Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

U.S. Department of the Interior
U.S. Geological Survey

USGS
science for a changing world

Compiled October 2015

http://water.usgs.gov/owq/FieldManual/

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Comments and Errata (not in this document, internet connection needed)

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Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

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Chapter A1.

PREPARATIONS FOR WATER SAMPLING

Revised 2005
By **Franceska D. Wilde**

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science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192
This report is accessible online at http://pubs.water.usgs.gov/twri9A/

Foreword

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and quality-assured data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that the data collected are of the quality required to fulfill our mission.

(signed)

Robert M. Hirsch
Associate Director for Water

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PREPARATIONS FOR WATER SAMPLING

National Field Manual for the Collection of Water-Quality Data

Chapter A1.

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Note:

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Chapter A1.
PREPARATIONS FOR WATER SAMPLING

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ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) provides guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses field-trip preparations, including selection of sample-collection sites for studies of surface-water quality, site reconnaissance and well selection for studies of ground-water quality, and the establishment of electronic files and field files and folders for a sampling site.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters are posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed Jan. 31, 2005).

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. A high degree of reliability and standardization of these data are paramount to fulfilling this mission. Documentation of nationally accepted methods by USGS personnel serves to maintain consistency and technical quality in data-collection activities. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect water-quality data. Chapter A1 addresses preparations for collecting water samples at surface-water and ground-water sites. **Formal training and field apprenticeship are needed in order to correctly implement the protocols and guidelines described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to Chapter 4 on "Collection of Water Samples." NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within designated limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

This chapter of the *National Field Manual* informs field personnel of the major steps needed to: prepare for water-quality data-collection activities; select surface-water sampling sites; make reconnaissance visits to ground-water sampling sites and select wells that will meet scientific objectives; and set up electronic and paper files. Study design and data-network design are beyond the scope of this publication. This chapter does not address statistical methods for site selection or well installation.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual* the terms "required" and "recommended" have the following USGS-specific meanings:

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and other professionals who have the appropriate expertise. Technical memorandums or other documents that define the policy pertinent to such requirements are cited in this publication. USGS personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary for accomplishing specific data-quality requirements or study objectives must be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes one or several acceptable alternatives to a given procedure or equipment selection on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this publication to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints may affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

This is version 2.0 of chapter A1, "Preparations for Water Sampling," dated January 2005. The version number and date appear in the footer of each page. Each chapter of the *National Field Manual* is reviewed and revised periodically to correct any errors and incorporate technical advances.

Comments on the NFM, and suggestions for updates or revisions, should be sent to nfm-owq@usgs.gov. Newly revised and reissued chapters or chapter sections are posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed January 12, 2005). This page also contains a link to the NFM "Comments and Errata" page that chronicles revisions to each chapter.

ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include unpublished USGS training and field manuals and technical memorandums. The following individuals in the USGS developed the field and training manuals that provided the foundation for this *National Field Manual*: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, M.T. Koterba, C.E. Lamb, W.W. Lapham, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

Authors for the first version of chapter A1 included D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, whose expertise and integrity provided the goundwork for this and future chapters of the *National Field Manual*. The persistence and spirit that these colleagues brought to the process of developing a national field manual was invaluable.

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R.W. Lee and S.W. McKenzie were responsible for the final technical review of the original version of this report. They contributed to its accuracy, quality, and usability.

Special thanks to to T.L. Miller, whose encouragement and faith in this project has been instrumental to its achievement; and to D.A. Rickert for providing the support needed to produce a national field manual for water-quality studies.

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A1. PREPARATIONS FOR WATER SAMPLING

This chapter of the *National Field Manual for the Collection of Water-Quality Data* provides guidelines for field personnel as they prepare to select and (or) evaluate surface-water and ground-water sampling sites, establish site files, and prepare for sample-collection field trips.

SAMPLING—The act of collecting a portion of material for analytical purposes that accurately represents the material being sampled with respect to stated objectives.

Modified from Standard Methods, 1060A (APHA and others, 2001)

Fundamental to water-quality sampling is the fact that the analytical results can be no better than the sample on which the analysis was performed. Thus, the sample collector must accept primary responsibility for the quality and integrity of the sample up to the time that it is delivered to the analyzing laboratory or office. Communication and collaboration between field and laboratory personnel is essential to producing valid data from the sampling effort.

1.0 FIELD-PERSONNEL RESPONSIBILITIES

Before sample collection begins, field personnel must take steps to ensure that the samples collected will be representative of the aqueous system being investigated. A representative water sample is a sample that typifies ("represents") in time and space that part of the aqueous system to be studied and is delineated by the objectives and scope of the study. USGS data-collection efforts often take a whole-system approach, meaning that data-collection methods ensure representation of an entire stream reach or aquifer volume. A modified approach is needed for studies in which samples are representative of a specific part or aspect of an aqueous system instead of the entire system; for example, a study of aquatic ecology may establish nearshore boundaries on the system, and an oil-spill study may target only the surface of a water-table aquifer.

- **Be alert to sample representativeness.** The data are no better than the confidence that can be placed in how well the sample represents the aqueous system (Feltz and Culbertson, 1972; Horowitz and others, 1994).
- **Plan to collect quality-control samples.** Quality-control checks applied during laboratory analyses of the samples cannot compensate for data that are biased because samples were not representative of the aqueous system or because samples were improperly collected and processed.

Field personnel also are responsible for providing the necessary information to establish USGS National Water Information System (NWIS) site files for each sampling site and for checking to see that the site file is functional, that the information it contains is correct, and that updates are made promptly. NWIS is the hydrologic data base for the U.S. Geological Survey. Updated versions are released periodically.

Update files promptly:

- **The Ground-Water Site Inventory (GWSI)** file contains site information.
- **The Quality-of-Water Data (QWDATA)** file contains field and laboratory data.
- **The Automatic Data Processing System (ADAPS)** file contains time-series information.

FIELD-TRIP PREPARATIONS 1.1

All details of a field trip need to be planned well in advance. Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations; a common mistake is to put off these activities until the last minute.

Before selecting sites or making other preparations:

- Understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- Review the study workplan, especially types of measurements and samples needed.
- Make field reconnaissance trips before selecting sampling sites, if possible.
  - Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing wells, or site-access peculiarities).
  - Evaluate potential sources of contamination at the site, based on target analytes[1] to be collected.
- Review site files and field folders. (Note site location, description and access, and review any previously collected physical, chemical, and biological data.)
- Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

[1]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

Before selecting equipment:

Understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements[2] (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

Before starting field work:

- Review site files and update and review the field folder for each site from which samples and ancillary data will be collected (see sections 1.2.2 and 1.3.2).
- Review the safety plan. Be sure that you have the training needed if you will be working at sites designated as hazardous (see NFM 9).

Plan ahead! Take adequate time to prepare.

1.1.1 CHECKLISTS OF EQUIPMENT, SUPPLIES, AND ACTIVITIES

Each study needs to establish and follow a protocol for data-collection activities. Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 1-1). Most checklists are generic to all projects and sites (for example, vehicle and equipment maintenance checklists), but may need to be customized (for example, items listed, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment). The types of information and examples of items listed on the next page usually are included when developing checklists.

[2]As used in this publication, the term "data-quality requirements" refers to that subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the allowable variability to fulfill the scientific objectives of the study.

Types of information	Examples of items or activities in checklists
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.
Presampling activities	Prepare checklists; for example, field-trip preparations checklist (fig. 1-1) and well-information checklist (fig. 1-3).
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.
Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of-custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with respect to: analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, chemical treatment and preservation procedures; sample shipment; quality-control samples.
Field-folder contents	Prepare list of logistical information needed for each site, such as permission to access site, keys, maps.
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.

Data quality begins before the first sample is collected by taking care to use proper equipment, being aware of data-quality requirements, and being alert to potential sources of sample contamination.

FIELD-TRIP PREPARATIONS

PROJECT: _____

SITES: _____DATE:_____

✓	Prefield activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ , Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (Water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare field forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check field vehicle for safety equipment and supplies, such as material safety data sheets, flares, and remote communications system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update field folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with field-trip and call-in (check-in) schedule	Provided on _____ to _____
	Other	

Figure 1-1. Example of a presampling activities checklist.

DATA-QUALITY PLANS AND PREPARATIONS 1.1.2

USGS policy that water-quality data be of a defined and documented quality is described in Horowitz and others (1994) and Office of Water Quality Technical Memorandum 93.11 (see "Selected References and Documents"). Every study should prepare a sampling and analysis plan (SAP) and a quality-assurance plan (QAP) (Schertz and others, 1998) that include a description of the objectives, purpose, and scope of the study and its data-quality requirements. In addition, each USGS Water Science Center develops general quality-assurance plans that articulate its policies, responsibilities, and protocols. USGS water-quality specialists can provide guidance relating to quality-assurance procedures and policies for the collection of water-quality, surface-water, and ground-water data.

Field personnel are responsible for determining whether the equipment and methods being used could impair sample quality. For the most part, this determination involves collecting quality-control samples and analyzing the results.

- **Collect equipment blanks before beginning the field effort**.
  - Equipment blanks are processed through clean equipment in the controlled setting of an office laboratory.
  - **Process an equipment blank at least once a year for each set of sample-contacting equipment**. This applies to new equipment to be used for the first time, to equipment that will be cleaned with a new cleaning procedure, and to equipment that has not been tested with an equipment blank for 1 year.
  - **Do not collect or process environmental samples until the annual equipment blank data have been reviewed.** Ensure that the equipment blanks either are free of contamination or have concentrations small enough to be insignificant at the current analytical limits (Horowitz and others, 1994).
- **Examine field and laboratory results as soon as possible, preferably before the next sample-collection field trip.** Results indicating potential bias in the data will alert you to the changes needed in equipment, equipment-cleaning procedures, or field methods used.

- **Be prepared to collect additional blanks, replicates, or other field quality-control samples**, based on your judgment of the effects of field conditions on sample collection. Field conditions are unpredictable, and adverse or unexpected conditions could necessitate additional steps to document data quality.

Quality-control samples are collected either in the office laboratory or at the field site, depending on their specific purpose (see NFM 3, "Cleaning of Equipment for Water Sampling;" NFM 4, "Collection of Water Samples;" and NFM 5, "Processing of Water Samples"). Field personnel must be familiar with the various types of quality-control samples and know how and when to collect them in order to comply with USGS quality-assurance requirements. Collection of blank samples (blanks) is mandatory. Blanks are samples of laboratory-prepared and -analyzed water that are processed through the equipment in the same manner as the environmental sample, but after the equipment has been cleaned and prepared for field use.

In preparation for collection of quality-control samples, solutions of the appropriate type and quality must be obtained for blank-water and standard reference material samples. USGS field personnel should use waters for blank samples (listed below) that are certified by the USGS National Water Quality Laboratory (NWQL) in Denver, Colo. and that can be obtained through the USGS One-Stop Shopping Web site. Laboratory certification should indicate that the blank water has target-analyte concentrations that are less than the method-detection limits. Standard/reference materials generally are obtained from the National Institute of Standards and Technology.

- Use pesticide blank water (PBW) to prepare blank samples to be analyzed for pesticides.
- Use nitrogen-gas-purged volatile/pesticide blank water (VPBW) to prepare blank samples to be analyzed for volatile organic compounds.
- Use inorganic blank water (IBW) to prepare blank samples to be analyzed for inorganic constituents. Alternatively, VPBW or PBW are designated "universal blank water" and may be used instead of IBW.

Collect field blanks at the field site under the same conditions as environmental samples. Field blanks can provide information on the efficacy of the equipment cleaning procedures used and on ambient atmospheric contamination.

SURFACE WATER 1.2

Before sample collection, sampling sites must be selected (section 1.2.1). For each sampling site, NWIS files and a field folder must be established, updated, and reviewed (section 1.2.2).

- The study team is responsible for selecting sampling sites and conditions (such as time of year, flow rate or stage) that will yield samples representative of the aqueous system being studied.
  - Each body of flowing and still surface water has a unique set of conditions that needs to be identified and considered in the site-selection process.
  - Field personnel must be trained in the correct and current water-quality data-collection procedures and must exercise judgment gained from field experience in order to make appropriate site selections.
- The study team is responsible for establishing and maintaining accurate records for each sampling site.
  - Careful and complete documentation of site information and the data collected must be input to electronic and paper files.
  - The field folder must include all the information necessary for efficient field operations.

SELECTION OF SAMPLING SITES 1.2.1

Field personnel must select the point(s) or transect(s) at which samples will be collected. In most bodies of flowing or still water, a single sampling site or point is not adequate to describe the sampling area's physical properties and the distribution and abundance of chemical constituents or biological communities. Location, distribution, and number of surface-water sampling sites can affect the quality and applicability of the resulting data. Generic guidelines for selecting flowing-water and still-water sites are described in this section.

When selecting surface-water sampling sites:

- Consider the study objectives, types of data needed, equipment needs, and sampling methods.
- Obtain all available historical information.
- Consider physical characteristics of the area, such as size and shape, land use, tributary and runoff characteristics, geology, point and nonpoint sources of contamination, hydraulic conditions, climate, water depth, and fluvial-sediment transport characteristics.
- Consider chemical and biological characteristics of the area (aquatic and terrestrial).

1.2.1.A Flowing-Water Sites

Flowing-water sites can refer to streams (fast or slow, intermittent, ephemeral, or perennial), canals, ditches, and flumes of all sizes and shapes, or to any other surface feature in which water moves unidirectionally. All or parts of reservoirs and estuaries that flow unidirectionally are considered to be flowing water. Determine latitude and longitude from maps or by land-survey techniques. Global-positioning system (GPS) equipment is useful to identify sampling-site location.

Flowing-water sampling sites optimally are located:

- At or near a stream-gaging station, to obtain concurrent surface-water discharge data required for computing constituent-transport loads and to determine discharge/constituent-concentration relations. (Measure discharge at time of sampling if a stream-gaging station is not at or near the sampling site or if discharge cannot be rated or estimated with sufficient accuracy.)
- In straight reaches having uniform flow, and having a uniform and stable bottom contour, and where constituents are well-mixed along the cross section.
- Far enough above and below confluences of streamflow or point sources of contamination to avoid sampling a cross section where flows are poorly mixed or not unidirectional.

- In reaches upstream from bridges or other structures, to avoid contamination from the structure or from a road surface.
- In unidirectional flow that does not include eddies. (If eddies are present within the channel, sample only the unidirectional flow.)
- At or near a transect in a reach where other data are collected (such as data for suspended sediment, bedload, bottom material, or biological material) and (or) for which historical data are available.
- At a cross section where samples can be collected at any stage throughout the period of study, if possible.

After a tentative selection of a sampling site, develop a preliminary profile of field measurements[3] at various locations along the cross section (NFM 4 and NFM 6). Final site selection is based on a comparison of field measurements with the data requirements of the study.

> **TECHNICAL NOTE:** The preferred sampling method and number of verticals to be sampled within the stream cross section that are needed to obtain a sample that is sufficiently representative depends on stream homogeneity as indicated by the field-measurement profile and stream-discharge or other data, as well as by study objectives. Sampling methods are described in NFM 4. Note that the field-measurement profile is a useful guideline, but might not be representative of chemical homogeneity for the analytes of interest. Also, it might be desirable to move to a sampling site upstream or downstream to adjust for seasonal variation or extreme flow conditions.

The guidelines used for selecting sampling sites on ephemeral and intermittent streams are the same as those for perennial streams. Ephemeral and intermittent stream sites need additional planning and examination to account, for example, for conditions related to rapidly changing stage and discharge that can occur as a result of flash flooding or urban runoff.

[3]The profile of the cross section usually includes specific electrical conductance (conductivity), pH, temperature, dissolved-oxygen, and turbidity measurements.

CAUTION: Any stream, including an ephemeral or intermittent stream, can rapidly become too deep and swift to wade safely.

1.2.1.B Still-Water Sites

Still-water sites refer to all sizes and shapes of lakes, reservoirs, ponds, swamps, marshes, riverine backwaters, or any other body of surface water where water generally does not move unidirectionally. All or parts of reservoirs that do not flow unidirectionally could be considered to be still water.

When locating still-water sampling sites:

- Use in situ field measurements to help determine vertical and spatial distribution of sampling locations.
- Avoid areas near structures such as harbors, boat ramps, piers, fuel docks, and moored houseboats (to avoid point sources of contamination), unless these structures are part of the study.
- Select sites with a record of historical data, if possible.

NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES AND FIELD FOLDERS 1.2.2

Field personnel are responsible for establishing and maintaining electronic and paper site files and ensuring their accuracy and completeness. The information required for establishing electronic records in NWIS and for creating field folders for surface-water sampling sites is summarized below.

NWIS Files 1.2.2.A

USGS policy requires specific information on surface-water sampling sites to be stored in the site file in NWIS (Hubbard, 1992; WRD Memorandum 92.59). Results of chemical water analyses are stored in the water-quality file (QWDATA) of NWIS (Gellenbeck, 2005). The Automatic Data Processing System (ADAPS) contains continuous records of water levels and water quality (Bartholoma, 2003). The minimum information required for establishing electronic files in NWIS for surface water is listed in table 1-1. Individual studies and USGS Water Science Center offices may have additional data-storage requirements.

If the site location has been identified:

- Establish or check the NWIS site file before the field trip.
- Update the files promptly after the field trip.
- Fill in information that is needed by, or could be useful to, the study in addition to the information shown on table 1-1. Refer to the Web page “Data Elements for Reporting Water Quality Results of: Chemical and Microbiological Analyses” for more information.The URL for this page is http://wi.water.usgs.gov/methods/tools/wqde/ (accessed Jan. 12, 2005).

- If real-time data are being served on the Web, ensure that current policies and quality-assurance measures are understood and implemented (see U.S. Geological Survey Water Resources Policy Memorandum No. 99.34, at http://water.usgs.gov/admin/memo/WRD/wrdpolicy99.34.html (accessed Jan. 12, 2005).

RULE OF THUMB:

Before starting field work—Make sure the NWIS file is established.

After field work—Input updates to NWIS files promptly.

1.2.2.B Field Folders

Selected information that is needed for reference while at a surface-water site is kept in a field folder. The field folder contains information needed by trained personnel to locate and safely collect and process water samples. The field folder is taken along on each sampling trip. General contents of the field folder are listed on the field-folder checklist (fig. 1-2), but the folder should be customized according to study needs.

Table 1-1. Minimum information required for electronic storage of site and surface-water-quality data in the U.S. Geological Survey (USGS) National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Required information for creation of a surface-water site in NWIS[1, 2]		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number	C1	11530500
Station Name	C12	Klamath River near Klamath, Calif.
Latitude	C9	413052
Longitude	C10	1235957
USGS Water Science Center (formerly "District")/User	C6	06 (California)
State	C7	06 (California)
County	C8	015 (Del Norte)
Agency Use	C803	A (Active)
Station Type	C802	SW
Required information for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	11530500
Sample Medium	MEDIM	9 (surface water)
Sample Type	STYPE	9 (regular sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	9 (stable stage)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields are available in NWIS that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.
[2]Modified from Ground-Water Site Inventory Schedule Form 9-1904-A, Revised June 2004, NWIS 4.4

Field-folder checklist: surface-water quality		
✓	**Item**	**Comments**
	Station description: • Location of gaging station (if one is present). • Location of sample-collection sites: high and low streamflows. • Hydrologic and geologic sections. • Name of landowner, tenant, or other responsible party. • Site access instructions (for example, call owner or site operator before arrival at site, obtain key to unlock security gate). • Photographs to document site conditions.	
	Maps to site (State and local)	
	Profiles of cross section of stream channel at sampling location(s). • Stream-bottom geometry. • Physical and chemical measurements.	
	Safety information (NFM 9): • Nearest emergency facilities. • Phone numbers (home) of study chief or supervisor. • Traffic condition and traffic plan showing where to park, placement of flags and cones. • Location of power lines. • Environmental hazards, such as weather and animals.	
	Sampling schedule: • Laboratory analyses to be requested and associated codes. • When to collect samples (high or low flow).	
	Bottle types needed for each analytical schedule.	
	Analytical Services Request form(s) and example of a completed form.	
	Sampling instructions: • Cumulative-discharge curves at about 10-, 50-, and 90-percent duration. • Velocity cross sections at about 10-, 50-, and 90-percent duration. • Equipment to use at various flows. • Flow-duration curve. • Discharge rating curves and (or) tables.	
	Shipping instructions: • Amount of ice to use. • Mailing labels to and from laboratory. • Location of nearest post office or shipping agent.	
	Surface-water field form and an example of completed form.	
	A tabulation sheet for each type of bacteria enumerated at the site (include example with date of sample, streamflow, volumes filtered, dilutions, plate counts).	
	Plots of field-measured data (last 5-10 years of record); if there is a good enough relation to show outliers, include: • Conductivity versus streamflow. • Conductivity versus alkalinity. • Temperature versus time.	
	Statistical summary of historical water data: • Seasonal, maximum-minimum values. • Discharge-related maximum-minimum values.	
	Special equipment needed to address site-specific conditions: • Sampling. • Safety.	

Figure 1-2. Checklist for contents of surface-water-sampling field folder.

GROUND WATER 1.3

Ground water is sampled either from various types of existing wells or from wells that are installed specifically for a study.

- **Water-supply wells** are wells that are installed primarily for supply of public, irrigation, domestic, commercial, or industrial water and usually are equipped with a dedicated high-capacity pump. The term "supply well" is used in this publication.
- **Observation wells** are wells or piezometers that are installed (usually without a dedicated pump) for the purpose of collecting hydrologic data. The term generally has been applied to wells installed to observe and determine hydrologic characteristics of an aquifer (Lapham and others, 1997).
- **Monitor wells** are observation wells that are installed specifically for assessment of physical, chemical, and biological characteristics of the aquifer. Low-capacity portable pumps are commonly used for sampling, but monitor wells can be equipped with a dedicated pump. The term "monitoring well" is used in this publication.

Information is compiled about the well and well site during site-reconnaissance visits, well installation, and subsequent data-collection efforts at the site. This information is used to help select the well(s) needed for study. The ground-water site inventory is compiled in the office and verified in the field. In an office inventory, the study team identifies existing wells or well sites and compiles background information and available records for those wells. The field inventory is completed during reconnaissance trips in which well location is verified, additional information is collected, and the suitability of the site for study objectives is determined. For each well, the inventory of site and well information is entered into the NWIS water-quality (QWDATA) and ground-water site inventory (GWSI) data bases and is added to the file created for the well (well file).

1.3.1 SITE RECONNAISSANCE AND WELL SELECTION

Field personnel critically evaluate existing and installed wells to determine whether they will yield samples that are representative of the environment targeted for study.

As a member of the study team:

- Be prepared to participate in office- and field-related aspects of selecting and installing wells (see Lapham and others, 1997).
- Be familiar with study objectives and requirements for data collection and quality.
- Be familiar with considerations for well selection and well installation (summarized in table 1-2).

Information gathered from a site reconnaissance visit can help determine whether an existing well or a proposed well-installation site meets the criteria established by the study. Site reconnaissance visits also ensure efficient field operations and could be a critical factor in site selection or rejection. These site visits commonly are needed to verify the location and condition of wells, evaluate site characteristics, and make modifications to the site and adjustments to sampling plans to allow sampling to proceed. Before leaving for the site, determine the activities that are to be completed and make the necessary preparations (table 1-3).

Keep in mind the primary concerns for water-quality studies:

- The sample must represent the system intended for study.
- Sample integrity must be maintained.

Site visits also can be used to identify areas of ground-water recharge and discharge, test field equipment, test well-purging and sampling procedures, conduct aquifer tests, make preliminary field measurements, and identify the presence of target analytes.

Review safety plans and procedures before leaving for the field.

Table 1-2. Considerations for well selection and well installation

[Modified from Lapham and others, 1997]

Well location
• Location conforms to the study's network design for areal and depth distribution.
• Land-use/land-cover characteristics, if relevant, are consistent with study objectives.
• Site is accessible for equipment needed for well installation and sample collection.
Hydrogeologic unit(s)
• Hydrogeologic unit(s) that contribute water to the well can be identified.
• Depth and thickness of targeted hydrogeologic unit(s) are known or can be determined.
• Yield of water is adequate for sampling (typically, a minimum of 1 gallon (3.785 liters) per minute).
Well records, description, design, materials, and structure
• Available records (for example, logs of well drilling, completion, and development) have sufficient information to meet the criteria established by the study.
• Borehole or casing/screen diameter is adequate for equipment.
• Depth to top and bottom of sample-collection (open or screened) interval is known (to determine area contributing water to well).
• Length of well screen is proportional to the vertical and areal scale of investigation.
• Well has only one screened or open interval, if possible. (Packers can be used to isolate the interval of interest, but packers might not completely isolate zones in unconsolidated or highly fractured aquifers. If packers are used, materials of construction must be compatible with analytes to be studied.)
• Top of well screen is several feet below mean annual low-water table to reduce chances of well going dry and to avoid sampling from unsaturated intervals.
• Filter pack is of a reasonable length (a long interval compared with length of screened or open interval usually results in uncertainty as to location of the source of water to well).
• Well-construction materials do not leach or sorb substances that could alter ambient target-analyte concentrations.
• Well-structure integrity and communication with the aquifer are sound. (Checks include annual depth-to-bottom measurements, borehole caliper and downhole-camera video logs, and aquifer tests.)
Pump type, materials, performance, and location of sampler intake
• Supply wells have water-lubricated turbine pumps rather than oil-lubricated turbine pumps. (Avoid suction-lift, jet, or gas-contact pumps, especially for analytes affected by pressure changes, exposure to oxygen, or that partition to a gas phase.)
• Pump and riser-pipe materials do not affect target-analyte concentrations.
• Effects of pumping rate on measurements and analyses have been or will be evaluated.
• Sampler intake is ahead of where water enters treatment systems, pressure tanks, or holding tanks.

Table 1-3. Example of ground-water site-reconnaissance activities

Before the site visit
Review considerations for well selection and installation (summarized in table 1-2).
Review background information collected.
Obtain permission to gain access to the site and to collect samples from the well.
Update well files: record changes in ownership and land use.
Contact utility companies (gas, water, and electric) before digging or drilling.
Determine whether the pump may or may not be removed from well by field personnel. (Owner's permission is required to remove a pump—you could be liable for damage to pump or well.)
Be sure that you get information needed about the site that could interfere with or interrupt sampling. For example, • Hours of pump operation and scheduled downtime. • Pumping rate or rates. • Holding tanks or chemical treatments. • Electrical service to the site. • Scheduled maintenance for pumps or related equipment. • Scheduled site maintenance, such as painting, construction, and defoliation. • Seasonal water-level declines that make the well unusable. • Times of denied access; for example, no access while the owner is out of town. • Special site-access needs; for example, clearance with a site owner or site operator, keys to unlock access to the site, animals. • Restrictions on the location.
Record conditions that could compromise study objectives, including potential point or nonpoint sources of contamination. For example, • Nearby wells that could affect well hydraulics. • Condition of well—for example, rusting or punctured casing, poor surface seal. • Land use and land cover or changes in land use and land cover. • Application of salt on nearby roads during winter, or application or use of herbicides and pesticides. • Landfills or other waste-management facilities. • Industrial, commercial, and agricultural complexes and discharges.
During the site visit
Measure water level in each well. Record water-level data on the appropriate form(s).
Identify potential difficulties with the type of equipment and sample-collection methodology to be used. (Note that sampling plans will have to be modified accordingly.)
Update field folders. • Note site conditions that could affect the quality of data collected from that well. • Note change(s) in land use.
Verify well identification number and make sure that it is clearly and permanently labeled. • Check that identification corresponds with what is in the field folder and on site and location maps. • Correct any mistakes or uncertainty about well identification and well location.
Verify type of pump, well diameter, and use of holding tanks, pressure tanks, chemical treatments. • Check whether oil is floating on the water column in a well equipped with an oil-lubricated pump. • Make sure that the downhole treatment system is turned off before collecting water samples. • Determine if a portable pump or another intended sampling device is suitable for use.

Table 1-3. Example of ground-water site-reconnaissance activities—*Continued*

During the site visit—*Continued*
Establish optimum pumping rate(s) for purging and sample collection and decide where to route excess discharge. • Adjust pumping rate to ensure adequate purging of the well without entrainment of atmospheric gases due to excessive drawdown. • Route water away from the well to prevent (1) creating muddy and slippery conditions and (2) damage to or defacement of the property to which you were granted access.
Check that well structure is intact. • Wells used for ground-water studies should be "sounded" annually to check whether depth to bottom corresponds with well construction information or whether the well is filling with loose materials (U.S. Geological Survey, 1980; Lapham and others, 1997). A decrease in depth to bottom could indicate that the well casing is collapsing, or that there is a breach or corrosion of well screen or casing, or that the well is improperly designed to retain aquifer materials. • Borehole caliper and downhole-camera video logs can identify a damaged or broken well casing. A downhole camera can identify a plugged screen or accumulation of sediment in the well. • Aquifer tests, such as slug tests, can be used to check the hydraulic connection between the well and the aquifer. Aquifer tests, however, are generally beyond the scope of site reconnaissance. • The surface seal of a USGS monitoring well should be intact and the well should be capped. Concrete pad should be repaired if cracked or separated from outer casing. A tight-fitting well cap should have a small ventilation hole.
Check well access for sample-collection points. • Sample-collection points need to be near the wellhead, ahead of where water enters pressure tanks, holding tanks, or treatment systems. • At wells where an access point close to the well is not available, it might be possible to install a hose bibb or tap at the wellhead. Because it usually is not possible to control the pumping rate of a supply well, the field person may need to set up a hose-and-valve system to control the rate at which water is sampled and to reduce the likelihood of backflow of water stored in plumbing lines.
Check well access for water-level measurements. The construction of some supply wells makes water-level measurements difficult or impossible. • Although it is often possible to slip a weighted steel or electric well tape below the pump to get a water-level measurement, the pump can be damaged if the weight or tape becomes entangled in the pump. The weight should be attached so that it will snap off of the tape under stress. • Water levels can be estimated through the air line on some wells. • Sometimes field personnel are permitted to remove the pump from the well to get a measurement; however, pump removal can be difficult, time consuming, and potentially unsafe, and could damage the pump. • A note should be made in the well file if there is no access for a depth measurement.

1.3.2 NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES, WELL FILES, AND FIELD FOLDERS

USGS policy requires specific information on ground-water sampling sites to be stored in NWIS. NWIS is the public portal to USGS water resources data (Hubbard, 1992; WRD Memorandum 92.59). Paper documents, such as agreements between the well owner and the USGS for use of the well, also are necessary and are stored in well files and field folders (U.S. Geological Survey, Office of Ground Water Technical Memorandum No. 2003.03).

- Much of the information needed to set up files for existing wells can be obtained from well owners, drillers, records from state or local jurisdictions, and well-construction logs.
- Information that will be needed to set up well files for new wells is recorded by field personnel as the new well is installed (Lapham and others, 1997).

RULE OF THUMB:

Before starting field work—Make sure the site file is established in NWIS.

After field work—Update NWIS promptly.

NWIS Files 1.3.2.A

Within the NWIS system, well information, ground-water levels, and water-quality data are stored in three subsystems: the Ground-Water Site Inventory (GWSI), Quality of Water Data (QWDATA), and the Automatic Data Processing System (ADAPS). All wells for which data are stored must be identified by an electronic record in the NWIS site file.

- GWSI primarily contains (1) descriptive information about the site and well, (2) construction information, and (3) noncontinuous water-level data (Hoopes, 2004).
- QWDATA contains (1) results of field and laboratory water-quality sample analyses and measurements, (2) noncontinuous water-level data, and (3) other data related to water-quality samples or sample analysis (Gellenbeck, 2005).
- ADAPS contains continuous records of water levels and water quality (Bartholoma, 2003).
- NWISWeb displays real-time water-level data (http://waterdata.usgs.gov/nwis/gw), and real-time water-quality data for selected wells (http://waterdata.usgs.gov/nwis/qw). (Websites accessed Jan. 12, 2005).

The minimum information required for establishing electronic files in GWSI and QWDATA is shown in table 1-4. Individual studies and USGS Water Science Center offices may have additional data-storage requirements. For example, the GUNIT (geologic unit) code provides important information for ground-water studies.

When creating or updating a GWSI site-file record, fill in information that is needed by, or useful to, the study, in addition to the required information shown in table 1-4.

Table 1-4. Minimum information required for electronic storage of site and ground-water-quality data in the U.S. Geological Survey (USGS) National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Required information for creation of a ground-water site in NWIS[1, 2] (GWSI)		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number (Latitude/longitude/sequence no.)	C1	394224075340501
Station Name	C12	KE Be 61
Latitude	C9	394224
Longitude	C10	0753405
Country	C41	US
Lat/Long Accuracy	C11	S (seconds)
Lat/Long Method	C35	M (Map)
Lat/Long Datum	C36	NAD83
Time Zone	C813	EST
Daylight Savings Time Flag	C814	Y (Yes)
District/User	C6	24 (Maryland)
State	C7	10 (Delaware)
County	C8	003 (Sussex)
Station Type	C802	6 (Well)
Data Reliability	C3	C (Field Checked)
Site Type	C2	W (Well)
Use of site	C23	O (Observation)

Required information for storage of sample analyses in the water-quality subsystem (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	394224075340501
Sample Medium	MEDIM	6 (ground water)
Sample Type	STYPE	2 (blank sample)
Hydrologic (“Hydro”) Event	EVENT	9 (routine sample)
Hydrologic (“Hydro”) Condition	HSTAT	A (not determined)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields from those shown are available in GWSI and QWDATA that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]From Ground-Water Site Inventory Schedule Form 9-1904-A, Revised June 2004, NWIS 4.4.

Well Files 1.3.2.B

A well file also must be established for each well selected or installed for the study or in a data network. At the outset of the study, it is useful to refer to a checklist of the items and types of information needed for the well file (fig. 1-3).

The well file is the repository of the information compiled for the well, and it should contain documentation for site selection, well inventory, well installation, and sample collection.

- Include owner-signed and dated permission forms for site access, well construction (OGW 2003.03, Form 9-4183), well ownership, sample collection and analysis, and data publication.
- Include well-construction information to the extent that it is available (Lapham and others, 1997).
- Include water-quality information, hydrogeologic field forms and logs, and plots of water-quality data and other hydrologic, geologic, geochemical, or geophysical information available for the well or field site.
- Include a log of well-maintenance and well-integrity checks and tests, geophysical logs and surveys, results of aquifer tests, analyses of cores or cuttings of geologic materials, and analyses from previously collected samples from the well or from a nearby well.

Field Folders 1.3.2.C

Selected information related to the well file and electronic records is kept in a field folder. The field folder contains information needed by personnel to locate and gain access to the site and to collect and process ground-water samples. The field folder should be taken along on each visit to the well for reference at the field site and should not contain original data records. The generic contents of a field folder are listed in the field folder checklist (fig. 1-4). Examples of site-location maps and a site sketch are shown in figure 1-5.

WELL-INFORMATION CHECKLIST, Page 1 of 2

Project name and identification number: _____
Latitude-longitude: _____ Sequence number: _____
Other site or well ID: _____ Station name: _____

Indicate use of water/site:

Public Supply	Irrigation
Domestic	Observation
Commercial	Monitoring
Industrial	Other _____

Item in well file	Date item filed
Criteria for well selection or installation	_____
Station Analysis	_____
Station Description	_____
ADR (Automatic Data Recorder) Manuscript	_____
Ground-Water Site Inventory (GWSI) data entered into National Water Information System (NWIS)	_____
Paper copy of GWSI form (9-1904-A)	_____
Copies of agreement to complete activity (drilling, sampling, etc.) _____	_____
List agreements _____	_____
Copies of field forms and logs:	
Well-drilling record	_____
Driller's log	_____
Lithologic log: Cuttings	_____
Cores	_____
Aquifer tests: (list types) _____	_____
_____	
Geophysical logs: (list types) _____	_____
_____	
Well-construction record	_____
Well-development record	_____
Well-maintenance checks: (list types) _____	_____
_____	
Well-location information:	
Latitude-longitude, datum, method of determination, and any changes	_____
Well-location map(s)	_____
Site-sketch map	_____
Written description of location	_____
Well-casing elevation (elevation, and method and date of determination)	_____
Photographs of well and vicinity (with measuring/sampling points identified)	_____
Land use/land cover form (Lapham and others, 1997)	_____

Figure 1-3. Example of a well-information checklist for a well file and field folder.

WELL-INFORMATION CHECKLIST, Page 2 of 2

Item in well file	Date item filed
Water-quality records for each sampling event (for example, purging, field measurements, field forms, sampling history) and copies of laboratory analyses requested	_____
	_____
	_____
	_____
	_____
Water-level measurements - current:	_____
	_____
	_____
Water-level measurements - historical:	_____
	_____
	_____
Record of well leveling (survey)	_____
Datum Corrections	_____
Pumping schedule/history	_____
Type of pump in well and location of intake	_____

Description of measuring point for water levels: _____

_____

_____

Description of collection point for samples from

Supply wells _____

_____

Monitoring wells _____

Other information (for example, geologic unit, aquifer name): _____

_____

_____

_____

Figure 1-3. Example of a well-information checklist for a well file and field folder—*Continued*.

Field-folder checklist: ground-water quality		
✓	Item	Comments
	Forms (new forms and (or) examples of completed forms): • Permission forms—must be signed by proper authority. • Analytical Services Request form(s). • Ground-water field form and well-inventory form.	
	Equipment and supplies checklists.	
	Field-techniques manuals.	
	Safety information: • Nearest emergency facilities; home phone number of supervisor. • Diagram of where to park, placement of flags and cones. • Traffic conditions; location of power lines. • Environmental hazards such as weather and animals.	
	Site location and description: • Maps showing location and identification number of well(s). • Name of landowner, tenant, or other responsible party. • Site access instructions (call owner; get keys or tools needed for security gate, well house, well protective casing). • Photographs and land use/land cover form to document site conditions. • Well dimensions and construction.	
	Sampling schedule and instructions: • Laboratory analyses, codes, and bottle types. • Preservation requirements. • Quality-control samples. • Location of sampler intake during sample collection. • Pumping rate for purging and sampling.	
	Purging instructions: • Number of well volumes. • Rate of pumping; containment and discharge of purge water. • Location of sampler intake during purging. • Field measurements and stability protocols. • Previous field-measurement and purge-volume records. • Place to discharge excess water.	
	Water-level measurements: • Location of measuring point. • Previous records from well.	
	Ancillary information: • Geologic section(s). • Hydrologic section(s). • Borehole geophysical logs.	
	Shipping instructions: • Mailing labels; location of nearest post office or shipping agent. • Ice or holding time requirements.	

Figure 1-4. Checklist for contents of ground-water-sampling field folder.

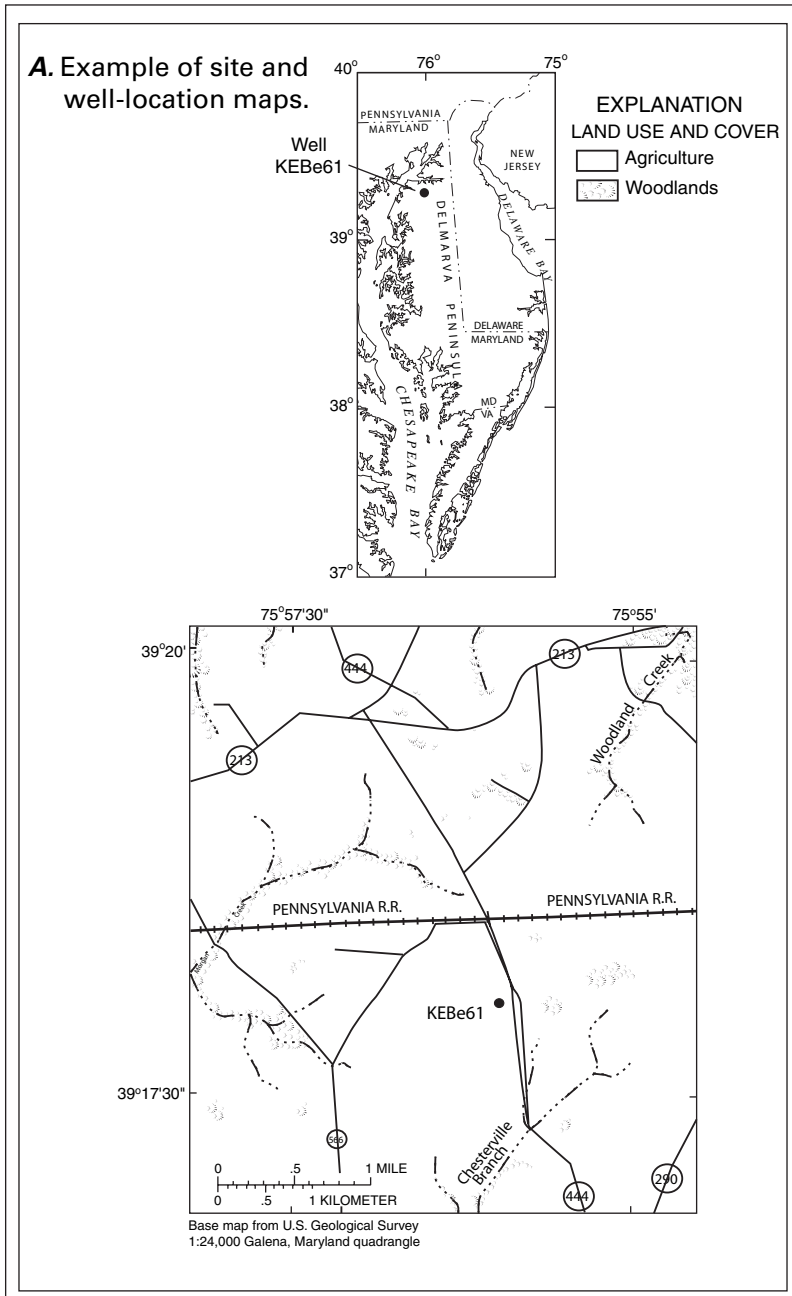
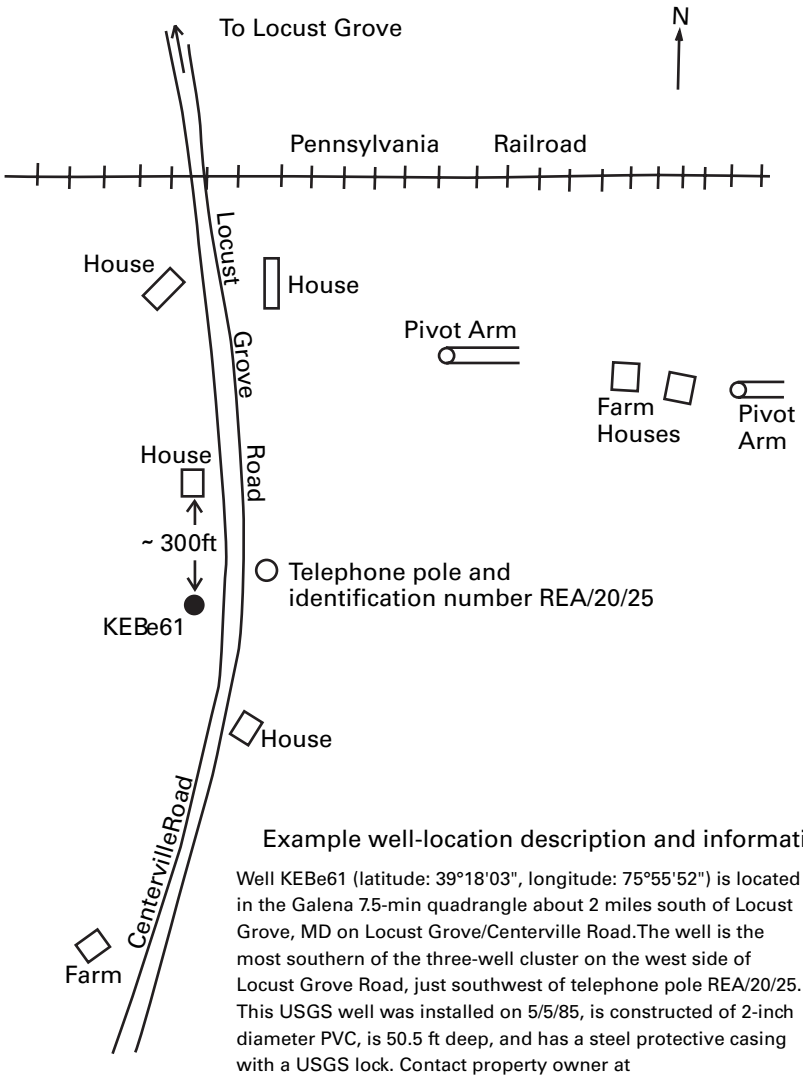


Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch.

B. Example of well-site sketch (with well-site information).



Example well-location description and information:

Well KEBe61 (latitude: 39°18'03", longitude: 75°55'52") is located in the Galena 7.5-min quadrangle about 2 miles south of Locust Grove, MD on Locust Grove/Centerville Road.The well is the most southern of the three-well cluster on the west side of Locust Grove Road, just southwest of telephone pole REA/20/25. This USGS well was installed on 5/5/85, is constructed of 2-inch diameter PVC, is 50.5 ft deep, and has a steel protective casing with a USGS lock. Contact property owner at ( )___-____ one day before sampling.

Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch—*Continued.*

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Ground Water

Memo No.	Title	Date
gw 03.03	Agreement Forms for Gaging Station and Observation Well Installations and Transfers	Sept. 17, 2003

Water Quality

Memo No.	Title	Date
qw 93.11	PROGRAMS AND PLANS: Implementation of the Protocol for Collecting and Processing Surface-Water Samples for Low-Level Inorganic Analyses	July 15, 1993

Water Resources Policy

Memo No.	Title	Date
wrdpolicy 92.59	Policy for Management and Retention of Hydrologic Data of the U.S. Geological Survey	Oct. 20, 1992
wrdpolicy 99.34	Quality Assurance Measures for Serving Real-time Water Data on the World Wide Web	Feb. 28, 2000

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National Field Manual for the Collection of Water-Quality Data

Chapter A2

SELECTION OF EQUIPMENT FOR WATER SAMPLING

Revised by Franceska D. Wilde, Mark W. Sandstrom, and Stanley C. Skrobialowski

Techniques of Water-Resources Investigations Book 9, Chapter A2

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

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Preface

The Water Mission Area of the U.S. Geological Survey (USGS) provides the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a national field manual is necessary to achieve consistent application of the scientific methods and procedures used, to maintain USGS technical expertise and data integrity, and to publish USGS water-quality field methods for ready reference and review by others. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.

Acknowledgments

The information included in this chapter of the National Field Manual is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise.

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Chapter A2. Selection of Equipment for Water Sampling

Revised by Franceska D. Wilde, Mark W. Sandstrom, and Stanley C. Skrobialowski

Abstract

The *National Field Manual for the Collection of Water-Quality Data* (National Field Manual) describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and groundwater resources. This chapter addresses the selection of the equipment commonly used by USGS personnel to collect and process water-quality samples.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters can be accessed at *http://pubs.water.usgs.gov/twri9A* or from the USGS Water-Quality Information Pages (*http://water.usgs.gov/owq/index.html*) under the heading "Methods: Data Collection, Analysis, & Interpretation".

Introduction

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual*) describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and groundwater resources. Chapter A2 provides information about equipment used to collect and process water samples to determine physical and chemical properties and composition. Requirements, recommendations, and guidelines are described that pertain to the selection and use of field equipment by USGS personnel. **Formal training and field apprenticeship are needed in order to correctly implement the requirements and recommendations described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapters are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to chapter A4 titled "Collection of Water Samples". NFM 4.1 refers to chapter A4, section 1, titled "Surface-water sampling". NFM 4.1.2 refers to chapter A4, section 1, subsection 2, titled "Selection of surface-water sampling sites". This report is chapter A2, "Selection of Equipment for Water Sampling," and therefore is referred to as NFM 2. When referencing a chapter section within the same chapter, however, "NFM" is omitted and the section is identified; for example, as section 2.1 (Sample collection), or 2.1.1 (Surface-water equipment), or 2.1.1.A (Isokinetic depth-integrating samplers).

Purpose and Scope

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias

and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of chapter A2 of the *National Field Manual* is to provide information regarding the requirements, recommendations, and guidelines routinely used for equipment selection in USGS studies involving the collection and processing of water-quality samples. (The terms "required" and "recommended," as used in this manual, are explained below under "Requirements and Recommendations.") The information provided covers topics fundamental to the collection and processing of surface-water and groundwater samples that are representative of the ambient environment. This chapter does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies.[1]

Requirements and Recommendations

As used in this *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

- **Required** (require, required, or requirements) and "must" pertain to USGS protocols and indicate that USGS policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected Water Science Centers[2] or other professional personnel, as appropriate.
  - Technical memorandums and other documents that define the policy pertinent to such requirements are referenced in this manual.
  - Personnel are instructed to use required equipment or procedures as described herein.
  - Departure from or modifications to the stipulated requirements that might be necessary to accomplish specific data-quality requirements or study objectives must be based on referenced research and good field judgment and must be quality assured and documented in permanent and readily accessible records.
- **Recommended** (recommend, recommended, recommendation, and "rule of thumb") indicates that USGS policy recognizes one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus, with respect to established good-science practices, including the professional judgment of field scientists. References to technical memorandums and selected publications pertinent to such recommendations are cited in this chapter to the extent that such documents are available.
  - Specific data-quality requirements, study objectives, or other constraints affect the choice of recommended equipment or procedures.
  - Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented.

[1] *National Field Manual* chapters 7 and 8 describe equipment used to collect and process samples for analysis of biological indicators and suspended solids, respectively.

[2] Water Science Center" refers to an organizational unit of the USGS in any of the States or Territories of the United States.

— Departure from or modifications to recommended procedures must be quality assured and documented in permanent and readily accessible records.

Field Manual Review and Revision

Each chapter of the *National Field Manual* is reviewed and revised periodically to correct errors, incorporate technical advances, and address additional topics or emerging areas of relevance to water-quality studies. *National Field Manual* chapters are issued in electronic format only. The version number for a given chapter is shown in the footer on each page. A major update or revision will be designated as a new version by the number that precedes the decimal point, and updates that are limited in scope or importance with respect to the chapter as a whole are designated by an increase in the version number after the decimal point. Minor nontechnical changes, such as URL or editorial updates, are designated by a second number that follows the decimal point (for example, version 3.01).

Comments, questions, and suggestions related to the NFM should be sent to *nfm-owq@usgs.gov*. Newly revised and reissued chapters or chapter sections replace the former versions, which are archived and linked to the home page for that chapter. The home page also contains a link to the NFM "Comments and Errata" page (*http://water.usgs.gov/owq/FieldManual/mastererrata.html*) that chronicles changes to each chapter.

Chapter A2. Selection of Equipment for Water Sampling

This chapter assists field personnel conducting water-quality investigations to select the sample-collection and sample-processing equipment[3] appropriate for study objectives, data-quality requirements,[4] and site conditions. The selection of equipment for collecting or processing water-quality samples depends on the physical constraints and safe operation of the equipment and on its suitability with respect to achievement of study objectives.

Criteria for selecting equipment for water sampling depend on (1) the mechanical constraints of the equipment to perform adequately under given environmental conditions, (2) the adequacy of equipment operation to obtain water-quality samples that represent the environmental conditions of the sample source, and (3) the adequacy of the equipment materials and construction to maintain sample integrity and not to be a source of leaching and sorption of target analytes.

- **Always operate equipment safely.**
- Be thoroughly familiar with requirements for equipment operation and maintenance.
- Be aware of the limitations as well as applications of the equipment with respect to your field site.
- Maintain and test equipment on a regular schedule.

2.0 Chemical Compatibility with the Water Sample

The materials used to construct equipment and the materials that contact equipment can alter sample chemistry (table 2–1). Equipment designed for water-quality sampling commonly is constructed of a combination of materials, the most inert being used for components that will contact the sample. Nonsample-wetted components and manual contact with sampling equipment can be a source of sample contamination. Field personnel must wear gloves and use other techniques to minimize potential contamination, implement quality-assurance procedures, and quantify potential effects by analyzing quality-control samples collected using laboratory-certified deionized and blank water.

When selecting equipment to be used, consider keeping several sets of precleaned equipment available. Using a clean set of equipment for each sampling site can lessen the chance of cross contamination between sites and eliminate the need for time-consuming equipment cleaning in the field. An extra set of precleaned equipment could also serve as a backup should equipment break or become contaminated.

Check that the equipment to be used will not affect the sample chemistry.

[3] NFM 6 describes equipment used for field measurements of physical or chemical properties of water (temperature, dissolved oxygen, specific electrical conductance (conductivity), pH, reduction-oxidation potential, alkalinity, and turbidity). NFM 7 describes equipment used for determinations of biological indicators. NFM 8 describes equipment used for bottom-material sampling. NFM 9 describes equipment related to safety in field activities.

[4] The term “data-quality requirements” (as used in this field manual) refers to that subset of data-quality objectives specifically pertaining to the analytical detection level for concentrations of target analytes and the variability (or error brackets) allowable to fulfill the scientific objectives of the study.

Table 2–1. General guidelines for selecting water-sampling equipment to avoid sample contamination from materials used in equipment construction.

[‡, generally appropriate for use shown; Cr, chromium; Ni, nickel; Fe, iron; Mn, manganese; Mo, molybdenum; $^3H/^3He$, tritium/helium-3; CFC, chlorofluorocarbon; SF_6, sulfur hexafluoride]

Construction materials[1]		Inorganic and organic analyte(s) targeted for analysis	
Material	**Description**	**Inorganic**	**Organic**
Plastics[2]			
Fluorocarbon polymers[3]	Chemically inert for most analytes	‡, but potential source of fluoride	‡, sorption of some organics
Polypropylene	Relatively inert for inorganic analytes	‡	Do not use
Polyethylene (linear)	Relatively inert for inorganic analytes	‡	Do not use
Polyvinyl chloride (PVC)	Relatively inert for inorganic analytes	‡	Do not use
Silicone	Very porous. Relatively inert for most inorganic analytes	‡, but potential source of silica	Do not use
Nylon	Relatively inert for inorganic analytes	‡	Do not use.
Metals[3]			
Stainless steel, 316-grade (SS 316)	SS 316—metal with the greatest corrosion resistance. Comes in various grades	‡, but potential source of Cr, Ni, Fe, and possibly Mn and Mo if corroded[4]	‡, but do not use if corrosion is evident[5]
	Used for submersible pump casing[4]	**Do not use for surface-water sampling:** equipment must have a plastic coating (this does not apply to submersible pumps)	
Other metals: brass, iron, copper, aluminum, and galvanized and carbon steels	Refrigeration-grade copper or aluminum tubing is used routinely for collection of $^3H/^3He$, CFC, and SF_6 samples	Do not use (except as noted for isotopes)	‡, routinely used for CFCs. Do not use if corroded
Glass			
Glass, borosilicate (laboratory grade)	Relatively inert. Potential sorption of analytes	‡, but glass is potential source of boron and silica	‡
Ceramic			

[1]This table does not address the suitability of well-casing materials for given sampling and quality-assurance objectives. Such information is provided in Lapham and others (1997).

[2]Plastics used in connection with inorganic trace-element sampling must be uncolored or white (Horowitz and others, 1994).

[3]Fluorocarbon polymers include materials such as Teflon®, Kynar®, and Tefzel® that are relatively inert for sampling inorganic or organic analytes.

[4]Most submersible sampling pumps have stainless steel components. One usually can minimize effects on samples collected for analysis of inorganic constituents by, to the extent possible, using fluorocarbon polymers in the construction of sample-wetted components (for example, for a bladder, stator, impeller).

[5]Corroded/weathered surfaces are active sorption sites for organic compounds and can leach trace elements.

2.0.1 Equipment Materials

Materials used in the construction of water-sampling equipment can include glass, plastics, ceramics, and metals. Chemical reactivity varies widely within the same group of materials, depending on the chemical composition, the physical configuration, and the manufacturing process. Thus, regarding reactivity with water and most other chemical substances, fluorocarbon polymers are less reactive than plastics such as polyethylene, and 316-type stainless steel (SS 316) is less reactive than brass, iron, or galvanized steel (table 2–1). For plastics and metals in general:

- The softer or more flexible forms of any plastic or metal are more reactive than the rigid forms.
- The more polished the surface, the less reactive the material tends to be.

2.0.2 Disposable Gloves

Wearing disposable, powderless gloves is required when handling equipment used to collect and process water-quality samples. Gloves protect field personnel from contact with pathogens and chemical contaminants and preservatives. Wearing gloves also helps to avoid sample contamination that could result from improper sample handling. Neither gloved nor ungloved hands should come in contact with the sample or with an equipment surface that the sample could contact. Refer to NFM 4.0.2 for a detailed description of the Clean Hands/Dirty Hands requirements for using gloves.

Although common glove types include those made of vinyl, latex, and nitrile, nitrile is in standard use for USGS sampling work because of its resistance to most of the chemicals to which it typically will be exposed for an exposure time that is usually less than 15 minutes. Field personnel are cautioned that skin contact with materials such as latex or nitrile may cause severe allergic reactions in some individuals, and any changes to skin texture or color should be monitored.

- Wear powderless nitrile gloves when handling equipment and chemical solutions. Do not allow the water that enters the sample bottle to contact gloved (or bare) hands.
- When working in a sampling chamber, **wearing elbow-length gloves** is recommended if sampling for pharmaceutical or personal-care analytes—this will minimize exposure of the sample to chemicals (such as DEET (n,n-Diethyl-meta-toluamide)) that have been applied to skin.
- Check the manufacturer's chemical resistance chart for any compound, such as acid, base, or organic solvent, to which the glove might be exposed.

Physical properties to consider when selecting disposable gloves are glove length, slip protection, puncture resistance, heat and flame resistance, cold protection, and comfort. These factors can vary among manufacturers. **Visually inspect gloves for defects.**

- During field work, routinely check for tears, punctures, and other flaws that can prevent the glove from being an effective shield.
- After putting the gloves on, rinse them with deionized water (DIW) while gently rubbing hands together to remove any surface residue before handling sampling equipment.

2.0.3 Blank Water and Chemical Reagents

USGS personnel are required to use the blank water that is quality assured by the USGS National Water Quality Laboratory (NWQL) and available to USGS field studies from the National Field Supply Service (NFSS) through the USGS One Stop Shopping service (*http://1stop.usgs.gov*). The NWQL provides a laboratory-certified analysis that documents the chemical composition and concentration of each lot of NFSS-supplied blank water that field personnel use to condition or rinse sampling equipment, as well as to collect quality-control samples.[5] Several grades of blank water are available from One Stop Shopping; selecting the appropriate grade depends on the sample analysis to be performed.

- **VPBW** (volatile/pesticide-grade blank water). Blank water that is suitable for collecting blank samples to be analyzed for volatile organic compounds (VOCs), pesticides, and organic carbon; purged with nitrogen gas.
  - The shelf life of an unopened bottle of VPBW for analysis of VOCs is no more than 2 weeks after VPBW has been purged of VOCs by the NWQL (purge date is listed on the bottle label). For organic compounds other than VOCs, the expiration date varies for each lot certified by the NWQL and is available to USGS personnel at *http://wwwnwql.cr.usgs.gov/qas.shtml?obw*.
  - Do not use VPBW to collect blank samples for analysis of inorganic constituents.
- **PBW** (pesticide-grade blank water). Blank water that is suitable for collecting blank samples to be analyzed for pesticides or organic carbon.
  - The expiration date varies for each lot certified by the NWQL and is available to USGS personnel at *http://wwwnwql.cr.usgs.gov/qas.shtml?obw*.
  - Do not use PBW for collecting blank samples for analysis of inorganic constituents.
- **IBW** (inorganic-grade blank water): Blank water that is suitable only for collecting blank samples that are to be analyzed for inorganic trace elements, major ions, or nutrients.
  - IBW also can be used for blank samples for dissolved organic carbon (DOC), depending on project objectives and quality-assurance plans. DOC is listed on the IBW Certificates of Analysis provided by the NWQL.
  - The expiration date varies for each lot certified by the NWQL and is available to USGS personnel at *http://wwwnwql.cr.usgs.gov/qas.shtml?ibw*.
  - Do not use IBW to collect blank samples for analysis of organic compounds.

[5] USGS personnel can access the certificates of analysis for the type and lot of blank water they are using at *http://wwwnwql.cr.usgs.gov/qas.shtml?nfssqa_certificates*.

Deionized water (DIW) produced by a USGS Water Science Center (WSC), although quality assured periodically for concentrations of organic analytes (organic-grade water or OGW) and (or) inorganic analytes (DIW and ASTM International[6] Type 1 water from other sources), **are not acceptable substitutes for VPBW, PBW, and IBW for the collection of blank samples**.

- OGW and DIW that have been quality controlled through laboratory analyses may be used as equipment-cleaning solutions, as appropriate, for the equipment to be used and as instructed in NFM 3.
- Unopened bottles of NWQL-certified inorganic and organic blank water must be stored in a location with no exposure to vehicle exhaust, cleaning fluids, or other solvents (Office of Water Quality Technical Memorandum 2009.04; technical memorandums cited in this report are listed in the section "Selected References and Technical Memoradums"). No open bottles of blank water are to be stored for later use to collect blank samples. These requirements pertain also to WSC-produced water used for sampling activities; that is, the water should be produced and stored apart from exposure to potential sources of contamination.

Chemical preservatives, standards, buffers, and other reagents and substances used in the process of water-quality field and laboratory activities are not to be used beyond the expiration date listed. Discard expired chemical substances in a manner that conforms with Federal and local regulations and good environmental stewardship.

[6] ASTM International formerly was known as American Society for Testing and Materials.

2.1 Sample Collection

Guidelines for selecting sample-collection equipment and related supplies differ, depending on the chemical nature of the target analyte and on whether samples are collected for surface water or groundwater. Routine use should be made of checklists, field forms (see NFM 6.0.1 and 6.0.2), and logbooks. Examples of checklists for sample-collection equipment and supplies are provided in section 2.4.

A bound logbook must be maintained that is dedicated to keeping calibration and maintenance records for each field-measurement, field-analysis, and multiparameter instrument. A field book in which the equipment and methods used for project activities and field-site observations are recorded also is strongly recommended. Logbooks and other records documenting field activities may be requisitioned if the project data are a likely candidate for litigation. Documentation of equipment use and extra quality-control analyses are required if study objectives or site conditions result in a departure from published USGS required and recommended procedures.

- Logbooks must be bound so that pages are not readily removable (no looseleaf notebooks); pages should be preprinted with consecutive numbers.
- Entries in logbooks or on field forms must be dated and written with ballpoint pen or a permanent, non-smudge marker **(not with pencil or liquid ink)**.
- Incorrect entries or mistakes must not be erased: draw a single line through the mistake and initial and date it.

All equipment should be maintained and tested on a regular schedule (NFM 6). For example, the calibration of thermistor and liquid-in-glass thermometers should be checked at least annually (NFM 6.1). Equipment checks, calibrations, maintenance, and repairs must be entered in the logbook.

2.1.1 Surface-Water Equipment

Study objectives, flow conditions, and structures (such as a bridge, cableway, or boat) from which sample-collection equipment (a sampler) is deployed must be considered when determining which equipment to use. **Isokinetic depth-integrating samplers** and **nonisokinetic samplers** are the primary types of surface-water samplers in common use for USGS surface-water studies. USGS personnel obtain the surface-water sampling equipment described below either from commercial sources or from the USGS Hydrologic Instrumentation Facility (HIF; *http://water.usgs.gov/hif/*).

The equipment to be selected depends on whether or not the stream can be waded. To determine whether stream depth and velocity are too great to safely wade the stream (NFM 9), field personnel are advised to use professional judgment, but **at a minimum**, should not wade in flowing water if the measured depth (in feet) of the stream, multiplied by its velocity (measured in feet per second), equals 10 or greater. Application of this rule varies among individuals according to their weight and stature and depends on streambed conditions.

RULE OF THUMB: DO NOT wade in flowing water when the product of depth (in feet) and velocity (in feet per second) equals 10 or greater.

2.1.1.A Isokinetic Depth-Integrating Samplers

An isokinetic depth-integrating sampler is designed to accumulate a representative water sample continuously and isokinetically (that is, streamwater approaching and entering the sampler intake does not change in velocity) from a vertical section of a stream while transiting the vertical at a uniform rate (ASTM International, 1999; see NFM 4, Appendix A4–A). Isokinetic depth-integrating samplers are categorized into two groups, based on the method of suspension: handheld samplers and cable-and-reel samplers.

Types and pertinent characteristics of isokinetic depth-integrating samplers recommended for sampling in flowing water are summarized in table 2–2, illustrated on figure 2–1, and described below. For detailed descriptions of isokinetic depth-integrating samplers, refer to Szalona (1982), Ward and Harr (1990), Horowitz and others (1994), Edwards and Glysson (1999), Davis and the Federal Interagency Sedimentation Project (2005), and publications and information provided by the Federal Interagency Sedimentation Project (*http://water.usgs.gov/fisp/*).

- **Operational limits for isokinetic rigid-bottle samplers:**
  - The maximum allowable transit rate (R_t) relative to mean velocity (V_m) for a given rigid-bottle sampler varies with nozzle size and sample-bottle size (equipment properties were designed using English units; refer to Conversion Factors section for conversion to metric units) (table 2–2).
  - **Do not exceed the listed R_t/V_m ratio for the given nozzle and bottle size.** A lower R_t/V_m is better for ensuring that a representative velocity-weighted sample is collected, but care must be taken to not overfill the sampler bottle.
  - **Do not exceed the maximum depth of deployment for a rigid-bottle sampler** (table 2–2).
- **Operational limits for isokinetic bag samplers:**
  - The maximum allowable transit rate to collect an isokinetic sample for all depth-integrating bag samplers is the product of 0.4 and the maximum mean stream velocity.
  - The bag-sampler intake efficiency is tested before each set of samples is collected during a site visit. Nonisokinetic samples may be collected with a bag sampler if the efficiency test and the extenuating circumstances are documented.

For collection of an isokinetic sample, the minimum mean stream mean velocity must be greater than 1.5 ft/s for a rigid-bottle depth-integrating sampler, and varies for a depth-integrating bag sampler.

Table 2–2. Isokinetic depth-integrating water-quality samplers and sampler characteristics.

[Rt, transit rate in feet per second (ft/s); V_m, mean stream velocity in the vertical being sampled, in ft/s; DH, depth-integrating handheld sampler; PN, polypropylene cap and plastic (Delrin®) nozzle; PFA, perfluoroalkoxy bottle or bag; C&N, cap and nozzle; PC, plastic coated; PT, polypropylene or PFA bottle; PDC, plastic dip coated; D, depth-integrating sampler; P, plastic nozzle; TFE, tetrafluoroethylene nozzle]

Sampler designation	Sampler construction material	Sampler dimensions[1]			Unsampled zone[2] (inches)	Suspension method	Minimum calibrated velocity, (feet per second)	Maximum calibrated velocity, (feet per second)	Maximum depth, (depth at sea level, in feet)	Sampler container size (liters)	Nozzle intake size[3] (inches)	Maximum transit rate ratio,[4] R_t/V_m
		Length (inch)	Width (inch)	Weight (pound)								
US DH-81	PN or PFA-C&N	[1]6.5	3.2	[1]0.5	[2]4	Handheld (PC)	[5]2.0 [5]1.5 [5]2.0	6.2 7.6 7.0	15 15 13.3	1 (PT)	3/16 1/4 [1]5/16	0.2 0.3 0.4
US DH-95	Bronze (PDC) with PN or PFA-C&N	22	66	29	4.8	Handheld or reel and cable	[5]2.0 1.7 2.1	6.2 7.4 7.0	15 15 13.3	1 (PT)	3/16 1/4 5/16	0.18 0.32 0.4
US DH-2	Bronze (PDC) with P or TFE nozzle	19	6	30	4	Handheld or reel and cable	[5]2.0 2.0 2.0	6.0 6.0 6.0	35 20 13	1 (P or PFA)	3/16 1/4 5/16	0.4 0.4 0.4
US D-95	Bronze (PDC) with PN or PFA-C&N	26	6.7	64	4.8	Reel and cable	[5]1.7 [5]1.7 [5]2.0	6.2 6.7 6.7	15 15 13.3	1 (PT)	3/16 1/4 [1]5/16	0.18 0.32 0.4
US D-96	Bronze (PDC) with P or TFE nozzle	35	8	132	4	Reel and cable	[5]2.0 [5]2.0 [5]2.0	12.5 12.5 12.5	110 60 39	3 (P or PFA)	3/16 1/4 5/16	0.4 0.4 0.4
US D-99	Bronze (PDC) with P or TFE nozzles	47	10	285	9.5	Reel and cable	[5]3.0 [5]3.0 [5]3.0	15 15 15	220 120 78	6 (P or PFA)	3/16 1/4 5/16	0.4 0.4 0.4

[1]Length, width, and weight will depend on specific bottle dimensions. Weight indicated is for cap and nozzle only. Handle is plastic coated with clear heat-shrinking tubing.

[2]Distance from nozzle to the channel bottom will depend on specific bottle dimensions.

[3]Nozzle sizes are those recommended for the application shown.

[4]Refer to NFM 4, appendix A, for maximum transit-rate ranges, and to Office of Surface Water Technical Memorandum 94.05, *http://water.usgs.gov/admin/memo/SW/sw94.05.html.*

[5]Pertains to water temperature greater than 27 degrees Celsius. For water temperatures less than 27 degrees Celsius refer to Office of Surface Water Technical Memorandum 2013.03 and Office of Water Quality Technical Memorandum 2013.02, "Guidelines for FISP bag sampler intake efficiency tests and operational velocities policy," and released jointly, *http://water.usgs.gov/admin/memo/QW/qw2013.02.pdf.*

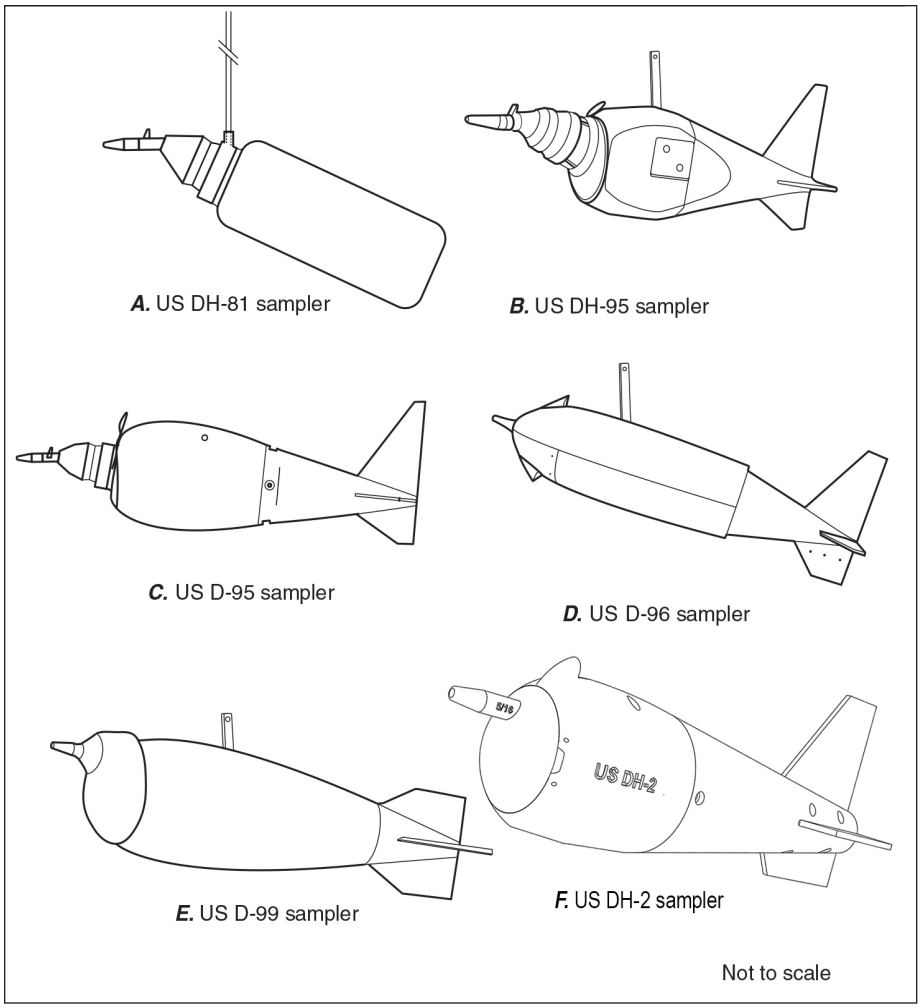


Figure 2–1. Isokinetic depth-integrating samplers: (*A*) US DH-81, (*B*) US DH-95, (*C*) US D-95, (*D*) US D-96, (*E*) US D-99, and (*F*) US DH-2. Illustrations *A*–*E* courtesy of Federal Interagency Sedimentation Project, Waterways Experiment Station, Vicksburg, Miss; illustration *F* courtesy of Carnet Technology, *carnettechnology.com*.

The cap-and-nozzle assembly is available in fluoropolymer and polypropylene materials. The same cap and nozzle can be used for the US DH-81, US DH-95, and US D-95 samplers. Owing to advances and improvements in sampler technology, and to keep abreast with data needs, sampling devices are periodically reevaluated to ensure they are appropriate for USGS data-collection activities. The US DH-81, US DH-2,7 US DH-95, US D-95, US D-96,[7] or US D-99 samplers are approved for collecting samples in flowing waters for all analyses except for samples to be analyzed for inorganic gases and VOCs (fig. 2–1). Technical Note 1 below lists samplers whose use has been discontinued by USGS water-quality personnel for the routine collection of surface-water samples.

- Water samples for which trace elements will be determined must contact only noncontaminating materials—typically a fluorocarbon polymer or polypropylene material.

[7] The US DH-2A incorporates some improvements to the DH-2, but components are interchangeable and it looks and functions identically. The US D-96A-1 is an aluminum version of the US D-96.

► Water samples for which organic compounds will be determined must contact only noncontaminating materials—typically a metal (such as stainless steel), a fluoropolymer or fluorocarbon polymer (such as Teflon®[8]), or a ceramic (such as hard-fused microcrystalline alumina).

TECHNICAL NOTE 1. Discontinued sampling devices

- The US D-77, US D-77 Bag, and Frame Bag (FB) samplers have been phased out for all USGS water-quality and sediment studies (Office of Water Quality Technical Memorandum 2002.09; see, "Selected References and Technical Memorandums").
- The US DH-48, US DH-59, US DH-76, US D-74, US P-61, US P-63, and US P-72 no longer are used for the collection of trace-element samples, but may be acceptable when sampling only for major ions, nutrients, and suspended sediments, depending on the data-quality requirements of the project. Collect additional quality-control samples if it is necessary to use any of these samplers (Horowitz and others, 1994).

Handheld samplers

Handheld samplers (table 2–3) are used to collect water samples where flowing water can be waded or where a bridge is accessible and low enough from which to suspend the sampler. The rigid-bottle sampler components (cap, nozzle, and bottle) are interchangeable. Both inorganic and organic samples can be collected with the DH series samplers (DH 81, DH 95, DH 2 (or DH 2A) provided the construction material of the sampler components (table 2–1) does not affect ambient concentrations of target analytes. Isokinetic depth-integrated samples for bacteria analysis also can be collected with these samplers because the cap, nozzle, and bottle can be autoclaved. All handheld samplers should be tested and maintained as described in table 2–3. The checklist also applies to cable-and-reel samplers.

► **When using the US DH-81 (fig. 2–1*A*) and US DH-95 (fig. 2–1*B*)**, use the 1-L bottle and adhere to the depth limit for the sampler deployment to avoid collecting a nonisokinetic sample. The depth limit depends on the nozzle diameter.

— To collect an isokinetic sample when using a 3/16-in. nozzle, flow velocity must be between 2.0 and 6.2 ft/s (~0.61 to 1.89 m/s).

— To collect an isokinetic sample when using a 1/4-in. nozzle, flow velocity must exceed 1.5 ft/s (~0.46 m/s) but be no greater than 7.6 ft/s (~2.32 m/s).

— To collect an isokinetic sample when using a 5/16-in. nozzle, flow velocity should be between 2.0 and 7.0 ft/s (~0.61 to 2.13 m/s), and depth of deployment should not exceed 13.3 ft (~4 m).

► **When using the US DH-2 (or DH-2*A*) bag sampler (fig. 2–1*F*) for isokinetic sampling:**

— Use a 3/16-, 1/4-, or 5/16-in. nozzle and mount. (Do not use the DH-2 sampler 1/8-in. nozzle.)

— The minimum flow velocity is 3.7 ft/s for the 3/16-in. nozzle when the water temperature is less than 27 °C and for the 1/4- and 5/16-in. nozzles when the water temperature is less than 10 °C. Make sure that flow velocity is no greater than 6 ft/s (~1.83 m/s). The minimum flow velocity is 2 ft/s for the 3/16-, 1/4-, and 5/16-in. nozzles when the water temperature is greater than 27 °C.

— Use in water with a maximum depth between 13 and 35 ft (~3.96 to 10.67 m), depending on nozzle diameter, for an isokinetic, depth-integrated sample.

— Water temperature must be equal to or greater than 4 °C.

[8] Teflon is a registered trademark of the DuPont Corporation.

Table 2–3. Pre-field checklist for handheld and cable-and-reel samplers.

Sampler Checklist	Comment
Mechanical operation	Test the working condition of the sampler. If tailfin is damaged or broken, sampler will not swim correctly.
Nozzles	Replace nozzles that have burrs or are damaged. Use only nozzles purchased from the Federal Interagency Sedimentation Project (*http://water.usgs.gov/fisp/*).
Plastic coating	If plastic coating is damaged or any metal parts are exposed, recoat or touch up with a plastic dip product.
Cleanliness of sampler	Before field work, clean appropriate parts of the sampler according to procedures described in NFM 3 and store parts in plastic for transport to the field site.
Laboratory results from analysis of the sampler and equipment blank(s)	Make sure the sampler has been quality assured with an annual equipment blank and certified for water-quality use (see NFM 1 and NFM 4).
Have separate sets of sampler components and backup equipment available	If at all feasible, for a given field trip when collecting multiple water samples, prepare and use separate sets of sampler bottles, caps, and nozzles for each sampling site. Have backup equipment available onsite.
Have field-cleaning supplies and blank water available	If separate sets of sampler components are not available, then clean equipment between sampling sites (see NFM 3) and be prepared to process the number of field blanks needed to document that equipment was adequately cleaned.

Cable-and-reel samplers

Cable-and-reel samplers are used to collect water samples where flowing water should not be waded. These include the US D-95 bottle sampler and the US D-96 and US D-99 bag samplers. (Refer to table 2–2 for sampler characteristics and sampling limitations.) Like the handheld US DH-81, US DH-2, and US DH-95, these cable-and-reel samplers can be used to collect inorganic and organic samples; however, appropriate sampler components (cap, nozzle, and bottle or bag) must be selected so as not to bias concentrations of target analytes. Isokinetic, depth-integrated samples collected for the analysis of bacteria also can be collected with these samplers because the cap, nozzle, bottle, and bags can be autoclaved.

The US D-96 bag sampler uses a perfluoroalkoxy (PFA) or polyethylene bag that is placed in a sliding tray that supports the bag and holds the nozzle holder with nozzle in place. The bag is attached to the nozzle holder with a hook-and-loop (for example, Velcro®) strap. The US D-99 bag sampler uses a 6-L PFA or polyethylene bag that is placed in a chamber behind the nozzle, through an access door.

Metal parts of the US D-95 bottle sampler and the US DH-2 bag, US D-96 bag, and US D-99 bag samplers must be coated with plastic (for example, Plasti Dip®) and recoated periodically to prevent possible sample contamination from metallic surfaces. **All cable-and-reel samplers should be tested and receive any necessary maintenance before use, as described in table 2–3**.

► **When using the US D-95 bottle sampler (fig. 2–1*C*):**

— Use a 3/16-, 1/4-, or 5/16-in. nozzle. US DH-81 and US DH-95 nozzles can be used.

— Make sure that flow velocity exceeds 1.7 ft/s (~0.52 m/s), but is no greater than 6.7 ft/s (~2.04 m/s), depending on the nozzle diameter used.

— Use in water less than 13.3 to 15 ft (~4 to 4.6 m) deep (at sea level)—depending on the nozzle used and the altitude at the site—for an isokinetic, depth-integrated sample.

- **When using the US D-96 bag sampler (fig. 2–1*D*):**
  - Use only the 3/16-, 1/4-, or 5/16-in. nozzles designed specifically for this sampler.. The nozzles needed are unique to the D-96 sampler and mounts.
  - The minimum flow velocity is 3.7 ft/s for the 3/16-in. nozzle when the water temperature is less than 27 °C and for the 1/4- and 5/16-in. nozzles when the water temperature is less than 10 °C. Make sure that flow velocity is no greater than 12.5 ft/s (~3.8 m/s)
  - Use in water with a maximum depth of 39 to 110 ft (~11.9 to 33.5 m), depending on the nozzle diameter for an isokinetic, depth-integrated sample.
  - Water temperature must be equal to or greater than 4 °C. The sampler has been tested at temperatures equal to or greater than 4 °C and found to function properly, provided the flow velocities are greater than the minimums noted above.
- **When using the US D-99 bag sampler (fig. 2–1*E*) for isokinetic sampling:**
  - Use a 3/16-, 1/4-, or 5/16-in. nozzle and mount. (Do not use a 1/8-in. nozzle that is designed for the D-99 sampler.)
  - The minimum flow velocity is 4.0 ft/s for the 3/16-in. nozzle when the water temperature is greater than 4 °C. The minimum flow velocity for the 1/4- and 5/16-in. nozzles is 3 ft/s when the water temperature is greater than 27 °C, and 3.7 ft/s when the water temperature is less than 10 °C. Be sure that flow velocity is no greater than 12.5 ft/s (~3.8 m/s).
  - Use in water with a maximum depth of 78 to 220 ft (~23.8 to 67 m), depending on nozzle diameter, for an isokinetic, depth-integrated sample.
  - Water temperature must be equal to or greater than 4 °C.

2.1.1.B Nonisokinetic Samplers

Nonisokinetic samplers are sampling devices in which the sample enters the device at a velocity that differs from ambient stream velocity. All of the isokinetic samplers described in 2.1.1.A can be used to collect depth-integrated, although nonisokinetic, samples, when used beyond the minimum and maximum ranges of velocity and depth (table 2–2). When collecting a nonisokinetic sample, the sampler intake should not enter the unsampled zone. As with all samplers, the materials that contact the sample must not bias concentrations of target analytes by sorbing or leaching target analytes.

Open-mouth samplers

Open-mouth samplers used for the collection of water samples include the handheld bottle, the weighted-bottle sampler, the biochemical oxygen demand (BOD) sampler, and the VOC sampler (fig. 2–2).

- **The handheld bottle sampler** is the simplest type of open-mouth sampler. A bottle is dipped to collect a sample (fig. 2–2*A*) where depth and velocity are less than the minimum required for depth-integrating samplers.
- **The weighted-bottle sampler** is available in stainless steel (US WBH-96) (fig. 2–2*B*) or polyvinyl chloride. The weighted-bottle sampler can be used to collect samples where flow velocities do not meet the minimum requirement for isokinetic depth-integrating samplers and where the water body is

too deep to wade. An open bottle is inserted into a weighted holder that is attached to a handline for lowering. Sampling depth is restricted by the capacity of the bottle and the rate of filling.

► **The BOD sampler** and the VOC sampler (fig. 2–2 *C–D*, respectively), are open-mouth samplers designed to collect non-aerated samples.

— The BOD sampler accommodates 300-mL glass BOD bottles specifically designed to collect non-aerated samples for dissolved-oxygen determination (American Public Health Association and others, 1992, p. 4–99).

— The VOC sampler is specifically designed to collect non-aerated samples in 40-mL glass septum vials for determination of VOCs.

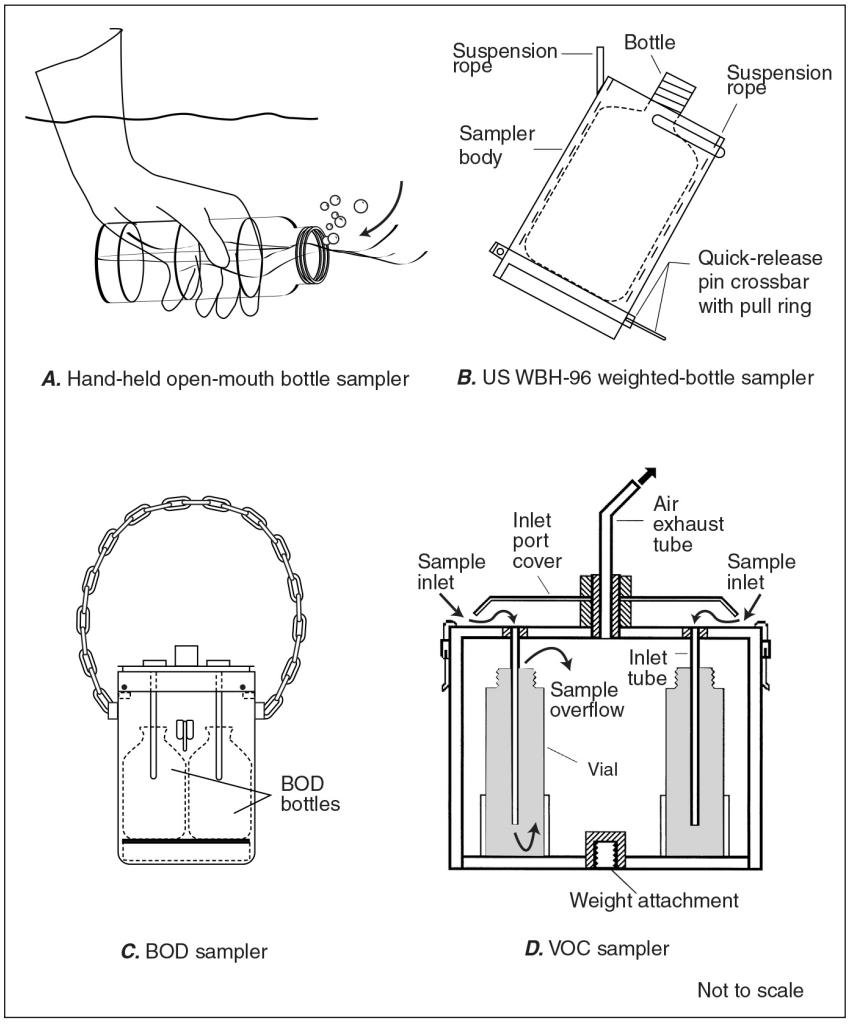


Figure 2–2. Nonisokinetic open-mouth samplers: (*A*) handheld open-mouth bottle sampler, (*B*) US WBH-96 weighted-bottle sampler, (*C*) biochemical oxygen demand (BOD) sampler, and (*D*) volatile organic compound (VOC) sampler. *A*, from U.S. Environmental Protection Agency, 1982b; B, courtesy of Federal Interagency Sedimentation Project, Waterways Experiment Station, Vicksburg, Miss.; *C*, published with permission of Wildlife Supply Company; *D*, from Shelton (1997).

Thief samplers

Thief samplers are used to collect instantaneous discrete samples. Thief samplers have been used primarily to collect samples from lakes, reservoirs, and some areas of estuaries. Smaller versions, designed to collect groundwater samples, also have been used in still and flowing surface water. The most commonly used thief samplers are the Kemmerer sampler, Van Dorn sampler, and double check-valve bailer with bottom-emptying device (fig. 2–3). These samplers are available in various sizes and mechanical configurations, and in various types of construction material (such as stainless steel, glass, polyvinyl chloride, fluorocarbon polymer). Disposable fluorocarbon polymer bailers also are available. For descriptions of additional thief samplers, see U.S. Environmental Protection Agency (1982b), Ward and Harr (1990), and American Public Health Association and others (1992), or consult the manufacturer of the environmental sampling equipment.

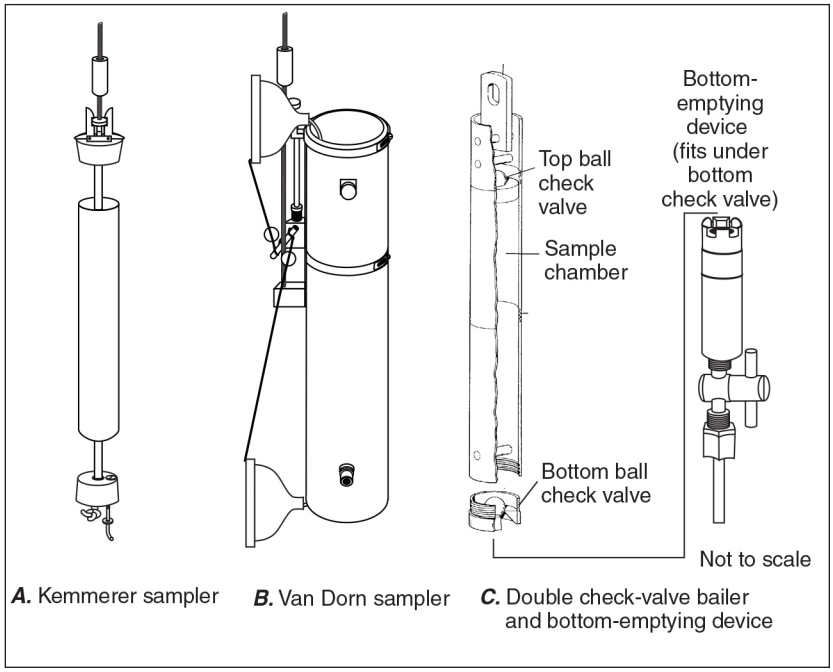


Figure 2–3. Nonisokinetic thief samplers: (*A*) Kemmerer sampler, (*B*) Van Dorn sampler, and (*C*) double check-valve bailer with bottom-emptying device. *A* and *B*, from the American Public Health Association and others (1992); used with permission. *C*, published with permission of Timco Manufacturing Inc.

Single-stage samplers

Single-stage samplers such as the US U-59 (fig. 2–4*A*) are designed to obtain suspended-sediment samples from streams at remote sites or at streams where rapid changes in stage make it impractical to use a conventional isokinetic, depth-integrating sampler. Single-stage samplers can be mounted above each other to collect samples from various elevations or times as streamflow increases and the hydrograph rises (fig. 2–4*B*) (Edwards and Glysson, 1999).

- **The US U-59** is a sample container mounted to collect a water sample as stage rises above the sampler intake.
  - The vertical-intake sampler is used to sample streams carrying sediments finer than 0.062 millimeter (mm). When compared to a horizontal-type intake, the vertical intake is less likely to become clogged or fouled by floating solid materials.
  - The horizontal-intake sampler is used to sample streams carrying sediment coarser than 0.062 mm.
- **The US U-73**, which can be used to sample water during either rising or falling stage, is constructed to provide some protection from trash or other solids that could clog or foul the intake.

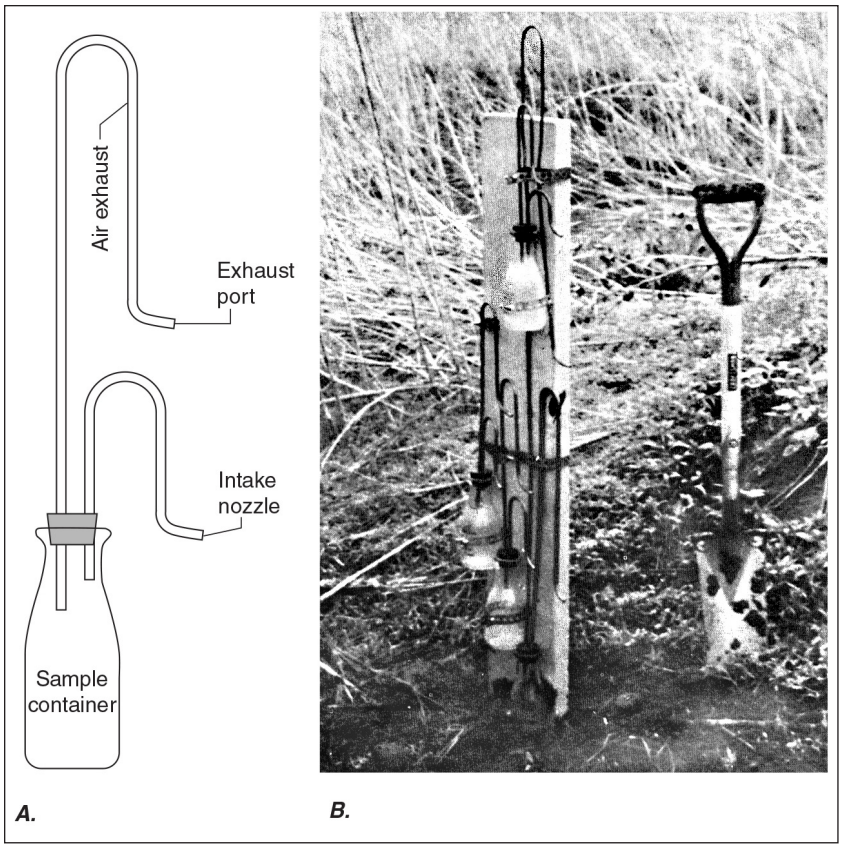


Figure 2–4. US U-59 sampler: (*A*) single stage and (*B*) a bank of U-59 samplers installed on a plank post. *A*, from Edwards and Glysson (1999); *B*, photograph by J.C. Mundorff, U.S. Geological Survey.

Automatic samplers and pumps

Automatic pumping samplers (autosamplers) with fixed-depth intake(s)[9] can be used to collect samples at remote sites; from ephemeral, small streams; or from urban storm drains where stage rises quickly (American Public Health Association and others, 1992; Edwards and Glysson, 1999). These samplers can be programmed to collect samples under a combination or variety of conditions such as precipitation, stage, or discharge. Samples from automatic samplers or pumps are considered point-integrated samples.[10]

Pumps used for water sampling are grouped into two general categories: suction-lift pumps and submersible pumps. Pumps can be used to collect water samples from lakes, reservoirs, and estuaries (Radtke and others, 1984; Radtke, 1985; Ward and Harr, 1990). Suction-lift and submersible pumps are described in section 2.1.2, "Groundwater Equipment."

2.1.1.C Support Equipment

Clean Hands/Dirty Hands techniques, described in NFM 4, are required when sampling for trace elements (Horowitz and others, 1994) and are recommended as a general practice in sample collection, particularly when using heavy-duty support equipment.

Much of the equipment used to measure streamflow also can be used as support equipment when collecting water samples in water bodies that cannot be waded. Examples of commonly used support equipment are listed in section 2.4 near the end of this chapter.

Use of a vertical transit rate pacer, such as the US VTP-99 or the variable speed reel-drive system, can help to ensure an accurate flow-weighted sample after the appropriate transit rate has been determined (Office of Water Quality Technical Memorandum 2013.02; Edwards and Glysson, 1999, p. 53–60). Once programmed, the pacer produces an audible signal for pacing the raising and lowering of either handheld or mechanically hoisted samplers. The pacer is small enough to be carried in a shirt pocket, and the tone is audible for several feet in a quiet environment. The US VTP-99 can be used with a miniature phone-type monaural headphone jack; neither the jack nor the headphones are supplied. Tables for using the pacer when sampling with either a handheld sampler or a type "A," "B," or "E" reel can be found in the publication "Using the US VTP-99 vertical transit rate pacer."[11]

The variable speed reel-drive system consists of a variable speed electric motor that is mounted to a crane or boom. A pair of V-belts drives a B–56 or E–53 reel at a constant user-selected speed in both the up and down directions. The system includes an operator control that displays the selected speed, actual speed, direction, cable length deployed, and battery voltage.

Exercise great care to avoid sample contamination when handling support equipment for samplers used to collect trace-element samples.

[9] Automatic pumping samplers are available through commercial manufacturers, such as Hach Company Sigma samplers (www.Hach.com),Teledyne Isco, Inc. (http://www.isco.com), and Manning Environmental,Inc. (*http://www.manningenvironmental.com*).

[10] Periodically scan the National Field Manual Comments and Errata page (*http://water.usgs.gov/owq/FieldManual/mastererrata.html*) for chapters NFM 2 and NFM 44 for updates on automatic samplers (autosamplers) guidance.

[11] The publication is available at *http://water.usgs.gov/fisp/docs/Instructions_US_VTP-99_990722.pdf*.

2.1.2 Groundwater Equipment

The type of sampler or sampling system selected for collecting groundwater samples depends on the type and location of a well, the depth to water from land surface, physical characteristics of the well, groundwater chemistry, and the analytes targeted for study. Selecting the appropriate equipment for collecting groundwater samples is important in order to obtain data that will meet study objectives and data-quality requirements. Groundwater sampling equipment is available from a variety of commercial sources. Support equipment (for example, tubing, valves, manifolds) is available commercially or, for USGS personnel, through the USGS Hydrologic Instrumentation Facility (HIF).

Groundwater most commonly is collected using either pumps designed specifically for water sampling from monitoring wells, pumps installed in supply wells, or a bailer or other point or thief-type sampler.[12] General considerations for selecting groundwater equipment are listed in table 2–4.

- Monitoring wells: Samplers can be portable, dedicated, or permanently installed in the well.
  - Portable equipment is commonly used at multiple well sites and cleaned after each use.
  - Portable samplers and sample tubing commonly are dedicated to a site with large contaminant concentrations.
  - Some types of portable equipment can be installed in a well for the duration of the monitoring program. Remove the sampler from the well periodically for cleaning.
- Supply wells (for domestic, municipal, industrial or commercial, or agricultural use): Equipment selection is limited, as supply wells normally are equipped with permanent, large-capacity pumps.
  - Choice of equipment usually depends on well configuration and type of pump installation (permanent or temporary).
  - Modifications to the well and ancillary equipment attached at the wellhead are necessary in some cases (see section 2.1.2.A.)

Sampling equipment must not be a source of contamination or otherwise affect analyte concentration (table 2–1). Of specific importance for groundwater sampling is a potential change in groundwater chemistry due to atmospheric exposure.

- Select equipment that minimizes sample aeration.
- Select equipment that will not leach nor sorb significant concentrations of the target analytes, with respect to data-quality requirements.
  - Submersible pumps that tested successfully[13] for inorganic constituents[14] included the Grundfos Redi-Flo2®, Fultz SP-300, Bennett, and several types of bladder pumps with Teflon® bladders.

[12] Sampling equipment not described in this report includes multilevel collection systems (LeBlanc and others, 1991; Smith and others, 1991; Gibs and others, 1993); samplers designed to collect groundwater under natural-gradient flow conditions (Margaritz and others, 1989; Vroblesky, 2001a); and pump-and-packer systems.

[13] Unpublished results of testing by the USGS in 1994 confirmed that commonly used sampling equipment with fluorocarbon polymer interior parts does not, in general, affect sample concentrations of inorganic constituents or organic compounds (U.S. Geological Survey Office of Water Quality, written commun., 1994) after being precleaned according to NFM 3 protocols and fitted with new, cleaned tubing. Water-quality sampling equipment developed or modified since the 1994 testing have not been similarly evaluated. USGS projects are directed to collect presampling equipment blanks to quality assure the appropriateness of the equipment to be used to produce samples of the quality required by the project.

[14] Trace-element concentrations in blank samples processed through these samplers were within the margin of analytical variability at a method reporting level of 1 microgram per liter.

Double-check-valve fluorocarbon polymer bailers also were found to be capable of producing uncontaminated samples for inorganic analyses.

— Samplers tested that achieved a greater than 95-percent recovery of VOCs included Grundfos Redi-Flo2®, Fultz SP-300, bladder pumps, and the Bennett pump.

— Double-check-valve fluorocarbon polymer bailers scored a less than 95-percent recovery of known analyte concentrations, particularly for VOCs (U.S. Geological Survey, 1992a,b).

Choice of equipment is constrained by many factors, including equipment construction and equipment specifications. For example, it is necessary to consider power requirements, lift capability, and discharge capacity of submersible pumps. Ideal equipment for sample collection might not exist, and compromise is often necessary. **Field personnel must understand the application, advantages, disadvantages, and limitations of the available equipment, with respect to study objectives and site characteristics, and must document how any compromises made might affect the data and data-quality objectives.**

Table 2–4. General requirements and considerations for selecting groundwater sampling equipment (thief samplers and pumps).

Requirements	Considerations
Construction materials	• Is the sampler constructed from materials that (initially or over time) could leach targeted analytes? If left in the well, is the sampler constructed of materials that will degrade appreciably within the lifetime of the study? • Can the sampler be cleaned? Can it withstand the level of decontamination needed and subsequently produce clean equipment blanks?
Operation, capabilities, and limitations	• Could operation of the sampler compromise sample integrity with respect to study objectives or data quality? For example, does the sampler heat or aerate the sample, or subject the sample to negative pressure, leading to volatilization of purgeable organic compounds, oxidation of target analytes, or changes in partial pressure of carbon dioxide or other gases? • Is the sampler capable of evacuating standing water (that is, can it be used for purging in addition to sample collection)? • Is the sampler capable of providing flow or sample volumes sufficient for sample collection and in a manner that minimizes suspension of sediments or colloids that could bias chemical measurements? • Is the sampler mechanically capable of withdrawing formation water from the desired depth?
Power requirements	• What are the power requirements of the sampler or the manner in which it will be deployed? Will it require electrical power (alternating or direct current), gasoline or other fuel-powered generators, or compressed gas such as air or nitrogen? • Will the capacity of the power source be sufficient to allow the sampler to run continuously throughout purging and sample collection? • Could the power source contaminate samples? (For example, gasoline-powered generators or compressors are a potential source of volatile organic compounds.) • Could the fuel be changed to a noncontaminating type (for example, convert a gasoline-powered generator to propane fuel)?
Transport	Is the sampler easily transported to remote sites and rugged enough for field use?
Sampler repair	Can the sampler be repaired in the field?
Availability and cost	• Are the available samplers suitable for study use? Are funds available to purchase, operate, and maintain the sampler? • Are funds available to purchase a spare pump head (or other equipment)? This would allow for sampling to continue while, for example, one pump head is being repaired.

2.1.2.A Pumps

Pumps transport water from depth to land surface either by suction lift or positive pressure.[15] The pumping mechanism for most suction-lift pumps (peristaltic, jet, and some nonsubmersible centrifugal pumps) is at land surface. Positive-pressure pumps (helical rotor, gear, bladder, piston, inertial submersible, and centrifugal) are grouped together as submersible pumps because they are placed below the static water level.

Supply-well pumps

Centrifugal and jet (venturi) pumps (fig. 2–5) that have the pumping mechanism above land surface, as well as high-capacity submersible pumps and turbine pumps, are common in domestic, municipal, and other supply wells.

- **Note that large- and small-capacity pumps used in supply wells can affect analyte concentrations** (see NFM 1 and Lapham and others, 1997).
  - Erroneous data produced as a result of using these pumps are most likely for dissolved gases, VOCs, and reduction-oxidation (redox) chemical species.
  - Oil in the water column is common for oil-lubricated pumps.
  - Chemical treatment systems, pressure tanks, and holding tanks can compromise sample integrity.
- Install a hookup system for transfer of sample from the wellhead to the chamber or the area where samples will be processed (NFM 4 and 5). Clean such equipment to remove oils and other manufacturing and shipping residues (NFM 3) before use.
  - Ensure that the point of sample discharge from the hookup system on supply wells is ahead of chemical treatments or holding tanks. Obtain permission to modify the discharge point by installing a spigot or other plumbing appropriate to preserve the quality of the sample, if possible. Otherwise, do not use the well. The spigot or other plumbing also must be cleaned before use.
  - Install an anti-backsiphon device in line with the hookup system.
  - Install an optional needle valve with flow-regulating capabilities in line with the hookup system (fig. 2–6*A*).

[15] For more detailed information on pumps, refer to manufacturers' instructions and specifications and to U.S. Environmental Protection Agency (1982b), Morrison (1983), Driscoll (1986), Imbrigiotta and others (1988), Ward and Harr (1990), American Public Health Association and others (1992), Gibs and others (1993), Sandstrom (1995), Koterba and others (1995), and Edwards and Glysson (1999).

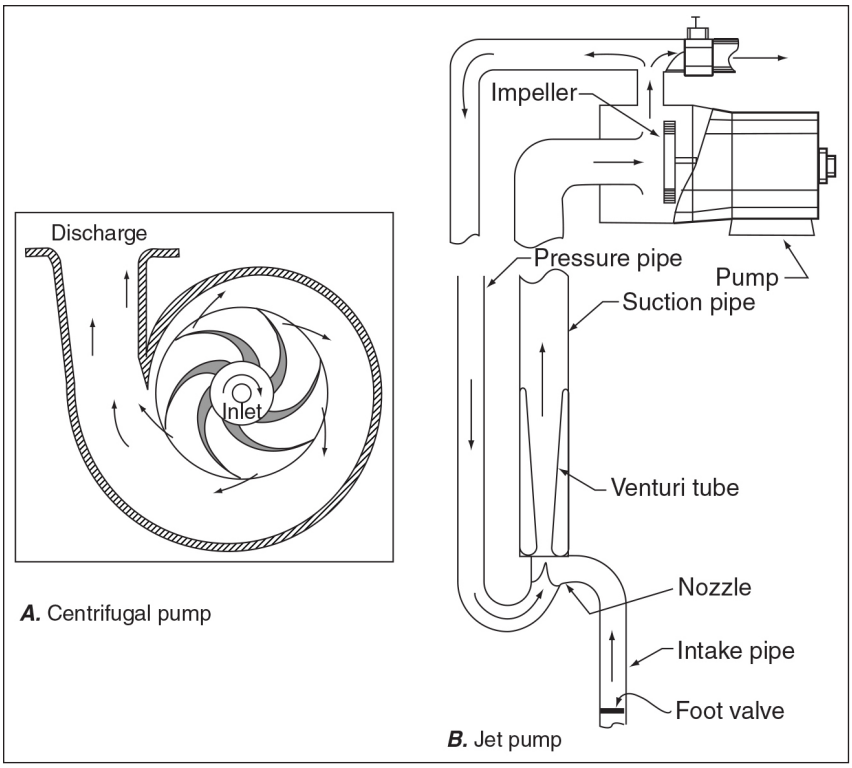
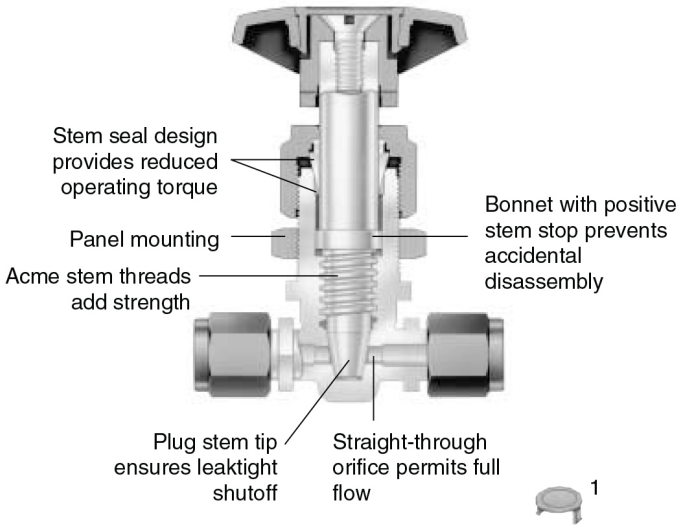


Figure 2–5. Above-land-surface pumps typically used to obtain water from supply wells are the (*A*) centrifugal pump and (*B*) jet pump. From Driscoll (1986); published with permission of US Filter/Johnson Screens.

A. Swagelok® PFA Needle Valve number PFA-4RPS8 (fits 1/2-inch tubing)



B. Materials of Construction

Component	Material Grade/ASTM Specification
1 Handle insert	PFA 440-HP/ D3307
2 Screw	
3 Handle	
4 Packing nut	
5 Upper packing	
6 *Lower packing*	
7 *Stem stop*	
8 Panel nut	
9 *Stem*	
10 *Body, ferrules*	
11 Nut	
Lubricant	PTFE based

Wetted components listed in *italics*.

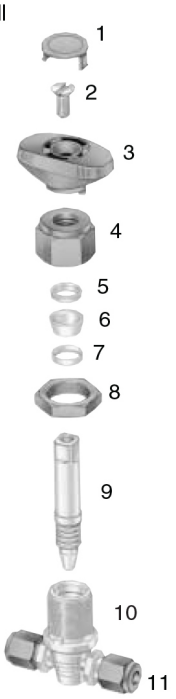


Figure 2–6. Swagelok® perfluoroalkoxy needle valve showing (*A*) front view and (*B*) exploded view.

Monitoring-well pumps

Suction-lift and positive-displacement pumps are commonly used to collect water samples from monitor (monitoring) wells. Field personnel should consider the criteria and guidelines listed in tables 2–4 and 2–5 when selecting a pump for sampling from monitoring wells.

- Suction-lift pumps create a vacuum in the intake line that draws the sample up to land surface (fig. 2–7*A*).
  - The vacuum can result in the loss of dissolved gases and VOCs.
  - Intake tubing could diffuse atmospheric gases sufficiently to affect some target analytes unless thick-walled low-diffusion tubing is used.
  - Use of a peristaltic pump (1- to 2-L/min pumping rate) is limited to wells in which depth to water is less than about 25 ft (~9 m). The operation lift may be as small as 20 ft.
  - Peristaltic pumps have the advantages of few moving parts, easily replaceable tubing and heads, and portability.
  - Provided that data quality is not compromised, properly operated peristaltic pumps can be used to obtain samples from shallow wells, especially those that produce small volumes of water.
- Submersible pumps (positive pressure or other types of positive-displacement pumps) designed specifically for the collection of water samples from monitoring wells are preferred, generally, because they do not create a vacuum (fig. 2–7*B–F*).
  - Install an anti-backsiphon device in-line (on top of the pump before the tubing connection) to prevent backflow from contaminating the groundwater.
  - Select suitable materials for sample line, sample-line connectors (see “Pump Tubing,” section 2.2.4), and sample-line reels (see “Support Equipment,” section 2.1.2.C, and “Checklists for Equipment and Supplies,” section 2.4) for use with submersible pumps.
- The suitability and application of commonly used submersible pumps depends on pump and well characteristics and on practical constraints (tables 2–4 and 2–5). Determine that:
  - The rate of pumping is suitable for a given lift (table 2–5).
  - The maximum lift of the pump at the water surface is greater than the lift to land surface.
  - The power source and pump characteristics are sufficient to allow the pump to run continuously throughout purging and sample collection.
  - The height of the water column must be at least 5 ft above the top of the submersible pump (to avoid setting the pump intake too close to the bottom of the well).
  - The pumping rate will not cause excessive drawdown, which could result in the intersection of the water level with the well screen or open interval or causing the well to go dry.

Portability and repairability are important logistical considerations when selecting a pump.

- Portability. The pumps shown in figure 2–7 are made for transport to and from the field, but fuel or electrical power requirements make some more awkward to transport and to operate at remote sites than others (not shown is the inertial-lift pump, which has no fuel or electrical power requirement when operated manually).
- Repairability:
  - Ruptured bladders for bladder pumps can be replaced easily in the field.
  - Fluorocarbon polymer impellers used in gear pumps are easily abraded and can be ruined by particulate-laden water. Such impellers can be replaced in the field, but usually with some difficulty.
  - Submersible centrifugal pumps and piston pumps generally are not easily repaired in the field. Such pumps, however, include features such as variable-speed capability that make them favored for many applications.
  - When selecting a pump for sampling, consider purchasing an additional pump head (the submerged motor component), because most repairs involve the pump head. The pump heads for some pump types or models (such as the Fultz pump) are constructed for quick connect and disconnect to ease pump head replacement under field conditions.

Table 2–5. Examples of pump capability as a function of well and pump characteristics in a 2-inch-diameter well.

[Table modified from Koterba and others (1995), p. 18–19; ft, foot; m, meter; gal, gallon; L, liter; TDH, total dynamic head; gal/min, gallon per minute; L/min, liter per minute; ~, approximately; ---, not available]

Well Characteristics			Pump Characteristics			
			Fultz SP-400: Lift capacity is exceeded at ~150 ft (~45.7 m)		Grundfos RediFlo2®: Lift capacity is exceeded at ~260 ft (~76.2 m)	
Water-column height, in ft (m)	Lift or TDH,[1] in ft (m)	Three-well-volume purge protocol,[2] in gal (L)	Pumping rate at lift or TDH shown, in gal/min (L/min)	Maximum volume after 2 hours of pumping,[3] in gal (L)	Pumping rate at lift or TDH shown, in gal/min (L/min)	Maximum volume after 2 hours of pumping, in gal (L)
20 (~6.1)	25 (~7.6)	10 (37.85)	1.0 (3.785)	120 (~454)	7.0 (~26.5)	840 (~3,179)
40 (~12.2)	160 (~48.7)	20 (75.7)	---	---	~4.8 (~18.2)	538 (~2,036)

[1]In these examples the lift is equivalent to TDH and is estimated as the depth to water in the well (see Koterba and others, 1995, for more information).

[2]Standard procedure is to purge a minimum of three well volumes while monitoring field measurements (NFM 4, NFM 6): purge volume = $V=0.0408HD^2$, where H is water-column height (in feet) and D is the well diameter (in inches).

[3]Maximum pumped volume is calculated from the pumping rate for a given pump system (from manufacturer's specifications) at the lift (or TDH) multiplied by an assumed total purging time of 2 hours (Koterba and others, 1995).

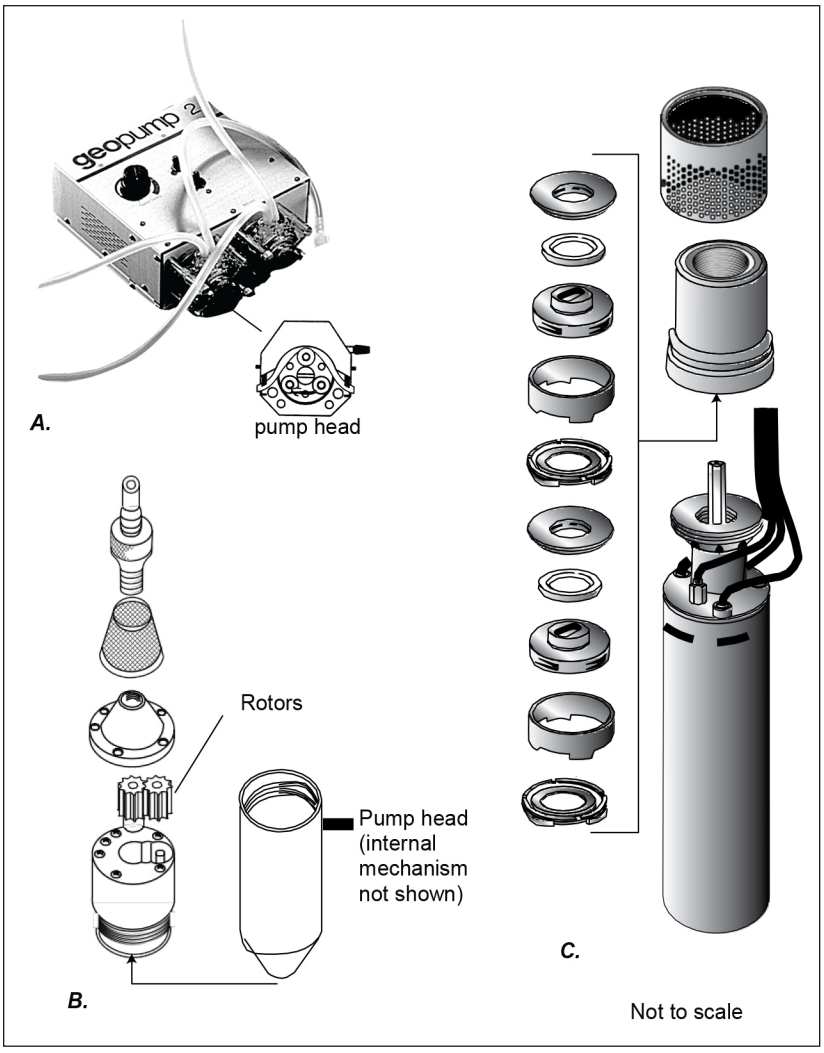


Figure 2–7a. Pumps typically used for withdrawal of water samples from monitoring wells: (*A*) peristaltic suction-lift pump and (*B–F*) examples of submersible positive-displacement pumps. *A*, peristaltic pump showing detail of pump head. *B*, electrical gear or rotor pump. *C*, electrical centrifugal impeller pump showing detail of impeller assembly. Illustrations published with permission: *A*, GeoTech Environmental Equipment, Inc., with pump head from Cole Parmer Instrument Company; *B*, Fultz Pumps, Inc.; *C*, Grundfos Pumps Corporation.

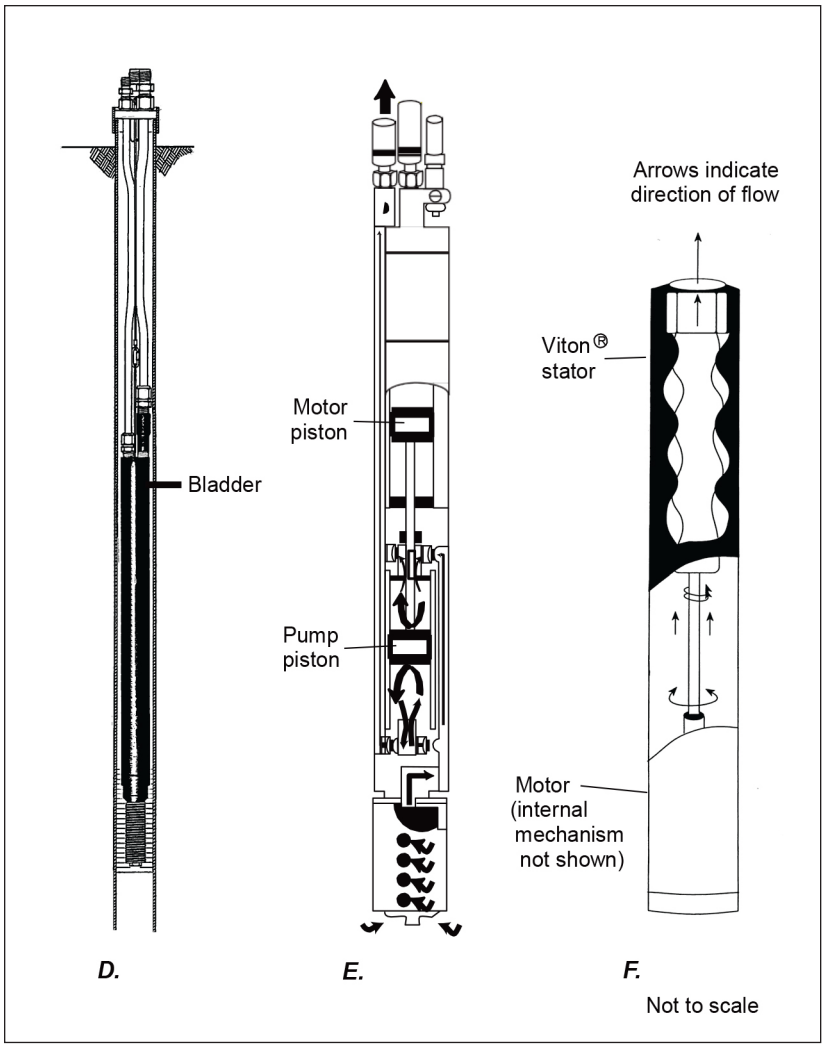


Figure 2–7b. Pumps typically used for withdrawal of water samples from monitoring wells: (*A*) peristaltic suction-lift pump and (*B–F*) examples of submersible positive-displacement pumps. (*D*) bladder pump, (*E*) reciprocating piston pump, and (*F*) progressive cavity pump. Illustrations published with permission: *D* and *F*, Geotech Environmental Equipment, Inc.; *E*, Bennett Sample Pumps, Inc.

Well-development pumps

Wells need to be developed after construction to remove sediment and other debris at the bottom of the well and to improve hydraulic connection to the aquifer. Wells might need to be redeveloped after long periods of inactivity before water-quality samples are collected. Sounding of the well (confirming the well depth) may indicate that the well should be redeveloped in preparation for collecting a representative sample.

- In general, the submersible pump that is used to purge and sample the well is not recommended for well development or redevelopment. Using the sampling pump to redevelop a well can ruin or shorten its functional life and (or) damage the smooth internal surfaces of the pump, which in turn can result in leaching of target analytes to the sample, thus causing an analytical bias (Lapham and others, 1997).

- Inertial pumps can be fitted with a surge block to provide an effective and easily operated method for well development or redevelopment (*http://www.waterra.com/pages/Applications/well_develop2011.html*; *http://www.solinst.com/Text/textprod/404text.html*).
  - Adding a surge block to an inertial pump creates a strong bidirectional churning effect that helps to remove sediment that collected at the bottom of the well.
  - Inertial pumps work well in silty/sandy environments; they can be successfully operated in wells with depths to 100 ft (~30.6 m) when using a hand pump, depths to 200 ft (~61 m) when using a pump powered by an electric motor, and depths to 250 ft (~76 m) when using a pump powered by a gasoline motor (Lapham and others, 1995; Waterra Pumps Limited, 2011; Solinst Canada Ltd., 2012.
- Another inexpensive option to consider in well development is to use inexpensive disposable plastic (clear or white) tubing with a suction-lift pump. This method, however, is limited to shallow wells with water table depths less than 25 ft (~7.6 m) from the land surface (Lapham and others, 1995).
  - To aid in removing sediments from the bottom of the well, add a surge block and one-way valve to the bottom of the tubing as described above. The tubing can be physically raised and lowered, producing a purging effect.
  - To prevent cross contamination of wells, it is recommended that new tubing and a new surge block and valve be used and quality-assured for each well that is developed or redeveloped.
- Wells can also be developed using the air/gas-lift method. This method is not recommended for shallow wells, but may be the only method available for very deep wells, especially for wells that approach 2,000 ft (~610 m) in depth (Lapham and others, 1995).
  - In this method, compressed air is forced down the well and replaces the water and debris in the casing. The displaced water and debris in the well casing is then forced up and out of the well.
  - **Air introduced into the aquifer can change the aquifer's geochemistry, either temporarily or permanently.** Ensure that air is not forced from the well screen into the surrounding aquifer system by determining the volume of water to be displaced, slowly removing and monitoring the volume being displaced, and halting the process when the required volume of water has been removed. This should be followed by pumping at least one well volume upon recovery of the water level in the well while monitoring the concentration of dissolved oxygen.

2.1.2.B Bailers, Thief Samplers, and Passive Diffusion Bag Samplers

Bailers and other thief samplers disturb the water column, especially when raised and lowered repeatedly; for this reason, use of these devices is not recommended. The disturbance can stir up or mobilize particulate matter, including colloidal or mineral precipitates that are artifacts of well construction and are not part of the ambient groundwater flow. This, in turn, can result in the analysis of substantially greater than ambient concentrations of trace elements and hydrophobic organic compound(s). Passive diffusion bag (PDB) samplers do not disturb the water column.

Bailers and thief samplers

Although bailers are not, in general, recommended for groundwater sampling because of the potential aeration of the sample, bailers can have some necessary and useful applications and may be the only

sampling option, especially when sampling at great depth. Use of a bailer may be preferred, for example, for sampling sites at which contaminant concentrations are extremely large, because bailers are easier to clean or are disposable and less expensive to replace than pumps. **The following recommendations apply in situations where bailers are a reasonable choice for collecting samples at wells.**

- Select bailers with double check valves (fig. 2–3*C*) to ensure that a point sample has been collected and to help prevent sample aeration. The material of choice normally is fluorocarbon polymer (Teflon®) because it can be used when sampling for both inorganic and organic analytes and it can be readily cleaned.
- Consider using disposable fluorocarbon polymer bailers at sites where concentrations of contaminants are large. Discard disposable equipment after one use.
- Use a bottom-emptying device through which the rate of sample flow can be controlled. Place the bailer into a holding stand while emptying sample from the bailer through the bottom-emptying tube.
- Use either a fluorocarbon polymer-coated or colorless (white) polypropylene line for lowering the sample; keep the line on a reel. Polypropylene is easy to clean, inexpensive, and can be discarded after one use.

Specialized sealed downhole samplers, grouped loosely under the thief-sampler category (fig. 2–3), are designed to capture and preserve in situ groundwater conditions by precluding sample aeration and pressure changes from sample degassing (escape of VOCs) or outgassing (escape of inorganic gases). Such sampling equipment includes syringe samplers (Gillham, 1982), true thief samplers (Ficken, 1988), samplers using hermetic isolation methods (Gibs and others, 1993; Torstensson and Petsonk, 1988), and a combined well-bore flow and depth-dependent water sampler (Izbicki and others, 1999).

Passive diffusion bag samplers

Water-filled passive diffusion bag samplers (PDBs) are suitable for obtaining samples to be analyzed for selected VOCs.[16] A typical PDB sampler consists of a low-density polyethylene (LDPE) lay-flat tube closed at both ends and containing deionized water. The sampler is positioned at the target horizon of the well by attachment to a weighted line or fixed pipe. Sampler construction and application are described in Vroblesky (2001a,b).

2.1.2.C Support Equipment

The support equipment used during groundwater sampling depends on the type and size of the pump or sampler used, field conditions, and depth to water or to sampling interval in the well. A reel should be used for efficient and clean deployment of the sample line. Commonly used support equipment is listed in section 2.4. A detailed description of the various types of support equipment is beyond the scope of this manual.

[16] PDBs are not suitable when collecting samples to be analyzed for inorganic ions, methyl-*tert*-butyl, acetone, or phthalates, and PDBs have limited applicability for other non-VOCs.

2.2 Sample Processing

Water samples must be processed as quickly as possible after collection. The equipment most commonly used for sample processing includes sample splitters, disposable capsule and disk filters, filtration assemblies, solid-phase extraction systems, and chambers in which samples are processed and treated with chemical preservatives. Having several sets of cleaned processing equipment on hand is recommended. The equipment and supplies commonly used to process surface-water and groundwater samples are listed in section 2.4.

The collection of surface water generally results in a single composite sample. A groundwater sample generally is not collected as a composite; instead, the sample is pumped directly, one after the other, into separate bottles for designated analyses (NFM 4.2). There are exceptions. For example, groundwater samples withdrawn using a bailer or thief sampler can be collected as a composite, provided that sample integrity for the analytes of interest can be maintained.

2.2.1 Sample Splitters

A composite sample often is subdivided (split) into subsamples for analysis. Each whole-water subsample should contain suspended and dissolved concentrations of target analytes that are virtually equal to those in every other subsample. Use of the fluorocarbon polymer churn splitter, the polypropylene/polyethylene (poly) churn splitter, and the fluorocarbon polymer cone splitter are discussed in sections 2.2.1.A and 2.2.1.B, respectively. Testing and comparative data between the splitters are described in Capel and Larson (1996), Horowitz and others (2001), and Office of Water Quality Technical Memorandum 97.06. Advantages and limitations of these sample splitters are shown in table 2–6.

Table 2–6. Advantages and limitations of sample splitters.

[L, liter; mg/L, milligram per liter; µm, micrometer; mL, milliliter; >, greater than; ≤, less than or equal to]

Splitter	Advantages	Limitations
Fluorocarbon polymer (fluoropolymer) churn splitter	• Can be used to process samples for inorganic and nonvolatile organic analyses. • Simple to operate. • Easy to clean. • No modification of the splitter design is necessary.	• Although it can be used to split samples with mean particle sizes ≤ 250 µm[1] and suspended-sediment concentrations ≤ 1,000 mg/L, splitting accuracy becomes less efficient for mean particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. • Sample volumes less than 4 L or greater than 13 L cannot be split for whole-water subsamples from this 14-L churn. • Samples for bacteria determinations are not to be taken from a churn splitter because the splitter cannot be autoclaved.
Polypropylene/polyethylene (poly) churn splitter	• Used only to process samples for inorganic analyses. • Simple to operate. • Easy to clean.	• Poly churn splitters must not be used to composite samples for determination of organic compounds. • Although it can be used to split samples with mean particle sizes ≤ 250 µm and suspended-sediment concentrations ≤ 1,000 mg/L, splitting accuracy becomes less efficient for mean particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. • When using the 14-L churn, sample volumes that total less than 4 L or greater than 13 L cannot be split for whole-water subsamples. • Requires a modified spigot and construction of a funnel assembly. • Samples for bacteria determinations are not to be taken from a churn splitter because the splitter cannot be autoclaved.
Fluorocarbon polymer (fluoropolymer) cone splitter	• Used to process samples with suspended-sediment concentrations from 0 to 10,000 mg/L. • Samples containing sediment particles ranging in size from very fine clay and silt (1 to 10 µm) to mean sand-size particles (250 µm) can be split. • Samples as small as 250 mL can be split into 10 equal subsamples. • Samples greater than 13 L can be processed. • Can be used to process samples for both inorganic and nonvolatile organic analyses.	• Accuracy of the volume equivalents must be verified before using a new or modified cone splitter. • Splitter is awkward to operate and clean in the field. • Sample is vulnerable to contamination from atmospheric sources or from improper operation. • Splitting accuracy for mean sediment particles >250 µm or sediment concentrations >10,000 mg/L must be quantified by the user. • Samples for bacteria determinations are not to be processed through the cone splitter because the splitter cannot be adequately sterilized. • The cone splitter must be level for proper operation.

[1]Refer to Office of Water Quality Technical Memorandum 97.06 (*http://water.usgs.gov/admin/memo/QW/qw97.06.html*).

2.2.1.A Churn Splitter

Churn splitters are available in either fluorocarbon polymer (fluoropolymer or Teflon®) (fig. 2–8A) or polypropylene/polyethylene (poly) (fig. 2–8B) plastic. Both churn types are available in 14-L and 8-L sizes. A 4-L churn is available but it has not been evaluated for splitting efficiency and is not recommend for use. Splitter advantages and limitations are described in table 2–6. The 8- or 14-L poly churn splitter is recommended to composite and split surface-water samples for inorganic analyses. The 8- or 14-L fluoropolymer churn splitter is recommended to composite and split samples for either inorganic or nonvolatile organic analyses.

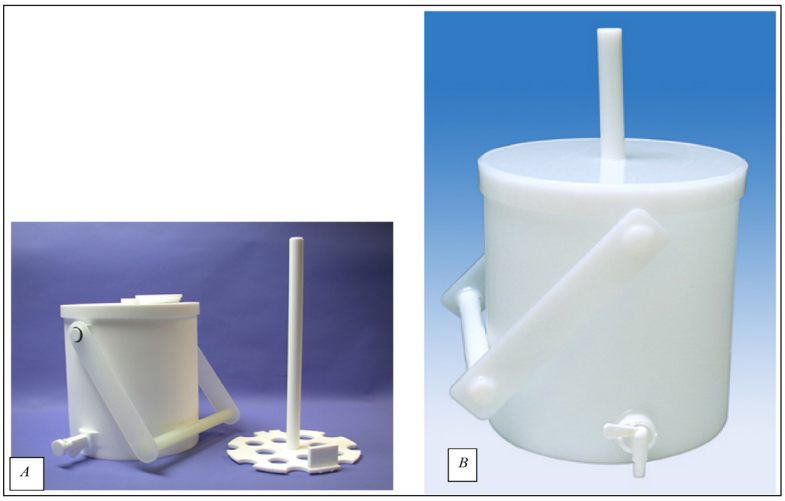


Figure 2–8. Churn-type sample splitters: (*A*) Fluorocarbon polymer (Teflon) churn splitter and (*B*) Polyethylene churn splitter. Photographs courtesy of the U.S. Geological Survey Hydrologic Instrumentation Facility.

- **Trace-element samples.** Use either the poly or fluoropolymer churn splitter. **Do not split samples for trace-element analyses from a metal compositing container.**
- **Organic compound samples.** Use only the fluoropolymer churn to collect or extract samples for analysis of organic compounds. Stainless-steel and glass containers and the plastic churn also can be used to composite samples for analysis of dissolved organic compounds. **Do not collect or extract samples for trace-element analyses from a metal container.**
- **Churn covering.** Place the churn splitter inside two pliable, clear plastic bags (double bagged) to **keep the entire churn-splitter assembly clean during sampling and to prevent potential contamination**. These bags should be large enough to completely enclose the churn splitter, including funnel and churn handle, with enough excess material so that the bag openings can be gathered, folded over, and kept closed.
- **Churn carrier.** The carrier is a white plastic container, with lid, large enough to hold the double-bagged churn splitter assembly.
  - The lid of the carrier serves both as a seal for the carrier and as a windbreak when the collected subsample is poured into the churn funnel.
  - The purpose of the carrier is to minimize contamination during transport. In exposed areas, such as bridges and roadways, the carrier can protect against atmospheric sources of contamination, particularly fumes and particulate material from motor vehicles.

- **Sample-volume requirements.** For a valid whole-water sample analysis, a limited volume of water should be withdrawn from the churn. The water level inside the churn should be no more than 2 in. (5.08 cm) from the top of the churn and no less than 2 in. (5.08 cm) above the spigot (Quality of Water Branch Technical Memorandum 78.03). The remaining volume of sample/sediment mixture in either churn (about 4 L in the 14-L churn and 3 L in the 8-L churn) can be used for filtered samples.

Modifications to the spigot and lid of the poly churn splitter are described below.

- **Spigot.** The original spigot on the poly churn splitter contains a metal spring that introduces a potential source of metal contamination and must be replaced if the churn is used to process samples for trace-element analysis (Horowitz and others, 1994). The churn splitter spigot can be replaced or refurbished with noncontaminating components by the manufacturer (USGS personnel can refer to the Office of Water Quality internal communication "Water-Quality Information Note 2005.07" at *http://water.usg.gov/usgs/owq/WaQI/index.html*.
- **Funnel assembly for plastic churn lid.** To meet requirements for trace-element sampling, a funnel assembly is inserted into a 1-in.- (2.54 cm) diameter hole drilled through the lid of the churn splitter (fig. 2–8).
  - The funnel is used when pouring whole-water samples into the churn splitter so that the churn lid can be left on, thus minimizing exposure of the composite sample to atmospheric contamination.
  - To make the funnel assembly, cut the top section (at the shoulder line) from a 1-L polypropylene sample bottle and insert it into the hole drilled in the churn lid. Cut the bottom two-thirds from a 1-L Nalgene® or other larger diameter sampler bottle and use this as a funnel cap.

2.2.1.B Cone Splitter

The cone splitter is a pour-through device constructed entirely of fluorocarbon polymer with 10 ports that can accommodate 10 fluorocarbon sample-discharge tubes (fig. 2–9). The cone splitter can be used to process samples for analysis of inorganic as well as nonvolatile organic analytes. The primary function of the cone splitter is to divide the sample simultaneously into as many as 10 equal-volume samples. **The cone splitter may be used to process samples with mean particle sizes of ≤250 micrometers (µm) and suspended-sediment concentrations of ≤10,000 milligrams per liter (mg/L)** (table 2–6).

Some cone splitters have a 2-mm mesh screen in the reservoir funnel to retain large debris, such as leaves and twigs, which could clog or interfere with the splitting process. Below the funnel is a short standpipe that directs sample water in a steady stream into a splitting chamber that contains a notched, cone-shaped splitting head with 10 equally spaced exit ports around its base. **There should be no ridges, benches, or surfaces inside the splitting chamber that could retain material or interfere with the splitting process.** The cone splitter is supported either by tripod legs or with an adjustable clamp and stand.

The cone splitter is built to very close tolerances in order to achieve accurate and reliable operation. **Bias to data can result from splitter imperfections or improper operation; therefore, calibration and proper use is necessary when processing samples.**

- **Cone-splitter covering.** Once leveled, place one pliable, clear plastic bag over the entire splitter, including tubes, to keep the entire cone-splitter assembly clean during sample splitting and to prevent potential contamination. The bag should be large enough to enclose the top of the splitter and the top of the receiving containers at the end of each tube.

► **Sample-volume requirements.** Because the cone splitter is a pour-through device, the volume that can be split is unlimited. The minimum volume that can be split is 250 mL. Larger volumes are split more effectively (Capel and Larson, 1995 and 1996).

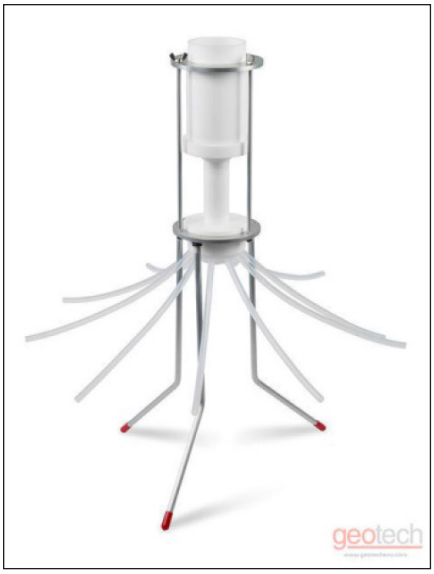


Figure 2–9. Dekaport® fluorocarbon cone splitter with 10 fluorocarbon discharge tubes. Illustration courtesy of Geotech Environmental Equipment, Inc.

Before using a new or modified cone splitter, test the splitter to be used as follows *(from Quality of Water Branch Technical Memorandum 80.17):*

1. Inspect the cone splitter housing and outlet ports. They should be smooth and symmetrical without any visible burrs or chips. **The cone splitter must be clean.**
2. Connect the 10 fluorocarbon discharge tubes to the outlet ports. The tubes must be the same length and as short as possible. Label the outlets from 1 to 10.
   - All tubes must be solidly seated in the cone-splitter base. The ends should be flush with the bottom of the inside of the port.
   - Tubes need only extend into the receiving containers sufficiently to prevent spillage.
   - Tubes must not extend in so far that the ends become submerged during the split.
3. Place the cone splitter on a stable platform or bench. **The splitter must be level for proper operation.** Use a bull's-eye level to check leveling and recheck during use; the level may change as personnel move inside the field vehicle.
4. Wet the cone splitter by pouring several liters of deionized water through it.
   - Lightly tap the system to dislodge adhering water drops, and discard the water.
   - Place an empty sample bottle under each outlet tube.

5. Accurately measure 3 L of deionized water into a 1-gal. narrow-mouth plastic bottle. Check that the splitter is level and adjust if necessary.
6. Rapidly invert the 1-gal. bottle over the reservoir, letting deionized water flow out as fast as possible. For proper operation, the standpipe must be discharging at its full flowing capacity.
7. After all deionized water has passed through the splitter, tap the assembly several times to dislodge adhering water drops. Check for spills and leaks. If any are observed, stop the test, correct the problem, and repeat steps 1–7.
8. Measure the volumes of the 10 subsamples carefully, within an accuracy of ±1.0 mL. Record the volumes for each outlet on a form similar to table 2–7.
9. Repeat the test a minimum of three times. Use the same initial volume for each test.

Calculate and document the results of the cone-splitter accuracy test as follows:

1. Referring to the example in table 2–7, calculate the mean volume of each subsample ($\bar{x}$) and standard deviation (S_x):

$$\bar{x} = \frac{\sum x_i}{n} \tag{1}$$

and

$$S_s = \sqrt{\frac{\sum (x_i - \bar{x})^{-2}}{n-1}}, \tag{2}$$

where

x_i is the measured volume for each subsample, and
n is the number of subsamples (outlet ports).

2. Calculate the standard deviation in percent (E_x):

$$E_x = \frac{S_x}{\bar{x}} \text{ x } 100. \tag{3}$$

3. Calculate the error for each subsample (E_i):

$$E_i = \frac{x_i - \bar{x}}{\bar{x}} \text{ x } 100. \tag{4}$$

4. Compute the mean standard error ($\bar{E}_{\bar{x}}$) for the three tests and document the maximum and minimum errors (E_i) for all tests in field notes.
5. If data-quality requirements warrant, note the error patterns for individual outlets to determine which outlets produce consistent bias and label them with their mean percent bias error. Depending on the objectives of the sampling effort and professional judgment of the project water-quality specialist, this pattern of error may not be of concern.

TECHNICAL NOTE 2. A cone splitter is considered acceptable for sample processing if the mean standard error ($\bar{E}_{\bar{x}}$) for the three tests is 3 percent or less, and no individual error (E_i) exceeds ±5 percent.

Table 2–7. Example of six cone-splitter accuracy tests using deionized water.

[Modified from Quality of Water Branch Technical Memorandum 80.17; na, not available]

Test number initial sample weight (grams)	1 2,499.4		2 2,499.5		3 2,499.5		4 2,499.5		5 2,499.5		6 2,499.4		Averages	
Outlet number	**Outlet volume (x_i)**	**Percent (E_i)**	**Outlet volume (x_i)**	**Percent (E_i)**	**Outlet volume (x_i)**	**Percent (E_i)**	**Outlet volume (x_i)**	**Percent (E_i)**	**Outlet volume (x_i)**	**Percent (E_i)**	**Outlet volume (x_i)**	**Percent (E_i)**	**Outlet volume (x_i)**	**Percent (E_i)**
1	248.4	-0.5	249.5	-0.1	247.4	-0.9	248.1	-0.7	247.8	-0.8	249.2	-0.2	248.4	-0.5
2	246.8	-1.2	246.8	-1.2	245.6	-1.6	248.4	-0.6	246.3	-1.4	246.7	-1.2	246.8	-1.2
3	249.4	-0.1	251.0	0.5	250.6	0.4	251.1	0.5	249.8	0	248.7	-0.4	250.1	0.1
4	250.7	0.4	252.6	1.1	252.5	1.1	251.3	0.6	251.8	0.8	250.5	0.3	251.6	0.7
5	248.1	-0.6	248.3	-0.6	249.8	0	249.3	-0.2	250.2	0.2	248.1	-0.6	249.0	-0.3
6	252.2	1.0	250.3	0.3	252.7	1.2	252.0	0.9	252.7	1.2	250.6	0.4	251.8	0.8
7	245.7	-1.6	246.2	-1.4	246.0	-1.5	246.3	-1.4	246.6	-1.3	245.9	-1.5	246.1	-1.5
8	252.7	1.2	254.2	1.8	252.9	1.3	253.3	1.4	253.1	1.3	254.6	2.0	253.5	1.5
9	248.7	-0.4	247.3	-1.0	247.5	-0.9	247.1	-1.1	248.3	-0.6	249.5	-0.1	248.0	-0.7
10	253.9	1.7	252.1	0.9	251.8	0.8	250.6	0.3	251.7	0.8	253.0	1.3	252.0	1.0
Final sample weight	2,496.6		2,498.3		2,496.8		2,497.5		2,498.2		2,496.8		2,497.4	
Sample loss	2.8		1.2		2.7		2.0		1.3		2.6		na	
Mean weight ($\bar{x}$)	249.7		249.8		249.7		249.8		249.8		249.7		249.8	
Standard deviation (S_x)	2.7		2.7		2.8		2.3		2.5		2.7		na	
Error percent (E_x)	1.1		1.1		1.1		0.9		1.0		1.1		na	

2.2.2 Sample-Processing Chambers

Working within a sample-processing chamber reduces the possibility of random atmospheric contamination during sample bottling, filtering, and chemical preservation. **Use of sample-processing chambers is a routine requirement when filtered samples will be analyzed for trace elements** (Horowitz and others, 1994); is recommended strongly when sampling for trace organic compounds; and also when sampling for most other analytes, such as major and minor inorganic ions and total or dissolved organic compounds. Field personnel should consult NFM 4 and NFM 5 in addition to their project quality-assurance plan and project data-quality objectives for project-specific guidance related to the use of sample-processing chambers and the collection of blank samples inside and outside of the chambers.

Use of separate chambers for sample collection, sample processing, and sample preservation generally is the most efficient approach. Space permitting, multiple preservation chambers can be dedicated to a specific chemical treatment. Alternatively, use of a single preservation chamber requires replacement of the bag covering with each change in chemical treatment. If insufficient space is available in which to set up a processing and preservation chamber, the processing-chamber frame also can function as a preservation-chamber frame by changing the clear plastic bag (chamber cover) after sample collection is completed and before preserving samples with a chemical treatment. The PVC chamber frames should be kept clean of dirt and exposure to chemical substances. Chamber covers must be replaced with each change in the sample collection and (or) type of filtration and chemical treatment.

- The **sample-collection chamber** is where sample water is pumped, either directly into sample bottles or through the filter unit, and then into sample bottles.
  - The processing chamber either sits over a fixed or portable sink or contains a basin to which a waste-disposal funnel or hose has been attached, allowing excess water to drain readily to waste.
  - The tubing through which sample is delivered to the chamber may be supported by the frame (or clipped to the outside) and inserted through a hole in the top of the chamber, allowing it to be connected to a filtration device inside the chamber.
- The **sample-preservation chamber** is the same as or similar to the sample-collection chamber but without an inlet for sample tubing or an outlet for drainage. The bottled sample is passed from the processing chamber to the preservation chamber, in which a chemical treatment is added to the sample in accordance with the specific sequence and instructions given in NFM 5.
  - Also placed in the preservation chamber are preservative-containing vials required for the type of sample and a suitable waste container for storage of spent preservative ampoules (see NFM 5).
  - Chemical reagents used to preserve samples are not to be used beyond their expiration date; they should be discarded in a manner that conforms with local and Federal regulations and good environmental stewardship.

Processing chambers can be portable and easily transferable between field sites and field vehicles or can be installed as permanent fixtures; for example, in a water-quality field vehicle or laboratory. These chambers are designed for use during sample collection and sample processing or preservation to prevent potential airborne contaminant sources from having contact with the sample (fig. 2–10 *A* and *B*). Glove boxes (fig. 2–10*C*) are a type of chamber designed to isolate the sample from contact with atmospheric oxygen when adding chemical preservatives or while performing a titration on the sample by filling the chamber with a clean inert gas, such as nitrogen or argon. Glove boxes typically are used for research projects and not for routine sampling. The most common type of sample-processing chamber used for routine USGS

water-quality field work is portable and self-constructed (see fig. 2–10 *A* and *B* and refer to the appendix. While there is no standard design for constructing the chamber, the materials used for the frame and cover should be dedicated to analyte-specific processing so as to prevent sample contamination, as follows:

- Use tubing that is either nonmetallic or completely covered by or embedded in nonmetallic material (for example, PVC) to prevent contamination of samples to be analyzed for concentrations of trace elements.
  - This chamber is inexpensive and the frame is easily constructed with ≤1/2-in.-diameter white polyvinyl chloride (PVC) pipe or tubes (see fig. 2–10*A* and the appendix).
  - The frame supports a clear plastic covering (large, clear plastic bags are available from One Stop Shopping) (fig. 2–10*B*). The transparent bag forms a protective tent within which to work while collecting, processing, or preserving samples. The plastic covering (chamber bag) should be secured to the frame using white or clear plastic clips or clamps.
- The PVC tubing and clear plastic bag covers have been bench tested, and it was determined that a chamber constructed with these materials is appropriate for use for samples to be analyzed for trace organic compounds. The analysis of blank samples resulted in no detection of volatile organic substances.[17]

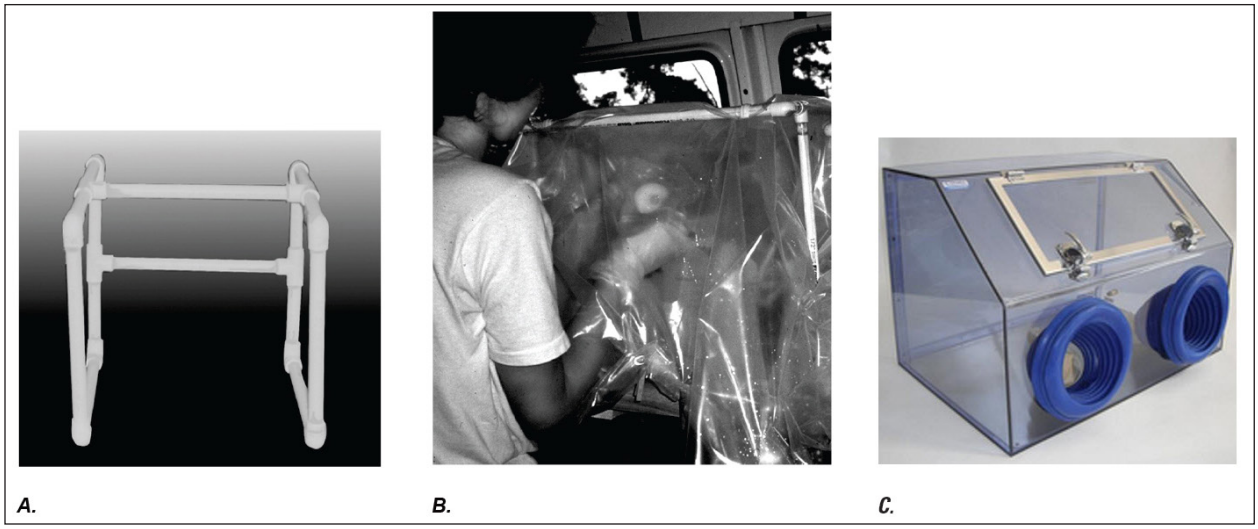


Figure 2–10. Photographs showing (*A*) a polyvinyl chloride frame of a processing or preservation chamber, (*B*) a covered chamber frame with a sample being processed inside the chamber, and (*C*) a simple glove box by Cleatech®, LLC. *A*, Photograph by B.A. Bernard, U.S. Geological Survey. *B*, photograph by Jacob Gibs, U.S. Geological Survey. *C*, Cleatech® 2200 Series PVC Mini-Glovebox ; photograph courtesy of Cleatech, LLC (*http://www.laboratory-supply.net/contact_us.php*, accessed December 30, 2013).

[17] Internal communication from the USGS National Water Quality Laboratory to the USGS Office of Water Quality, 2006. Depending on data-quality objectives, projects may further substantiate data quality by preparing an ambient blank for volatile organic compound (VOC) analysis that is collected and (or) preserved in the chamber(s).

2.2.3 Filtration Systems

Filtration systems separate particulate substances (solid phase and biological materials) from the solute or aqueous phase of a water sample. Water samples are filtered for analysis of inorganic constituents, organic compounds, and biological materials to help determine the environmental fate and quantify the transport of these target analytes. Additional information relevant to the selection of filtration systems can be found in NFM 5. Depending on sample type and analysis to be performed:

- For surface-water applications, the most common filtration systems consist of a variable-speed peristaltic pump or a metering pump that forces the whole-water sample through tubing into either (1) a plate-filtration assembly or (2) a disposable capsule or disk filter.
- For groundwater applications, the sample ordinarily is pumped directly from the well into a disposable capsule (or disc) filter or other filtration assembly. If the sample is collected by bailer, some bailers can be directly connected to a filtration device and hand-pump system, or the sample is decanted to a churn or other vessel and transferred to the filtration device by means of a peristaltic pump.
- For small-volume samples to be analyzed for pesticide and selected other organic analytes (for example, samples to be analyzed by direct-aqueous injection liquid chromatography tandem mass spectrometry (DAI LC-MS/MS), a syringe is used to push the sample through a small disposable filter in situations where an in-line pump (for example, when sampling groundwater) or another means is not available to push the sample through the designated filter.

TECHNICAL NOTE 3. Separation of solid from aqueous phases can be achieved by methods other than filtration, and data requirements may dictate the need for an alternative method such as centrifugation, ultracentrifugation, dialysis or lipid-membrane separation, or reverse-flow osmosis and tangential-flow filtration.

The filter membrane material to be used depends on the class of target analyte(s) (table 2–8):

- **Inorganic Samples.** The filter membrane through which water samples are passed for analysis of inorganic constituents typically is composed of polyethersulfone, cellulose nitrate, or a polycarbonate polymer. The disposable capsule filter that is in routine use by the USGS water-quality program is an acrylic copolymer material (Versapor®). The direction of the water flow through the filter is critical in order to prevent the filter from separating from the support medium and thereby allowing particulates to bypass the filter and enter the sample container.
- **Trace-Organic Samples.** Samples to be analyzed for trace organic compounds are filtered through a glass fiber (microfiber) (GF/F) membrane. The filter membrane material described above for inorganic samples should not be used for organic samples unless instructions specifically state that the material is acceptable (for example, see the information for dissolved organic carbon (DOC) samples described below).
- **Dissolved Organic Carbon Samples.** Samples for DOC analysis may be filtered either through GF/F disks using the Savillex DOC-25 mm unit (described below), GF/F disks using an inline 47-mm fluorocarbon assembly, or the disposable capsule (polyethersulfone) filter. The choice of filtration unit depends on the analytical, technical, and data-quality objectives of the project.

- **Total Particulate Carbon (TPC) and Total Particulate Nitrogen (TPN) Samples.** Samples to be analyzed for TPC and (or) TPN must be filtered through a GF/F disk using the 25-mm fluorocarbon pressure filtration assembly by Savillex (the U.S. Geological Survey DOC-25 filter-holder assembly).[18]

The filter-membrane pore size is determined by the type of samples to be analyzed. A filtered sample is defined operationally by the nominal pore size of the filter membrane. The filter pore size selected depends on study objectives, data requirements, and industry standards. The standard pore sizes of filters used by the USGS are:

- 0.45 µm for inorganic constituents (including major ions, radiochemicals, and trace elements), some bacteria (NFM 7), and possibly DOC, depending on project requirements.
- 0.7 µm for pesticides, DOC, and most other organic compounds (0.7 µm is the smallest nominal pore size available for GF/F) membranes.
- 0.65 µm for some bacteria (see NFM 7.1).

TECHNICAL NOTE 4. A filter pore size of 0.2 µm or less is used for trace-element samples that will be analyzed for some geochemical applications and interpretive studies, as well as for nutrient samples for which the exclusion of bacteria at the 0.2-µm threshold is desirable.

- **Construction materials and membrane material in filtering systems must not be a source of sample contamination with respect to the substances for which the sample will be analyzed.**
- **Only use equipment that is specified for the analyte schedule or for the analytical method of interest.**

2.2.3.A Inorganic Constituents

The standard device for filtering samples for analysis of inorganic constituents is the disposable capsule filter, which has replaced routine use of the plate-filter assembly for most applications (table 2–8). **Construction materials in filtering systems must not be a source of sample contamination with respect to the substances for which the sample will be analyzed.**

Disposable capsule and disk filters

The routine procedure for filtering a sample for analysis of inorganic constituents requires using a disposable capsule filter,[19] such as the Pall GWV® high-capacity 700 cm^2 sampling capsule with acrylic copolymer (Versapor®) filter membrane material (fig. 2–11)[20] or the Pall AquaPrep 19.6 disk filter with polyester-reinforced polysulfone (Thermopor®) filter membrane material.

[18] This 25-mm pressure filter-holder assembly is produced for the USGS by Savillex Corporation (*http://www.savillex.com/ProductDetail.aspx?ProductName=Filter-holder-assembly-US-Environmental-Protection-Agency*).

[19] This disposable capsule filter also can be used for processing samples for analysis of dissolved organic carbon, conditional according to project-dependent criteria (refer to section 2.2.3.B and NFM 5.2.2.C).

[20] The Pall Corporation groundwater capsule filter (AquaPrep 600) with a polyethersulfone membrane and a 600-cm2 filtration area (accessed November 19, 2013, at *http://www.pall.com/main/laboratory/product.page?id=20009*) was used originally in the USGS operational water-quality program.

- The high-capacity capsule is recommended when filtering sediment-laden waters (usually surface water) or at sites at which a large volume of sample will be collected.
- The 19.6 disk filter is used at surface-water and groundwater sites at which water is typically clear of sediment or other particulate matter and for which the required volume of sample is small.

These filtration devices are quality assured for the USGS use by the NWQL and are supplied by One Stop Shopping; however, quality-assurance tests have confirmed that, within a day of use, the capsule filter must be rinsed with a minimum of 2 L of IBW or quality-controlled DIW, and the AquaPrep disk filter must be rinsed with a minimum of 50 mL of IBW or quality-controlled DIW (NFM 3, amended version 2.0 or update; NFM 5.2.1, version 3.0, table 5–5).[21] USGS project personnel can access NWQL quality-assurance results (certificates of analysis) for each lot of capsule and disk filters (*http://wwwnwql.cr.usgs.gov/qas.shtml?filters_home*).

Figure 2–11. Disposable filtration devices: (*A*) GWV® high-capacity capsule filter, 0.45-µm pore size, 700-cm² pleated Versapor® filter membrane; and (*B*) Small-capacity AquaPrep® disk filter, 0.45 µm, 19.6 cm² Versapor/Thermopor® filter membrane. *A*, image courtesy of Pall Corporation; *B*, photograph by S.C. Skrobialowski, U.S. Geological Survey.

Do not reuse the disposable filtration devices. Discard after one use, in an environmentally appropriate manner.

Table 2–8. Analyte requirements and recommendations for filtering surface-water and groundwater samples using the disposable capsule and disk filters.

[The table, modified from Horowitz and others (1994), includes only those constituents evaluated in the experiments described in the reference and in Office of Water Quality Technical Memorandum 2000.08, *http://water.usgs.gov/admin/memo/QW/qw00.08.html*]

Analytes for which the disposable capsule or disk filter is required[1]			Analytes for which the disposable capsule or disk filter is recommended[2]
Aluminum	Cobalt	Molybdenum	Anions (chloride, sulfate)
Antimony	Copper	Nickel	Calcium
Barium	Iron	Silver	Dissolved organic carbon
Beryllium	Lead	Thallium	Magnesium
Boron	Lithium	Uranium	Nutrients (nitrogen, phosphorus)
Cadmium	Manganese	Zinc	Radiochemicals (excluding radon gas)
Chromium			Silica
			Sodium
			Strontium

[1]Requirements for surface-water and groundwater sample filtration are described in NFM 5.

[2]The plate-filter method, while rarely in use, is acceptable contingent on the correct application of equipment-cleaning protocols (NFM 3) and the project's data-quality objectives.

[21] USGS personnel can refer to internal communication, Water-Quality Information Notes 2009.10 and 2009.11. In addition, users of this *National Field Manual* are advised to check the NFM "Comments and Errata" Web page for recent and proposed protocol changes (*http://water.usgs.gov/owq/FieldManual/mastererrata.html*).

Plate-filter assemblies

Before 1994, the most common filtration assembly used for USGS studies for filtering inorganic samples was the nonmetallic backflushing plate-filter assembly designed to hold a 142-mm filter (fig. 2–12). Because this method allows greater exposure of the sample to the air, and because the equipment is time-consuming to field clean and quality assure, **this equipment no longer is recommended for routine filtering of inorganic samples (table 2–8)**. Information and instructions are provided below, however, because the plate-filter method might be necessary or useful for certain research-oriented studies, especially those that require filtration through a membrane with 0.2 µm or smaller pores and (or) a prerinse with nitric or other acid.

- Types of plate-filter assemblies available for inorganic samples include:
  - Fluorocarbon polymer filtration assembly designed for 47-mm-diameter filters; can be used for inline filtering of inorganic or organic samples by using an appropriate filter membrane. The device is illustrated in the organic compounds section 2.2.3.B.
  - Plastic pressure or vacuum filtration assembly for a 47-mm-diameter filter; used with either a hand vacuum pump or a peristaltic pump.
  - Plastic backflushing assembly, available for 142-mm- and 293-mm-diameter filters (no longer in common use for USGS studies) (fig. 2–12).
- A smooth-tipped plastic forceps is needed to transfer the filter to the plate of the filter assembly. Kennedy and others (1976) give detailed instructions for use of the plate-filter assembly.

Figure 2–12. Nonmetallic backflushing plate-filter assembly for a 142-millimeter-diameter filter membrane. Illustration reproduced with permission of Pall Corporation.

2.2.3.B Organic Compounds

Filtering whole-water samples isolates suspended solid-phase substances from the aqueous phase, thus allowing for separate determinations of organic compounds in the solid and aqueous phases. Filtering also helps to preserve samples for organic determinations by removing microorganisms that could degrade compounds in the sample (Ogawa and others, 1981).

- Hydrophobic compounds are analytes that preferentially partition to particulate matter. Filtering concentrates particulate matter on the disk (filter), enhancing extraction efficiency and lowering analytical detection limits. This is especially useful for whole-water samples with small concentrations of suspended material and for which large volumes of sample (4 to 40 L) must be filtered to provide an analyzable mass of suspended materials.
- Hydrophilic compounds are analytes that are water soluble. Filtering is used to remove suspended material or other particulate matter from the water sample, to identify concentrations of dissolved analytes, and to remove any solid-phase substances containing constituents that could interfere with the analysis and that could be co-extracted with target analytes.

Use only equipment that is specified for the analyte schedule or analytical method of interest. Equipment needed to filter samples for determination of trace organic compounds, such as pesticides, is described in detail in Sandstrom (1995).[22] Equipment and components used for filtering whole-water samples for trace organic determinations should be made of materials (a) that will not contaminate the sample or sorb analytes, and (b) that can withstand organic cleaning solvents without being damaged. Such materials include stainless steel or aluminum, fluorocarbon polymer, glass, and nonporous ceramics (hard-fused microcrystalline alumina).

- **Avoid using plastics, rubber, oils, and other lubricants because their use can result in sample contamination, analytical interference, and (or) sorptive losses.**
- In contrast, some new analytical techniques, such as tandem mass spectrometry, are very selective and are not affected by interferences from leaching of plastics; consequently, specified high-purity plastic components can be used for the collection of samples for methods that use this analytical technique (for example, LC-MS/MS).

Valveless piston metering pump, tubing, and PTFE diaphragm pump head

The valveless piston metering pump consists of a pump head with a reciprocating piston driven by a 12-volt direct current (DC), variable-speed motor (fig. 2–13). It has a delivery rate of up to 500 mL per minute.

- The pump head and all wetted parts are constructed of ceramic, fluorocarbon polymer, or stainless steel components, which are resistant to organic solvents and thus appropriate for use when collecting samples for pesticides and many other organic compounds.
- These pumps can tolerate some suspended materials in the sample being pumped, but large concentrations of suspended materials can cause excessive wear of pump parts and strain on the pump's motor.
- The ceramic piston and shaft of these pumps will break if motor amperage exceeds 4 amps. To avoid this, either a 4-amp DC circuit breaker connected in-line with the pump power line, or an alternating to direct current converter with a 4-amp maximum output should be used.

[22] Contact the USGS National Water Quality Laboratory for additional information about this method (*http://nwql.usgs.gov/mrdp.shtml?MRDP*).

The pump and filtration assembly are connected by 1/4-in.-diameter convoluted fluorinated ethylene polypropylene (FEP) tubing (fig. 2–14) with appropriate fittings. The convoluted tubing does not crimp when bent and is available only in fixed lengths with smooth ends.

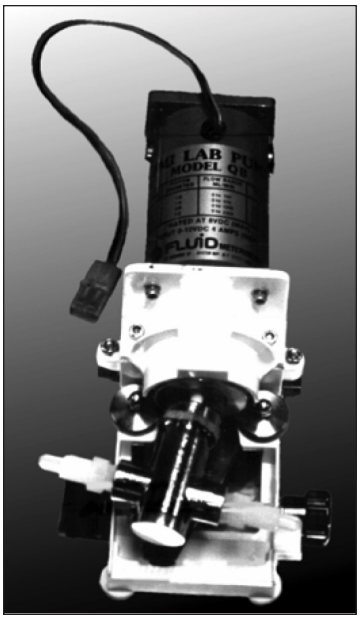
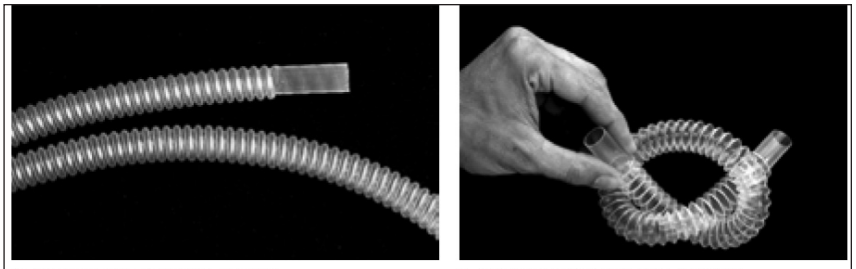


Figure 2–13. Valveless piston metering pump. Photograph by B.A. Bernard, U.S. Geological Survey.



A. Convoluted (spiral) design ***B.*** Corrugated (parallel) design

Figure 2–14. Flexible fluorinated ethylene polypropylene (FEP) tubing showing the (*A*) convoluted design and (*B*) corrugated design. Published with permission of Cole-Parmer Instrument Company: *A*, Copyright 1992. *B*, Copyright 1987. Cole-Parmer does not warrant these illustrations to be current, accurate, or suitable for any purpose.

When an alternative to the metering pump is necessary, a peristaltic pump fitted with a polytetrafluoroethylene (PTFE)-diaphragm pump head can be used (fig. 2–15). This system has a diaphragm through which repeated compression and decompression motions transfer the sample (similar to the action of piston pumps); sample water is sealed off from the outside, entering through an inlet check valve during decompression and exiting through an outlet check valve during compression.

- All the wetted components are constructed of PTFE and glass.
- The diaphragm (membrane) pump commonly is driven hydraulically and has a delivery rate of up to 800 mL/min.

Figure 2–15. Polytetrafluoroethylene diaphragm pump head. Photograph by D.A. Evans, U.S. Geological Survey, 2013. Photograph copyright© Cole-Parmer, published with permission.

Filtration equipment: samples of organic compounds for routine and DAI LC-MS/MS analyses and samples of organic carbon

Various types of devices are used routinely for filtration of samples to be analyzed for organic compounds. Selection of the filtration device depends on the analysis to be requested or the field method selected. Samples for organic-compound analyses are filtered through 0.7-um pore size media (see section below titled “Filter-membrane material”).

Plate-filter assemblies are available for filters with disk diameters ranging from 13 to 293 mm. The 47-mm PFA filter holder delivers sample in-line from the source to the sample container. The assembly diameter selected is determined by the sample volume to be filtered, by the concentration of suspended materials in the sample, and by the method for delivering sample to the filtration unit. For example, the 25-mm Savillex pressure-filtration assembly (described more fully in the section below on DOC filtration) was developed specifically for water samples to be analyzed for dissolved and particulate organic carbon.

Samples to be filtered for analysis of organic compounds by direct-aqueous injection liquid chromatography tandem mass spectrometry (DAI LC-MS/MS) are processed using a syringe-filtration method (table 2–9).

- **Trace organic compounds.** Filter-holder assemblies commonly used for filtering wastewater, pharmaceutical, hormone, and some pesticide samples include either the three-legged aluminum (or stainless steel) plate-filter assembly (fig. 2–16*A*) or the PFA in-line filter-holder assembly (fig. 2–16*B*). The aluminum plate-filter assembly consists of two machined aluminum or stainless-steel plates (designed to contain a 142-mm-diameter filter) held together by locking bolts or a locking ring.
  - The plates have fluorocarbon polymer-coated silicone or Viton® O-rings set in grooves to seal the filtration assembly. A stainless-steel screen on the lower plate supports the filter. A valve is built into the upper plate to exhaust trapped air. Connectors are built into the center of the top and bottom plates so that inlet and outlet fluorocarbon polymer tubing can be attached.

— O-rings should be inspected for cracks and abrasions every time they are cleaned and should be replaced when appropriate.

— The PFA in-line filter-holder assembly with a Tefzel® ETFE clamp nut holds a 47-mm-diameter glass fiber filter (GF/F) (0.7-µm nominal pore size). (Similar assemblies currently are available from commercial manufacturers such as Savillex, Cole-Parmer, and Berghof.)

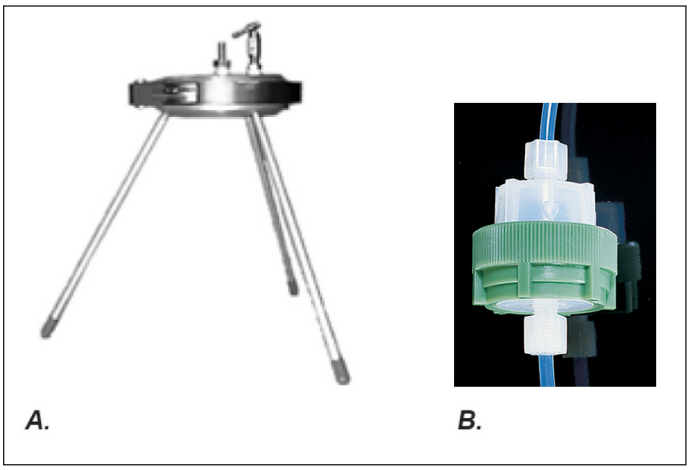


Figure 2–16. Examples of filter-holder assemblies: (*A*) Aluminum plate-filter assembly for a 142-millimeter-diameter filter GF/F disk and (*B*) Perfluoroalkoxy (PFA) filter holder for a 47-millimeter-diameter filter (Cole-Parmer EW-06103-13 PFA inline filter holder shown). Photographs published with permission: *A,* GeoTech Environmental Equipment, Inc. and *B* , Cole-Parmer Company (photograph copyright© Cole-Parmer), published with permission.

► **Organic compounds by DAI LC-MS/MS analysis.** Samples for analysis of organic compounds using direct aqueous injection (DAI LC-MS/MS)[23] may be filtered using an inline 25-mm disposable syringe filter unit (syringe filter), as explained below.[24] Filtration devices and other equipment made of plastic components generally are not to be used to process water-sediment samples for the determination of organic compounds; however, the syringe filter with plastic components has been approved and is an efficient and technically appropriate option for a specific DAI LC-MS/MS analysis. For detailed information regarding syringe filter, syringe, blunt needle, and other equipment needed for the syringe filtration process, and on how to connect the syringe filter to the syringe, refer to NFM 5, version 3.0 or later, or contact the USGS National Water Quality Laboratory (*http://nwql.usgs.gov/mrdp.shtml?MRDP)*.

— The disposable syringe-tip filter consists of a 25-mm-diameter GF/F membrane with a graded multifilter (GMF)[25], nominal 0.7-µm pore diameter, enclosed in a polypropylene housing with Luer inlet and outlet fittings (table 2–9; fig. 2–17*A*). **The syringe filter is discarded after a single use.**

— A disposable 20-mL syringe constructed of high-purity polypropylene and polyethylene is used to contain the sample and provide pressure to push the sample through the filter (table 2–9; fig. 2–17*B*). **The syringe is discarded after a single use.**

[23] Direct aqueous injection-liquid chromatography/tandem mass spectrometry.

[24] Alternatively, either a plate-filter assembly or PFA inline filter-holder assembly can be used, as described above in the bulleted item "Trace organic compounds."

[25] The graded multifilter (GMF) is a prefilter consisting of a coarse top layer of borosilicate glass microfibers meshed with a fine bottom layer.

— A blunt stainless-steel needle, 2 in. long, with Luer connector (needle), is used to withdraw sample into the syringe.

— The 25-mm filter unit is appropriate for the DAI LC-MS/MS methods because the required volume of filtered sample is only 10 mL.

Table 2–9. Equipment needed for filtration of water samples for analysis by DAI LC-MS/MS.

[DAI LC-MS/MS, direct aqueous injection-liquid chromatography/tandem mass spectrometry; NFSS, National Field Supply Service; GF/F, glass fiber filter; mm, millimeter; µm, micrometer; mL, milliliter; HSW®, Henke Sass Wolf Norm-Ject® sterile Luer-Lock syringe; NWQL, National Water Quality Laboratory; in., inch]

Item	NFSS Catalog Number	Description
Syringe filter	Q762FLD	Disposable syringe-tip filter, GF/F, 25-mm diameter, 0.7µm nominal pore diameter, polypropylene housing (Whatman 6890-2507 "GF/F with glass microfiber membrane")
Syringe	Q763FLD	Disposable syringe, 20 mL, with Luer-Lock outlet, high-purity polyethylene with polypropylene plunger, free of rubber, latex, and silicone oil (HSW® Norm-Ject®).
Blunt needle	Q764FLD	Stainless-steel needle, 1 in. long, with Luer fitting and blunt tip (NFSS catalog number Q764FLD).
DAI LC-MS/MS kit	Q765FLD	Kit includes the syringe filter, syringe, blunt needle, and 20-mL glass amber vial. (The 40-mL vial in which 20 mL of sample is collected is being replaced with a 20-mL vial that requires only 10 mL of sample. Contact NWQL if further clarification is needed.)

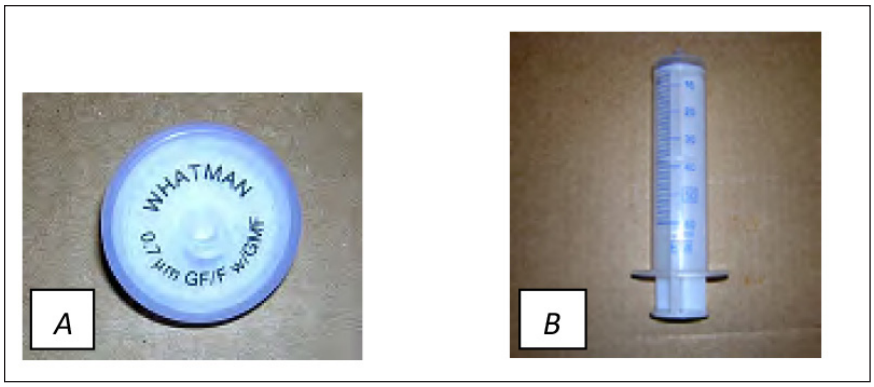


Figure 2–17. Syringe-tip filter and syringe for processing samples for analysis by DAI LC-MS/MS: *(A)* 25-millimeter disposable syringe-tip filter disk (National Field Supply Service (NFSS) catalog number Q762FLD) and *(B)* 20-milliliter disposable syringe with Luer-Lock outlet (NFSS catalog number Q763FLD). (A 1-inch blunt-tip stainless-steel needle with Luer fitting (NFSS catalog number Q764FLD) is not shown). Photographs from U.S. Geological Survey collection.

- **Dissolved organic carbon (DOC), total particulate carbon (TPC), particulate inorganic carbon (PIC), and total particulate nitrogen (TPN).** Depending on the types of analyses for dissolved organic carbon to be performed on the sample, **DOC samples** are processed through either (1) a Savillex DOC 25 fluorocarbon pressure filtration unit[26] with a baked 25-mm, 0.7-micron pore size GF/F disk, loaded on a 25-mm stainless steel or polysulfone filter-support screen, or (2) one of the disposable filters—either the large-capacity Versapor® capsule filter or the 19.6-cm^2 capacity Thermopor® disk filter (NFM 5.2.2.C). **Samples for TPC and TPN analyses** must be processed either through the Savillex pressure filtration assembly or a vacuum filtration assembly (fig. 2–18*A* and *B*), loaded with a baked 25-mm, 0.7-micron pore size GF/F disk on a 25-mm stainless steel screen.
  - Either a hand-pressure pump or a peristaltic pump fitted with clean tubing can be used to move the TPC, TPN, and PIC sample through the filtration assembly.
  - A peristaltic or submersible groundwater pump can be used to move the DOC sample through the capsule filter.
  - A detailed description of the methods and equipment needed for the analysis of carbon samples can be found in NFM 5.2.2.C, "Procedures for processing samples for carbon analysis." See also the equipment lists provided in section 2.4.

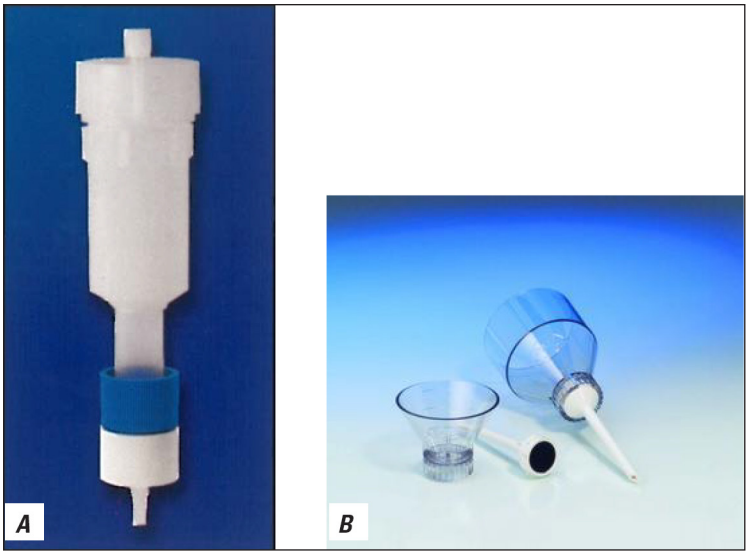


Figure 2–18. Filtration assemblies used to process samples for analysis of total particulate carbon and nitrogen: *(A)* Savillex DOC 25-mm fluorocarbon pressure assembly, and *(B)* Pall® Life Sciences, Inc. small-capacity (left) and large-capacity (right) polysulfone vacuum assemblies. Phographs published with permission: A, courtesy of Savillex Corporation; B. courtesy of Pall Corporation.

Filter-membrane material

Tortuous-path depth filters made of borosilicate glass microfibers are used to filter most samples to be analyzed for organic compounds because the material is considered inert for its intended use, can withstand organic solvents, and can withstand laboratory preparation (being baked at 450 °C). **Filter membranes made of cellulose, polycarbonate, or polyethersulfone polymers commonly are used to process**

[26] Part number for the "Savillex U.S. Geological Survey – DOC 25 configuration" is Savillex part #401-61-25-53-60-2.

samples for the determination of nutrients and other inorganic constituents. These are not suitable for filtering samples for the determination of most organic compounds, mainly because they are not resistant to the organic solvents used to preclean sampling and processing equipment. DOC samples, however, may be processed through the disposable capsule filter) (NFM 5), if study objectives permit.

- For most organic analytes, use GF/F (glass-microfiber filters) with a 0.7-µm nominal pore size that have been baked at 450 °C for at least 2 hours.[27]
  - The 25-mm syringe-tip GF/F disk used for DAI LC-MS/MS sample analysis is not baked at 450 °C but is field rinsed prior to use.
  - The 25-mm GF/F disk is used in the Savillex and vacuum filtration assemblies (see section 2.2.3.A.).
- Use only filters without binders. (Acrylic resin binders might leach from the filter and contaminate samples, or might not be completely combusted when baked at 450 °C.)

2.2.4 Pump Tubing and Tube Connectors

Pump tubing refers to the sample lines that are used with various pumps to collect and process groundwater and surface-water samples. Tubing connectors join the tubing to pumps, filters, or other sections of tubing that may be of the same or different diameter or material. The tubing and connectors for surface-water samples usually are consistent in material and diameter. The tubing and connectors for groundwater samples can vary according to the type of well to be sampled and the data quality objectives. Tubing and connections for groundwater may be used to pump water from the well or to connect to groundwater wells having preinstalled pumps. Field personnel are cautioned to **evaluate possible artifacts in a sample associated with pump tubing and tubing connectors and connections**.

When connecting to an existing supply well with a garden-hose type connection, the disposable, one-use only "Tuff-Lite" adapter (garden hose connection kit, part # CSK001) available from One Stop Shopping can be adapted to one-half inch NPT (National Pipe Thread Taper) standard threads to which project-appropriate fittings and tubing can be connected.

- Tubing connectors and connections that contact the sample should be made of inert material, to the extent possible. Stainless-steel connections should be the highest grade available (SS 316). If flexible copper, aluminum, or stainless-steel tubing is used for chlorofluorocarbon (CFC) sampling, it should be refrigeration grade. Such fittings ordinarily are delivered with coatings of machining lubricants, which must be removed by cleaning before use.
  - Greaseless fittings can be specified and ordered on the open market.
  - For filtering groundwater samples that are pumped directly from the well to a filtration assembly, **fluorocarbon polymer tubing ordinarily is preferred and recommended**.
  - Fluorocarbon polymer, silicone, C-Flex® pump tubing commonly are used with portable submersible pumps and with peristaltic or metering pumps. Use of a fluorocarbon polymer material generally is recommended because fluorocarbon polymers are relatively inert with respect to many inorganic and organic analytes (table 2–10).

[27] USGS personnel can obtain baked, quality-assured 142-mm-, 47-mm-, and 25-mm-diameter GF/F disks and quality-assured 25-mm syringe-tip filters from One Stop Shopping.

- Silicone tubing is suitable when sampling for inorganic analytes only, **and only after appropriate cleaning** (see NFM 3).
  - Measurable concentrations of silica (0.09 to 0.24 mg/L) have been detected in blank samples passed through silicone tubing (Horowitz and others, 1994). These concentrations are likely to be problematic only if low-ionic-strength water is being sampled or if the concentrations are unsuitable to meet the data-quality requirements of the study.
  - Silicone tubing is not designed for use with acids.
  - Silicone tubing is gas permeable and very sorptive of organic compounds.
- C-Flex® tubing is made from a thermoplastic elastomer and is suitable for use when sampling for all inorganic analytes and DOC, but not for other organic compounds.
  - C-Flex® tubing is not compatible with alcohols or organic solvents, and therefore cannot be used when sampling for organic analytes. DOC is an anomaly because organic solvents are a source of contamination for DOC analysis.
  - C-Flex® tubing is relatively resistant to acid. Acid resistance is important because dilute hydrochloric acid is required for most equipment-cleaning procedures, especially for decontamination of equipment used for sampling inorganic analytes (see NFM 3).
  - C-Flex® tubing is less permeable to gas than silicone tubing.
- Fluorocarbon polymer tubing is recommended when sampling for most inorganic and organic analytes. Fluorocarbon polymer tubing is available in corrugated and convoluted, as well as in straight-wall configurations (fig. 2–14).[28]
  - Fluorocarbon polymer tubing is available that is customized to the shape of the pump head.
  - Convoluted fluorocarbon polymer tubing is flexible and easy to handle. Attach convoluted tubing to each end of the premolded tubing.
  - Fluorocarbon polymer tubing sheathed in another plastic is available at lower cost and can be a good alternative for one-time use or short-term use and cleaning cycles.
    - The fluorocarbon polymer liner may twist, constrict, and crack within its sheathing, such that a smooth flow of water is impeded.
    - A fluorocarbon polymer tubing liner sheathed in another plastic requires frequent inspection to ensure that the liner has not cracked, allowing sampled water to pass between the liner and plastic sheathing.

[28] The convoluted tubing usually is available in fixed lengths with smooth surfaces at the ends, whereas the corrugated tubing is produced in alternating ribbed and smooth sections.

- Polyvinyl chloride (PVC) tubing (Tygon®) is suitable for inorganic samples only and must be appropriately cleaned prior to contact with inorganic samples.
  - PVC tubing can be washed with dilute acid.
  - PVC tubing has the lowest gas permeability of any peristaltic pump tubing.
  - When used with a peristaltic pump, PVC tubing has a shorter life than silicone, C-Flex®, or Norprene®.
  - **PVC tubing may leach plasticizers.**
- Nylon, polyethylene (PE), and polypropylene are all inexpensive, rigid tubing that can withstand high pressure and are relatively impermeable to gases and moisture. PE and polypropylene are suitable for sampling inorganic analytes. Nylon tubing is more resistant to organic compounds than other plastic tubing, but to date has not been tested as a potential source of trace-element or organic-compound contamination.
- Norprene® tubing is made from a thermoplastic elastomer (a polypropylene base with USP mineral oil) and **is suitable only when sampling for inorganic analytes**. It must be appropriately cleaned prior to contact with samples collected for inorganic analysis. (Norprene® tubing has the longest life of any manufacturer-recommended tubing material.) Norprene tubing®:
  - Can be washed with dilute acid.
  - **May leach USP mineral oil.**
  - Is acceptable for use with a peristaltic pump.
  - The gas permeability of Norprene® tubing is lower than that of silicone tubing and greater than that of PVC tubing.

Table 2–10. Common varieties and characteristics of fluorocarbon polymer tubing.

Varieties of Fluorocarbon Polymer Tubing.	Characteristics of Fluorocarbon Polymer Tubing.
FEP (fluorinated ethylene polypropylene)	• Most transparent • Best abrasion resistance • High flexibility • Least expensive of the Teflon® varieties
PFA (perfluoroalkoxy)	• Less transparent than FEP • Virtually nonporous (nonpermeable) • Most expensive of the Teflon® varieties
PTFE (polytetrafluoroethylene)	• Least transparent; milky to white • High flexibility • Midpriced between FEP and PFA
Kynar® (polyvinylidene fluoride)	• Translucent • Low flexibility • Less expensive than the Teflon® varieties
Tefzel® (Ethylene tetrafluoroethylene)	• Withstands higher pressure than Teflon® • Most expensive

2.3 Field Vehicles

Water samples should be processed within vehicles that are designed, designated, prepared, and dedicated for that purpose. If multiple-use vehicles are used for water-quality work, then use of portable processing and preservation chambers is mandatory, and additional quality-control samples should be collected to document that the quality of the data has not been compromised. **Contamination of the sample for target analytes is much more likely when multiple-use vehicles are used for the collection of water-quality data.**

Whether using a field vehicle dedicated for water-quality work or a multi-use vehicle, every effort should be made to keep the work area clean and to eliminate sources of sample contamination, as is emphasized in the examples listed below.

- Containers of blank water, solvents, buffers, standards, and other chemical substances should be properly labeled, dated, secured, and stored in a manner that prevents accidental spills. Some solutions may need to be stored separately to protect them from contamination.
- Keep metallic objects, such as surface-water and groundwater sampling support equipment, out of the inorganic sample-processing and -preservation area.
- Install a dustproof barrier between the vehicle's cab and the sample-processing and -preservation area.
- Cover metallic surfaces (cabinets or shelving that cannot be replaced) with plastic sheeting in areas where samples will be processed for the analysis of inorganic constituents and cover all work surfaces with heavy-duty aluminum foil in areas where samples will be processed for the analysis of organic constituents.
  - Keep the sheeting free of spills and dust.
  - Replace sheeting on a routine basis (as suitable for the site environment) and whenever it cannot be cleaned completely.
- Store chemical substances so that chemical fumes will not enter the sample-processing and -preservation area. Containers of solvents, blank waters, and liquid waste should be stored in separate areas or compartments.
- If transporting a nitrogen tank, ensure that the tank is fastened securely to the vehicle with a bracket. Brackets specially designed for gas tanks/cylinders can be obtained from companies that sell gas-supply equipment.

For additional discussions about recommendations and requirements for field vehicles, refer to Horowitz and others (1994) and Koterba and others (1995).

CAUTION! Store acids, bases, and solvents in separate storage areas so that the chemicals cannot mix if a spill occurs (NFM 9).

2.4 Checklists for Equipment and Supplies

Examples of checklists for equipment and supplies commonly used to collect and process water samples are provided in tables 2–11 through 2–18 to aid field personnel when selecting equipment for a water-quality field trip. These checklists are not intended to be exhaustive and should be modified to meet specific study needs. Many of the items listed are explained in greater detail in other NFM chapters, as indicated. Refer to other chapters of the NFM for lists of equipment and supplies for field measurements (NFM 6), biological indicators (NFM 7), and bottom-material samples (NFM 8). **Field equipment must be cleaned and tested before commencing with field work (NFM 3).**

Remember to test backup equipment and bring it to the field in good operating condition.

Table 2–11. Suggested support equipment for surface-water sampling.

[A detailed description of the various types of support equipment is beyond the scope of this manual; refer to Corbett and others (1943), Buchanan and Somers (1969), and Rantz and others (1982)]

Cranes		
Type		Maximum recommended weight of sampler (pounds)
	Type A	100
	Type E	30,000
	Bride board	50
	Other (add to checklist)	
Crane bases		
Type		Maximum recommended weight of sampler (pounds)
	Three-wheel	100
	Four-wheel	150

Miscellaneous	
	Battery or hydraulic power motor system for B-56 or E-53 reel
	Hanger bars, connectors, and pins for connecting sampler to cable
	Counterweights for four-wheel crane base
	Safety equipment (flotation jacket, cable cutter, bridge safety plan, traffic cones, and warning signs)
	Vertical transit rate pacer (US VTP-99)
	Variable speed reel drive system for B-56 or E-53 reel (batteries, spare belts)
	Handlines or ropes for operating weighted bottle sampler, VOC sampler, or DH 95, or DH 2
	Plastic coated wading rod for DH-81
	Other (add to checklist)

Table 2–11. Suggested support equipment for surface-water sampling.—Continued

[A detailed description of the various types of support equipment is beyond the scope of this manual; refer to Corbett and others (1943), Buchanan and Somers (1969), and Rantz and others (1982)]

Reels[1]						
	Reel	**Cable diameter (inches)**	**Maximum weight (pounds)**	**Cable capacity (feet)**	**Brake**	**Operation type**
	A-55	0.084 0.10	50 100	95 80	No	Hand
	B-56	0.10 0.125	150 200	144 115	Yes	Hand or power
	E-53	0.10 0.125	150 300	206 165	Yes	Power
	Other (add to checklist)					

[1]Selection of a type of reel should be based primarily on the maximum cable length needed and the weight of the sampler that must be supported.

Table 2–12. Suggested support equipment for groundwater sampling.

Groundwater support equipment	
	Handline or manual/power reel with line
	Tripod assembly with manual or power reel
	Wellhead guide for flexible sample line to pump
	Wheeled carts to transport portable sampling equipment
	Energy source for reels and pumps (batteries, compressor, or generator)
	Extension cords
	Other (add to checklist)

Table 2–13. Sample-collection equipment for surface water and groundwater.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*]

Sample collection equipment: surface water (refer to NFM 4)	
	Weighted bottle (plastic or stainless steel), handline, and bottle
	US DH-95 and US D-95 (plastic dipped) • Bottle (1 liter) • Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) and cap
	US DH-81 (handle and collar) • Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) and cap • Plastic or fluorocarbon polymer bottle (1 liter)
	US DH-2, US D-96, US D-96-A1, and US D-99 (plastic dipped) • Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) • Polyethylene or perfluoroalkoxy (PFA) bag • Extra tailfin section, nozzles, adapters, sampler head, and so forth • Bag sampler intake efficiency requires: ○ Graduated pitcher or cylinder (2 or 4 L) ○ Stop watch
	Crane with 3- or 4-wheel base and counterweights
	Reel, hanger bars, and pins
	Current meter/ADCP for US DH-95, US D-95, US DH-2, US D-96, US D-96-A1, and US D-99
	Bridge board and reel
	Plastic sheeting with weighted corners to cover bridge rail, 2 millimeters thick
	Vertical transit rate pacer
	Biochemical oxygen demand (BOD) sampler
	Volatile organic compound (VOC) sampler
	Thief sampler
	Pumping sampler(s)
	Other (add to checklist)
Sample collection equipment: groundwater (refer to NFM 4)	
	Positive-displacement submersible pump, discharge line, and reel
	Water-supply-well sample line and garden-hose threaded adaptor
	Thief-type sampler (for example, bailer, single or double-check valve, and bottom-emptying device)
	Suction-lift pump (peristaltic or centrifugal)
	Antibacksiphon device

Table 2–13. Sample-collection equipment for surface water and groundwater.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*]

	Sample collection equipment: groundwater (refer to NFM 4)
	Sample-water manifold (to split sample water flow)
	Flowthrough chamber for field-measurement electrodes (pH, conductivity, dissolved oxygen, water temperature, oxidation/reduction)
	Tubing, appropriate for type of pump and target analytes
	Tubing connectors and "Tuff-Lite" adapters (compatible with tubing material and target analytes)
	Water-level measuring tape (steel or electric) and bleach/water solution or disinfectant wipes (commercially available). For electric tapes, be sure to check with the manufacturer before exposing the tape and tape housing to the bleach or other solvent solution. Follow the detailed instructions for disinfecting and subsequent rinsing of well tapes given in NFM 3 and updated in the Comments and Errata for NFM 3, dated 11/21/2005 (*http://water.usgs.gov/owq/FieldManual/mastererrata.html*)
	Water-level indicator (blue chalk for steel tape)
	Weight (to attach to water-level measuring tape or sample line). Do not use a lead weight; use stainless steel or other relatively noncontaminating material.
	Power source for pump or reel; batteries for electronic sounder
	Graduated bucket (to measure rate of discharge) and stopwatch
	Containers (for disposal of purge water)
	Flow controller (for sampling pump)
	Plastic sheeting, 2 millimeters or thicker
	Other (add to checklist)

[1]Use only nozzles purchased from the U.S. Geological Survey Federal Interagency Sedimentation Project.

Table 2–14. Sample-processing equipment and supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DAI LC-MS/MS, direct aqueous injection liquid-chromatography/tandem mass spectrometry; OGW, organic-grade water; L, liter; mm, millimeter; µm, micrometer; in., inch; g, gram; mL, milliliter]

Sample splitters (refer to NFM 5)	
	Churn splitters • Plastic churn splitter, 8 L or 14 L, modified spigot and funnel (NFM 2.2.1.A) (inorganic analytes) • Fluoropolymer churn splitter, 8 L or 14 L (organic and (or) inorganic analytes), modified spigot • Extra fluoropolymer churn spigot, nylon screws and o-rings
	Churn carrier
	Cone splitter • Splitting chamber for cone splitter • Bull's-eye bubble level and shims for cone splitter
	Large clear plastic bags: protective • Covering for transporting clean churn splitter or cone splitter • Covering for sample processing and preservation chambers
	Subsample bottle kits for whole-water samples
	Other: Gloves (nitrile, powderless, disposable)
Filtration systems for inorganic-constituent filtration (refer to NFM 5)	
	Peristaltic pump and batteries
	Pump tubing for groundwater and peristaltic pump (refer to section 2.2.4, table 2–10)
	Filtration devices • Filter units, disposable capsule filter, "high-capacity" Versapor® membrane, 0.45-µm pore size • Disk filter, small capacity, Thermopor® membrane, 0.45-µm pore size
	Filter membranes for nondisposable (plate-filter) filtration assemblies (various diameters, pore sizes, and materials); plate-type filtration assemblies; forceps, plastic or ceramic (to handle filter membranes)
	Subsample bottle kits (for filtered inorganic samples)
	Inorganic grade blank water (IBW) (obtained by USGS personnel from One Stop Shopping)
	Deionized water (DIW), Water Science Center-produced and quality assured)
	Gloves (powderless, disposable, nitrile)
	Other (add to checklist)
Filtration systems for organic-compound filtration (refer to NFM 5)	
	Plate-filter assembly • Aluminum or stainless steel (for 13-, 142-, or 293-mm-diameter filter disk) • PFA filter holder (for 25-mm or 47-mm-diameter filters)
	Filter disk, borosilicate glass fiber (GF/F); 0.7-µm pore size, baked. (Select diameter: 293 mm, 142 mm; 13 mm, 25 mm; 47 mm, as required)
	Pump, ceramic piston valveless metering, with fluorocarbon polymer convoluted tubing or groundwater pump tubing, and batteries. (Alternatively, peristaltic pump with FTPE diaphragm pump head: alternative to valveless metering pump, as appropriate for project needs and data-quality requirements.)

Table 2–14. Sample-processing equipment and supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DAI LC-MS/MS, direct aqueous injection liquid-chromatography/tandem mass spectrometry; OGW, organic-grade water; L, liter; mm, millimeter; µm, micrometer; in., inch; g, gram; mL, milliliter]

Filtration systems for organic-compound filtration (refer to NFM 5)	
	DAI LC-MS/MS kit (refer to table 2–9) that includes: • Disposable syringe-tip filter, GF/F, 25-mm diameter, 0.7 µm, polypropylene housing • Disposable syringe, 20 mL, HSW® Norm-Ject® with Luer-lock outlet, high-purity polyethylene with polypropylene plunger • Stainless-steel blunt-tip needle, 1 in. long, with Luer fitting • 20-mL glass amber vial
	Organic carbon: Savillex fluorinated ethylenepropylene pressure-filtration assembly and 25-mm stainless steel or polysulfone filter support screen. (Refer also to section 2.2.3.B for use of the disposable capsule or disk filter for dissolved organic carbon sample analysis, listed above under "Filtration systems for inorganic-constituent filtration")
	Subsample bottle kits
	Volatile/pesticide-grade blank water (VPBW) (obtained by USGS personnel from One Stop Shopping)
	Pesticide-grade blank water (PBW) (obtained by USGS personnel from One Stop Shopping)
	Deionized, charcoal-filtered organic-grade water (OGW), Water Science Center-produced and quality assured
	Forceps (stainless steel, ceramic, or Teflon-coated)
	Other (add to checklist)
Miscellaneous processing equipment and supplies: inorganic and organic sampling	
	Sample processing chamber; supply of transparent plastic covers (bags) for portable chamber and disposable powderless gloves to handle equipment
	Gloves, powderless, disposable, made of nitrile or other chemical-resistant material (as required by the intended application)
Filtration system for carbon analysis (refer to NFM 5)	
	Fluorocarbon-polymer filtration assembly and baked glass-microfiber filter disks (GF/F) (25-mm, 0.7-µm pore size)
	Disposable capsule filter for dissolved organic carbon sample analysis (if consistent with study protocols and objectives)
	Hand pressure or peristaltic pump
	C-flex tubing with inline 0.2-µm air filter
	Cylinder (graduated, glass)
	Holding stand, ring, and medium three-prong clamp
	Forceps, stainless steel
	Whirl-Pak bags (6 ounce and 18 ounce)
	Aluminum foil squares
	Cooler and ice
	Organic-grade water
	Power source for pump (battery, generator, other)
	Other: Gloves (powderless, disposable, nitrile)

Table 2–14. Sample-processing equipment and supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DAI LC-MS/MS, direct aqueous injection liquid-chromatography/tandem mass spectrometry; OGW, organic-grade water; L, liter; mm, millimeter; µm, micrometer; in., inch; g, gram; mL, milliliter]

Solid-phase extraction (SPE) system (refer to NFM 5)	
	Valveless piston metering pump (ceramic) (with fluorocarbon polymer convoluted tubing)
	Fluorocarbon polymer tubing, 1/8-in. outside diameter
	Variety of tubing fittings, adaptors, connectors, and unions
	Portable balance, 1 to 6,000 g
	Graduated glass cylinders
	Beaker (plastic, 1,000 mL)
	Spike mixture and micropipette kit
	Surrogate mixture and micropipette kit
	SPE column (C-18); checklist and reporting form
	Methanol (pesticide grade), ascorbic acid, sodium chloride, and pesticide-grade organic water, all in fluorocarbon polymer dispenser bottles
	Gloves (powderless, disposable, nitrile)
	Stopwatch
	Aluminum foil
	CFCs, dissolved gases SF_6, $^3H/^3He$, and low-level VOCs)
	Consult the USGS Reston Chloroflurocarbon Laboratory at http://water.usgs.gov/lab/ for sample-collection or –processing equipment for CFCs and dissolved gases (N_2, Ar, Co_2, CH_4, O_2, He-4), SF_6, $_3H/_3He$, and low-level VOCs.
	Passive diffusion bag (PDB) samplers[1] for investigating selected volatile organic compounds in groundwater (see NFM 5)
	1- to 2-ft-long low-density polytheylene (LDPE) lay-flat tubes
	Polyethylene mesh (sleeve for PDB)
	Deionized water (used to initially fill the PDB before deployment)
	Weighted line or fixed pipe (to hold PDB in place in well)
	Cable ties or stainless steel spring clamps (to hold PDB to weighted line or fixed pipe)
	Heat source (to seal ends of PDB)

[1]Vroblesky (2001b) includes photographs of sampling equipment and deployment.

Table 2–15. Sample-preservation equipment and supplies.

[NFM, *National Field Manual for the Collection of Water-Quality Data*; *N*, normal]

	Preservation equipment and supplies (refer to NFM 5)
	Preservation chamber(s)
	Chamber covers (large, transparent bags)
	Waste containers for spent preservative ampoules (uniquely dedicated for each chemical used)
	Chemical reagents (such as nitric, hydrochloric, and sulfuric acids) and project requirements for sample preservation for the analytes targeted and analytical method selected. *Note that although several analytes might require the same type of acid preservative, the normality, volume, and grade specified by the laboratory may differ; it is important to follow the explicit laboratory directives concerning the chemical treatment of a sample, including handling, storage, and expiration date of the preservative.*
	Nitric acid (HNO_3): 7.57 to .7*N*, Ultrex grade
	6*N* ultrapure hydrochloric acid vial (for mercury sample)
	Sulfuric acid (H_2SO_4): • 4.5*N* for nutrients and carbon samples • 18*N* for chemical oxygen demand (COD) and phenol samples
	Hydrochloric acid (HCl) for volatile organic compound sample
	Phosphoric acid/cupric sulfate
	Sodium hydroxide (NaOH)
	Ascorbic acid
	Zinc acetate
	Phytoplankton kit
	Radon kit
	Preservation equipment and supplies (refer to NFM 5)
	Cooler, ice or chilling agent, 12-volt freezer or dry ice for chlorophyll
	Other: For example, apron, goggles, gloves (powderless, disposable nitrile)

Table 2–16. Cleaning and quality-control sampling equipment and supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; FEP, fluorinated ethylene polypropylene]

	General cleaning equipment and supplies (refer to NFM 3)
	Basins or standpipes (clear or white plastic, fluorocarbon polymer, stainless steel)
	Brushes (nonmetallic, clear or white)[1]
	Detergent, laboratory phosphate-free (0.1 to 2 percent by volume)
	Tap water
	Deionized water, produced in a Water Science Center laboratory or equivalent (ASTM International Type 1) (Office of Water Quality Technical Memorandum 92.01), distilled water purchased from commercial supplier

Table 2–16. Cleaning and quality-control sampling equipment and supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; FEP, fluorinated ethylene polypropylene]

General cleaning equipment and supplies (refer to NFM 3)	
	Wash bottles
	Material Safety Data Sheet (MSDS) for each chemical to be used
	Sealable plastic bags (without color closure strips) • Large plastic storage bags
	Other safety equipment; for example: • Laboratory coat or apron • Gloves • Eyewash station • Acid spill kit; solvent spill kit • Safety shower
Inorganic constituents	
	Hydrochloric acid, analytical grade (5 percent by volume)
	Neutralization container and marble chips
	Wash bottle (for hydrochloric acid)
	Inorganic-grade blank water (IBW)[2] (National Water Quality Laboratory Technical Memorandum 1992.01)
	Large plastic bags (clear or white)
	Plastic sheeting (clear or white)
Organic compounds	
	Methanol, pesticide grade[3]
	Waste container, methanol[3]
	Waste container for buffers and standards
	Wash bottle, for methanol (FEP-grade fluoropolymer)[3]
	Aluminum foil
	Fluorocarbon polymer bags/sheeting
	Pesticide- or volatile-grade blank water (PBW or VPBW)[2]
	Deionized water, district-produced or equivalent (ASTM International Type 1) and quality assured

[1]Restaurant-supply stores are an excellent source for these types of brushes.

[2]USGS personnel should obtain blank water from the "One Stop Shopping" Web site using the following item numbers: IBW - Q378 FLD; PBW - N1590 or N1600; VPBW - N1580 or N1570

[3]Methanol supplies must not be used or stored where contact is possible with samples or equipment dedicated for the analysis of organic carbon.

Table 2–17. Shipping equipment and supplies.

[NFM, *National Field Manual for the Collection of Water-Quality Data*]

Shipping equipment and miscellaneous shipping supplies (refer to NFM 5[1])	
	Coolers (1- to 5-gallon sizes)
	Boxes (sturdy)
	Packing material (foam sleeves, bubble wrap), ice
	Large plastic bags (for lining coolers and boxes)
	Sample-bottle labels
	Analytical Services Request (ASR) form, return address label, and account number
	Sealable plastic bag for forms and return address label
	Tape (fiber reinforced)
	Shipping label (forms)

[1] The additional equipment needed for shipping chain of custody samples is not included on this table.

Table 2–18. Field-measurement and miscellaneous field supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DO, dissolved oxygen; NIST, National Institute of Standards and Technology; USGS, U.S. Geological Survey]

Field-measurement and miscellaneous field supplies (refer to NFM 6)	
Field Measurements	
	Instruments for measurement of barometric pressure, water temperature, dissolved oxygen, specific electrical conductance, pH, redox, alkalinity, turbidity, and other water properties (Refer to each section in NFM 6.)
	Barometer (NFM 6.2) (most DO meters include an internal barometer)
	Calibration buffers and standards (NFM 6.2, 6.3, 6.4, 6.5, 6.7)
	Digital counter for alkalinity titration (NFM 6.6)
	Buret (NFM 6.6)
	Beakers
	Volumetric pipettes (have a backup supply of various capacities)
	Magnetic stirrer
	Titrant (NFM 6.6)
	Titrant cartridges (NFM 6.6)
	Titrant delivery tubes (NFM 6.6)
	Thermometers and (or) thermistors (NFM 6.1), NIST-certified or NIST-traceable
Miscellaneous Equipment and Supplies	
	Printout or online access to relevant sampling procedures and USGS field protocols
	Emergency contact information for field personnel: names, phone numbers, e-mail addresses, etc.

Table 2–18. Field-measurement and miscellaneous field supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DO, dissolved oxygen; NIST, National Institute of Standards and Technology; USGS, U.S. Geological Survey]

Field-measurement and miscellaneous field supplies (refer to NFM 6)—Continued	
Miscellaneous Equipment and Supplies—Continued	
	Bound notebook (logbook) and ballpoint pen (indelible ink, non-smudge)
	Laptop or tablet computer with power adapter
	Thumb drive for data backup
	Field folder(s) with station, site, and well information and permission form
	Field documentation forms
	Calculator and extra batteries
	Watch
	Tagline
	Discharge measurement equipment
	Hip boots
	Chest waders
	Rain gear
	Personal flotation device
	Traffic safety vest, cones, signs, warning lights
	First aid kit
	Highway emergency kit
	Tool kit
	Tape (electrical, fiber, fluorocarbon polymer, other)
	Plastic-coat spray
	Fire extinguisher
	Flashlight with extra batteries
	Backup batteries for sampling devices
	Keys to sampling site, security locks, and vehicle (extra set)
	Weather report
	Field trip itinerary (copy to supervisor); sampling and safety plans, Job Hazard Analysis form
	Satellite phone or cellular phone
	Camera with extra batteries, memory card, etc.
	Work gloves

Table 2–18. Field-measurement and miscellaneous field supplies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DO, dissolved oxygen; NIST, National Institute of Standards and Technology; USGS, U.S. Geological Survey]

	Field-measurement and miscellaneous field supplies (refer to NFM 6)—Continued
	Miscellaneous Equipment and Supplies—Continued
	Shovel, ice chisel/auger
	Boat, motor, gasoline, oil, paddle, oars
	Drinking water
	Soap (antibacterial)
	Sunscreen (wash hands thoroughly after application; do not use a spray application or aerosol)
	Insect repellent. Instead of a DEET repellent, try (a) oil of lemon eucalyptus or (b) picaridin: (see *http://en.wikipedia.org/wiki/Icaridin*; *http://wwwnc.cdc.gov/travel/yellowbook/2014/chapter-2-the-pre-travel-consultation/protection-against-mosquitoes-ticks-and-other-insects-and-arthropods*). Additional insect-repellent information from U.S. Environmental Protection Agency: *http://cfpub.epa.gov/oppref/insect/* (accessed April 29, 2014).
	Paper towels (lint free)
	Safety plan(s) (NFM 9)
	Map(s); Global Positioning System (GPS)-capable device
	Locations of and phone numbers for hospitals and other emergency facilities (police, fire department, animal control, etc.) (NFM 9)
	USGS photo identification should be with all field personnel at all times in the field.
	Direct current/alternating current (DC/AC) power inverter
	Other (add to checklist)

Conversion Factors, Selected Terms and Symbols, and Abbreviations

Conversion Factors

Inch/Pound to SI

inch (in.)	25.4	millimeter (mm)
square inch (in^2)	645.16	square millimeter (mm^2)
foot (ft)	0.3048	meter (m)
foot per second (ft/s)	0.3048	meter per second (m/s)
gallon (gal)	3.785	liter (L)
pound, avoirdupois (lb)	0.4536	kilogram (kg)

SI to Inch/Pound

meter (m)	3.281	foot (ft)
meter per second (m/s)	3.281	foot per second (ft/s)
centimeter (cm)	0.3937	inch (in.)
micrometer (µm)	3.9372×10^{-5}	inch (in.)
millimeter (mm)	0.03937	inch (in.)
square centimeter (cm^2)	0.155	square inch (in^2)
liter (L)	0.2642	gallon (gal)
milligram per liter (mg/L)	0.5841	grains per gallon
milliliter (mL)	0.0338	ounce, fluid (oz)
milliliter (mL)	2.64×10^{-4}	gallon (gal)
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound (lb)

Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$°F = 1.8(°C) + 32$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Selected Terms

Analyte (target analyte). "Substances being determined in an analysis" (from Bennett, 1986). The term "target analyte" is used in this report to refer to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, conductivity, dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity.

Fluorocarbon polymers and fluoropolymers. Fluorocarbon polymers (polyfluorocarbons) or fluoropolymers are composed of monomers (smallest repeating compound segment of a polymer) consisting of carbon, fluorine, hydrogen, and, for one polymer, oxygen. The fluoropolymers have tradenames that include, for example, Teflon® and Tefzel® (ethylene tetrafluoroethylene) (products of the DuPont Company) and Kynar® (a polyvinylidene fluoride, a product of the Atofina Chemicals Company). Common types of fluoropolymers include FEP (fluorinated ethylene polypropylene), PFA (perfluoroalkoxy), PTFE (polytetrafluoroethylene), and PVDF (polyvinylidene fluoride). Each fluorocarbon polymer has different chemical and physical properties; however, all are relatively nonreactive chemically at ambient temperatures and do not leach monomers.

Trace element(s). For the purpose of this report and to maintain consistency with common usage, the term "trace element(s)" is used to refer to metals and other elements such as arsenic, antimony, selenium, and tellurium that usually are present in natural surface-water and groundwater systems in concentrations less than 1 mg/L (modified from Hem, 1985). Common usage of this term, as defined above, is inexact and not rigorous with respect to the aqueous chemistry discipline.

Whole water. Water as sampled from its source and not subjected to filtration or other phase-separation process. Common synonymous terms include: raw (water) sample and unfiltered (water) sample.

Selected Symbols

~	approximately
>	greater than
≤	less than or equal to
±	plus or minus

Abbreviations

BOD	biochemical oxygen demand
CFC	chlorofluorocarbon
DAI	direct aqueous injection
DAI LC-MS/MS	direct aqueous injection-liquid chromatography/tandem mass spectrometry)
DC	direct current
DIW	distilled/deionized water DOC dissolved organic carbon
DOC	dissolved organic carbon
ETFE	ethylene-tetrafluorethylene
FEP	fluorinated ethylene polypropylene
FISP	Federal Interagency Sedimentation Project of the U.S. Geological Survey
gal/min	gallon per minute
GF/F	glass fiber filter, sometimes referred to as glass microfiber filters (GMF)
GMF	graded glass microfiber prefilter, consisting of a coarse top layer of borosilicate glass microfibers meshed with a fine bottom layer
GPS	Global Positioning System
HIF	USGS Hydrologic Instrumentation Facility, Stennis Space Center, Mississippi
IBW	inorganic-grade blank water (water that is laboratory-certified to be free of specified inorganic analystes within the given analytical detection or reporting levels)
L/min	liter per minute
LC/MSMS	liquid chromatography-tandem mass spectrometry
LDPE	low-density polyethylene
mL/min	milliliter per minute
NFM	*National Field Manual for the Collection of Water-Quality Data*
NFSS	National Field Supply Service
NPT	National Pipe Thread Taper
NWQL	USGS National Water Quality Laboratory
OGW	organic-grade water produced and analyzed in a USGS Water Science Center laboratory
PBW	pesticide-grade blank water (water that is laboratory-certified to be free of specified pesticide compounds within given analytical detection or reporting levels
PDB	passive diffusion bag sampler

PE	polyethylene
PFA	perfluoroalkoxy
PIC	particulate inorganic carbon
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
SPE	solid-phase extraction
SS	stainless steel
TPC	total particulate carbon
TPN	total particulate nitrogen
USGS	U.S. Geological Survey
USP	United States Pharmacopeia
VOC	volatile organic compound
VPBW	volatile/pesticide grade blank water (water that is laboratory-certified to be free of specified volatile and pesticide compounds within given analytical detection or reporting levels)

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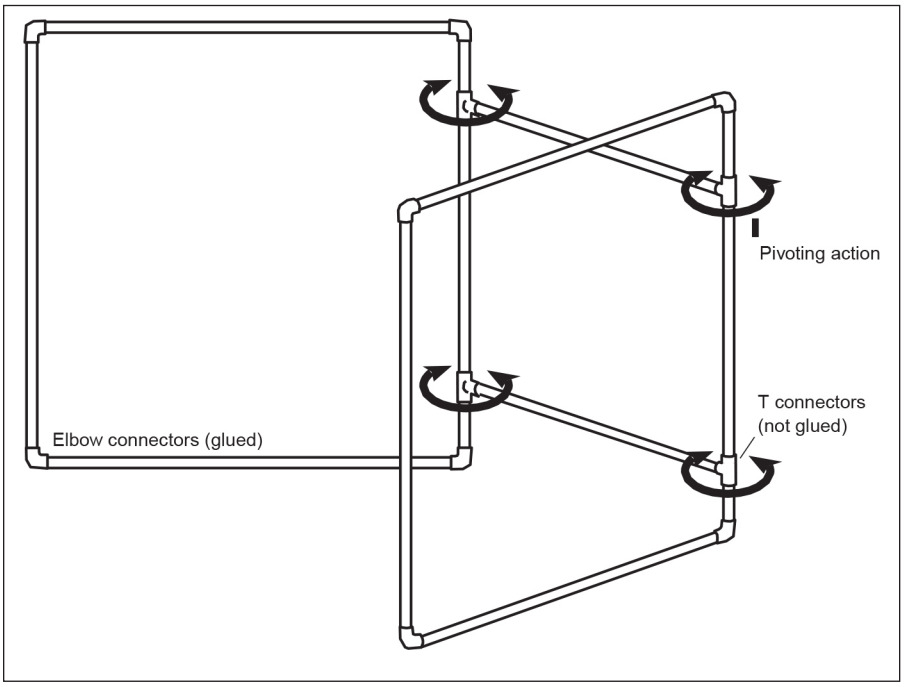
Appendix: Construction of a Collapsible Sample-Processing/ Preservation Chamber.



This frame can be pulled apart at the four joints that are left unglued and will swivel or fold at these joints. Schedule 40 polyvinyl chloride pipes can be used for greater rigidity. The dimensions of a chamber depend on its use (processing or preservation) and the space available in the field vehicle.

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A3.

CLEANING OF EQUIPMENT FOR WATER SAMPLING

Revised 2004
Edited by **Franceska D. Wilde**

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192
This report is online at http://pubs.water.usgs.gov/twri9A/

Foreword

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and quality-assured data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that the data collected are of the quality required to fulfill our mission.

(signed)

Robert M. Hirsch
Associate Director for Water

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CLEANING OF EQUIPMENT FOR WATER SAMPLING

A3.

National Field Manual for the Collection of Water-Quality Data

Chapter A3.

Illustrations

Table

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Chapter A3. CLEANING OF EQUIPMENT FOR WATER SAMPLING

Revised 2004

Edited by **Franceska D. Wilde**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. Chapter A3 describes procedures for cleaning the equipment used to collect and process samples of surface water and ground water and procedures for assessing the efficacy of the equipment-cleaning process. This chapter is designed for use with the other chapters of this field manual.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be posted on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed September 20, 2004).

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A3 describes procedures for cleaning the equipment used to collect and process samples of surface water and ground water and procedures for assessing the efficacy of the equipment-cleaning process.

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to chapter 4, "Collection of Water Samples," and NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to *(1)* establish and communicate scientifically sound methods and procedures, *(2)* provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, *(3)* encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The equipment-cleaning procedures presented in this chapter are adequate for routine environmental conditions. A modification of the cleaning procedures might be required, for example, in order to decontaminate equipment adequately after sampling at sites where analyte concentrations are large. Modifications to the standard procedures described in this chapter must be quality controlled and documented.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and District[1] or other professional personnel, as appropriate. Technical memorandums or other documents that define the policy pertinent to such requirements are referenced in this manual. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplish specific data-quality requirements or study objectives must be based on referenced research and good field judgment and must be quality assured and documented in permanent and readily accessible records.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this chapter to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented in permanent and readily accessible records.

[1]**District** refers to a water-data collecting organizational unit of the USGS located in any of the States or Territories of the United States.

FIELD MANUAL REVIEW AND REVISION

This is version 2.0 of chapter A3, "Cleaning of Equipment for Water Sampling," dated April 2004. The version number and date appear in the footer of each page. Each chapter of the *National Field Manual* is reviewed and revised periodically to correct any errors and incorporate technical advances.

Comments on the NFM, and suggestions for updates or revisions, should be sent to nfm-owq@usgs.gov. Newly revised and reissued chapters or chapter sections are posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed September 20, 2004). This page also contains a link to the NFM "Comments and Errata" page that chronicles revisions to each chapter.

ACKNOWLEDGMENTS

The information included in the original and revised versions of chapter 3 of the *National Field Manual* is based on the work of Sandstrom (1990), Horowitz and others (1994), Shelton and Capel (1994), and Koterba and others (1995). Credit for the production of this report belongs chiefly to the original editors, including D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo.

The editors wish to thank and pay tribute to those who have been responsible for technical review and who contributed to the accuracy, quality, and usability of this report: S.L. Lane, R.W. Lee, and T.D. Oden. Appreciation also is extended to the following colleague reviewers who helped to improve this report: H.D. Ardourel, B.A. Bernard, K.K. Fitzgerald, D.S. Francy, S.R. Glodt, V.J. Kelly, S.W. McKenzie, S.K. Sando, C.A. Silcox, and W.R. White. In addition, the editor is indebted to I.M. Collies and L.J. Ulibarri for their editorial and production assistance.

Special thanks go to T.L. Miller and S.K. Sorenson, whose encouragement and faith in this project have been instrumental to its achievement.

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A3. CLEANING OF EQUIPMENT FOR WATER SAMPLING

USGS policy requires that equipment for water samples be properly cleaned before contacting the sample and that the effectiveness of the cleaning procedures be quality controlled (Sandstrom, 1990; Horowitz and others, 1994; Koterba and others, 1995). Additional specific and more stringent requirements than the standard procedures described in this chapter may be required to meet specific project or program needs.

The goal of equipment cleaning is to help ensure that the equipment is not a source of foreign substances that could affect the ambient concentrations of target analytes in samples or otherwise affect sample chemistry. Standard procedures are described in this chapter for when, where, and how to (1) clean equipment constructed of various materials and (2) collect equipment blanks and field blanks for quality control.

Equipment cleaning (decontamination): Applying cleaning solutions to the external and internal surfaces of equipment or using other nondestructive procedures (such as steam cleaning) to remove foreign substances that could affect the concentrations of analytes in samples.

Space commonly is dedicated in a workplace laboratory for equipment cleaning and for storage of cleaning supplies. In this report this work space can include the Field Service Unit or other dedicated workspace.

Document the use of standard USGS equipment-cleaning and quality-control procedures.

- Clean all sample-collection and sample-processing equipment before use.
  - — Manufacturing residues must be removed from new equipment.
  - — Dust and any other foreign substances must be removed from equipment that has been in storage or transport.
  - — Equipment must be decontaminated immediately after use.
- Prevent cross contamination between sampling sites by rinsing equipment with deionized water (DIW) while equipment is still wet from sampling, and then clean equipment as prescribed in this chapter before transporting it to the next site.
- Do not substitute a "sample-water field rinse" for the equipment-cleaning procedures described in this chapter.
- Collect equipment blanks and field blanks for quality control of the cleaning procedure. The frequency of collecting blanks normally is based on study objectives and site conditions. **However, a minimum of one equipment blank per year is required for each piece of equipment.**

You must adhere to any additional or specific protocols mandated by the study or program for which the data are being collected.

SUPPLIES FOR EQUIPMENT CLEANING 3.1

By **D.B. Radtke, A.J. Horowitz, and M.W. Sandstrom**

The supplies commonly used to clean sample-collection and sample-processing equipment are listed in table 3–1. Cleaning supplies are to be stored in a contaminant-free cabinet. Follow safety instructions regarding the storage of chemical reagents (NFM 9).

Before gathering the cleaning supplies, check the construction materials (for example, metal, glass, or plastic) of washbasins and other cleaning items relative to the samples to be collected.

- **For analysis of inorganic constituents**—Basins, brushes, and other items used for cleaning should be constructed of a suitable nonmetallic material, preferably uncolored or white polypropylene, polyethylene, or other plastic. **Do not use cleaning agents or items that might leach or sorb metals if the equipment to be cleaned will be used for samples to be analyzed for trace elements.**

- **For analysis of organic compounds**—Basins and other cleaning items can be constructed of metal, glass, or plastic materials. Stainless steel is recommended for methanol use. **Do not use cleaning agents or items that might leach, sorb, or leave residues of organic substances that could bias or interfere with the analysis.**

CAUTION: Refer to Material Safety Data Sheets (MSDS) before handling any chemicals.

- **Wear safety gloves, glasses, and apron when working with corrosive and oxidizing solutions.**
- **Work in a well-ventilated area.**

Table 3–1. Supplies for cleaning equipment used for water-sampling activities

[ACS, American Chemical Society; DIW, distilled/deionized water; µS/cm, microsiemens per centimeter at 25 degrees Celsius; PBW, pesticide-grade blank water; VPBW, volatiles and pesticide-grade blank water (nitrogen-purged); IBW, inorganic-grade blank water; L, liter; cm, centimeter; NAWQA, National Water-Quality Assessment; TPC, total particulate carbon; TPN, total particulate nitrogen; DOC, dissolved organic carbon; NFM, *National Field Manual*; PVC, polyvinyl chloride]

Item	Description and Comments
Acid solution[1]	Hydrochloric: ACS trace-element grade (5 percent by volume in DIW). Nitric: ACS trace-element grade (10 percent by volume in DIW).
Aluminum foil	Organics only: Heavy duty, for work surfaces and equipment.
Bags, plastic or fluorocarbon polymer	Sealable bags with uncolored closure strips, various sizes. Recyclable trash bags are recommended for large equipment storage.
Noncolored plastic sheeting	Clean sheeting used to provide a clean work surface.
Brushes and sponges	Uncolored; plastic components needed for inorganic work.
Distilled/deionized water (DIW)	Maximum specific electrical conductance, 1 µS/cm (usually District produced; Office of Water Quality Memorandum 92.01). Must not be used as a substitute for blank water.
Office-produced organic-grade deionized water	Usable only as a cleaning solution and only as specified in the text. Must not be used to substitute for PBW or VPBW.[2]
Detergent	Nonphosphate laboratory soap (for example, Liquinox™).
Gloves, disposable	Powderless, nitrile, assorted sizes.
Inorganic-grade blank water (IBW)[2]	Blank water with certificate of analysis prepared and (or) quality assured by the analyzing laboratory, and is required for collecting inorganic blank samples.
Jerricans or carboys	For waste solutions and as neutralization container. Neutralization container: 25- to 30-L, polyethylene, wide-mouth, with layer of marble chips. Methanol waste container: Appropriate for flammable liquid.
Methanol[3]	ACS pesticide-grade. Methanol is the organic solvent in common use for cleaning organic-compound sampling equipment and is mandated for the NAWQA Program. Study requirements might dictate use of a different ACS pesticide-grade solvent.
Neutralization materials	Marble landscape chips (1- to 2-cm chips recommended).[4]
Pesticide-grade blank water (PBW); volatile-grade blank water (VPBW)[2]	Blank water prepared and (or) quality assured by the analyzing laboratory; required for collecting blank samples as follows: PBW for pesticide analysis; VPBW for volatile compounds analysis and pesticide analysis; and either PBW or VPBW for TPC, TPN, and DOC analyses.
Safety equipment and guidelines (NFM 9)	For example, Material Safety Data Sheets (MSDS), safety glasses, chemical spill kit, apron, emergency phone numbers.

Table 3–1. Supplies for cleaning equipment used for water-sampling activities—*Continued*

Item	Description and Comments
Standpipes for submersible pump	Plastic, glass, or other suitable material; for example, pipette jars or capped PVC casing; one standpipe labeled for blank water and one each for each cleaning solution. (Do not use PVC for methanol.)
Tap water	If quality is questionable, substitute DIW. Tap water is more effective for initial and rapid removal of detergent residue.
Tissues	Laboratory grade, lint free, various sizes (for example, Kimwipes™).
Washbasins	One washbasin dedicated per cleaning solution; white or uncolored for containing acid or DIW solutions. Plastic, nonleaching. (Stainless steel is recommended for methanol.)
Wash bottles - polyethylene or fluorocarbon (dispenser or squeeze)	Labeled to indicate contents (for example, ACID, DIW, TAP). Fluorocarbon polymer needed for methanol, PBW, VPBW, and IBW.

[1]Hydrochloric acid is required if analyzing for nitrogen species; otherwise, nitric acid is acceptable.
[2]USGS personnel can order IBW, PBW, and VPBW from One Stop Shopping.
[3]Methanol is extremely flammable and potentially explosive, emits noxious fumes, and is absorbed through the skin. Observe safety practices when handling methanol or other organic solvents.
[4]Agricultural limestone, soda ash, baking soda, and crushed shells are not recommended (Horowitz and others, 1994).

11/2005 - Add a row to table 3-1:
Disinfectant - Hypochlorite (0.525 percent) wipes (commercially available), dilute bleach solution (0.005 percent, see text), or methyl or ethyl alcohol solution.

Note: Refer to NFM 7.1 for disinfection requirements when sampling for microbial organisms.

CAUTION: Methanol is extremely flammable and potentially explosive, emits noxious fumes, and is absorbed through the skin. Observe safety practices when handling methanol or other organic solvents.

- **Wear safety gloves, glasses, and apron.**
- **Work in a well-ventilated area and away from an open flame or sparks.**
- **Make sure that all electrically powered equipment is grounded; alternating current equipment must have a ground-fault interrupter.**
- **Inspect electrical wiring for cuts, breaks, or abrasions where the metal wire is exposed.**
  - **Exposed wires can cause sparks if a short to ground occurs.**
  - **Replace faulty wires—do not rely on fixing with electrical tape.**

GENERAL CLEANING PROCEDURES 3.2

By **A.J. Horowitz and M.W. Sandstrom**

Equipment should be cleaned in an area protected from airborne or other sources of contamination. Procedures to remove contaminants to concentrations below the targeted method-detection levels can vary, depending on the cleaning supplies used, the type of equipment being cleaned, the solubility and concentration of contaminant(s), and the length of time equipment is exposed to contaminant(s). **Examine equipment-blank and field-blank data to determine whether adjustments to the cleaning protocol are needed** (section 3.4)**.**

The cleaning procedure to be used depends on the type(s) of water samples that will be collected and processed. Figure 3–1 summarizes the sequence of cleaning procedures for equipment used to collect samples for inorganic and (or) organic analytes (Sandstrom, 1990; Horowitz and others, 1994; and Koterba and others, 1995).

- **Inspect equipment for stains, cuts, or abrasions. Replace parts as needed.**
  - — Replace chipped or cracked glassware.
  - — Replace bent sampler nozzles or samplers with bent fins (surface-water samplers).
  - — Replace tubing if mold, mildew, or imbedded sediment cannot be removed.
  - — Replace cracked or severely crimped O-rings.
  - — Repair pump intakes and anti-backsiphons that have loose or missing screws.
  - — Check the flow manifold and sample tubing to ensure that valves and quick-connect fittings are in good working order; repair or replace as necessary to eliminate any problems.
  - — Cover exposed metal surfaces on surface-water samplers with "plasti-dip."

- **Rinse equipment with DIW directly after use while equipment is still wet, then use cleaning procedures.**

- **Place cleaned equipment in doubled storage bags.**

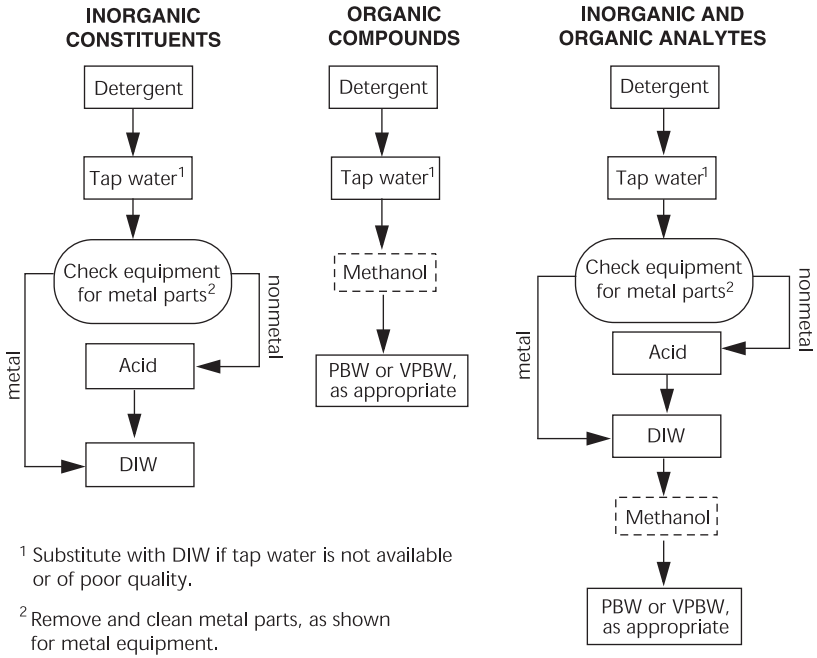


Figure 3–1. General sequence for cleaning equipment before sampling for inorganic and (or) organic analytes.

Do not allow collection and processing equipment to sit uncleaned in a field vehicle or elsewhere between field trips.

INORGANIC-CONSTITUENT SAMPLING EQUIPMENT 3.2.1

Cleaning of equipment used to collect and process water for analysis of inorganic constituents involves a five-step workplace-laboratory procedure or a five-step field-site procedure. (These procedures do not apply to field-measurement instruments—see NFM 6.) These procedures are effective for cleaning equipment exposed to water containing concentrations of as much as 50,000 µg/L of iron, 5,000 µg/L each of manganese and zinc, 400 µg/L of copper, 125 µg/L of cobalt, and large concentrations of the other trace elements (Horowitz and others, 1994).

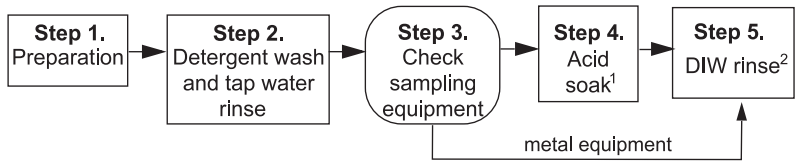
Equipment should be cleaned periodically in the workplace laboratory, where complete disassembly is more practical and more thorough procedures are possible. Compared to cleaning at the field site, cleaning procedures carried out in the workplace laboratory involve longer exposure of equipment to cleaning solutions, more frequent changes of cleaning solution, and greater volumes of rinse water.

- To minimize field cleaning of equipment between sampling sites, preclean a separate set of equipment for each site.
- If individual or dedicated sets of equipment for each field site are not available or cannot be precleaned, clean the equipment onsite and process additional field blanks during each field trip (Horowitz and others, 1994; Koterba and others, 1995).
- Return excessively contaminated equipment to the workplace laboratory for rigorous cleaning before reuse.
- After cleaning, document completion of and any modifications to the cleaning procedures. Note that procedure modifications must be sanctioned by the data-collection program and be consistent with study data-quality objectives.

Standard procedures for workplace-laboratory and field-site cleaning of equipment used to collect and process samples for analysis of inorganic constituent are described below and summarized in figures 3–2 and 3–3. Not all the steps listed apply to all equipment, however. For example,

- Omit detergent step when cleaning plastic bags for surface-water samplers.
- Omit acid step when cleaning submersible pumps or other equipment constructed of stainless steel or other metallic material (for example, the original polyethylene churn with a metal-spring spigot).
- Omit detergent and acid steps when cleaning sample bottles.

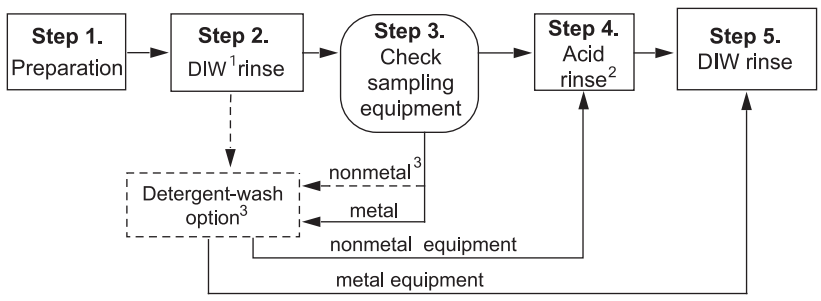
Be sure to check the specific procedures for sample bottles and other selected equipment listed in section 3.3 before proceeding with the workplace-laboratory and field-site procedures. Wear powderless laboratory gloves during the cleaning procedures, changing to a fresh pair of gloves with each change in procedure. Minimize the length of time that the gloves are in contact with any cleaning or rinse solution.



[1]Acid soak used for nonmetal equipment.

[2]DIW = deionized water (table 3-1).

Figure 3–2. Workplace-laboratory cleaning procedures for equipment used to sample for inorganic constituents.



[1] DIW = deionized water (table 3-1).

[2] Acid rinse used for nonmetal equipment.

[3] Detergent wash is routine only for field cleaning of submersible pumps, metal equipment components, or excessively contaminated equipment.

Figure 3–3. Field-site cleaning procedures for equipment used to sample for inorganic constituents.

To clean equipment used when sampling for inorganic constituents:

Step 1. Preparation at the workplace laboratory or field site (figs. 3–2 and 3–3).

a. Prepare a contaminant-free space for cleaning and drying the cleaning supplies and sample-collection and sample-processing equipment.

i. Gather the cleaning supplies, the equipment to be cleaned, and the plastic bags or other material with which to wrap the cleaned equipment. Check table 3–1 for the cleaning supplies needed.

ii. Place clean plastic sheeting over the work surface.

iii. Put on disposable, powderless gloves[2], a laboratory coat or apron, and safety glasses.

iv. Prepare the detergent solution, using a nonphosphate, laboratory-grade detergent.

- **Workplace laboratory** (fig. 3–2). Use 0.1- to 2-percent solution, volume-to-volume (v/v), using a higher concentration for dirtier equipment.
- **Field site** (fig. 3–3). Use 0.1- to 0.2-percent solution, v/v. Do not use greater than 0.2-percent solution for field cleaning.

v. Prepare the acid solution, using a 5-percent v/v dilution of ACS trace-element-grade hydrochloric acid (HCl) in DIW.

- **Add the acid to the water**, not water to acid (NFM 9).
- If nitric acid (HNO_3) will be used, prepare a 10-percent solution (v/v) of ACS trace element-grade acid in DIW.

vi. Label each washbasin, standpipe, and wash bottle to indicate the solution it will contain.

vii. Unwrap the equipment to be cleaned and discard the storage bags. Change gloves.

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[2]Refers to laboratory gloves that are nonpowdered and intended for disposal after one use. Glove materials must be appropriate for the work to be carried out and the solutions and equipment to be contacted. For example, nitrile gloves are rated as resistant to the acids and solvents commonly encountered in water-quality field work. **Be aware of possible allergic reactions to latex or other glove materials; discontinue use immediately if an allergic reaction occurs.**

b. Clean the items used to clean the equipment.

i. Fill washbasins and (or) standpipes with the nonphosphate detergent solution. Put wash bottles, scrub brushes, and other small items used for cleaning into a washbasin. **Soak for 30 minutes.**

ii. Scrub interior and exterior sides of basins and standpipes with soft scrub brushes. Fill wash bottles with a soapy solution and shake vigorously.

iii. Rinse all items thoroughly with tap water to remove detergent residue. No detergent bubbles should appear when fresh tap water is agitated in the basin, standpipe, or wash bottle.

iv. Rinse washbasins with DIW.

v. Pour 5-percent HCl (or 10-percent HNO_3) solution into washbasins, standpipes, and wash bottles. Soak for 30 minutes. **Do not soak items with metal parts (exposed or hidden) in an acid solution.**

vi. Discard used acid solution into a neutralization container containing a bottom layer of marble chips (Step 4d).

vii. Rinse washbasins, standpipes, and wash bottles with DIW. Dispose of DIW using directions in Step 4d.

c. Disassemble sample-collection and sample-processing equipment. Change gloves.

- Submersible pumps should be disassembled periodically for workplace cleaning, but they are not usually disassembled for field cleaning.
- Processing and preservation chamber frames should be cleaned periodically using workplace-laboratory cleaning procedures. Field cleaning is needed only if the cover is slipped over the frame instead of being clipped to the inside of the frame.

Step 2. Detergent wash and tap water rinse—Workplace laboratory (fig. 3–2).

a. Place small equipment parts into washbasin labeled for detergent and fill with a 0.1- to 2-percent solution of nonphosphate laboratory detergent. The amount of detergent depends on the hardness of the tap water and the degree to which the equipment is dirty or contaminated.

b. Soak equipment and tubing for 30 minutes: fill tubing with solution and keep submerged.

c. Scrub exterior and interior of equipment surfaces to the extent possible, using a firm sponge or soft brush to remove any adhering material such as oil and grease, sediment, algae, and chemical deposits. Pay particular attention to grooves and crevices, O-rings, nozzles, and other spaces where inorganic or organic materials might be trapped. Change gloves.

d. Rinse equipment thoroughly with warm tap water to remove detergent residue. Equipment rinsing is completed when no soap bubbles appear after the rinse water is agitated. Change gloves.

Step 2. DIW rinse and detergent-wash option—Field site (fig. 3–3).

For the DIW rinse:

a. Rinse equipment and tubing with DIW. Pay particular attention to removing material from grooves and crevices, O-rings, nozzles, and places where materials might be trapped. Note that equipment should already have had one DIW rinse directly after contact with sample water and before the equipment had a chance to dry.

b. Change gloves. Proceed to field detergent-wash option only for metal equipment components or for equipment that has become excessively contaminated.

For the detergent-wash option:

A field detergent wash is used for between-site cleaning of submersible pumps, metal components of equipment, or for equipment that has become greasy or otherwise coated and requires detergent to remove foreign materials; specific instructions for submersible pumps are given in section 3.3.10.

a. Place small equipment, tubing, and parts into basin labeled "detergent" and fill with a 0.1- to 0.2-percent detergent solution. Soak for about 10 minutes, or keep equipment assembled and circulate the solution through pump tubing for 5 to 10 cycles.

b. Scrub equipment surfaces with a firm sponge or soft brush to remove any adhering material such as oil and grease, sediment, algae, or chemical deposits. Pay particular attention to grooves and crevices, O-rings, nozzles, and other places where inorganic materials might be trapped. Change gloves.

c. Rinse equipment thoroughly with tap water to remove detergent residue. Use DIW if tap water is unavailable or is suspected of having a quality so poor as to contaminate the equipment. If necessary, use a wash bottle filled with DIW or tap water to rinse hard-to-reach places; pump tap water through assembled equipment for five or more tubing volumes. Equipment rinsing is complete when no soap bubbles appear after agitating the rinse water. If nonmetal equipment has been detergent-washed, go to Step 4.

d. Place equipment into acid-solution washbasin. Change gloves.

Step 3. Check equipment—Workplace laboratory and field site (figs. 3–2 and 3–3).

— Nonmetal equipment or equipment with removable metal parts: remove any metal parts and go to Step 4.

— Metal equipment components or excessively contaminated equipment: use the detergent-wash option at the field site (step 2) and then go to Step 5, DIW rinse.

Step 4. Acid soak/rinse—Workplace laboratory and field site (figs. 3–2 and 3–3).

For equipment constructed primarily of glass or fluorocarbon polymer or some other plastic, soak (workplace laboratory) or rinse (field site) in a 5-percent (v/v) HCl solution to remove any remaining organic films and inorganic deposits.

> **TECHNICAL NOTE:** A 10-percent (v/v) HNO_3 solution can be used instead of HCl if samples to be collected with the equipment will not be analyzed for nitrogen species.

CAUTION: Wear safety glasses and other protective apparel when working with acids.

a. Place nonmetal equipment and tubing into the washbasin labeled "acid solution."

b. **Workplace laboratory.** Fill basin with dilute HCl solution (see TECHNICAL NOTE above). Soak equipment and tubing for 30 minutes. Carefully swirl the acid solution several times during the 30-minute soak to enhance removal of mineral encrustations.

c. **Field site.** Using a wash bottle filled with 5-percent HCl solution (see TECHNICAL NOTE above), rinse exterior of equipment and tubing. Pump acid solution through the equipment and tubing, using a peristaltic pump.

d. Carefully pour or pump the used acid solution into a neutralization container with marble chips covering the bottom (table 3–1). Do not reuse the acid solution.

   - Do not fill the neutralization container more than three-fourths full of acid solution.
   - Ventilate container and workspace to allow for safe escape of carbon dioxide gas during dissolution of marble chips.
   - Check the solution pH periodically using narrow range pH indicator strips. Neutralization is complete when the solution pH is greater than 6.0 or the original DIW pH.
   - Discard the neutral solution, as appropriate.
   - Rinse the container with tap water but retain any undissolved marble chips. Replenish chips to form a layer on the bottom of the neutralization container.

Step 5. DIW rinse—Workplace laboratory or field site (figs. 3–2 and 3–3).

a. Place equipment into the cleaned washbasin labeled DIW. Change gloves.

b. **Workplace laboratory.** Rinse exterior and interior of each piece of equipment and tubing thoroughly with DIW and place on a clean surface to dry or into a clean IBW washbasin if blank samples will be collected to quality control the cleaning procedures.

c. **Field site.** Pump DIW through equipment.

d. Pour or discharge DIW rinse water into neutralization container. Change gloves.

e. Continue DIW rinsing until rinse-water pH is greater than 6.0 or the original DIW pH.

f. Allow equipment to air dry in an area free from potential airborne contaminants.

Storage of clean equipment

- Place dry, clean equipment inside doubled plastic bags. For small equipment, parts, and tubing, use sealable plastic bags.
- Place the churn splitter into doubled plastic bags and then place churn splitter inside of the churn carrier.

Clean equipment at the sampling site while equipment is still wet and before leaving for the next site.

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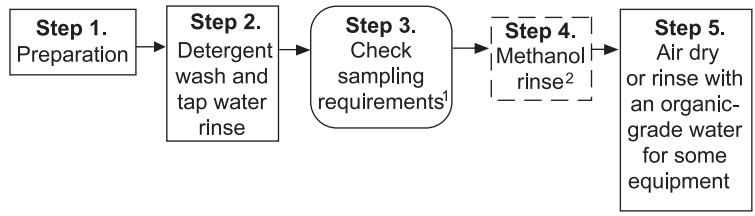
ORGANIC-COMPOUND SAMPLING EQUIPMENT 3.2.2

Nearly identical procedures are used in the workplace laboratory and at the field site to clean equipment used to sample for organic compounds. The workplace laboratory provides an environment in which equipment can be cleaned over an extended time using greater volumes of cleaning and rinsing solutions than in the field. The five-step cleaning procedure summarized in figure 3–4 is described in this section. If inorganic constituents also will be sampled for, check the sequence of cleaning solution to be used as shown in figure 3–1 before proceeding.

- Preclean a separate set of equipment for each site in order to avoid field cleaning of equipment between sampling sites. Always rinse equipment with DIW directly after use, however.

- If individual or dedicated sets of equipment for each field site are not available or cannot be precleaned, field clean equipment before moving to the next sampling site and process additional field blanks for each field trip (Koterba and others, 1995).

- Collect additional field blanks after cleaning equipment that was exposed to high levels of contamination (NFM 4) and before the equipment is reused for environmental sampling.



[1] If also sampling for inorganics, then acid soak/rinse nonmetal equipment before the methanol rinse.

[2] Omit when cleaning equipment used to sample for organic-carbon analyses.

Figure 3–4. Cleaning procedures for equipment used to sample for organic compounds.

Standard procedures for workplace-laboratory and field-site cleaning of equipment used to collect and process samples for organic-compound analysis are described below and summarized in figure 3–4. Not all the steps listed apply to all equipment, however. For example,

- **Omit any cleaning procedure for sample bottles for organic compounds** (for example, pesticides, volatiles, and total particulate or dissolved organic carbon). Bottles for organic analyses that arrive from the laboratory should be capped and ready for use and should not be rinsed by field personnel. Discard these bottles if received uncapped.

- **Omit the methanol rinse when cleaning the equipment used to collect and process samples for total particulate carbon, particulate organic carbon, and dissolved and suspended organic carbon (TPC, POC, DOC).** If equipment (such as a submersible pump) has been in contact with methanol or other organic solvent and must be used for TPC, POC, or DOC sampling, then flush the equipment with copious quantities of sample water before collecting the sample; collection of a blank sample for DOC quality control is recommended.

Before proceeding with the workplace-laboratory and field-site procedures, be sure to check the specific procedures that are listed in section 3.3 for cleaning selected equipment. Also check for cleaning procedures that are specific to the needs of your study (for example, the NAWQA Program permits no deviation from the methanol-cleaning protocol).

To clean equipment used when sampling for organic compounds:

Step 1. Preparation (fig. 3–4).

a. Prepare a contaminant-free space for cleaning and drying the cleaning supplies and sample-collection and sample-processing equipment.

   i. Gather the cleaning supplies, the equipment to be cleaned, and clean storage bags and aluminum foil with which to wrap the cleaned equipment. (Check table 3–1 for the cleaning supplies needed.)

   ii. Cover the cleaning area with aluminum foil.

   iii. Put on disposable, powderless gloves,[3] a laboratory coat or apron, and safety glasses. **Gloves provide protection from direct contact with solvents only for a limited period of time.**

   iv. Prepare the detergent solution, using nonphosphate laboratory-grade detergent. A 0.1- to 0.2-percent (v/v) solution is normally of sufficient strength, unless equipment is very oily or greasy. **Do not use greater than a 0.2-percent solution for field cleaning.**

b. Clean the items to be used to clean the equipment.

   i. Label each washbasin, standpipe, and wash bottle with a black waterproof marker to indicate the solution it will contain.

   ii. Follow Steps 2–5, listed below, to clean the washbasins, standpipes, wash bottles, and other items to be used for equipment cleaning.

c. Disassemble sample-collection and sample-processing equipment. Submersible pumps should be disassembled periodically for workplace cleaning but usually are not disassembled for field cleaning.

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[3]Refers to laboratory gloves that are nonpowdered on and intended for disposal after one use. Glove materials must be appropriate for the work to be carried out and the solutions and equipment to be contacted. Use nitrile or other solvent-resistant gloves when cleaning with organic solvents. **Be aware of possible allergic reactions to latex or other glove materials; discontinue use immediately if an allergic reaction occurs**.

Step 2. Detergent wash and tap water rinse (fig. 3–4).

a. Place small equipment parts into washbasin labeled for detergent. Fill washbasin with a 0.2-percent solution of nonphosphate, laboratory-grade detergent. (The specific concentration of detergent solution depends on how contaminated the equipment might be and on the hardness of the tap water.) Change gloves.

   - **Workplace laboratory.** Soak equipment in detergent solution for 10 to 30 minutes.
   - **Field site.** Rinse equipment exterior and interior with detergent solution.

b. Scrub the exterior and interior of equipment surfaces to the extent possible, using a firm sponge or soft brush to remove any adhering material such as oil and grease, sediment, algae, or chemical deposits. Pay particular attention to removing material from areas where particulate materials might be trapped, such as grooves and crevices, O-rings, and nozzles.

c. Place equipment into tap water washbasin.

d. Rinse equipment thoroughly with tap water to remove detergent residue. Use an organic-grade water (PBW, VPBW, or workplace-produced) if tap water is unavailable or is of a quality so poor as to contaminate the equipment. If necessary, use a wash bottle filled with organic-grade water or tap water to rinse hard-to-reach places. Equipment rinsing is complete if no detergent bubbles appear when rinse water is agitated. Change gloves.

Step 3. Check sampling requirements (fig. 3–4).

a. If samples will be collected for organic analysis only, go to Step 4.

b. If samples will be collected for inorganic analysis in addition to organic analysis, follow the procedure for the acid wash and DIW rinse before proceeding with the methanol rinse (see figs. 3–1 and 3–4).

Step 4. Methanol rinse[4] (fig. 3–4).

a. Use gloves that are chemically resistant to any solvent being used. Place cleaned equipment into a clean stainless steel or organic-solvent-resistant washbasin. Methanol-rinse area must be outside of the field vehicle and away from the sample-processing site. **Sample-collection, processing, and preservation areas must remain free of solvent vapors.**

b. Use pesticide-grade methanol (or appropriate organic solvent) dispensed from a methanol fluorocarbon-polymer wash bottle (workplace laboratory) or pumped through tubing (field site) (see **TECHNICAL NOTE** below).

   i. Rinse equipment exterior and interior with a minimum amount of methanol.

   ii. Rinse only the interior (not the exterior) of pump tubing with methanol if collecting samples for analysis of organic compounds such as pesticides.
   Exception: A methanol rinse of pump tubing is not recommended if TPC, POC, or DOC samples will be withdrawn through that tubing.

   iii. Place equipment components and tubing on a clean aluminum foil surface. If also collecting samples for analysis of metals, use clear plastic sheeting instead of aluminum foil.

   iv. Pour or discharge used methanol (or other organic solvent) into an appropriate waste container for flammable liquids (Water Resources Discipline Memorandum 94.007). Change gloves. Dispose of gloves used for methanol rinse appropriately.

CAUTION: Use methanol or other organic solvents sparingly and work under a fume hood or in a well-ventilated area, away from where an open flame or sparks can occur. Wear safety gloves, glasses, and apron.

[4]The methanol rinse is used to remove organic contaminants from equipment and represents standard procedure for all USGS studies. The NAWQA Program mandates use of the methanol rinse with no exceptions.

TECHNICAL NOTE: Rinse equipment with dichloromethane or hexane if the methanol rinse is not sufficient to clean equipment contaminated with excessive concentrations of hydrophobic organic compounds. If rinsing with dichloromethane or hexane, use pesticide-grade solutions, wear nitrile gloves, and use only on dry equipment (dichloromethane and hexane are not soluble in water). Do not rinse equipment with any organic solvent if equipment will be used for TPN, POC or DOC samples.

Step 5. Air dry equipment or rinse with organic-grade water (fig. 3–4).

a. Allow methanol-rinsed equipment to air dry in an area free from dust and potential airborne contaminants (place an aluminum foil tent loosely over the drying equipment; if also collecting samples for metals analysis, use lint-free, nonabrasive wipes instead of aluminum foil).

b. If it is not practical for the methanol to evaporate from the interior of equipment components or sample tubing, either

- dry by blowing clean, filtered, inert gas through equipment; or
- rinse methanol from equipment with pesticide-grade or volatile-grade blank water, dispensed from a wash bottle or pumped with a valveless fluid metering pump. This rinse water should be collected and disposed of properly, according to the regulations in effect for your locality (consult your safety officer).

Storage of clean equipment

Cover all equipment orifices with aluminum foil or fluorocarbon polymer bags, then place equipment into sealable storage bags. Isolate equipment used to collect trace-element samples from aluminum foil.

SPECIFIC PROCEDURES FOR CLEANING SELECTED TYPES OF EQUIPMENT 3.3

By **A.J. Horowitz, M.W. Sandstrom, and F.D. Wilde**

The equipment-cleaning steps described in sections 3.2.1 and 3.2.2 apply to most, but not all, equipment. This section describes the cleaning procedures needed for specific equipment for which the general protocols are modified or do not apply, or for which more detailed instructions might be useful. Always wear appropriate disposable, powderless gloves throughout each cleaning procedure, and change gloves with each change of cleaning solution (see section 3.2).

INORGANIC-SAMPLE BOTTLES 3.3.1

Bottles for samples to be analyzed for inorganic constituents include translucent colorless polyethylene, opaque brown polyethylene, and transparent glass bottles.Translucent polyethylene bottles that were acid rinsed at the laboratory should arrive capped with colorless, translucent plastic caps. ~~Glass bottles for samples for mercury analysis also are acid rinsed and should arrive capped~~. Deleted 02/17/2011.

- **Discard acid-rinsed bottles that are received uncapped.**
- The more rigorous cleaning procedure that follows is required for bottles that will contain samples to be analyzed for trace elements. This bottle-cleaning procedure also is recommended for bottles that will contain samples to be analyzed for major ions and nutrients.

Before leaving for the field, clean polyethylene and glass sample bottles, including acid-rinsed bottles, as described in the steps that follow:

1. Put on powderless, nitrile gloves.
2. Fill each bottle about one-quarter full of DIW and cap.
3. Shake vigorously and decant DIW.
4. Repeat the DIW rinse (Steps 2 and 3 above) two more times.
5. Following the last rinse, fill each bottle half full with DIW and cap the bottle.
6. Rinse exterior of bottle with DIW and dry with lint-free laboratory tissue.
7. Store bottles in doubled plastic bags.

CHURN SPLITTERS 3.3.2

The plastic (non-fluorocarbon) churn splitter is used primarily for samples to be analyzed for inorganic constituents, whereas the fluorocarbon churn splitter can be used to process samples for organic-compound analysis as well as for inorganic constituents (NFM 2).

When using the detergent wash/tap water rinse for the churn splitter—Workplace-laboratory procedure (fig. 3–2, Step 2):

1. Fill churn splitter through the top (using a funnel, if necessary) with detergent solution.
2. Soak for 30 minutes.
3. Scrub interior and exterior surfaces with a soft brush, taking care not to abrade the surface.
4. Pay particular attention to cleaning the paddle and the area around the spigot.
5. Make sure the churn spigot opening and funnel are free of sediment, including fine particulates (clay), organic matter, and stains.
6. Drain some of the cleaning solution through the spigot before discarding the remaining solution.
7. Fill churn splitter about one-third full with tap water; swirl and shake the churn vigorously to remove detergent residues. Allow tap water to pass through the spigot.
8. Repeat rinse procedure until no bubbles remain in rinse water after the water is agitated.

When using the acid rinse for the churn splitter—Workplace-laboratory or field-site procedures (figs. 3–2 and 3–3, Step 4):

1. Using a 1-L wash bottle filled with a 5-percent HCL or 10-percent HNO_3 acid solution (table 3–1), rinse the entire inside surface of the churn, allowing the acid solution to drain through the spigot. **Exception:** Do not use this step if using a plastic churn splitter with a metal spring in the spigot.

2. Decant acid solution into the neutralization container.

When using the DIW rinse for the churn splitter—Workplace-laboratory or field-site procedures (figs. 3–2 and 3–3, Step 5):

1. Fill the churn splitter with DIW to about one-third full.

2. Swirl the DIW vigorously and pour it out of the top of the churn into the neutralization container.

3. Repeat the fill-and-swirl procedures of 1 and 2 above at least twice, checking the pH of the DIW after each swirl with narrow-range pH indicator strips.

4. **Pass a portion of the DIW through the spigot only after the DIW pH equals or is greater than either 6.0 or the pH of the DIW before acidification. Pour the rest of the DIW into the neutralization container.**

When using the methanol rinse (fig. 3–4, Step 4):

1. Rinse only the fluorocarbon churn with methanol. Do not methanol rinse the plastic churn splitter.

2. Using a fluorocarbon wash bottle filled with pesticide-grade methanol (table 3–1), rinse the entire inside surface of the churn, allowing the methanol to drain through the spigot and into an appropriate container designated for methanol waste.

For storage of a cleaned churn splitter—Workplace-laboratory or field-rinse site procedures:

1. Package a clean, dry churn splitter in two new plastic bags and loosely tie or secure with a nonmetal clip. If a churn splitter must be packaged while wet, use within 1 to 3 days and (or) keep chilled to prevent bacterial growth.

2. Place entire package into the churn carrier.

CONE SPLITTERS 3.3.3

The fluorocarbon-polymer cone splitter (NFM 2) is appropriate for splitting samples for inorganic or organic analyses. When cleaning the cone splitter (Office of Water Quality Technical Memorandum 97.03), pay particular attention to removing foreign material from threaded and hard-to-access parts. Field cleaning can be minimized by having separate, precleaned cone splitters available for each site and by keeping a supply of clean tubes to replace the used tubes for each site to be sampled.

When inorganic constituents will be analyzed in samples processed through the cone splitter:

Workplace laboratory. Follow the steps as described for figure 3–2.

Field site. Referring to figure 3–3:

1. Prepare the field site as described in section 3.2.1. Put on disposable, powderless gloves.
2. Rinse the splitter thoroughly with DIW.
3. Inspect the cone splitter. If it looks dirty, is suspected of being contaminated, or was allowed to dry between field sites without a thorough DIW rinse, or if the splitter will be used for sampling both inorganic and organic analytes, use the detergent-wash option. Change gloves.
4. Acid rinse by passing 1 L of 5-percent HCl solution through the cone splitter. Collect used acid solution into a neutralization container. Change gloves.
5. Rinse the cone splitter with at least 3 L of DIW. Collect the rinse solution into a neutralization container. Change gloves.
6. Allow the cone splitter to dry and then store in a clean plastic bag. Seal the bag and store in a second plastic bag or plastic storage container for transport to the next site. A cone splitter that is packaged into bags while wet should be used within 1 to 3 days and (or) kept chilled to prevent bacterial growth.

When organic compounds will be analyzed in samples processed through the cone splitter (fig. 3–4):

Workplace Laboratory. Follow the steps described for figure 3–4.

Field Site.

1. Prepare site as described in section 3.2.2. Put on appropriate disposable, powderless gloves; if a solvent will be used, select gloves that will withstand contact with the solvent.
2. Detergent wash and rinse equipment as described for figure 3–4.
3. Check equipment and sampling requirements. If splitter will also be used for inorganic sampling, follow acid-rinse directions before rinsing with methanol or other organic solvent.
4. Proceed with the methanol (or other organic solvent) rinse, if required (section 3.2.2). (The methanol rinse is required for the NAWQA Program, for example). A methanol-rinsed cone splitter, however, must not be used if the cone splitter will contact samples for analysis of TPC, POC, or DOC.

For storage of a cleaned cone splitter:

1. Allow the cone splitter to air dry.
2. If the cone splitter will not be used to process samples for inorganic constituents at the next site, wrap the spigot and other orifices in aluminum foil.
3. Place the cone splitter into a clean plastic bag and seal.
4. Store in a second plastic bag or plastic storage container for transport to the next site.

If a cone splitter must be packaged while wet, use within 1 to 3 days and (or) keep chilled to prevent bacterial growth.

FILTRATION EQUIPMENT 3.3.4

Filtration equipment includes disposable filtration devices and various reusable plate-filter and pressure-filter assemblies. Cleaning procedures for these types of equipment are described below.

DISPOSABLE FILTRATION DEVICES 3.3.4.A

Disposable filter units have a one-time use for processing samples to be analyzed for inorganic and carbon constituents, but must be rinsed with IBW or VPBW[5] before use to remove any manufacturing residues and condition the filter membrane. The filtration device can be prerinsed in the workplace laboratory rather than at the field site as long as the device is kept chilled and used in less than 1 day. After filtering the sample, discard the filter unit and clean or replace the sample-delivery tubing (section 3.3). The procedure below describes sufficient cleaning of the filter for analysis of inorganic constituents at the low parts-per-billion (ppb) concentration level (Horowitz and others, 1994).

Rinse the disposable filtration device before use as follows:

1. Put on disposable, powderless gloves. Use Clean Hands/Dirty Hands techniques described in NFM 4. Remember: the Dirty Hands team member performs operations that are outside of the processing chamber and the Clean Hands team member performs operations that are inside the chamber.

2. In a processing chamber, remove the filter unit from any protective bags. Attach pump tubing to the inlet connector of the filter unit, keeping the tubing as short as possible. **When using the large-capacity capsule filter, make sure the direction of flow through the filter unit matches the direction-of-flow arrow on the filter housing.**

[5]If samples for DOC analysis will be filtered, then rinse the disposable unit with VPBW instead of IBW.

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3. Pump IBW (or VPBW[5]) through the filter unit. Discharge the rinse water through a sink funnel or to a toss bottle.
   - Use 1 L of IBW (or VPBW[5]) to rinse the large-capacity[6] (≥ 600 cm^2 Effective Filter Area (EFA)) filter.
   - Use ~~100~~ 50 mL of IBW (or VPBW[5]) to rinse the small-capacity[7] (19.6 cm^2 EFA) (disc) filter.
   - Operate the pump at a low speed.
   - Hold the filter unit so the discharge end is pointing up at an acute angle from the horizontal plane. (This expels any trapped air; do not allow water to spray onto chamber walls.)
4. Remove tubing from the IBW (or VPBW) reservoir and continue to operate the pump in the forward, mid-range speed position to drain as much as possible of the IBW (or VPBW) that remains in the filter unit. While the pump is operating, shake the capsule filter to help remove any entrained IBW (or VPBW).
5. Detach the filter unit from the peristaltic pump tubing, put into a clean, sealable plastic bag, and store chilled until ready for use.

3.3.4.B PLATE-FILTER ASSEMBLIES AND IN-LINE FILTER HOLDER

To clean filtration equipment used for samples to be analyzed for inorganic or organic analytes, consult sections 3.2.1 and 3.2.2, respectively. Use Clean Hands/Dirty Hands techniques, as appropriate (NFM 4). The aluminum plate-filter assembly and the fluorocarbon (PFA) in-line filter holder are used most commonly for filtering samples for analysis of non-volatile organic compounds, such as pesticides. The plastic 144-mm-diameter plate-filter assembly no longer is in common use; if used, it should be cleaned by using the procedures prescribed in section 3.2.1 and by following the guidelines below and in figure 3–3. See section 3.3.4.C for information about cleaning filtration equipment used for carbon (TPC, PIC, and DOC) samples.

[6]For example, Pall-Gelman AquaPrep™ 600 or Whatman Inc. Polycap™ groundwater capsule filters.

[7]For example, Pall-Gelman AquaPrep™ sampling device.

- **Preclean in the workplace laboratory** one filtration device per site to be sampled, if possible, in order to save the time that would be needed to clean the plate-filter assembly during the field effort.
- **During the detergent wash and (or) DIW rinse,** pay particular attention to grooves and crevices, O-rings, and support structures for the filtration device, where sediment or organic matter might be lodged. Detergent wash and DIW rinse the pressure valve.
- **Remove and discard the used filter membrane or disc (filter) at the field site;** rinse the filtration device immediately with DIW while still wet from filtering the sample, even if clean equipment is available for the next site.

Always remove the used filter media from the plate-filter assembly before cleaning and storage.

When field cleaning the aluminum plate-filter or PFA in-line filter-holder assembly, use the general cleaning instructions in section 3.2.2 for figure 3–4, as follows:

1. Inspect the filtration assembly for damage or excessive contamination and replace if necessary.
2. Wearing disposable, powderless gloves, prepare the area to be used for cleaning the plate-filter assembly by lining the table or counter surface with aluminum foil.
3. Disassemble the filter assembly and carefully remove the used glass-fiber filter media to avoid spilling any of the filter cake. Place used filter into a sealable plastic bag, seal the bag, and put aside for disposal. Place components of the filtration assembly and tubing into a washbasin for detergent. Change gloves.

4. Detergent wash by using a 0.1- to 0.2-percent nonphosphate-detergent solution. Scrub each component of the filtration assembly with a soft brush to remove any adhering material such as oil and grease, sediment, algae, or chemical deposits. Pay particular attention to grooves and crevices, O-rings, and support structures for the filter disc, where particulate materials might be lodged. Pump detergent solution through tubing. Place components of the filtration assembly onto a clean, aluminum-foil-covered surface.

5. Discard detergent solution from basin, rinse basin with tap water, and place components of the filtration assembly into the basin. Change gloves.

6. Rinse each component thoroughly to remove detergent residue, paying particular attention to grooves and crevices. Use a wash bottle filled with DIW or tap water to rinse hard-to-reach places. Place rinsed components onto a dry section of clean aluminum foil or basin.

7. Change to solvent-resistant gloves. Place components of the filtration assembly into a clean, solvent-resistant washbasin.

8. Rinse the filtration assembly components with pesticide-grade methanol or an equivalent grade for other organic solvents while outside of the field vehicle and downwind of sampling activity. Do not methanol rinse any tubing or filtration assembly to be used for collecting or processing samples for TPC, PIC, or DOC analysis (see section 3.3.4.C). **The instructions for the methanol rinse apply also for use of any other organic solvent.**

   a. Dispense methanol from a fluorocarbon-polymer wash bottle. Rinse all sample-contacting surfaces of filtration-assembly components and tubing over a solvent-resistant basin or waste container. **Methanol-laced rinse water must be collected into an appropriate waste container designed for flammable liquids.**

   b. Place methanol-rinsed equipment components onto a clean aluminum foil surface to air dry. (Cover equipment components loosely with an aluminum foil tent, to protect from airborne contaminants.)

9. Reassemble the filtration assembly. Wrap nozzles with aluminum foil and seal the filtration assembly in plastic bags. Double bag for transport or for long-term storage.

PRESSURE-FILTRATION AND VACUUM-FILTRATION APPARATUS 3.3.4.C

The cleaning procedures described in section 3.2.2 for figure 3–4 must be modified for the pressure- and vacuum-filtration equipment used to filter for samples to be analyzed for TPC, PIC and DOC (DOC samples also may be filtered through the disposable devices described in section 3.3.4.A). The gas-pressurized filtration assembly for processing carbon samples is constructed of either stainless steel or fluorocarbon-polymer material. Vacuum-filtration equipment consists of a polypropylene flask and a polysulfone filter funnel.

- C-Flex tubing and glass graduated cyclinders also are used. **Do not bring the pressure-filter assembly in contact with methanol or other organic solvent or organic-solvent vapors.**
- **Do not clean the pressure-filter assembly with detergent. Exception:** see Step 3 below.
- In general, workplace-produced organic-grade water that is prepared by being passed through appropriate columns to remove organic compounds is of adequate purity for cleaning this equipment; PBW or VPBW also can be used. Workplace-produced organic-grade water, however, must not be used instead of PBW or VPBW for preparing blank samples.

When cleaning carbon-sample filtration equipment:

1. Wearing disposable, powderless gloves, disassemble the filtration assembly before it dries and place the components and other carbon-related equipment into a clean washbasin. Change gloves.

2. Using workplace-produced organic-grade water, thoroughly rinse the equipment components and place into a washbasin or onto a clean surface. Generally, these steps should be sufficient to field clean the pressure-filter assembly.

   - If necessary, use a soft-bristled toothbrush to remove sediment, chemical deposits, and other foreign material from threaded components, gaskets, O-rings, support screens, grooves, and nozzles. Take care not to scratch or mar inner surfaces.

   - Rinse the filtration equipment thoroughly with workplace-produced organic-grade water, or PBW, or VPBW.

3. If the pressure- or vacuum-filtration assembly or other carbon-sample equipment is very dirty or contaminated, clean as follows:

   a. Disassemble and soak components for at least 1 hour in a 0.1-percent solution of nonphosphate laboratory-grade detergent.

   b. Clean with a soft-bristled toothbrush, as described above in step 2.

   c. Rinse repeatedly with workplace-produced organic-grade water, being sure to remove all traces of detergent.

4. Place all components of the pressure-filter assembly onto aluminum foil or other clean surface and allow to air dry thoroughly under a protective aluminum-foil tent.

5. Reassemble equipment components in preparation for sample filtration, wrapping nozzles and other equipment apertures with aluminum foil. Seal in a storage bag.

Do not use methanol or other organic solvents on the equipment used to filter samples for organic-carbon analyses.

SAMPLE TUBING 3.3.5

Cleaning procedures are described below for the tubing and nozzles used with peristaltic and valveless metering pumps. Cleaning procedures for submersible pump tubing are described in section 3.3.10.B. Wear appropriate, disposable, powderless gloves throughout the cleaning process, changing gloves with each change in cleaning solution (section 3.2).

- Preclean the number of tubing sections needed at each site in the workplace laboratory rather than recleaning tubing in the field, in order to save time during field work. Place into doubled plastic bags and store tubing dry or store wet tubing chilled to prevent bacterial growth. If bacterial growth is present, reclean tubing before use.

- Use disposable tubing if possible, especially at contaminated sites, to avoid the cleaning process and prevent the possibility of cross contamination.

When using workplace-laboratory or field-site procedures for cleaning plastic (including fluorocarbon-polymer) tubing for inorganic-constituent samples:

Follow the general sequence of procedures summarized in figures 3–2 or 3–3.

1. Pump 1 L of 5-percent HCl solution through the tubing, discharging the used acid solution into a neutralization container. Pinch and release tubing near tubing outlet while pumping the acid through to ensure that all interior surfaces are acid rinsed.

2. Pump 2 L of DIW through tubing, using the pinch-and-release method. Discharge used DIW to an acid-neutralization container, and check that the rinse-water pH is greater than 6.0 or the original DIW pH.

3. Discard neutralized solutions appropriately.

4. Clean stainless steel connections or metal tubing using detergent-wash and tap water/DIW-rinse procedures.

When using workplace-laboratory or field-site procedures for cleaning tubing for organic-compound samples:

Follow the general sequence of procedures described for figures 3-1 and 3–4. Proceed with the methanol rinse after the detergent wash and tap water rinse, unless the tubing will be in contact with samples for organic-carbon analysis. If samples also will be collected for inorganic-constituent analysis, however, acid rinse the nonmetallic tubing and components after the detergent wash/tap water rinse and before continuing with the methanol rinse.

1. Pump 1 L of nonphosphate, laboratory-grade detergent solution through tubing, followed by sufficient tap water or DIW to remove detergent residue. Pinch and release tubing near tubing outlet while pumping the solution to ensure that all interior surfaces are cleaned.

2. Place discharge end of tubing from peristaltic or valveless metering pump over methanol waste container.

    - Pass one tubing volume of methanol through the same pump system used for filtration, using the same pinch-and-release method.

    - Short sections of tubing can be held over the waste container while dispensing the methanol from a fluorocarbon-polymer wash bottle instead of pumping the methanol through the tubing.

    - **Do not methanol rinse tubing to be used for samples for TPC or DOC analysis.**

3. Store tubing in doubled plastic bags.

CAUTION: Do not use methanol around equipment that can create electrical sparks (see section 3.3.10.B).

PROCESSING AND PRESERVATION CHAMBERS AND FLOWTHROUGH CHAMBERS 3.3.6

Processing and preservation chambers are used to protect samples from atmospheric contamination generally are portable and are assembled at the field site. Large, clear plastic bags usually are clipped to the inside of the frame rather than stretched over the frame. Plastic clips are used to hold the cover tightly in place.

The flowthrough chamber, used when monitoring ground-water field measurements, is connected inline to the pump sampler. The flowthrough chamber should be kept free of sediment and dirt or deposits on the chamber walls. Air dry and store the chambers in sealable plastic bags.

When cleaning the processing and preservation chambers:

Workplace laboratory. Clean the frame of portable chambers in the workplace with detergent solution, then rinse thoroughly with tap water and dry and store in plastic bags.

Field site. Frames require regular cleaning after each use at a site if chamber covers are stretched over the outside of the frame rather than being clipped to the inside of the frame.

1. Discard the used bag.
2. Rinse the chamber frame with DIW and wipe dry with a lint-free cloth or tissue.
3. Replace chamber cover only when the next samples are ready to be processed.
4. If the processing chamber is a fixed installation (not portable), clean out any spilled sample water, solid materials, or wash solutions, and swab down the inside using DIW and lint-free laboratory tissue.
5. Use detergent solution followed by a thorough tap water or DIW rinse if a spill has contaminated the chamber.
6. Store chamber frames in plastic bags.

When cleaning the flowthrough chamber:

1. Clean the flowthrough chamber in the workplace laboratory with detergent solution and rinse thoroughly with tap water, followed by DIW. **Do not use acid solution or methanol.**
2. If the flowthrough chamber needs to be field cleaned, remove measurement sensors and clean with a dilute detergent solution; rinse thoroughly with tap water followed by DIW. If using the flowthrough cell of a multiparameter instrument, follow the manufacturer's instructions for cleaning the cell.

3.3.7 RADON SAMPLER

To clean radon samplers:

1. Soak radon samplers in a detergent solution for 10 minutes.
2. Rinse thoroughly with tap water to remove detergent residue, followed by three to five rinses with DIW.
3. Air dry the radon sampler and store in doubled plastic bags. **Do not use methanol on radon sampling equipment.**

3.3.8 WELL TAPES

Always inspect and clean well tapes after each use. Procedure 1 below describes general cleaning instructions for electric and steel tapes that are used to measure water levels in monitor or observation wells that do not have fecal contamination. Procedure 2 below describes disinfection instructions for well tapes that are used to measure water levels in wells susceptible to fecal contamination, including public-supply and domestic wells.

- Before using these procedures, check with the well owner or wellfield project manager to determine whether site restrictions would be compromised by the use of any of the cleaning substances described.
- Check the instructions provided by the manufacturer before using a cleaning or disinfection agent on your electric tape other than laboratory detergent and water.
- The term "electric tape" is used here to include the sensor and other wetted parts of electronic instruments that are used to measure water levels in wells.
- Spread clean plastic sheeting on the surface over which the tape will be cleaned, to prevent the tape from contacting the ground or other potential sources of contamination.

PROCEDURE 1. This cleaning procedure contains two options for cleaning well tapes used in monitor or observation wells **that are not susceptible to fecal contamination**, and therefore do not require disinfection. Option A is the standard procedure for cleaning well tapes when no oily substance is present on the water table. Option B describes how to clean oil residues from the well tape. Inspect the well tape before starting the cleaning procedure to determine whether Option A or Option B should be used.

Option A: Cleaning an electric or steel tape where no oily residue is noticeable on the tape:

When using an electric tape and sensor equipment, follow the manufacturer's instructions for equipment care and cleaning. Steps 1 through 3 can be used in the absence of manufacturer's instructions.

1. Wash the tape with a nonphosphate, 0.1- to 2-percent laboratory detergent solution (for example, Liqui-Nox[8]), using a soft cloth or a soft brush.
2. Rinse the tape thoroughly with DIW or tap water to remove all traces of the detergent solution.

[8]Liqui-Nox and Detergent 8 are products of Alconox, Inc. Reference to these products is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

3. Dry the electric or steel tape with a clean, soft cloth, and rewind the tape onto the reel. Place the tape into a clean plastic bag for transport and storage.
   Recommendation: If the tape will be stored for a month or more, put a drying agent such as a silica-gel packet into the plastic bag before sealing the bag.

Option B: Cleaning an electric or steel tape that is coated with oil:

When cleaning an electric tape, check with the manufacturer before exposing the tape to a solvent. This procedure should be carried out away from the well site.

1. Wearing solvent-resistant disposable gloves, prepare a nonphosphate, laboratory detergent solution (for example, 10-percent Liqui-Nox or 3-percent Detergent 8).

2. Use a soft brush, a clean terry cloth, or a sponge that is saturated with the detergent solution to remove oil from the wetted portion of the tape.

3. If an oily residue persists, use a clean cloth wetted with a solvent (such as a 10-percent naptha solution or a 70-percent ethanol, methanol, or acetone solution) and wipe down the oily portions of the tape. Allow the tape to air dry in a well-ventilated area.

4. Using tap water or DIW, thoroughly rinse the detergent from the tape, and then dry the tape with a clean cloth.

5. Rewind the tape onto the reel and place it into a clean plastic bag for storage and transport.
   Recommendation: If the tape will be stored for a month or more, put a drying agent such as a silica-gel packet into the plastic bag before sealing the bag.

Caution: Solvents mentioned above are flammable, explosive, and produce noxious fumes. Store these solvents in appropriate solvent-resistant containers that can be tightly capped and that are clearly labeled with its contents and hazards. A Material Safety Data Sheet (MSDS) must be displayed in the vicinity where the solvent is stored. Always wear disposable, solvent-resistant (for example, nitrile) gloves when working with solvents or other chemical substances. Do not leave the solvent in the sun or in a hot vehicle.

PROCEDURE 2. A well tape should be disinfected when it is being used to measure water levels in public-supply or domestic wells, or in wells susceptible to fecal contamination from other human or animal operations. **Begin Procedure 2 with a well tape that has been cleaned with a detergent solution, as described above in Procedure 1.**

Disinfecting an electric or steel tape:

1. Select a disinfectant: either a chlorine bleach solution (described below) or a methyl or ethyl alcohol solution. If using bleach, prepare a dilute 50 mg/L (0.005 percent) solution of common household chlorine bleach (1 mL of bleach to 900 mL water[9]). **If using an electric tape, check with the manufacturer before exposing the tape and related equipment to a solvent.**

   a. Label a polyethylene sample bottle as "Well-Tape Disinfectant" and record the date of preparation, using an indelible marker. The bleach solution should be prepared fresh for each day of use (NFM 7.3).

   b. Fill the bottle with the dilute disinfectant solution. Cap the bottle tightly, and double-bag it in a ziplock plastic bag for transport.

2. At the well site, put on disposable gloves. Wet a clean cloth with the disinfectant solution and use it to wipe down the section of the tape that was submerged in the well water.

3. Rinse the tape thoroughly with DIW or tap water. Using another clean cloth, wet and wipe the surface of the well tape through the entire chalked and wetted sections of the tape. Be thorough when rinsing bleach solution from a well tape; prolonged exposure of the tape to chlorine bleach can damage the tape.

4. Using a clean dry cloth, dry the steel tape thoroughly to prevent it from rusting.

5. Rewind the tape onto the reel and place it into a clean plastic bag for storage and transport.
   Recommendation: If the tape will be stored for a month or more, put a drying agent such as a silica-gel packet into the plastic bag before sealing the bag.

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[9]Prepare a 0.02 percent (200 mg/L) solution if pH is less than 6 or greater than 8 (NFM 7.3).

3.3.9 SURFACE-WATER SAMPLING EQUIPMENT

Disassemble surface-water samplers for cleaning and follow the sequence of procedures described in section 3.2 and figures 3–2, 3–3, or 3–4, as appropriate.

When using workplace-laboratory procedures for cleaning surface-water samplers:

1. Periodically disassemble samplers for workplace-laboratory cleaning. **Discard the bag sampler bag after one use**—do not attempt to scrub or detergent wash the used bag. Prepare cleaning solutions, cleaning equipment, and cleaning area as described in section 3.2.

2. Soak components in detergent solution for 30 minutes. Put on appropriate disposable, powderless gloves. Scrub components with a soft brush or sponge and rinse thoroughly (section 3.2.1 or 3.2.2). Change gloves.

3. Check the sequence of cleaning procedures (fig. 3–1).

   a. If the sampler is used for sampling inorganic constituents, soak each nonmetallic component in a 5-percent trace-metal-grade HCl solution for 30 minutes, followed by copious rinsing with DIW (section 3.2.1). **Acid rinse only nonmetal parts.** Change gloves.

      - Acid must not contact the metal collar on the DH-81 sampler.
      - Make sure that the nozzle is unscrewed from the cap.

   b. If the sampler is used for collecting organic-compound samples, rinse each component with pesticide-grade methanol dispensed from a fluorocarbon-polymer wash bottle and allow to air dry (section 3.2.2). **Do not methanol rinse tubing or components that will contact TPC or DOC samples.** Change gloves.

4. If collecting an equipment blank (section 3.4), change gloves and rinse each component with the appropriate blank water before collecting the blank sample.

5. Reassemble the sampler. If the sampler is dedicated to sampling for organic compounds, double wrap the sampler nozzle in aluminum foil. Place the sampler into double plastic bags and seal for storage and transport.

When using field-site procedures for cleaning surface-water samplers:

1. Unwrap precleaned washbasins (one for each cleaning solution to be used).

2. Disassemble the used sampler into its component parts (bottle, cap, nozzle) so that all of the pieces can be thoroughly wetted with the various rinses. **Discard the previously used bag-sampler bag** (do not attempt to clean the bag for reuse).

3. Wearing appropriate disposable gloves, thoroughly rinse the sampler components with DIW. Use a stream of DIW from the wash bottle, if required.

4. Check whether target analytes are inorganic constituents, organic compounds, or both. Review figure 3–1 for the appropriate cleaning sequence.

   a. If a sampler will be used for collecting samples for analysis of inorganic constituents only, change gloves and:

      i. Thoroughly rinse the sampler components with tap water or DIW.

      ii. Acid rinse nonmetallic components over a container using a stream of dilute acid solution from the appropriate wash bottle, if required.

      iii. Thoroughly rerinse the sampler components with DIW over the same washbasin, if possible (see section 3.2.1). Change gloves.

      iv. Place each component on a clean, plastic surface. Pour used acid solution and DIW rinse water into neutralization container.

      v. Check the pH of the rinse solution in the neutralization container. Discard when solution pH is greater than 6.0 or the original DIW pH. Change gloves.

b. If a sampler will be used for collecting samples for analysis of organic compounds only, change gloves and:

   i. Detergent wash, then rinse sampler components thoroughly with tap water or DIW until agitated rinse water produces no more suds. Change to solvent-resistant gloves.

   ii. Rinse sampler components with pesticide-grade methanol (section 3.2.2), collecting the used methanol into an appropriate container for safe storage until appropriate disposal is arranged. Omit this methanol rinse if sampler will be used for collection of TPC or DOC samples.

   iii. Place each component on a clean, aluminum-foil-covered surface to air dry and cover loosely with an aluminum foil tent, if airborne contaminants are a concern. Change gloves.

c. If sampler will be used for collecting samples for both organic and inorganic analyses, change gloves and:

   i. Proceed with a detergent wash and thorough tap water and (or) DIW rinse.

   ii. Acid rinse and DIW rinse nonmetallic components, as described above, discarding used solutions appropriately. Change to solvent-resistant gloves.

   iii. Rinse with methanol, as described above, except for equipment used to collect TPC or DOC samples.

   iv. Place cleaned items on a clean plastic surface to air dry.

5. Reassemble sampler. If the sampler is dedicated to sampling for organic compounds, double-wrap sampler nozzle in aluminum foil. Place sampler into doubled plastic bags for storage and transport.

Do not use methanol or other organic solvents on equipment used to collect organic-carbon samples.

GROUND-WATER SAMPLING EQUIPMENT 3.3.10

Ground water is sampled with nonpumping samplers (such as bailers, syringe samplers, and the Kemmerer sampler) and with pumping samplers (such as peristaltic and valveless metering pumps and submersible pumps) (NFM 2.1.2). Workplace-laboratory cleaning procedures are used before a sampler is used for the first time, after the sampler has been in long-term storage, and whenever the sampler has become excessively contaminated. Field-site cleaning procedures are used after sampling at a field site and before proceeding to the next sampling site. Caveats and modifications that apply to the general workplace-laboratory and field-site cleaning procedures (section 3.2) are described in this section. The cleaning procedures used should be documented on field forms.

The rinse with methanol, or other organic solvent, is appropriate only for samplers being used to collect samples for organic-compound analysis. **Solvents are never used to clean equipment when sampling for TPC or DOC.** Dispose of used methanol and all other cleaning solutions appropriately**.**

TECHNICAL NOTE: Sampler components made of fluorocarbon-polymer plastic generally can withstand a solvent rinse with methanol. Check with the manufacturer before using an organic solvent on pump components constructed of any other plastic material.

3.3.10.A BAILERS AND OTHER NONPUMPING SAMPLERS

Workplace-laboratory procedure. Clean nonpumping samplers in a designated area of the workplace laboratory. Follow the procedures described for figures 3–2 and 3–4, as appropriate for equipment used to sample for inorganic constituents or organic compounds, respectively.

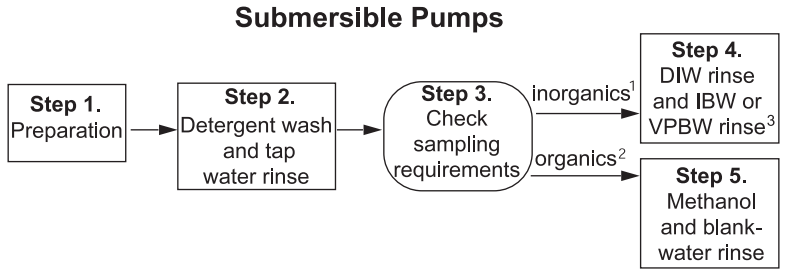
Field-site procedure. Follow the field-site cleaning procedures described for figures 3–3 and 3–4, as appropriate for equipment used to sample for inorganic constituents or organic compounds, respectively.

- Rinse the outside of the sampler with DIW directly after use.
- After filling the sampler with each cleaning solution, shake the sampler vigorously and drain solution through the bottom-emptying device, spigot, or nozzle of the sampler.
- If the sampler looks very dirty or is contaminated, disassemble and clean sampler components using the workplace-laboratory procedure.

SUBMERSIBLE PUMPS AND SUBMERSIBLE-PUMP TUBING 3.3.10.B

The general sequence shown in figure 3–5 is appropriate for cleaning most submersible pumps. The field-site cleaning procedure (described below after the workplace-laboratory procedure) is sufficient for routine cleaning of the pump in most cases. Collection of blank samples for quality control must be included as a standard protocol for every study in order to document and ensure the efficacy of the cleaning procedure for the field conditions encountered.

- Fluorocarbon-polymer tubing used to collect water containing large concentrations of volatile organic compounds (VOCs) can be difficult to clean adequately.
  - — Collect additional blanks if VOC concentrations in the last sample collected through the tubing were greater than 500 µg/L.
  - — Pump tubing should be replaced rather than cleaned if VOC concentrations in the last sample exceeded about 700 µg/L.
- Most submersible pumps have a stainless steel casing and other metal parts and should not be acid rinsed.
  - — To clean pumps that are excessively contaminated, a dilute acid rinse followed by copious water rinsing can be used occasionally without damaging the pump.
  - — Repeated rinsing with dilute acid solution can pit or corrode the pump's stainless steel surface. If the surface appears dulled, then the pump should not be used for collecting trace-metal samples.
- Lubrication water inside water-lubricated pumps (for example, the Grundfos RediFlo2™) can become contaminated and potentially result in contamination of subsequent samples. Replace the lubrication water with VPBW after sampling and when cleaning the pump. Follow manufacturer's instructions.



[1] Samples collected for inorganic-constituent analysis. If samples also are to be collected for organic-compound analysis, then rinse with deionized water (DIW) (Step 4), then methanol (Step 5).

[2] Samples collected for organic-compound analysis. When sampling for total-particulate or dissolved organic carbon, do not methanol rinse; complete cleaning by rinsing with organic-grade water.

[3] A rinse with inorganic blank water (IBW) or universal-grade blank water (VPBW) is needed only if collecting a blank sample for inorganics analysis directly after cleaning the pump.

Figure 3–5. Cleaning procedures for submersible pumps.

Workplace-laboratory pump-cleaning procedure:

Use workplace-laboratory procedures about once a year and more frequently if results of the pump blank or other information indicate that the pump is contaminated.

Step 1. Preparation.

a. Wearing appropriate gloves, prepare several gallons of a laboratory-grade nonphosphate detergent solution (about 0.1 or 0.2 percent, v/v; use up to 2-percent solution for excessively contaminated pump systems).

b. Preclean washbasins and standpipes (section 3.2).

c. Place pump into sink or waste basin and scrub exterior surfaces with soft brush and detergent solution; rinse thoroughly with tap water.

d. Disassemble the pump and place components into a detergent-solution washbasin.

Step 2. Detergent wash and tap water rinse pump components and tubing.

a. Soak pump components in the detergent solution for 30 minutes.

b. Clean pump components with soft sponge or brush.

c. Rinse thoroughly with tap water.

d. Raise discharge end of tubing above the rest of the tubing. Using a peristaltic or valveless fluid metering pump, fill the pump tubing with fresh detergent solution until solution rises to the end of the tubing. Plug the tubing end(s).

e. After 30 minutes remove plug from discharge end of tubing and flush detergent solution from tubing by pumping copious amounts of tap water through the tubing. Change gloves.

Step 3. Check sampling requirements.

— If pump will be used for collecting samples for inorganic-constituent analysis, then reassemble the pump and go to Step 4.

— Complete Step 4 if pump will be used for collecting samples for analysis of both inorganic and organic analytes before proceeding to Step 5.

— If the pump will be used for collecting samples for organic-compound analyses only, then go to Step 5.

Step 4. DIW rinse.

a. Place pump components into DIW washbasin and dispense DIW from a wash bottle to thoroughly rinse all pump components.

b. Using a peristaltic pump and appropriate clean tubing, pump DIW through the sample tubing to rinse.

c. Reassemble pump and connect pump tubing. Change gloves.

d. If collecting equipment blanks to verify that the pump has been adequately cleaned (section 3.4):

i. Rinse a clean standpipe dedicated to blank water with blank water.

ii. Insert pump into blank-water standpipe only after pump exterior has been rinsed with blank water or air dried after the methanol rinse.

iii. Pour IBW into the standpipe and pump at least one tubing volume to waste before collecting the blank sample.

Step 5. Rinse with methanol followed by a blank water rinse.

a. Wearing latex or nitrile gloves, put pump components into solvent-resistant washbasin.

b. Working under a fume hood, dispense methanol (or appropriate solvent) from a fluorocarbon-polymer wash bottle to rinse each pump component and the exterior pump casing. Collect the used solvent into a nonflammable container for storage until disposal.

- **Do not reuse methanol or other solvents.**
- **Work under a fume hood, if possible, or in a well-ventilated area outside of the workplace laboratory, as methanol fumes can contaminate other equipment.**
- **Do not methanol rinse organic-carbon sampling equipment.**

c. Place methanol-rinsed components on a clean, aluminum foil surface and allow the pump components and casing to completely air dry before reassembling the pump (see section 3.2.2). If also collecting samples for metals analysis, then use clean plastic sheeting instead of aluminum foil.

d. Using a valveless fluid metering pump and fluorocarbon-polymer tubing, pump about 2 L of methanol through sample tubing and discharge to the methanol waste container.

e. Reassemble the pump and connect the pump tubing. Change gloves and dispose of the methanol-contaminated gloves appropriately.

f. Pour organic-grade water (PBW or VPBW) into a clean PBW/VPBW standpipe. Insert pump and pass about two tubing volumes of organic-grade blank water (PBW or VPBW) through the pump and tubing to waste.

CAUTION: Pumping methanol or other flammable solvents through an electrical pump system could be dangerous in the event of sparks. Methanol emits noxious fumes and is absorbed through the skin. Wear a mask, safety glasses, and other protective apparel to protect yourself when working with organic solvents.

Field-site cleaning procedure for submersible pumps and pump tubing:

Step 1. Preparation.

a. Preclean the standpipes (one standpipe for each cleaning solution to be used, as described in 3.2.1). The standpipes need to be of sufficient height to supply necessary head for proper pump operation. Separate standpipes are designated for detergent solution and tap water rinse, DIW rinse, methanol rinse, and blank water (IBW/PBW/VPBW). Double-bag each cleaned standpipe for transport to the field site.

b. Estimate the volumes of cleaning solutions and blank water that will be needed for the field effort (refer to fig. 3–6).

c. Prepare the volumes of cleaning solutions needed for the field effort, using appropriate bottles for short-term storage and transport.

To estimate the volume of storage (V_s) in tubing of a set of pump-reel and extension tubing (in gallons)[1,2]:

$$\mathbf{V_s = [(L_p \times C_p) + (L_e \times C_e) + V_{sp}] \times C_{sp}}$$

where,

$\mathbf{V_s}$ is volume of storage in tubing, in gallons
$\mathbf{L_p}$ is length of pump-tubing segment being cleaned, in feet
$\mathbf{L_e}$ is length of extension tubing, in feet
$\mathbf{C_p}$ (or $\mathbf{C_e}$) = 0.023 liter per foot for a 3/8-inch inside-diameter (ID) tubing
or = 0.041 liter per foot for a 1/2-inch ID tubing
$\mathbf{V_{sp}}$ is volume of solution needed to fill standpipe to minimum level required to operate pump, in liters[3]
$\mathbf{C_{sp}}$ = 0.264 gallon per liter.

Examples

Given:

1. L_p - sample-wetted tubing segment is 100 feet for a pump-reel system that has a 1/2-inch ID tubing;
2. L_e - two, 10-foot, 3/8-inch-ID pieces of extension tubing, one running from pump-reel outlet to sample collection chamber, and another running from chamber back to pump-reel (return-flow tubing to standpipe); and
3. V_{sp} - minimum volume[3] of solution required in standpipe to operate pump is 0.8 liter.

To estimate the volume of detergent solution needed for the detergent wash cycle:

$$\mathbf{V_s = [(100 \times 0.041) + (20 \times 0.023) + 0.8] \times 0.264 = 1.4 \text{ gallons}}$$

The volume of workplace-produced deionized water needed to displace detergent solution and the volume of laboratory-produced organic-grade blank water needed to displace 2 liters of methanol just pumped into a system, ideally, would each be estimated to equal V_s[1,2].

---

[1]Estimate assumes no mixing of two solutions and ignores potential for detergent to adhere to tubing walls. Outflow from the discharge end of tubing should be checked for sudsing to determine that detergent has been removed.

[2]Estimate assumes no mixing at interface of two solutions and ignores potential for methanol to adhere to tubing walls. It is recommended that an additional 0.1 gallon (~ 0.4 liter) of blank water (pesticide-grade blank water or volatile-grade blank water) be used for each 10 feet of tubing to remove methanol residues from sample-wetted sections of tubing. Thus in the example above, another 1.1 (= (100 + 10) x (0.1/10)) gallons (4.2 liters) of blank water would be pumped from the system. This implies a total of about 2.5 (= 1.4 + 1.1) gallons (9.6 liters) of blank water would be used to remove methanol from the equipment setup.

[3]The minimum volume corresponds to the level of solution in the standpipe, which, if maintained, allows pump to operate without introducing air through the pump intake. Once this level is reached, remove pump, and measure this volume.

Figure 3–6. Estimation of cleaning-solution volumes for standpipe, pump, and pump tubing. [From Koterba and others, 1995, table 24.]

Step 2. Detergent wash and tap water rinse.

a. Put on disposable, powderless gloves. Rest pump in a washbasin or pail partially filled with detergent solution and clean exterior of pump and tubing with a soft brush. Rinse thoroughly with tap water. (DIW can be used instead of tap water, but is less efficient in detergent removal and requires a greater volume of water than tap water.)

b. Place pump into standpipe, add detergent solution to level above pump intake, and route the intake and discharge ends of pump tubing to the standpipe.

c. Begin pumping:

   i. Record the pumping rate.

   ii. Record the time it takes to fill the sample tubing.

   iii. Calculate the time it takes for a segment of solution to complete one cycle (fig. 3–6).

d. Circulate detergent solution for about three cycles through the tubing and back to the standpipe. If possible, pump detergent solution through tubing at alternating high and low speeds, and (or) introduce air segments between aliquots of the detergent solution to increase cleaning efficiency.

e. Remove the discharge end of tubing from the standpipe and pump about two tubing volumes of detergent solution to waste, adding fresh solution to the standpipe as needed. Remove pump from standpipe.

f. Rinse detergent from standpipe with tap water until sudsing stops.

g. Rinse pump exterior with tap water. Place rinsed pump into the tap water/DIW standpipe; add tap water/DIW to level above pump intake. Begin pumping through sample tubing. Do not recirculate rinse water, but add water as needed to maintain water level above pump intake. Continue for five or more tubing volumes. Direct rinse water to waste, away from the vicinity of the wellhead and sampling area and (or) contain as required for disposal.

h. Collect rinse water into a small bottle and stop the pump. Shake the bottle—if sudsing is observed in the rinse water, continue the rinse procedure until no suds appear in the rinse water. Change gloves.

Step 3. Check sampling requirements.

— If a pump will be used to collect samples for inorganic-constituent analysis, go to Step 4.

— Complete Step 4 if a pump will be used to collect samples for analysis of both inorganic and organic analytes and then go to Step 5.

— If a pump will be used to collect samples for organic-compound analysis only, go to Step 5.

Step 4. DIW rinse.

A separate DIW rinse is not required if DIW was substituted for tap water.

a. Use a clean DIW-dedicated standpipe (not the tap water standpipe) and rinse the standpipe with DIW. Rinse pump exterior with DIW. Place pump into the DIW standpipe and add DIW to level above pump intake. Change gloves.

b. Start pumping DIW. Rinse DIW through sample tubing without recirculating, using about three tubing volumes of DIW. Keep the DIW level above pump intake.

c. If collecting field blanks to verify that the pump has been adequately cleaned (section 3.4):

   i. Change gloves. Rinse clean blank-water standpipe with IBW (or VPBW). Rinse pump exterior with blank water.

   ii. Place pump into the standpipe and add IBW (or VPBW) to cover the pump intake.

   iii. Turn on pump and displace any water residing in the pump and tubing. Continue pumping IBW (or VPBW) for one tubing volume before collecting the blank sample.

Step 5. Methanol rinse.[10]

Make certain that the pump or other nearby electrically powered equipment is grounded, the power cord is intact, and potential sources of sparks do not exist before rinsing pump with methanol.

TECHNICAL NOTES:

– Inspect the integrity of the seals and O-rings on the pump-motor/pump-body housing. Water inside the motor housing may indicate that methanol vapors could enter the motor. Direct-current motors inherently spark because of the commutator ring. AC motors might spark if the insulation is frayed or burnt on the motor windings or any associated wiring.

– If flammable liquids are required for cleaning electrical pump systems, use extreme caution. Vapors from solvents such as methanol can ignite if a disruption in the motor lead-insulation system occurs in the vapor-enriched zone. (Ignition from a spark from an AC induction-type motor in good operating condition is not a concern if rated as using the National Electrical Code (NEC) at Class 1, Group D.[11])

a. Wear latex or nitrile gloves, safety glasses, and apron. Work in a well-ventilated area outside of the field van and downwind of the sampling area.

b. Place pump into a clean, dedicated, solvent-resistant standpipe and route discharge end of sample tubing to a methanol waste container. Add methanol solution to level above pump intake.

c. Pump about 2 L of methanol through the sample tubing into the methanol waste container, keeping the level of solution above the pump intake. The operator should stand back from the pump as a safety precaution in the event that an electrical spark ignites the methanol. Carefully pour any unused methanol that is in the standpipe into a methanol waste container. Let the methanol in the standpipe evaporate to dryness. Change gloves.

[10]Reminder to NAWQA Program personnel: the methanol rinse is mandated for cleaning equipment to be used to collect samples for analysis of all organic compounds other than organic carbon.

[11]NEC Class 1; Group D: Areas in which flammable gases or vapors may be present in the air in sufficient quantities to be explosive; atmospheres such as acetone, alcohol, ammonia, benzene, benzol, butane, gasoline, hexane, lacquer solvent vapors, naphtha, natural gas, propane, or gas or vapors of equivalent hazard (Cole-Parmer Instrument Company, 1997).

d. Rinse pump exterior with organic-grade water and place pump into the standpipe. Add organic-grade water to the standpipe to push the methanol out of the tubing and into the methanol waste container. Pump at least an additional 0.1 gallon (about 0.38 L) of organic-grade water through the system for every 10 ft (about 3.05 m) of methanol-wetted tubing. Discharge this water to the methanol waste container.

> **TECHNICAL NOTE:** The recommended organic-grade water is PBW or VPBW (designated for blank samples). Workplace-produced organic-grade water might not be of adequate purity, especially after being stored, and its use requires collection of additional blank samples for quality control (see section 3.4).

e. Repeat (d) above with blank water (PBW or VPBW) pumped from a blank-water standpipe if blank samples will be collected for analysis of organic compounds.

A methanol rinse is most safely accomplished under a laboratory hood or in another well-ventilated, clean environment.

Storage of the cleaned submersible pump and tubing:

1. Place pump into two clean, noncontaminating storage bags and tie the bags shut.

2. Cover the pump reel and tubing with doubled plastic bags or sheeting for transport to the next site.

For long-term storage (longer than 3 days), the pump and exterior and interior of the tubing must be dry before being placed into plastic bags. Tubing can be dried by blowing filtered air or filtered (inert) gas through the tubing. If tubing cannot be dried, store chilled to prevent bacterial growth. If bacterial growth has occurred, reclean before use.

3.4 QUALITY CONTROL FOR EQUIPMENT-CLEANING PROCEDURES

By **A.J. Horowitz, M.W. Sandstrom, and F.D. Wilde**

Quality-control samples are required for any sampling and analysis program. Without quality-control information, the quality of the environmental data collected can be neither evaluated nor qualified. If the user has no means of knowing the associated errors, the data cannot be interpreted properly.

The purpose for obtaining quality-control (QC) samples following equipment cleaning is to ensure that the equipment and the procedures used for cleaning the equipment do not contaminate or otherwise affect the environmental samples that were or will be collected. The QC sample used to assess the adequacy of cleaning procedures before field work commences is called the equipment blank. QC sampling guidelines for microbiological sampling differs and can be found in NFM 7.

- **Blank water**. Blank water is used to develop specific types of QC samples (National Water Quality Laboratory Memorandum 92.01). The water is a solution that is free of analyte(s) of interest at a specified detection level. USGS personnel are required to use blank water that has been analyzed and certified to be of a specific grade and composition.
  - — Use IBW, PBW, or VPBW (nitrogen-purged) to collect blank samples for analysis of inorganic constituents.
  - — Use PBW to collect blank samples for analysis of pesticides. (Do not use PBW when collecting samples for VOC analysis.)
  - — Use VPBW, which is nitrogen-purged, to process blank samples for analysis of VOCs. VPBW also is suitable as a blank sample for pesticide and inorganic-constituent analyses.
  - — Use PBW or VPBW as the quality-control sample for total-particulate carbon and dissolved organic-carbon analyses (TPC and DOC). This cannot be strictly documented as a blank sample because neither PBW nor VPBW is certified to be free of organic carbon.

- **Equipment blank.** An equipment blank is blank water that is processed under controlled conditions in the workplace laboratory by being passed sequentially through each component of the sample processing and collection equipment. **An equipment blank represents an entire sampling system (fig. 3–7) and is required:**

  — Annually.

  — When a cleaning procedure is followed for the first time.

  — When new equipment will be used for the first time.

To fulfill equipment-blank requirements:

1. Allow enough time in the study workplan to collect the annual equipment blank, complete laboratory analyses, and review analytical results before field work for the study commences.

2. Process the annual equipment blank in a clean, controlled environment in the workplace laboratory, after the equipment has been cleaned using workplace-laboratory procedures.

3. Analyze the annual equipment-blank data before collecting and processing the first water-quality sample of either the fiscal year or the study.

   - If the equipment-blank data indicate that the equipment does not introduce contaminants that will bias study results, then sampling can proceed.

   - If the equipment-blank data indicate unacceptable concentrations of analytes of interest, then the cause must be identified and the equipment or cleaning procedures must be changed or modified before sampling can proceed.

Plan ahead: Assess equipment-blank data before environmental samples are collected.

- **Field blank.** The field blank is blank water that is processed at the field site by being passed sequentially through each component of the equipment being used to collect environmental samples. The procedure for processing the field blank, like the equipment blank, can also result in a set of sequentially collected blank samples (fig. 3–7) (Horowitz and others, 1994). Other types of blank samples also are collected at the field site (NFM 4). **At least one field blank per sampling run is recommended; the numbers and distribution of QC samples depend on study objectives, the target analytes, and site conditions.**

  — Process field blanks through clean equipment.

  — If equipment is used at several sites during a field trip, process a field-equipment blank after the last sample has been collected and again after the equipment has undergone the prescribed field-cleaning procedures.

  — If multiple sets of workplace-cleaned equipment are used during a field trip, process a field blank at any site during the course of the trip. In this case, the blank must be processed before sampling to avoid contaminating the blank with residues from an environmental sample.

  — Process field blanks onsite and under the same conditions as the environmental sample.

Before filling the QC sample bottle with the appropriate blank water:

1. Check that sample bottles are clean, are the correct type, and are labeled correctly.

2. Check the certificate of analysis for the lot of blank water to be sure that it is appropriate for quality control of target analytes.

3. Record the date and lot number of the IBW, PBW, and (or) VPBW used and of the preservative used. To the extent possible, use preservative from the same lot number for an entire sampling trip for both the environmental and quality-control samples.

4. Rinse sample bottles for inorganic constituents three times with a small quantity of the blank water.

Use the following strategy for QC data collection and analysis:

1. For inorganic-constituent samples, initially send only the final equipment-blank sample for the routine inorganic blank-sample analysis or for inorganic analytes targeted by the study.

    - Archive the remaining sequentially processed blank samples (fig.3-7) until the inorganic-constituent analysis of the equipment-blank sample has been received.

    - Do not archive blank samples for organic-compound analysis.

2. Check the analytical results for the equipment blank and field blanks as soon as possible and before the next field trip.

    - If analytical results indicate that the equipment is clean within acceptable limits, the equipment may be used for field work without additional testing or analysis.

    - **Use of equipment is not recommended if analysis of the equipment blank sample indicates greater than acceptable analyte concentrations.**

3. Additional QC data collection and (or) analysis is required if the equipment blank has greater than acceptable analyte concentrations.

    - **For inorganic-sample analysis.** Submit the rest of the sequential blank samples for laboratory analysis and use the analytical results from the sequential blank samples to identify potential source(s) of contamination. Modify equipment-cleaning procedures if contamination can be remedied by a change in cleaning procedure. Repeat collection of equipment blanks until the blank data verify that the equipment is suitable for use.

    - **For organic-sample analysis.** Modify the equipment cleaning procedure if the source of contamination is known or suspected and contamination can be remedied by a change in cleaning procedure. If the source of contamination is not known, reclean equipment using workplace-laboratory procedures and collect and analyze blanks for each part of the sampling system that could be a source of contamination. Repeat collection of equipment blanks until the blank data verify that the equipment is suitable for use.

The equipment blank is the last sample of a set of sequentially processed blanks collected in the workplace laboratory, and documents the suitability of the equipment for the samples that are to be collected and analyzed. **Field blanks** are collected in the field in the same manner as the equipment blank, but they document the effectiveness of the field-cleaning procedures plus any ambient contamination.

- **Surface water:** collect the series of five sequential blank samples listed below for routine surface-water sampling.
- **Ground water:** collect the source-solution blank (Sample 1) and either a sampler blank (Sample 2) or pump blank (Sample 4), depending on the type of sampling device being used along with the filter blank (Sample 5) .

Sample 1. SS blank	**Source solution (SS)** Put on disposable gloves. Pour the IBW, PBW, or VPBW directly into appropriate SS blank-sample bottle.[1] Add chemical treatment and (or) chill, as required for the analytes of interest.
Sample 2. Sampler blank	**SS + Sampler** Bottle or bag sampler: Fill sampler container with SS; attach sampler cap and nozzle; decant sample into blank-sample bottle through the nozzle. Preserve sample (add chemical treatment and (or) chill) as required (NFM 5). Bailer or thief sampler: Fill sampler with SS; install bottom-emptying device; empty sample into blank-sample bottle through the bottom-emptying device. Preserve sample, as required. Submersible or nonsubmersible pumps: Go to Sample 4 (Pump blank).
Sample 3. Splitter blank	**SS + Sampler + Splitter[2]** If a cone or churn splitter is used, decant remainder of the SS into sampler container, and then through splitter (through nozzle or bottom-emptying device). Refill sampler container with SS to fill churn with 3 to 5 liters of water. Alternatively, pour enough SS from samplers through cone splitter to fill splitter-blank bottle. Collect SS into blank-sample bottle through churn spigot or cone-splitter exit port(s). Preserve sample, as required.
Sample 4. Pump blank	**SS + Sampler + Splitter + Pump** Nonsubmersible pump (peristaltic, vacuum, or valveless metering pump): Secure intake end of clean pump tubing into churn splitter or into a subsample split with the cone splitter. Pump some sample to waste to rinse tubing, and fill pump-blank bottle directly from the discharge end. Preserve sample, as required. Submersible pump: Place pump in blank-water standpipe and fill standpipe with enough SS to cover pump intake and allow for drawdown. Start pump at low pumping rate, discharge 0.5 liter of SS to waste, then fill blank-sample bottle with SS. Preserve sample, as required.
Sample 5. Filter or equipment blank	**SS + Sampler + Splitter + Pump + Filter** Pump SS through a prerinsed filtration assembly (plate filter or capsule filter); pump the first aliquot to waste and then pump SS directly into the blank-sample bottle. Preserve sample, as required.

[1]Process the source-solution blank in the protected environment of the workplace laboratory only, not in the field (NFM 4).

[2]For ground-water quality control: A splitter blank is included if a cone splitter is used; a standpipe blank commonly is collected if a submersible pump is used.

Figure 3–7. Sequence of sample collection to obtain the equipment blank.

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CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
square centimeter (cm^2)	.1550	square inch
meter (m)	3.281	foot
milliliter (mL)	0.06102	$inch^3$ or cubic inch
liter (L)	0.2642	gallon
microgram (µg)	3.53×10^{-8}	ounce

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

ABBREVIATIONS

DIW	deionized water
DOC	dissolved organic carbon
HCl	hydrochloric acid
HNO_3	nitric acid
IBW	inorganic-grade blank water, laboratory-certified free of trace elements and other inorganic constituents
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter at 25°C
MSDS	Material Safety Data Sheet
NFM	*National Field Manual for the Collection of Water-Quality Data*
NAWQA	National Water-Quality Assessment Program of the U.S. Geological Survey
NWQL	National Water Quality Laboratory of the U.S. Geological Survey
PBW	pesticide-grade blankwater, certified free of pesticide organic compounds by the NWQL

ABBREVIATIONS—*Continued*

PIC	particulate inorganic carbon
PFA	perfluoroalkoxy
POC	particulate organic carbon
PVC	polyvinyl chloride
QC	quality control
SS	source solution
TOC	total organic carbon
TPC	total particulate carbon
TPN	total particulate nitrogen
TWRI	Techniques of Water-Resources Investigations
URL	Uniform Resource Locator
USGS	U.S. Geological Survey
VOC	volatile organic compound
VPBW	volatile- and pesticide-grade blank water, purged with nitrogen gas and certified free of volatile and pesticide compounds by the NWQL. VPBW also can be used instead of inorganic blank water (IBW).
v/v	volume to volume

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Office of Water Quality, National Water Quality Laboratory, and Water Resources Discipline numbered memorandums are available electronically on the Internet through the USGS Web site at http://water.usgs.gov/admin/memo/ (accessed March 4, 2004).

Office of Water Quality

Memo No.	Title	Date
qw 92.01	Distilled/Deionized Water for District Operations	Dec. 20, 1991
qw 97.03	Protocols for Cleaning a Teflon Cone Splitter to Produce Contaminant-Free Subsamples for Subsequent Determinations of Trace Elements	Feb. 7, 1997

National Water Quality Laboratory (NWQL)

Memo No.	Title	Date
92.01	Technology Transfer—Availability of Equipment Blank Water for Inorganic and Organic Analysis	Mar. 25, 1992

Water Resources Discipline

Memo No.	Title	Date
wrd 94.007	Safety--Storage, Transportation, Handling and Disposal of Methyl Alcohol	Dec. 3, 1993

U.S. Geological Survey
Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A4. COLLECTION OF WATER SAMPLES

Revised 2006

USGS
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U.S. DEPARTMENT OF THE INTERIOR
DIRK KEMPTHORNE, *Secretary*

U.S. GEOLOGICAL SURVEY
Mark D. Myers, *Director*

For additional information write to:

Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

This report is accessible online at http://pubs.water.usgs.gov/twri9A/

Foreword

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and quality-assured data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that the data collected are of the quality required to fulfill our mission.

Robert M. Hirsch
Associate Director for Water

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National Field Manual for the Collection of Water-Quality Data

Chapter A4.

COLLECTION OF WATER SAMPLES

Illustrations

Tables

Note:
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Chapter A4. COLLECTION OF WATER SAMPLES

Revised 2006
Franceska D. Wilde, Editor

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses preparations and appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are considerations and procedures to prevent sample contamination; establishing site files; instructions for collecting depth-integrated isokinetic and nonisokinetic samples at flowing- and still-water sites; and guidelines for collecting formation water from wells having various types of construction and hydraulic and aquifer characteristics.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection and quality control of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used inconjunction with eachother. Chapter numbersare preceded by an "A" to indicate that the report is part of the *National Field Manual*. Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that generally are applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and(4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples from bodies of surface water and ground water. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials. Collection of data related to onsite measurements such as pH and alkalinity is addressed in NFM 6, while collection of biochemical and microbiological data is addressed in NFM 7.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and other professionals who have the appropriate expertise. Technical memorandums or other documents that define the policy pertinent to such requirements are referenced in this chapter. USGS personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that, on the basis of research and (or) consensus, the USGS Office of Water Quality recognizes one or several acceptable alternatives for selecting equipment or procedures. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the alternatives must be based on referenced research and good field judgment, and reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* are reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be mailed to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or by e-mail to nfm-owq@usgs.gov). Newly published and revised chapters are posted on the USGS Web page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is: http://pubs.water.usgs.gov/twri9A/. The page contains links to an errata page and to the chapters of the *National Field Manual*. Information regarding the status and any errata of this or other chapters can be found near the beginning of the Web page for each chapter. Near the bottom of each chapter's Web page are links to archived versions.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on earlier manuals, various reference documents, and a broad spectrum of colleague expertise. Individuals in the USGS–too numerous to mention by name–developed the field and training manuals that provided the foundation for information on the collection and processing of water samples, and others have contributed through peer and editorial reviews to the technical quality of this document. Editorial assistance provided by Iris M. Collies and production assistance from Loretta J. Ulibarri have been indispensible in maintaining and enhancing the quality of this report.

The current editor owes a debt of gratitude to the original team of authors: Dean B. Radtke, Rick T. Iwatsubo, Jacob Gibs, Wayne W. Webb and Roger W. Lee, and to the following scientists who provided technical review, and who contributed significantly to the accuracy, quality, and usability of this report: Andrew Arnsberg, Bruce A. Bernard, William L. Cunningham, Ron G. Fay, Sarah Flanagan, Jacob Gibs, Kathleen K. Fitzgerald, Henry M. Johnson, Michael S. Lico, Jeffrey D. Martin, Timothy D. Oden, Kevin D. Richards, David A. Saad, Terry L. Schertz, Allen M. Shapiro, and Stanley C. Skrobialowski. Special thanks go to Timothy L. Miller for providing the support needed to produce a national field manual for water-quality studies.

Franceska D. Wilde
Managing Editor

A4. COLLECTION OF WATER SAMPLES

This chapter of the *National Field Manual* (NFM) describes standard USGS methods (sampling strategies, techniques, requirements, and recommendations) for the routine collection of representative water samples. Sample collection forms a continuum with sample processing; therefore, the information in this chapter overlaps with some of the information in NFM 5, *Processing of Water Samples*.

SAMPLING:
The act of collecting a portion of material for analytical purposes that accurately represents the material being sampled with respect to stated objectives.

Modified from Standard Methods, 1060A
(APHA and others, 2001)

Before sample collection begins, field personnel must take steps to ensure that the samples collected will be representative of the aqueous system being investigated. A representative sample is one that typifies ("represents") in time and space that part of the aqueous system to be studied, and is delineated by the objectives and scope of the study.

Obtaining representative samples is of primary importance for a relevant description of the environment. In order to collect a representative sample that will yield the information required, (1) study objectives, including data-quality requirements,[1] must be understood in the context of the water system to be sampled, and (2) artifacts of the sampling process must be minimized.[2] Field personnel must be alert to conditions that could compromise the quality of a sample.

- **Collect a representative sample.** Use appropriate methods and quality-assurance measures to ensure that the field sites selected and the samples collected accurately represent the environment intended for study and can fulfill data-quality objectives.

- **Think contamination!** To ensure the integrity of the sample, be aware of possible sources of contamination. Contamination introduced during each phase of sample collection (and processing) is additive and usually is substantially greater than contamination introduced elsewhere in the sample-handling and -analysis process. **Therefore, collect a sufficient number of quality-control samples, appropriately distributed in time and space, to ensure that data-quality objectives and requirements are met (section 4.3).**

[1] As used in this report, data-quality requirements refer to that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the variability allowable to fulfill the scientific objectives of the study.

[2] The degree to which a sample can be considered representative of a water body depends on many interrelated factors including, for example, temporal and spatial homogeneity of the water body, sample size, and the method and manner of sample collection.

4.0 RESPONSIBILITIES, FIELD PREPARATIONS, AND PREVENTING SAMPLE CONTAMINATION

This section of the NFM presents guidelines, requirements, and recommendations for USGS field personnel as they prepare for sample collection at field sites. Collecting comparable data over the duration of the sampling effort and among sampling sites is necessary for a valid analysis and interpretation of the data. This usually requires consistent use of the methods and equipment selected and collection of sufficient quality-control data to verify the quality and comparability of the data collected.

USGS data-collection efforts often take a whole-system approach, meaning that the data-collection methods used are designed so that the entire stream reach or aquifer volume is represented. A modified approach is needed for studies in which samples are representative of a specific portion or aspect of an aqueous system; for example, a study of aquatic ecology may establish nearshore boundaries on the system of study, and an oil-spill study may target only the surface of a water-table aquifer.

- **What do your data represent?** Data collectors need to know what questions the data being collected are meant to address, and understand the level of accuracy and precision that are needed in the data to answer those questions. The data are no better than the confidence that can be placed in how well the sample represents the aqueous system (Horowitz and others, 1994). Therefore, understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- **Are your data of appropriate quality?** Quality-control samples yield information by which confidence brackets can be applied to the environmental data. Field quality control is vital for data interpretation and assessment and yields different information than laboratory-performed quality-control checks.

Data quality begins before the first sample is collected, by taking care to use proper equipment, being aware of data-quality requirements, and being alert to potential sources of sample contamination.

4.0.1 RESPONSIBILITIES AND FIELD PREPARATIONS

Field personnel are responsible for their safety and for the quality of the work performed.

- **Never compromise the safety of field personnel.** Be familiar with the safety requirements and recommendations described in NFM 9. Get the appropriate training and certification needed if you will be working at sites designated as hazardous.
- **Collect data of known quality.** Fundamental to water-quality sampling is the fact that the quality of the analytical results can be no better than the quality of the sample on which the analyses were performed. The sample collector has primary responsibility for the quality and integrity of the sample up to the time that the sample is delivered to the analyzing laboratory or office. Data quality is determined from analysis of quality-control data.
- **Know what you need to do.** Before departing for field work, review the workplan, and plan for the types of measurements and samples specified.
  - — Be thoroughly familiar with your study objectives and requirements. Sampling plans, including quality-assurance and equipment requirements, need to be prepared and reviewed in advance. Some programs require a prescribed format for sampling, quality-assurance, and safety plans. Some projects require chain-of-custody documentation.
  - — Review and understand the USGS protocols for collecting and processing your samples before field work begins. Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

All details of a field trip need to be planned well in advance (fig. 4-1). Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations; a common mistake is to put off these activities until the last minute (table 4-1).

- **Make reconnaissance trips** before selecting repeat sampling sites, if possible.
  - — Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing or low-flow wells, or site-access peculiarities).
  - — Evaluate potential sources of contamination at the site, based on the analytes[3] to be targeted in the sample analysis.
- **Review site files and field folders** (see sections 4.1.1 and 4.2.1). Check the site location, description, and access. Review any previously collected physical, chemical, and biological data.
- **When selecting field equipment**, understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

[3]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

- **Prepare a workplan and checklists**.
  - The workplan delineates study activities and establishes the timeframe in which the activities are to be completed (table 4-1).
  - Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 4-1). Generic checklist items apply to most studies, and the checklist customized for specific study requirements (for example, special equipment or supplies, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment).
- **Data management.** Field personnel also are responsible for providing the necessary information to establish USGS National Water Information System (NWIS) site files for each sampling site and for checking to see that the site file is functional, that the information it contains is correct, and that updates are made promptly. NWIS is the hydrologic data base for the USGS, and includes the following subsystems in which study site files are to be maintained:
  - **Quality-of-Water Data (QWDATA)** – contains field and laboratory data.
  - **Automatic Data Processing System (ADAPS)** – contains time-series information.
  - **Ground-Water Site Inventory (GWSI)** – contains aquifer and ground-water site information.

PLAN AHEAD! Take adequate time to prepare.

Table 4-1. Example of work-schedule elements

Work-schedule elements	Examples of items or activities in checklists	Completed by
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.	
Presampling activities	Prepare checklists (see figs. 4-1 and 4-7). Prepare NWIS site files.	
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.	
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.	
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.	
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of-custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with respect to: analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, chemical treatment and preservation procedures; sample shipment; quality-control samples.	
Field-folder contents	Prepare a list of logistical information needed for each site, such as permission to access site, keys, maps.	
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.	

FIELD-TRIP PREPARATIONS

PROJECT: _____

SITES: _____DATE:_____

✓	Prefield activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ , Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (Water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare field forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check field vehicle for safety equipment and supplies, such as material safety data sheets, flares, and remote communications system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update field folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with field-trip and call-in (check-in) schedule	Provided on _____ to _____
	Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
	Other	

Figure 4-1. Example of a presampling activities checklist.

PREVENTING SAMPLE CONTAMINATION 4.0.2

The USGS prescribes specific protocols for avoiding contamination of water samples. In addition, collection of quality-control samples (section 4.3) – scaled as appropriate to the objectives of the study and site conditions – is mandated to check for, address, and measure sample contamination and any resulting bias to the data. The most common causes of sample contamination during sample collection include poor sample-handling techniques, input from atmospheric sources, inadequately cleaned equipment, and use of equipment constructed of materials inappropriate for the analytes targeted for study. To prevent or minimize sample contamination from these sources:

- **Implement good field practices**, summarized on table 4-2.

- **Use Clean Hands/Dirty Hands sampling techniques,** summarized on table 4-3.

USGS clean-sampling procedures (sometimes called the parts-per-billion or ppb protocol) involve (1) using equipment that is constructed of noncontaminating materials (NFM 2) and that has been cleaned rigorously before field work and between field sites (NFM 3); (2) handling equipment in a manner that minimizes the chance of altering ambient sample composition; (3) handling samples in a manner that prevents contamination; and (4) routinely collecting quality-control (QC) samples. **Good Field Practices and Clean Hands/Dirty Hands (*CH/DH*) are an integral part of routine USGS water-quality field work.**

The nine major elements that comprise Good Field Practices are listed on table 4-2. Four of the principles are further clarified below.

Field rinse equipment. Field rinsing of equipment used to collect or process samples should not be confused with the procedures used for equipment cleaning or decontamination; directions for field rinsing specific types of surface-water and ground-water equipment are described in sections 4.1.3 and 4.2.2.C, respectively. Collection of equipment blanks and field blanks is necessary to help identify potential sources of sample contamination (section 4.3). The same equipment that is used for collecting and processing environmental samples is used for collecting and processing blanks and other types of quality-control samples; however, equipment-cleaning and -rinsing procedures differ somewhat.

Follow a prescribed sampling order. One dictate of Good Field Practices is to follow a prescribed order for collecting samples. An aspect of this is that cross-contamination between sites can be avoided by planning the order in which field sites will be sampled. Sites should be sampled in the order of least to greatest potential for equipment fouling or contamination, if possible. The cleanest sites are often – although not always – those that are in pristine environments, in areas where concentrations of dissolved solids are low, or upstream or upgradient from known or suspected sources of contamination.

RULE OF THUMB: Collect samples first at sites having the least contamination or lowest chemical concentrations.

Table 4-2. Good field practices for collection of water-quality samples

[Modified from "Rules for Trace-Metal Sampling" by Howard Taylor, U.S. Geological Survey, written communication, 1992; NFM, *National Field Manual for the Collection of Water-Quality Data*]

- Be aware of and record potential sources of contamination at each field site.
- Wear appropriate disposable, powderless gloves:
  - Change gloves before each new step during sample collection (and processing).
  - Avoid hand contact with contaminating surfaces (such as equipment, coins, food).
  - Gloved as well as ungloved hands must not contact the water sample.
- Use equipment constructed of materials that are relatively inert with respect to the analytes of interest (NFM 2).
- Use only equipment that has been cleaned according to prescribed procedures (NFM 3).
- Field rinse equipment, but only as directed. Some equipment for organic-compound and other analysis should not be field rinsed.
- Use correct sample-handling procedures:
  - Minimize the number of sample-handling steps.
  - Use Clean Hands/Dirty Hands techniques (table 4-3) as required for parts-per-billion trace-element sampling. Adapt Clean Hands/Dirty Hands techniques for other sample types, as appropriate. Obtain training for and practice field techniques under supervision before collecting water samples.
- Collect (and process) samples in enclosed chambers so as to minimize contamination from atmospheric sources.
- Collect a sufficient number of blanks and other types of quality-control samples.
- Follow a prescribed order for collecting samples.

Table 4-3. Clean Hands/Dirty Hands techniques for water-quality sampling

- Clean Hands/Dirty Hands techniques require two or more people working together.
- At the field site, one person is designated as Clean Hands (*CH*) and a second person as Dirty Hands (*DH*). Although specific tasks are assigned at the start to *CH* or *DH*, some tasks overlap and can be handled by either, as long as the prescribed care is taken to prevent contaminating the sample.
- *CH* and *DH* wear appropriate disposable, powderless gloves during the entire sampling operation and change gloves frequently, usually with each change in task. (Wearing multiple layers of gloves allows rapid glove changes.) **Gloves must be appropriate to withstand any acid, solvent, or other chemical substance that will be used or contacted.**
- *CH* takes care of all operations involving equipment that contacts the sample; for example, *CH*
  - Handles the surface-water sampler bottle
  - Handles the discharge end of the surface-water or ground-water sample tubing
  - Handles the inner protective bag on the churn splitter
  - Transfers sample to churn or cone splitter
  - Prepares a clean work space (inside vehicle)
  - Sets up processing and preservation chambers
  - Places equipment inside chambers (for example, sample bottles, filtration and preservation equipment)
  - Works exclusively inside chambers during collection/processing and preservation
  - Changes chamber covers, as needed
  - Sets up field-cleaning equipment and cleans equipment
- *DH* takes care of all operations involving contact with potential sources of contamination; for example, *DH*
  - Works exclusively exterior to processing and preservation chambers
  - Prepares and operates sampling equipment, including pumps and discrete samplers, peristaltic pump switch, pump controller, manifold system
  - Operates cranes, tripods, drill rigs, vehicles, or other support equipment
  - Handles the compressor or other power supply for samplers
  - Handles tools such as hammers, wrenches, keys, locks, and sample-flow manifolds
  - Handles single or multiparameter instruments for field measurements
  - Handles the churn carrier, including outer protective bags
  - Handles stream-gaging or water-level equipment
  - Sets up and calibrates field-measurement instruments
  - Measures and records water levels and field measurements

Use Clean Hands/Dirty Hands (*CH/DH*) sampling procedures. *CH/DH* procedures were developed for collecting (and processing) samples vulnerable to contamination. *CH/DH* procedures separate field-duty chores and dedicate one individual (designated as Clean Hands or *CH*) to tasks related to direct contact with sample-wetted equipment and sample containers (table 4-3). Implementation of this protocol requires hands-on training and field-team coordination.[4]

- **Requirement:** *CH/DH* procedures are required when collecting samples for analysis of metals and other inorganic trace elements (hereafter referred to collectively as trace elements), as follows:
  - For trace elements with ambient concentrations at or near 1 µg/L.
  - For iron, aluminum, or manganese with ambient concentrations to about 200 µg/L.

- **Recommendation:** *CH/DH* procedures are recommended when collecting samples for analysis of most trace elements with concentrations to about 100 µg/L.

- **Recommendation:** *CH/DH* procedures are recommended when collecting samples for analysis of trace-organic compounds and major inorganic elements, particularly when the target analyte could be subject to contamination from field or laboratory procedures at a level that could exceed data-quality requirements.

[4]A detailed description of Clean Hands/ Dirty Hands techniques for surface-water sampling can be found in Horowitz and others (1994). Clean Hands/Dirty Hands techniques have been incorporated in the procedures for ground-water sampling (refer to section 4.2), equipment cleaning (NFM 3), and sample processing (NFM 5).

Minimize atmospheric contamination. Water bodies that are isolated from the atmosphere or that have dissolved-oxygen concentrations that are substantially less than that of air can be found in surface-water systems (deeper sections of stratified lakes and reservoirs, for example), but are more common in ground-water systems. For such sites, exposure of the sample to the atmosphere can increase dissolved-oxygen concentrations, causing reduced metal ions to oxidize and precipitate as a hydroxide.

Collection of environmental samples from water bodies for which concentrations of dissolved gases differ substantially from atmospheric concentrations might require special field equipment or procedures. Equipment and procedures should be selected that minimize contact with the atmosphere or minimize the effect of pressure changes from the source of the sample to the point of field measurement or sample processing. Sampling methods and equipment for preventing contact of anoxic and suboxic water samples with atmospheric gases are described in section 4.2.2.C.

> **TECHNICAL NOTE:** Exposure of anoxic or suboxic samples to atmospheric oxygen can cause reduced metal ions to oxidize and precipitate as a hydroxide (for example, oxidation of iron species from ferrous (Fe^{+2}) to ferric (Fe^{+3}) iron). Precipitation of an iron (or other metal) hydroxide can occur either before or during sample filtration, thereby lowering concentrations of soluble iron and co-precipitating metals in the sample. Examples of nonmetal analytes for which atmospheric exposure can compromise sample integrity include volatile organic compounds (VOCs), pH, alkalinity, sulfide, chlorofluorocarbons (CFCs), and some bacteria species.

SURFACE-WATER SAMPLING 4.1

The methods used to collect surface-water samples depend not only on flow characteristics of the surface-water body but also on the following considerations: safety of field personnel (NFM 9); suitability of the equipment with regard to the analytes of interest as well as that of the anticipated hydraulic conditions (NFM 2); field-measurement profiles (NFM 6); temporal and spatial heterogeneity; physical setting; ecological characteristics; weather conditions; fluvial-sediment transport; point and nonpoint sources of contamination; and study objectives, including data-quality requirements. Each sampling site needs to be selected and sampled in a manner that minimizes bias caused by the collection process and that best represents the intended environmental conditions at the time of sampling.

- Before beginning field work, USGS study teams should be thoroughly familiar with procedures and requirements described in this *National Field Manual* and in USGS Office of Water Quality Technical Memorandum 99.02.[5] Additional references that provide descriptions of surface-water sampling techniques include: Federal Interagency Sedimentation Project (1986), Ward and Harr (1990), and Edwards and Glysson (1999).
- Study requirements for collection of equipment blanks, field blanks, concurrent samples, and other relevant QC samples must be prepared for before field work begins (section 4.3). Equipment and supplies must be selected that are appropriate for the use intended.
- Ensure that the field team is staffed and equipped adequately. For example, additional personnel and equipment are required for collection of concurrently collected samples (concurrent replicate samples, section 4.3). Use of safety equipment and procedures is mandatory (NFM 9).
- Prior to sample collection, the study team must establish a NWIS site file and field folder for each sampling location (section 4.1.1).

[5]The U.S. Geological Survey (USGS) technical and policy memorandums referenced in this manual are available on the Web; see "Selected References and Documents" for numbered memorandum titles, dates, and the Web address.

4.1.1 SITE FILES

Field personnel are responsible for establishing and maintaining electronic and paper site files and ensuring their accuracy and completeness. The information required for establishing electronic records in NWIS and for creating field folders for surface-water sampling sites is summarized below.

4.1.1.A NWIS Files

USGS policy requires specific information on surface-water sampling sites to be stored in the site file in NWIS (Hubbard, 1992; USGS Water Resources Policy Memorandum 92.59). Site files should be established as soon as the sampling site has been selected. The minimum information required for establishing electronic files in NWIS for surface water is listed in table 4-4. Individual studies and USGS Water Science Center offices may have additional data-storage requirements.

- Results of chemical water analyses are stored in the water-quality file (QWDATA) of NWIS (Gellenbeck, 2005).
- The Automatic Data Processing System (ADAPS) contains continuous records of water levels and water quality (Bartholoma, 2003).

Once the site location has been established:

- Check the NWIS site file before each field trip.
- Update the files promptly after the field trip.
- Fill in information that is needed by, or could be useful to, the study in addition to the information shown on table 4-4. For guidance, refer to "Data Elements for Reporting Water Quality Results of: Chemical and Microbiological Analyses" (http://wi.water.usgs.gov/methods/tools/wqde/, accessed July 7, 2006).
- If real-time data are being served on the Web, ensure that current policies and quality-assurance measures are understood and implemented (USGS Water Resources Policy Memorandum No. 99.34, at http://water.usgs.gov/admin/memo/policy/wrdpolicy99.34.html (accessed July 7, 2006).

Before starting field work:
Make sure that the NWIS file has been established.
After field work:
Input updates to NWIS files promptly and have a second or third party check the input.

Table 4-4. Minimum information required for electronic storage of site and surface-water-quality data in the U.S. Geological Survey (USGS) National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Required information for creation of a surface-water site in NWIS[1, 2]		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number	C1	11530500
Station Name	C12	Klamath River near Klamath, Calif.
Latitude	C9	413052
Longitude	C10	1235957
USGS Water Science Center /User State	C6	06 (California)
County	C7	06 (California)
Agency Use	C8	015 (Del Norte)
Station Type	C803	A (Active)
	C802	SW

Required information for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	11530500
Sample Medium	MEDIM	9 (surface water)
Sample Type	STYPE	9 (regular sample)
Hydrologic (“Hydro”) Event	EVENT	9 (routine sample)
Hydrologic (“Hydro”) Condition	HSTAT	9 (stable stage)
Date (year/month/day)	DATES	20070909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields are available in NWIS that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.
[2]Modified from Ground-Water Site Inventory Schedule Form 9-1904-A, Revised June 2004, NWIS 4.4.

4.1.1.B Field Folders

Information that is needed for reference while working at a surface-water site is kept in a field folder. The field folder is taken along on each sampling trip. It includes all the information necessary for efficient field operations; for example, directions to and description of the site, safety precautions relevant to the site, and the specifics for sample collection and processing at the site. General contents of the field folder are listed on the field-folder checklist (fig. 4-2), but the folder should be customized according to study needs.

Field-folder checklist: surface-water quality		
✓	Item	Comments
	Station description: • Location of gaging station (if one is present). • Location of sample-collection sites: high and low streamflows. • Hydrologic and geologic sections. • Name of landowner, tenant, or other responsible party. • Site access instructions (for example, call owner or site operator before arrival at site, obtain key to unlock security gate). • Photographs to document site conditions.	
	Maps to site (State and local)	
	Profiles of cross section of stream channel at sampling location(s). • Stream-bottom geometry. • Physical and chemical measurements.	
	Safety information (NFM 9): • Nearest emergency facilities. • Phone numbers (home) of study chief or supervisor. • Traffic condition and traffic plan showing where to park, placement of flags and cones. • Location of power lines. • Environmental hazards, such as weather and animals.	
	Sampling schedule: • Laboratory analyses to be requested and associated codes. • When to collect samples (high or low flow).	
	Bottle types needed for each analytical schedule.	
	Analytical Services Request form(s) and example of a completed form.	
	Sampling instructions: • Cumulative-discharge curves at about 10-, 50-, and 90-percent duration. • Velocity cross sections at about 10-, 50-, and 90-percent duration. • Equipment to use at various flows. • Flow-duration curve. • Discharge rating curves and (or) tables.	
	Shipping instructions: • Amount of ice to use. • Mailing labels to and from laboratory. • Location of nearest post office or shipping agent.	
	Surface-water field form and an example of completed form.	
	A tabulation sheet for each type of bacteria enumerated at the site (include example with date of sample, streamflow, volumes filtered, dilutions, plate counts).	
	Plots of field-measured data (last 5-10 years of record); if there is a good enough relation to show outliers, include: • Conductivity versus streamflow. • Conductivity versus alkalinity. • Temperature versus time.	
	Statistical summary of historical water data: • Seasonal, maximum-minimum values. • Discharge-related maximum-minimum values.	
	Special equipment needed to address site-specific conditions: • Sampling. • Safety.	

Figure 4-2. Checklist for contents of a field folder for surface-water sampling.

4.1.2 SELECTION OF SURFACE-WATER SAMPLING SITES

The study team is responsible for selecting sampling sites, including the specific point(s) or transect(s) at which samples will be collected. The guiding principle for site selection is that data can be collected that accurately represent the intended conditions (such as time of year and flow rate or stage) of the aqueous system being studied with respect to study objectives. Generic guidelines for selecting flowing-water and still-water sites are described in this section.

- Each body of flowing and still surface water has a unique set of conditions that needs to be identified and considered in the site-selection process.
- Field personnel must be trained in the correct and current water-quality data-collection procedures and must exercise judgment gained from field experience to make site selections.
- Careful and complete documentation of site information and the data collected must be input to electronic and paper files.

In most bodies of flowing or still water, a single sampling site or point is not adequate to describe the physical properties and the distribution and abundance of chemical constituents or biological communities. Location, distribution, and number of sampling sites can affect the quality and applicability of the resulting data.

When selecting surface-water sampling sites:

- Consider the study objectives, types of data and quality of data needed, equipment needs, and sampling methods.
- Obtain all available historical information.
- Consider physical characteristics of the area, such as size and shape, land use, tributary and runoff characteristics, geology, point and nonpoint sources of contamination, hydraulic conditions, climate, water depth, and fluvial-sediment transport characteristics.
- Consider chemical and biological characteristics of the area (aquatic and terrestrial).
- Note the types of equipment that will be needed.

4.1.2.A Flowing-Water Sites

Flowing-water sites can refer to streams (fast or slow, intermittent, ephemeral, or perennial), canals, ditches, and flumes of all sizes and shapes, or to any other surface feature in which water moves unidirectionally. All or parts of reservoirs and estuaries that flow unidirectionally are considered to be flowing water. Determine latitude and longitude from maps or by land-survey techniques. Global-positioning system (GPS) equipment is useful to identify sampling-site location.

Flowing-water sampling sites optimally are located:

- At or near a streamgaging station, to obtain concurrent surface-water discharge data required for computing constituent-transport loads and to determine discharge/constituent-concentration relations. (Measure discharge at time of sampling if a streamgaging station is not at or near the sampling site or if discharge cannot be rated or estimated with sufficient accuracy.)
- In straight reaches having uniform flow, and having a uniform and stable bottom contour, and where constituents are well-mixed along the cross section.
- Far enough above and below confluences of streamflow or point sources of contamination to avoid sampling a cross section where flows are poorly mixed or not unidirectional.
- In reaches upstream from bridges or other structures, to avoid contamination from the structure or from a road surface.
- In unidirectional flow that does not include eddies. (If eddies are present within the channel, sample only the unidirectional flow.)
- At or near a transect in a reach where other data are collected (such as data for suspended sediment, bedload, bottom material, or biological material) and (or) for which historical data are available.
- At a cross section where samples can be collected at any stage throughout the period of study, if possible.

After a tentative selection of a sampling site, develop a preliminary profile of field measurements[6] at various locations along the cross section (section 4.1.3.A). Final site selection is based on a comparison of field measurements with the data requirements of the study.

> **TECHNICAL NOTE:** The preferred sampling method and number of verticals to be sampled within the stream cross section that are needed to obtain a sample that is sufficiently representative depends on stream homogeneity as indicated by the field-measurement profile and stream-discharge or other data, as well as by study objectives. Note that the field-measurement profile is a useful guideline, but might not be representative of chemical homogeneity for the analytes of interest. Also, it might be desirable to move to a sampling site upstream or downstream to adjust for seasonal variation or extreme flow conditions.

The guidelines used for selecting sampling sites on ephemeral and intermittent streams are the same as those for perennial streams. Ephemeral and intermittent stream sites need additional planning and examination to account, for example, for conditions related to rapidly changing stage and discharge that can occur as a result of flash flooding or urban runoff.

CAUTION: Any stream, including an ephemeral or intermittent stream, can rapidly become too deep and swift to wade safely.

[6]The profile of the cross section usually includes field measurements for specific electrical conductance (conductivity), pH, temperature, dissolved oxygen, and turbidity.

Still-Water Sites 4.1.2.B

Still-water sites refer to all sizes and shapes of lakes, reservoirs, ponds, swamps, marshes, riverine backwaters, or any other body of surface water where water generally does not move unidirectionally. All or parts of reservoirs that do not flow unidirectionally could be considered to be still water.

When locating still-water sampling sites:

- Use in situ field measurements to help determine vertical and spatial distribution of sampling locations.
- Avoid areas near structures such as harbors, boat ramps, piers, fuel docks, and moored houseboats (to avoid point sources of contamination), unless these structures are part of the study.
- Select sites with a record of historical data, if possible.

SAMPLING AT FLOWING-WATER AND STILL-WATER SITES 4.1.3

Flowing streamwater is collected using either isokinetic, depth-integrating or nonisokinetic sampling methods. At flowing-water sites, collection of an isokinetic, depth-integrated, discharge-weighted sample is standard procedure; however, site characteristics, sampling-equipment limitations, or study objectives constrain how a sample is to be collected and could necessitate use of other methods. If the QC plan calls for collection of concurrent samples, then the relevant procedures and equipment needs (section 4.3) must be reviewed before field work begins.

- Isokinetic, depth-integrating methods (section 4.1.3.A) are designed to produce a discharge-weighted (velocity-weighted) sample; that is, each unit of stream discharge is equally represented in the sample, either by dividing the stream cross section into intervals of equal width (EWI) or equal discharge (EDI) (USGS Office of Water Quality Technical Memorandum 99.02).
  - The analyte concentrations determined in a discharge-weighted sample are multiplied by the stream discharge to obtain the discharge of the analyte.
  - If used correctly and the sample is collected within the limitations of the sampling device being used, the EWI and EDI methods result in samples that have identical constituent concentrations.
- Nonisokinetic sampling methods (section 4.1.3.B), such as those involving use of an automated point sampler, generally do not result in a discharge-weighted sample unless the stream is completely mixed laterally and vertically. Thus, the analytical results cannot be used to directly compute analyte discharges.

Still-water samples generally also are collected at multiple locations in the water body and at multiple depths (section 4.1.3.C). The probability is small that any body of still water (lake, reservoir, pond, lock, storage pool) is relatively homogeneous with regard to any water-quality characteristic. Therefore, a single sampling point generally is not adequate to describe the physical and chemical properties of the water body, or the distribution and abundance of the inhabiting biological community. The number of sampling locations selected and the depths where samples will be collected depend on study objectives and the physical, chemical, and biological characteristics of the water body (Ward and Harr, 1990).

Document the sampling method used on the appropriate field form for each sample.

On-site preparations

When arriving at the field site, take the appropriate measures to avoid sample contamination, such as fumes from traffic or other sources and proper handling and care of sampling equipment. The selection and care of equipment employed for isokinetic and nonisokinetic surface-water sampling are described in NFM 2, while standard USGS equipment-cleaning procedures are detailed in NFM 3. Selection, maintenance, and proper cleaning of sampling equipment are of paramount importance in preventing sample contamination and these protocols should be carefully reviewed and consistently implemented. Only clean equipment should be transported to the field.

Once field work has begun, and before samples are collected, the sample-wetted portions of most of the collection and processing equipment require a field rinse with native water. Field rinsing helps to condition, or equilibrate, sampling equipment to the sample environment. Rinsing also serves to ensure that all cleaning-solution residues have been removed.

- The Clean Hands team member is responsible for field rinsing the equipment whenever *CH/DH* procedures are used.
- The use and field-rinsing procedures are summarized below for sampling devices and for sample-compositing and sample-splitting equipment. Samples for bacteria analysis are not to be taken from a churn splitter unless it has been sterilized as described in NFM 7.1.1, and has no metal parts in the spigot unit.
  - **Churn splitter:** The 14-L churn can be used to split samples with particle sizes 250 µm and suspended-sediment concentrations 1,000 mg/L; however, splitting accuracy becomes unacceptable for particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. Sample volumes less than 4 L or greater than 13 L cannot be split for whole-water subsamples. Churn lid requires a covered opening. To split a sample into subsamples for nonvolatile organic-compound analyses, use a Teflon-coated churn.
  - **Cone splitter:** Used to process samples with suspended-sediment concentrations from 0 to 10,000 mg/L, and to split samples containing sediment particles ranging in size from very fine clay and silt (1 to 10 µm) to sand-size particles (250 µm). Samples as small as 250 mL can be split into 10 equal subsamples. A Teflon cone splitter can be used to process samples with volume greater than 13 L and samples to be analyzed for inorganic constituents and nonvolatile organic compounds.

To field rinse a bottle sampler or bag sampler:

1. Put on appropriate disposable, powderless gloves (gloves).
2. Partially fill and rinse the sampler with the water to be sampled (rinse water).
   - Avoid getting sand in the rinse water.
   - To avoid suspended sand particles, collect water for rinsing at the edge of the stream in an area of low-flow turbidity.
3. Shake or swirl and then drain the rinse water from the sampler through the nozzle.
4. **For bag samplers** – the bag must be removed from the sampler to properly discard the final rinse water.
   a. Fill the bottom of the bag with approximately 100 to 200 mL of sample.
   b. Gently pull the bag into a tube-like shape and loosely fold over the top opening.
   c. Slosh the sample water back and forth from the bottom to the top of the bag.
   d. Keeping the bag in a tube-like shape, hold it horizontally and rotate it, making sure that the water flows into all of the folds of the Teflon® bag.

To field rinse a churn splitter:

1. Put on gloves.
2. Pour 2 to 4 L of rinse water from the sampler into the churn splitter (churn) through the top funnel.
3. Remove the churn from the churn carrier, leaving the outer plastic bag inside the carrier. Move the churn disk up and down several times to ensure that the inside of the churn is thoroughly wetted, then swirl the rinse water vigorously in the churn.
4. Pierce a hole through the inner plastic bag to expose the churn spigot and drain the rinse water through the spigot. **If sand is present**, swirl water vigorously in the churn, open the plastic bag, and partially lift the churn cover to pour the rinse water out of the top of the churn. (Draining the rinse water through the spigot will not adequately remove sand.)
5. After draining the rinse water from the churn, rotate the churn in the plastic bag so that the spigot is not exposed. Place the inner plastic bag holding the churn into an outer plastic bag and place into the churn carrier.

To field rinse the cone splitter:

1. Put on gloves.
2. Uncover the splitter reservoir and pour or pump 2 to 4 L of rinse water into the cone-splitter reservoir, one liter at a time.
3. Lightly tap the splitter to dislodge adhering water drops. Discard rinse water.
4. Cover the splitter.

Isokinetic, Depth-Integrated Sampling Methods at Flowing-Water Sites 4.1.3.A

Collection of isokinetic, depth-integrated samples involves using either an equal-width-increment (EWI) orequal-discharge-increment (EDI) sampling method. The EWI or EDI methods usually result in a composite sample that represents the discharge-weighted concentrations of the stream cross section being sampled.

The EWI and EDI methods are used to divide a selected cross section of a stream into increments having a specified width. The term vertical refers to that location within the increment at which the sampler is lowered and raised through the water column.

- EWI verticals are located at the midpoint of each width increment.
- EDI verticals are located at the centroid, a point within each increment at which stream discharge is equal on either side of the vertical.

If properly implemented, EDI and EWI methods should yield identical results. The uses and advantages of each method are summarized below and in table 4-5. Isokinetic samplers usually are used to obtain a discharge-weighted sample along the stream cross section. **When using an isokinetic sampler there should be no change in velocity (speed and direction) as the sample enters the intake** (fig. 4-3).

Table 4-5. Uses and advantages of equal-width-increment (EWI) and equal-discharge-increment (EDI) sampling methods

EWI method	Advantages of the EWI method
EWI is used when information required to determine locations of sampling verticals for the EDI method is not available, and (or) the stream cross section has relatively uniform depth and velocity. **Use EWI whenever:** • The location of EDI sampling verticals changes at the same discharge from one sampling time to another. This situation occurs frequently in streams with sand channels.	• EWI method is easily learned and implemented for sampling small streams. • Generally, less time is required onsite if the EWI method can be used and the information required to determine locations of sampling verticals for the EDI method is not available.
EDI method	**Advantages of the EDI method**
EDI is used when information required to determine locations of sampling verticals for the EDI method is available. **Use EDI whenever:** • Small, nonhomogeneous increments need to be sampled separately from the rest of the cross section. The samples from those verticals can be analyzed separately or appropriately composited with the rest of the cross-sectional sample. (Have the sampling scheme approved.) **or** • Flow velocities are less than the isokinetic transit-rate range requirement. A discharge-weighted sample can be obtained, but the sample will not always be isokinetic. **or** • The EWI sampling method cannot be used. For example, isokinetic samples cannot be collected because stream velocities and depths vary so much that the isokinetic requirements of the sampler are not met at several sampling verticals. **or** • Stage is changing rapidly. (EDI requires less sampling time than EWI, provided the locations of the sampling verticals can be determined quickly.)	• Fewer increments are necessary, resulting in a shortened sampling time (provided the locations of sampling verticals can be determined quickly and constituents are adequately mixed in the increment). • Sampling during rapidly changing stages is facilitated by the shorter sampling time. • Subsamples making up a sample set may be analyzed separately or may be proportionally composited with the rest of the cross-sectional sample. • The cross-sectional variation in constituent discharge can be determined if subsample bottles are analyzed individually. • A greater range in velocity and depths can be sampled isokinetically at a cross section. • The total composite volume of the sample is known and can be adjusted before sampling begins.

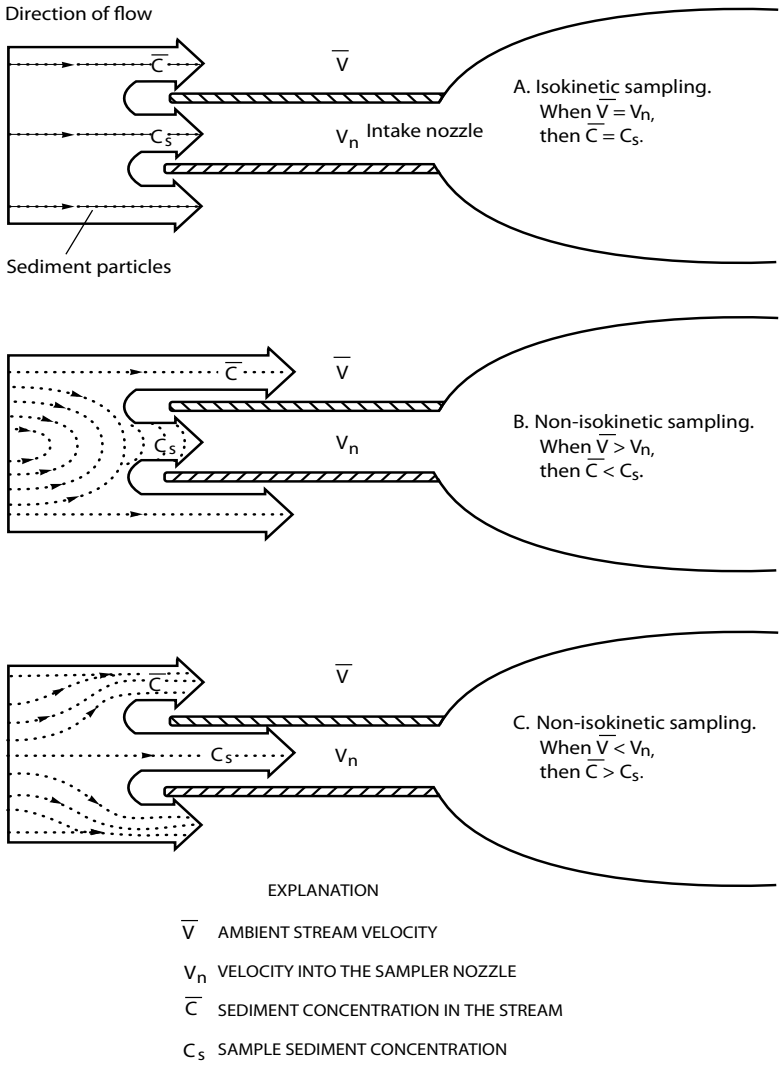


Figure 4-3. Relation between intake velocity and sediment concentration for isokinetic and nonisokinetic collection of water samples that contain particulates greater than 0.062 millimeters (modified from Edwards and Glysson, 1999, p. 14).

- Collect isokinetic, depth-integrated samples by using a standard depth- and width-integrating method if analysis of a representative sample from a cross section of flowing water is required for discharge computations. Appendix A4-A and Edwards and Glysson (1999, figures 39-43), provide detailed information about isokinetic, depth-integrating transit rates for collecting samples.
- For isokinetic sampling, the mean velocity of the vertical that is sampled must exceed the minimum-velocity requirement of an isokinetic sampler—the minimum velocity requirements are 1.5 ft/s for a bottle sampler, 2 ft/s for a 1- or 3-liter bag sampler, or 3 ft/s for a 6-liter bag sampler (Appendix A4-A).
  - The transit rate (the rate at which the sampler is lowered or raised) used to collect an isokinetic, depth-integrated sample is mainly a function of the nozzle diameter of the sampler, volume of the sampler container, stream velocity, and sampling depth (Appendix A4-A). The maximum allowable transit rate for a bag sampler is 0.4 multipied by the mean stream velocity.
  - An error in concentrations of suspended particulates coarser than 62 mm can be important when the velocity of the sample entering the nozzle and the stream velocity differ significantly. Too fast a transit rate will cause a sampler to undersample sand-sized particulates (Edwards and Glysson, 1999).
  - The transit rate must be kept constant during sampler descent through a vertical and also during sampler ascent through a vertical.

The number of increments needed in order to get a discharge-weighted sample at a site is related primarily to data objectives (for example, the accuracy needed) and how well-mixed or heterogeneous the stream is with respect to the physical, chemical, and biological characteristics of the cross section. The recommended number of increments for EWI and EDI methods are discussed in the sections to follow. Edwards and Glysson (1999) describe a statistical approach for selecting the number of increments to be used, based on sampling error and suspended-sediment characteristics.

Selecting the number of increments

- Examine the variation in field-measurement values (such as specific electrical conductance, pH, temperature, and dissolved oxygen) along the cross section (NFM 6).
- Consider the distribution of streamflow (discharge), suspended-materials concentration and particle-size distribution, and concentrations of other targeted analytes along the cross section. Consider whether the streamflow distribution or analyte concentrations will change during sample collection.
- Consider the type of sampler that will be used and the volume of sample that will have to be collected for the analysis of the target analytes.
- Avoid side-channel eddies. EDI and EWI methods cannot be used at locations with upstream eddy flow.

RULE OF THUMB: For isokinetic, depth-integrating sampling, do not exceed the designated maximum transit rate.

Equal-width-increment (EWI) method

For the EWI sampling method, the stream cross section is divided into a number of equal-width increments (fig. 4-4). Samples are collected by lowering and raising a sampler through the water column at the center of each increment. (This sampling location is referred to as the vertical.) The combination of the same constant transit rate used to sample at each vertical and the isokinetic property of the sampler results in a discharge-weighted sample that is proportional to total streamflow.

- **Isokinetic sampling is required for the EWI method.** Use isokinetic, depth-integrating sampling equipment (NFM 2.1.1.A).
  - **Use the same size sampler container (bottle or bag) and nozzle** at each of the sampling verticals (fig. 4-4).
  - **Collect samples using the same transit rate** at each vertical during descent and ascent of the sampler. The transit rate must be constant and within the operational range of the sampler (Appendix A4-A).
- Composite the subsamples from all verticals in a churn splitter or process subsamples through the cone splitter (NFM 2.2.1 and NFM 5.1.1).

Do not use EWI when stream velocities are less than the minimum velocity required for the isokinetic sampler selected:

1.5 ft/s for the bottle sampler.

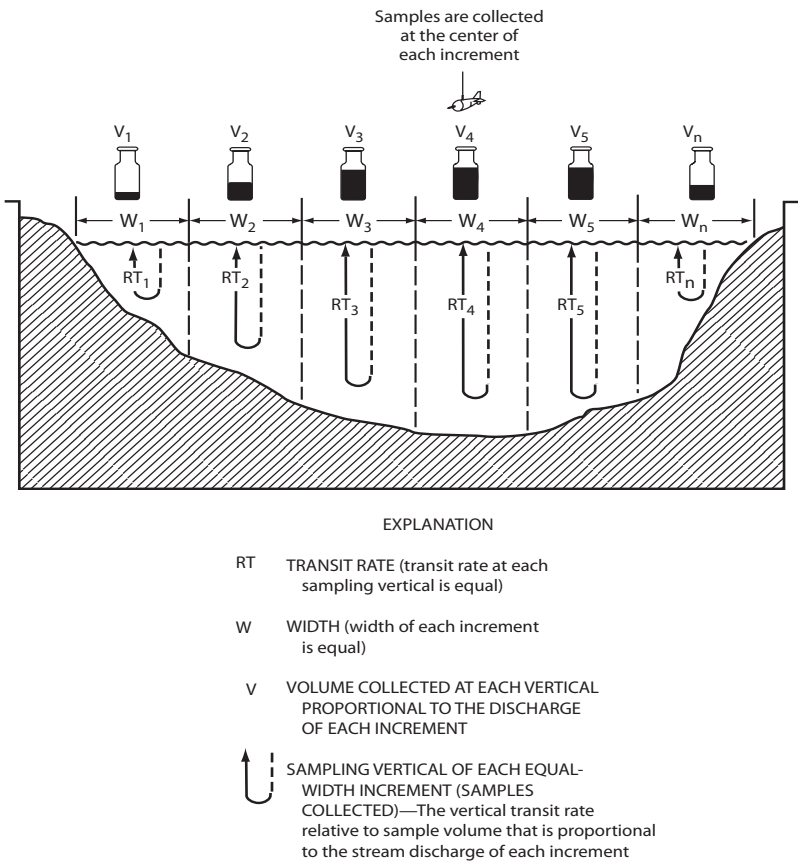
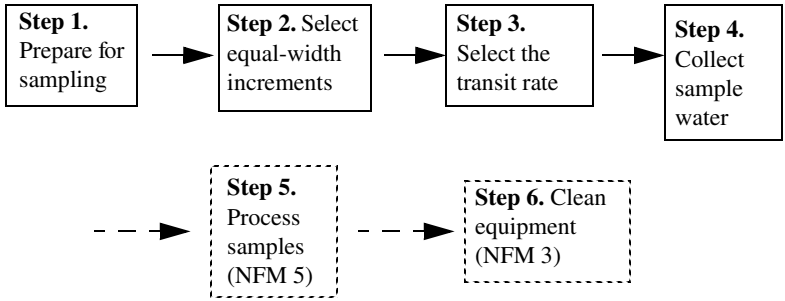


Figure 4-4. Equal-width-increment method for collection of water samples (modified from Edwards and Glysson, 1999).

Steps for the EWI sampling method



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Step 1. Prepare for sampling[7]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle in a location and direction so as to prevent sample contamination from vehicle emissions.

b. Assemble sampling equipment and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics other than fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- **Microbiological analyses**. Collect samples for microbiological analyses using equipment and techniques described in NFM 7.

[7]Preparations for water sampling are described in NFM 2 and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

Step 2. Select the number and width of equal-width increments.

a. Visually inspect the stream from bank to bank and longitudinally, observing velocity, width, and depth distribution, and apparent distribution of sediment and aquatic biota along the cross section. Note and document the location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other features along the cross section.

b. Determine stream width from a tagline or from distance markings on a bridge railing or cableway.

c. At sites with little sampling history, measure and record the cross-sectional variation of field measurements (such as specific electrical conductance, pH, temperature, and dissolved oxygen). Review the magnitude of the variations along the cross section.

d. Determine the width of the increment. To obtain the number of increments, divide the stream width by the increment width. **The number of increments must be a whole number**. Increment width is based on study objectives, variation in field measurements and flow, and stream-channel characteristics along the cross section.

   - Collect the subsample at the center of each equal-width increment (the vertical).
   - If the subsample does not represent the mean value for that increment, decrease the increment width until the mean value for the increment is represented. This will increase the number of increments sampled.

e. Locate the first sampling vertical at a distance of one-half of the selected increment width from the edge of the water. Locate all the other verticals at the center of each remaining equal-width increment along the cross section.

   Example:

   - If a stream 56 ft wide has been divided into 14 increments of 4 ft each, the first sampling vertical would be 2 ft from the water's edge and subsequent verticals would be at 6, 10, 14 ft from the water's edge, and so forth.
   - Even if streamflow is divided, as in a braided channel, equal-width increments must be identical from channel to channel, and the same constant transit rate must be used at each vertical.

f. Make slight adjustments to sampling locations, if necessary, to avoid sampling where the flow is affected by a pier or other obstruction.

TECHNICAL NOTE: Sampling near or downstream from large in-stream obstructions such as bridges and piers could result in artificially elevated concentrations of suspended sediments if the sampler is immersed in an eddy that is caused by the obstruction. If it is necessary to include an eddy in the cross section to be sampled, consider treating the eddy as a solid obstruction: subtract the eddy width from that of the total cross section, and determine the width of the increments based on the remaining stream width.

RULE OF THUMB

When selecting the number of equal-width increments:

- Cross-sectional width ≥ 5 ft—use a minimum of 10 equal-width increments
- Cross-sectional width <5 ft—use as many increments as practical, but equally spaced at a minimum of 3 inches apart.

Equipment limitations also constrain the number of increments selected; for example:

- When using a 1-L bottle sampler at maximum depth with a 14-L churn splitter, EWI samples can be collected at no more than 14 to 17 verticals.
- If an 8-L churn splitter is used, samples can be collected at no more than 10 verticals.
- A cone splitter must be used if the total volume collected will exceed the recommended volume for the churn splitter.

Step 3. Select the transit rate.

a. Refer to Appendix A4-A for guidelines for determining the transit rates for collecting isokinetic, depth-integrated samples. Unless the mean velocity is actually determined, use the trial-and-error method to determine the minimum transit rate.

b. Locate the equal-width increment containing the largest discharge (largest product of depth times velocity) by sounding for depth and either measuring or estimating velocity. At the vertical for this increment, use of the minimum transit rate results in the maximum allowable filling of the sampler bottle or bag during one vertical traverse.

c. Determine the minimum transit rateat this vertical for the type of sampler (bottle or bag), size of sampler nozzle, and the desired sample volume.

- Approximate the mean velocity of the vertical in feet per second by timing a floating marker (such as a peanut) as it travels a known distance. (A known length of flagging tape tied to the cable where the sampler is attached often is used to measure the distance.) Divide the distance (in feet) by the time (in seconds) and multiply by 0.86.
- Make sure that the transit rate does not exceed the maximum allowable transit rate to be used at any of the remaining verticals along the cross section. This can be determined by sampling the slowest increment. **If the minimum volume of sample (relative to depth of the vertical) is not collected at this vertical, then the EWI method cannot be used at this cross section to collect a discharge-weighted sample (Appendix A4-A).**
- Remember that you must keep the transit rate unidirectional, constant, and within the isokinetic transit range of the sampler when collecting isokinetic samples at each centroid.

Guidelines for selecting the transit rate for EWI sampling

- The descending and ascending transit rate must be constant in each direction and must be the same for each vertical along the cross section.
- **Do not exceed the maximum allowable transit rate if using EWI.** If the transit rate must exceed the maximum allowable rate, use EDI instead of EWI.
- The transit rate selected must be sufficiently rapid to keep from overfilling the sampler. The sampler is overfilled when the water surface in the sampler container is above the bottom edge of the nozzle when the sampler is held in the sampling position.
- The same size sampler nozzle and container must be used at all verticals along the cross section.
- If the total volume collected will exceed the recommended volume for the churn splitter, then a cone splitter must be used.

Step 4. Collect sample water.

The sample-collection procedure is the same whether you are wading or using the reel-and-cable suspension method. When sampling from a bridge, deploy the sampler from the upstream of the bridge, if possible, to avoid bridge-related contamination of the sample. **Use *CH/DH* techniques, as required (section 4.0.2). Always follow safety procedures (NFM 9)**.

a. Move to the first vertical (midpoint of first EWI near edge of water) and field rinse equipment (section 4.1.3). Collect the rinse water at the edge of the stream in a section of low stream velocity to minimize including suspended sediment.

b. Record start time and gage height.

c. Lower field-rinsed sampler at the predetermined constant transit rate until slight contact is made with the streambed. **Do not pause** upon contacting the streambed. Raise the sampler immediately at the same constant transit rate until sampler completes the vertical traverse.

   - Take care not to disturb the streambed by bumping the sampler on it; bed material may enter the nozzle, resulting in erroneous data.
   - Do not overfill the sampler container. Overfilling results in a sample that is not isokinetic and that could be enriched with heavy particulates because of secondary circulation of water through the sampler (from nozzle through air exhaust). This enrichment will result in an artificially increased sediment concentration and will bias particle-size distribution toward heavier and larger particulates.
   - Do not underfill the sampler container (Appendix A4-A). Underfilling will result in a sample that is not isokinetically collected because the maximum transit rate has been exceeded.
   - If the required volume cannot be collected, use the EDI method to obtain discharge-weighted samples.

d. Inspect each subsample as it is collected, looking for overfilling or underfilling of the sampler container and (or) the presence of anomalously large amounts of particulates that might have been captured because of excessive streambed disturbance during sample collection. **If you note any of these conditions, discard the sample, making sure there are no residual particulates left in the container, and resample.**

e. Move sampling equipment to the next vertical. Maintain the selected transit rate. The volume of the subsample can vary considerably among verticals. Subsamples can be collected at several verticals before emptying the sampler container, as long as the maximum volume of sample in a bottle or bag sampler has not been exceeded. If the container is overfilled, it is necessary to resample.

> **TECHNICAL NOTE:** The tables in Appendix A4-A apply to the first complete round-trip transit, starting with an empty sampler container. These tables cannot be used if the sampler is not emptied between verticals.

f. Continue to the next vertical until no more samples can be collected without overfilling the sampler container. Empty the subsample into a field-rinsed churn or cone splitter and repeat sample collection in the same manner until subsamples have been collected at all the verticals.

- If the total volume of the subsamples to be collected will exceed the operational capacity of the churn, select from the following options: use a smaller nozzle; or, use a cone splitter; or, use the EDI method, if appropriate.
- To ensure that all particulates are transferred with the sample, swirl the subsample gently to keep particulates suspended and pour the subsample quickly into the churn or cone splitter.
- Sample EWI verticals as many times as necessary to ensure that an adequate sample volume is collected as required for analysis, **but sample at each vertical an equal number of times.** (The composite cross-sectional sample will remain proportional to flow at the time of sampling.)
- If flow is stable during sampling, then multiple samples can be collected at each vertical during a single traverse along the cross section. If flow is changing, however, study objectives should determine whether to collect multiple samples at each vertical during a single traverse or to collect one sample at each vertical during multiple traverses along the cross section. Document on field forms the method used.

g. Record the following information after all samples have been collected:

- Sampling end time.
- Ending gage height.
- All field observations and any deviations from standard sampling procedures.

Step 5. Process Samples → Refer to NFM 5.

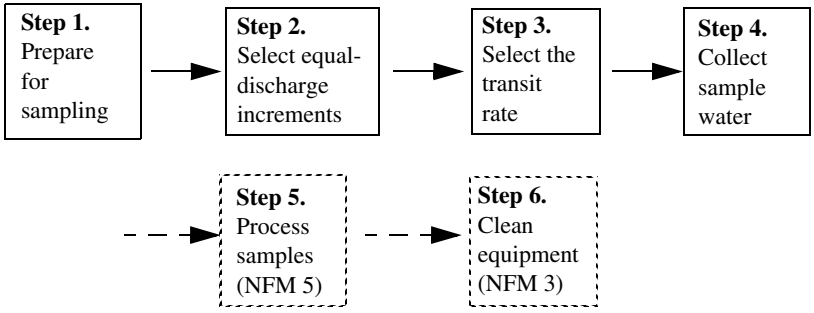
Step 6. Clean Equipment → Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse sampler components with deionized water before they dry and place them into a plastic bag for transporting to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling and then field-clean while at the sampling site using the prescribed procedures (NFM 3). Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place the cleaned sampler into a plastic bag and seal for transport to the next site.

Equal-discharge-increment (EDI) method

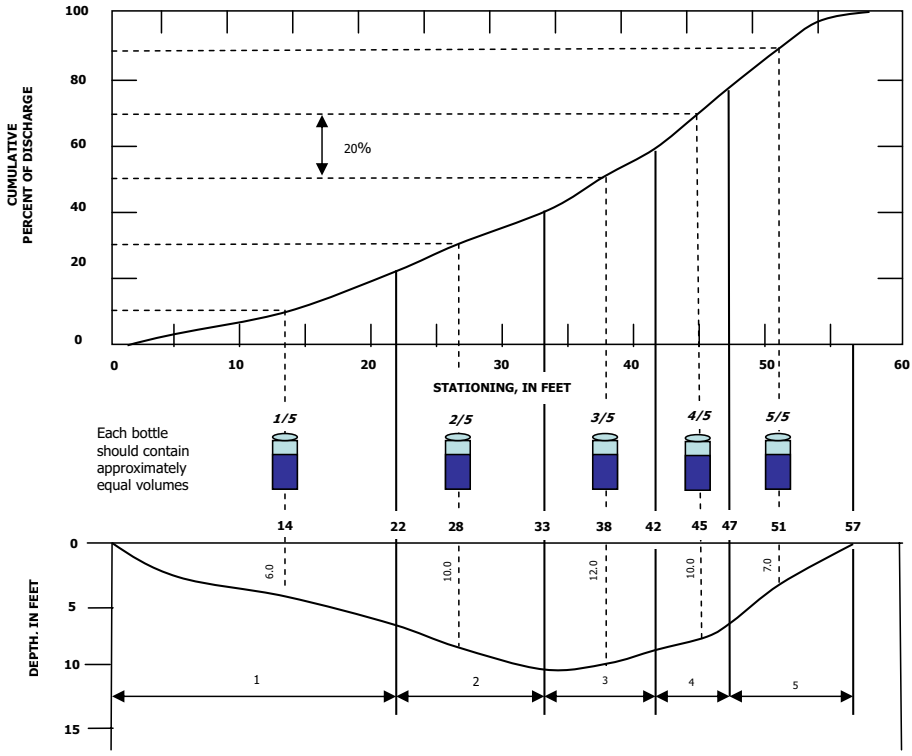
The objective of the EDI method is to collect a discharge-weighted sample that represents the entire flow passing through the cross section by obtaining a series of samples, each representing equal volumes of stream discharge. The EDI method requires that flow in the cross section be divided into increments of equal discharge. Equal-volume, depth-integrated samples are collected at the centroid of each of the equal-discharge increments along the cross section (fig. 4-5). Centroid is defined as that point in the increment at which discharge is equal on both sides of the point.

Steps for the EDI sampling method



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Example: Sampler D95; nozzle size 3/16 inches ID (inside diameter); 1-liter sampler bottle; width, 57 feet; maximum depth, 12 feet; maximum velocity, 6.1 feet per second (ft/s); width of section containing 20 percent of flow is variable, 5 to 22 feet; 20 percent of flow per section will give 5 sampling verticals; transit rate variable, 0.2 to 0.8 ft/s.



Sampling vertical/ bottle number	Percent discharge	Increment centroid from left edge of water, in feet	Increment depth, in feet	Mean velocity, in feet per second	Transit rate to give 800 milliliters, in feet per second
1/5	20	14	6	2.5	0.2
2/5	20	28	10	3.0	0.4
3/5	20	38	12	3.1	0.5
4/5	20	45	10	6.1	0.8
5/5	20	51	7	4.8	0.5

Figure 4-5. Equal-discharge-increment method for collection of water samples (modified from Bruce Ringen, U.S. Geological Survey, written commun., 1978).

Step 1. Prepare for sampling for inorganic and organic analytes.[8]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle in a location and direction so as to prevent sample contamination from vehicle emissions.

b. Assemble equipment needed and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics other than fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- **Microbiological analyses**. Collect samples for microbiological analyses using equipment and techniques described in NFM 7.

Step 2. Select the number and location of equal-discharge increments.

The number and location of equal-discharge increments should not be determined arbitrarily. Selection of increments for a sampling site is governed by factors described in a, d, and e below.

a. Visually inspect the stream from bank to bank, observing velocity, width, and depth distribution, as well as apparent distribution of sediment and aquatic biota along the cross section. Document location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other obstructions along the cross section.

b. Determine stream width from a tagline or from distance markings on bridge railings or on a cableway.

[8]Preparations for water sampling are described in NFM 2 and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

c. At sites with little sampling history—measure, record, and review the cross-sectional variation of field measurements (for example, specific electrical conductance, pH, temperature, and dissolved oxygen).

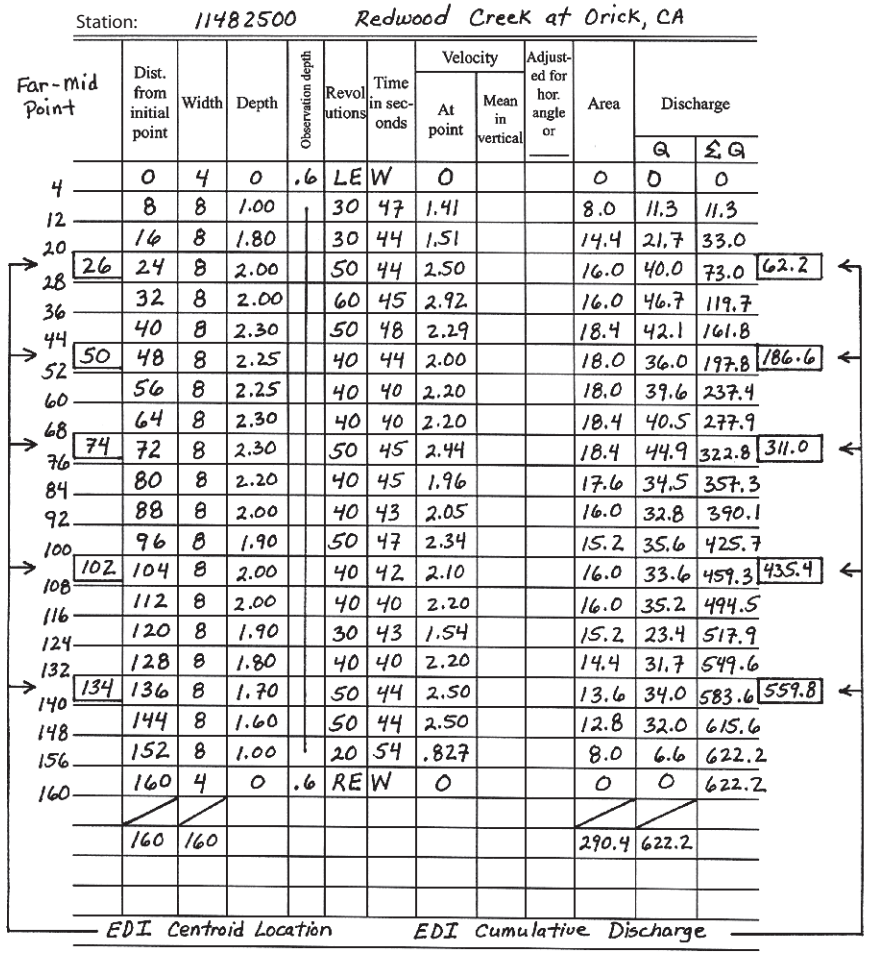
d. Measure discharge at the cross section to be sampled or use an existing EDI graph prepared from current or historical discharge measurements (fig. 4-5) (Edwards and Glysson, 1999). An existing EDI graph can be one prepared for the site that shows, for example, cumulative discharge or cumulative percent of discharge versus stationing.

e. Determine volume of discharge that will be represented in each EDI, based on data objectives for the study, variation in field measurements, flow and stream-channel characteristics along the cross section, and volume of sample required for analyses of target analytes.

f. Divide the cross section into equal-discharge increments.

- When determining the number of increments to be sampled, keep in mind that the subsample collected at the centroid of each EDI must represent the mean streamflow measured for that increment. If mean streamflow for the increment is not represented, increase the number of increments by decreasing the volume represented by each discharge increment until the mean streamflow value for the increment is represented.
- As a guide, a minimum of 4 sampling increments is recommended; the number of increments is usually less than 10.

g. Determine the location of the centroid of flow within each increment from the discharge measurement by (1) constructing a curve using cumulative discharge or cumulative percentage of discharge (fig. 4-5) plotted against cross-section stationing, or (2) determining EDI locations directly from the discharge measurement sheet (fig. 4-6; an explanation of this method and definition of midpoint are described in Edwards and Glysson, 1999). Centroid-of-flow locations also can be determined from an EDI graph, as described below and in the TECHNICAL NOTE that follows the example below.



Station: 11482500 Redwood Creek at Orick, CA

Far-Mid Point	Dist. from initial point	Width	Depth	Observation depth	Revolutions	Time in seconds	Velocity: At point	Velocity: Mean in vertical	Adjusted for hor. angle or	Area	Discharge: Q	Discharge: ΣQ	
4	0	4	0	.6	LEW		0			0	0	0	
12	8	8	1.00		30	47	1.41			8.0	11.3	11.3	
20	16	8	1.80		30	44	1.51			14.4	21.7	33.0	
28	26 24	8	2.00		50	44	2.50			16.0	40.0	73.0	62.2
36	32	8	2.00		60	45	2.92			16.0	46.7	119.7	
44	40	8	2.30		50	48	2.29			18.4	42.1	161.8	
52	50 48	8	2.25		40	44	2.00			18.0	36.0	197.8	186.6
60	56	8	2.25		40	40	2.20			18.0	39.6	237.4	
68	64	8	2.30		40	40	2.20			18.4	40.5	277.9	
76	74 72	8	2.30		50	45	2.44			18.4	44.9	322.8	311.0
84	80	8	2.20		40	45	1.96			17.6	34.5	357.3	
92	88	8	2.00		40	43	2.05			16.0	32.8	390.1	
100	96	8	1.90		50	47	2.34			15.2	35.6	425.7	
108	102 104	8	2.00		40	42	2.10			16.0	33.6	459.3	435.4
116	112	8	2.00		40	40	2.20			16.0	35.2	494.5	
124	120	8	1.90		30	43	1.54			15.2	23.4	517.9	
132	128	8	1.80		40	40	2.20			14.4	31.7	549.6	
140	134 136	8	1.70		50	44	2.50			13.6	34.0	583.6	559.8
148	144	8	1.60		50	44	2.50			12.8	32.0	615.6	
156	152	8	1.00		20	54	.827			8.0	6.6	622.2	
160	160	4	0	.6	REW		0			0	0	622.2	
	160	160								290.4	622.2		

EDI Centroid Location — EDI Cumulative Discharge

Figure 4-6. Example of discharge-measurement field notes used to determine the equal-discharge-increment centroid locations based on cumulative discharge and far-midpoint stationing (from Edwards and Glysson, 1999, p. 45).

Example:

In this example, each EDI equals 20 percent of discharge.

i. If the stream cross section will be divided into five equal-discharge increments, divide stream discharge by five to determine the discharge increment.

ii. Locate the centroid of the initial EDI where cumulative discharge equals half the discharge increment (10 percent). This is the location of the vertical from which the first subsample is collected.

iii. Locate each of the remaining centroids (four in this example) by adding the discharge increment (20 percent) to the previous centroid discharge (20 + 10 = 30) and determining where that cumulative discharge occurs along the cross section.

iv. The EDI centroids will correspond to locations of 10, 30, 50, 70, and 90 percent of the cumulative discharge along the cross section. In figure 4-5, these percentages of cumulative discharges correspond to locations at 14, 28, 38, 45, and 51 ft from the left edge of the water, whereas in figure 4-6, the centroid locations of the equal-discharge increments are at 26, 50, 74, 102, and 134 ft.

TECHNICAL NOTE: If the stream channel is stable at the cross section to be sampled, graphs of cumulative discharge or percentage cumulative discharge at various stages can be based on historical discharge measurements. Location of EDI centroids can be determined from these EDI graphs so that discharge measurements do not have to be made before each sampling. Linear interpolation based on discharge can be made between curves for different discharges on the EDI graphs. **EDI graphs require periodic verification by being compared to recent discharge measurements.**

Step 3. Select the transit rate.

a. Determine the sampling depth and the mean stream velocity at the centroid of each equal-discharge increment.

b. Determine the transit rate for each centroid that will yield subsamples with approximately the same volume (within 10 percent) using sampling depth, mean stream velocity, and information in Appendix A4-A. When compositing subsamples, the minimum volume for every equal-discharge increment is the minimum volume for the deepest vertical.

Guidelines for selecting the transit rate for EDI sampling

- Collect samples of equal volumes at each centroid. This is required for EDI if the sample will be composited (fig. 4-5). Generally, transit rates vary from centroid to centroid in order to collect equal volumes.
- Keep the transit rate unidirectional, constant, and within the isokinetic transit range of the sampler when collecting isokinetic samples at each centroid.
- **Do not exceed the maximum transit rate** (Appendix A4-A). The maximum transit rate will be exceeded if the minimum sample volume associated with stream velocity and the selected nozzle and bottle size is not collected. Exceeding the maximum transit rate will affect the concentration of particulates ≥ 0.062 millimeters.

Step 4. Collect sample water.

The procedures are the same whether you are wading or using a reel-and-cable suspension method. **Use *CH/DH* techniques, as required (section 4.0.2), and implement safety procedures (NFM 9).**

- Collect microbiological samples using equipment and techniques as described in NFM 7.
- Collect subsamples at EDI centroids as many times as necessary to ensure collection of sufficient sample volume for analysis. If the sample is to be composited, care must be taken to obtain approximately the same total volume (± 10 percent) from each EDI centroid so that the composited cross-sectional sample will be proportional to flow at the time of sampling.
- Stay within the isokinetic transit-rate range of the sampler at each centroid. If flow velocity is less than the isokinetic transit-rate range of the sampler, a discharge-weighted sample still can be obtained by collecting equal volumes at each centroid; however, this sample will not be isokinetic.

  a. Move sampling and support equipment to the centroid of the first increment to be sampled. Field rinse the sampling equipment (section 4.1.3). Collect the rinse water at the edge of the stream in a section of low stream volocity, to minimize including suspended sediment.

  b. Read and record the starting gage height. Record sampling start time.

c. Lower the sampler at the predetermined transit rate until slight contact is made with the streambed.

   - **Do not pause upon contacting the streambed.** Raise the sampler immediately at a constant transit rate to complete the vertical traverse. The descending transit rate does not have to equal the ascending transit rate, but each rate must be unidirectional, constant, and within the isokinetic transit range of the sampler.
   - Take care not to disturb the streambed with the sampler. Disturbing the streambed could cause bed material to enter the nozzle, resulting in erroneous data.
   - Ensure that the sampler container has not overfilled. Overfilling will result in enrichment of the sample with heavy particulates due to secondary circulation of water through the sampler (from nozzle through air exhaust). This enrichment will result in an artificially increased sediment concentration and will bias particle-size distribution towards heavier and larger particulates.

d. Inspect each subsample, looking for overfilling and (or) the presence of anomalously large amounts of particulates that might have been captured because of excessive streambed disturbance during sample collection. If you note either or both of these conditions, discard the sample, making sure there are no residual particulates left in the container, and resample.

e. Ensure that the sampler container is not underfilled (that the minimum volume indicated in Appendix A4-A has been collected). Underfilling will result in a subsample that is not isokinetically collected—usually because the maximum transit rate has been exceeded.

f. Depending on study objectives, either process and (or) analyze the subsample collected at the initial centroid as a separate sample, composite this subsample with other subsamples collected along the cross section, or split the subsample for further processing.

   - If the total volume of the subsamples that will be collected will exceed the operational capacity of the churn or cone splitter, decrease the number of increments or use a smaller nozzle.
   - Ensure that all particulates in the sampler bottle or bag are transferred with the sample by swirling the sample gently to keep particulates suspended, and quickly pouring the sample into the churn or cone splitter.

g. Move equipment to the next vertical.

- Determine the transit rate for this vertical. If the subsamples are composited, the total volume collected at each centroid must be equal.
- Repeat procedures, steps 4 c-f.
- Repeat this process at the remaining verticals along the cross section.

h. Record the following information after all samples have been collected:

- Sampling end time.
- Ending gage height.
- All field observations and any deviations from standard sampling procedures.

Step 5. Process samples → Refer to NFM 5.

Step 6. Clean equipment → Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse the components with deionized water before they dry and place them into a plastic bag for transport to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with deionized water while still wet from sampling, and then follow the prescribed cleaning procedures while at the sampling site (NFM 3). Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place cleaned sampler into a plastic bag and seal for transport to the next site.

Single vertical at centroid-of-flow (VCF) method

Samples may be collected at a single vertical at the centroid of streamflow if the section is known to be well mixed laterally and vertically with respect to concentrations of target analytes.

The VCF method for collecting water samples is identical to the EDI method except that there is one centroid of flow for the stream cross section and therefore only one vertical is sampled.

EDI and EWI methods are preferred for most USGS field applications. Do not use VCF unless you know your stream section to be well mixed with respect to your target analytes.

Guidelines for using the VCF method:

1. Measure discharge along the cross section where sampling is to be done. (This is not necessary if the section is stable and accurate historical discharge measurements are available.)
2. Locate the centroid of flow from the discharge measurement.
   - Either (a) construct an EDI graph using cumulative discharge or cumulative percentage of discharge plotted against cross-section stationing (for example, in fig. 4-5, the centroid location is station 38, which corresponds to 50 percent of cumulative flow), or (b) determine centroid location directly from the discharge measurement sheet (for example, in fig. 4-6, the centroid location is station 74).
   - EDI graphs of cumulative discharge at various stages can be based on historical discharge measurements if the stream channel is stable at the cross section to be sampled. The location of centroids can be determined from these EDI graphs so that discharge measurements do not have to be made before each sampling. **EDI graphs require periodic verification.**
3. Examine the cross section for uniformity of appearance.
4. Measure the cross-sectional variation of field measurements (such as specific electrical conductance, pH, temperature, and dissolved oxygen) at sites with little sampling history. Record and review variations along the cross section.
5. Evaluate data from steps 1–4 to decide if the VCF method is appropriate. Use either the EDI or the EWI sampling method if streamflow, field-measurement, or chemical-analysis data do not confirm that the stream section is well mixed vertically and laterally.
6. If the VCF method is used, follow steps 3 and 4 of the instructions for the EDI method for selecting transit rate and collecting samples.
7. **Process samples** → Refer to NFM 5.
8. **Clean equipment** → Refer to NFM 3, and to the information under Step 6 in either the preceding EDI or EWI methods.

4.1.3.B Nonisokinetic (Dip, Discrete, and Pump) Sampling Methods at Flowing-Water Sites

Most nonisokinetic samplers cannot be used to collect representative discharge-weighted samples from streams transporting sand-size or larger particulates. These samplershave important uses for unattended stream sampling and for sampling to determine constituent occurrence and distribution, but they have limited value for collecting samples used to calculate constituent discharge.

Guidelines for nonisokinetic sampling methods

Use nonisokinetic sampling methods when:

- Velocity of flow is so high that an isokinetic sampler cannot be lowered through the vertical properly and safely.
- Extreme low-flow conditions render use of an isokinetic sampler impractical. For example, when water depth is equal to or less than that of the unsampled zone or when stream velocity is less than the minimum velocity requirement for an isokinetic sampler (1.5 ft/s for bottle samplers, 2 ft/s for bag samplers).
- Automatic pumping samplers are needed for specific situations; for example, time-dependent regulatory monitoring, sampling at remote sites, or sampling of floods or urban runoff when discharge is rapidly changing and a large number of samples are needed from several locations within a relatively short time.
- Periods of extreme cold cause the nozzle or air-exhaust vent to freeze, rendering isokinetic, depth-integrating samplers inoperable.
- Study objectives dictate use of nonisokinetic sampling methods.

Three nonisokinetic sampling methods most commonly used are the dip (weighted-bottle), discrete, and pump methods. Ward and Harr (1990) and Edwards and Glysson (1999) provide detailed information on these sampling methods. General instructions are provided below.

- **Dip sampling method**. Dip sampling involves either (1) dipping a narrow-mouthed bottle into a water body, or (2) using either the DH-81 or D-95 sampler as described below. To use a DH-81 or D-95 sampler in a stream with velocity less than 1.5 ft/s, remove the nozzle from the sampler and proceed to sample the entire vertical. This is especially useful at a deep-water site. When sampling with a hand-held bottle, stand downstream of the bottle while it is being filled. Dip sampling is not recommended for discharge-weighted sampling when it is possible to obtain a depth-integrated, isokinetic sample. **The error introduced by dip sampling can be substantial if the target analytes are sorbed onto suspended materials that are not uniformly distributed along the cross section.** Care must be taken to avoid collecting particulates that are resuspended as the result of wading or bumping the sampler on the streambed.

  — To collect a dip sample in water that is too shallow to submerge an isokinetic, depth-integrating sampler, wade to where the sample(s) will be collected and immerse a hand-held, narrow-mouth bottle at the centroid of flow or at multiple locations along a cross section.

  — To collect a dip sample where water is too deep to wade and volocity is too great for use of an isokinetic sampler: lower a weighted-bottle sampler at the centroid of flow or at multiple locations along a cross section.

  — Collecting samples for biochemical oxygen demand (BOD) and volatile organic compounds (VOCs) are special cases of dip sampling that require special equipment. Instructions for BOD sampling can be found in NFM 7.0. **Instructions for VOC sampling are described at the end of this section 4.1.3.B under "Instructions for collecting VOC samples at flowing-water sites."**

- **Discrete sampling method**. Discrete (point) sampling involves either (1) lowering a sampler to a specified depth and collecting a sample by first opening, then closing the sampler, or (2) using a single-stage sampler, which fills when stream stage rises to a predetermined height.

  — Thief-type samplers are the most common point samplers used for collecting water-quality samples (NFM 2.1.1.B). Although these samplers are designed primarily to sample still waters, they can be adapted for slow-flowing water by attaching them to a weighted line. Samples can be collected at the centroid of flow or at multiple verticals and at selected depths along the cross section.

— Isokinetic point samplers (for example, the P-61 and P-63 described in Edwards and Glysson, 1999) are available for collecting samples for suspended-sediment concentration and particle-size determination, and for selected chemical constituents. **The P-61 and P-63 samplers are not suitable for collecting samples for organic-compound or trace inorganic-constituent analyses.**

— Single-stage samplers, such as the U-59 (NFM 2.1.1.B) and U-73 are useful for collecting samples for analysis of sediment and selected chemical constituents at stations located on streams or other locations susceptible to flash floods or where it is otherwise difficult to reach a station to manually collect samples (Edwards and Glysson, 1999). Before single-stage samplers can be installed, some knowledge of the seasonal stage characteristics of the stream is needed so that an appropriate sequence of samples can be obtained for a given storm season. The stream-stage and flow-velocity characteristics not only affect the design with respect to the vertical spacing of the samplers but also the support necessary for the samplers (Inter-Agency Committee on Water Resources, Subcommittee on Sedimentation, 1961, "The Single Stage Sampler for Suspended Sediment," St. Anthony Falls Hydraulic Laboratory Report 13). These samplers have not been certified as appropriate for collection of uncontaminated trace-element or trace-organic samples.

▶ **Pump-sampling method**. Pump sampling involves either suction-lift or submersible pump systems designed to collect water-quality samples (NFM 2.1.1.B). Pump systems can be portable or can be permanently installed and automated for sampling (see TECHNICAL NOTE below).

— Pump samplers generally are not used to collect isokinetic samples because of the difficulty in controlling the sample velocity through the sampler intake relative to the flow rate and direction of suspended particulates in the stream.

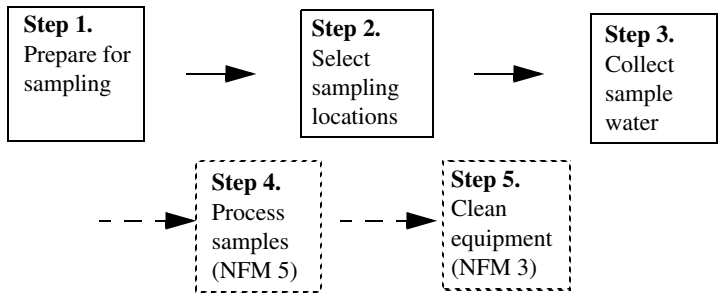
— Portable-pump samplers generally are used to collect a point sample by lowering the pump to a selected depth. A suction pump, such as a peristaltic pump, has a maximum lift of 30 ft or less. Refer to the manufacturer's instructions for the lift capacities of other types of pump samplers.

— A portable pump also can be used to collect a nonisokinetic, depth-integrated sample by continuous pumping at a constant rate as the intake is being lowered through the vertical.

Collection of useful data, especially with the use of automated pumping samplers, requires intensive planning and quality assurance, including careful site selection, selection of the type and construction material of the sampler, a review of historical hydrologic information, and collection of an adequate number and types of quality-control samples. The physical, chemical, and biological characteristics of the cross section, study objectives, and pump limitations must be considered when determining how and where to collect samples.

> **TECHNICAL NOTE:** The selection, deployment, use, and maintenance of automated samplers (auto samplers), such as those manufactured by ISCO, require training and detailed instructions that have not been incorporated into this manual; follow the manufacturer's instructions. Some tips for collecting autosampler samples appear in the steps below.

Steps for nonisokinetic sampling methods



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Step 1. Prepare for sampling for inorganic and organic analytes.[9]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle in a location and direction so as to prevent sample contamination from vehicle emissions.

[9]Preparations for water sampling are described in NFM 2 and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

b. Assemble equipment and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics unless they are fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- Collect samples to be analyzed for sediment concentration and (or) particle-size distribution using a separate set of clean sample bottles. Sediment samples generally are not field composited.
- Collect samples for microbiological analyses using equipment and techniques described in NFM 7.
- Calibrate field instruments as described in NFM 6.

Step 2. Select sampling locations.

Review data objectives to ensure they will be met at the sampling location(s) selected. If discharge-weighted samples are needed and the stream section is well mixed with respect to target analytes, locate multiple sampling points along the cross section using the EDI method.

a. Measure discharge at the cross section where samples will be collected.

b. At sites with very little sampling history, measure the variation within each field measurement (specific electrical conductance, pH, temperature, and dissolved oxygen) along the cross section and review these data.

c. Locate the centroid of flow if distribution of streamflow and the field-measurement data indicate that the section is well mixed (refer to the description of the VCF sampling method at the end of this section (4.1.3.A)).

Step 3. Collect sample water.

By applying EDI sampling methods and collecting equal-volume samples at the centroid of each equal-discharge increment, a sample can be collected that is discharge-weighted although it is not isokinetic. Using CH/DH techniques, as required (section 4.0.2):

a. Move sampling and support equipment to the first sampling location. Field rinse equipment (section 4.1.3).

b. Record starting gage height and sampling start time.

c. To collect a nonisokinetic sample with a dip or pump sampler:

- If a discrete sample is to be collected, lower the dip sampler to the desired depth, then sample.
- If a vertical traverse is made to collect the sample, **do not pause when contact with the streambed occurs**, but raise the dip sampler immediately until the traverse is completed. Take care not to disturb the streambed with the sampler, as bed material entering the sampler results in erroneous data.
- If a pump is used to collect a sample, lower the pump intake to the desired depth and pump about three sample-tubing volumes to field rinse sample tubing and then collect the sample.

d. Move to the next vertical (if more than one vertical will be sampled along the cross section).

i. Record the time and repeat sample collection as described in step 3c above.

ii. Inspect each sample, looking for anomalously large amounts of particulates that might have been captured because of excessive streambed disturbance during sample collection. If such a condition is observed, discard the sample, making sure there are no residual particulates left in the container, and resample.

iii. Depending on data objectives, either composite the samples collected or set aside each sample to be independently processed and analyzed.

- If pumped samples will be composited, pump the samples directly into the churn splitter.
- If transferring the subsample to a churn or cone splitter, ensure that all particulates in the sampler are transferred with the sample by swirling the sample gently to keep particulates suspended and pouring the sample quickly into a sample splitter.

e. After all the samples have been collected:

- Record sampling end time and gage height.
- For automated samplers: record beginning and ending dates and times for the sampling period. Retrieve samples from automated pumping samplers at the earliest possible time to reduce the chance of chemical or biological alteration of the sample. (Automatic samplers with refrigeration are available to help maintain sample integrity.) Samples collected by automatic samplers often are combined as a composite sample.
- Document all field observations and any deviations from standard sampling procedures.

Step 4. Process samples → Refer to NFM 5.

Step 5. Clean equipment → Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse the sampler components with deionized water before they dry and place them in a plastic bag for transport to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling and then field-clean while at the sampling site using the prescribed procedures. Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place the cleaned sampler into a plastic bag and seal for transport to the next site.

Instructions for collecting VOC samples at flowing-water sites:

Samples for analysis of volatile organic compounds (VOCs) are collected as a single-vertical point sample in a flowing stream. The VOC sampler should be deployed where the stream velocity represents the average flow, which typically is near mid-channel in the cross section. When collecting samples for VOC analyses, special care must be taken to avoid contamination from any oily film and debris floating on the stream surface.

1. VOC samples are collected directly into laboratory-supplied prebaked 40-mL amber-glass vials. If the stream is deep enough, use the VOC sampler described in NFM 2.1.1.B (fig. 2-2). If the sampler will not be used, skip to step 7.

   a. **Do not clean or field rinse the glass VOC vials – these are supplied by the laboratory ready to use.**

   b. The VOC sampler must be cleaned after each use and field rinsed before use. **To field rinse the sampler, either submerge it in the stream for several minutes or dowse it three times with native water before inserting the VOC vials.**

2. Change gloves. In an area protected from any direct source of contamination (preferably within a sample-processing chamber), uncap four 40-mL unlabeled VOC vials and place them into the VOC sampler. Secure and lock the sampler top in position. Store the vial caps in a clean, protected area.

3. Lower the sampler into the stream near mid-channel to about one half of the total depth at that vertical. Add weights to the sampler if the stream velocity is great enough to pull the sampler downstream. Use weights made of steel or other noncontaminating material; do not use lead weights.

4. Hold the sampler in one position until the sampler is full. Air bubbles will rise to the surface while the sampler is being filled, but may be difficult to see. This takes about 3 to 4 minutes. The sample will be retained in the vials during the last 15 to 20 seconds of sampling.

5. Remove the sampler when bubbles are no longer present or after about 5 minutes, and return it to the sample-processing chamber or other protected area.

6. Open the sampler carefully. Using metal tongs, slowly lift each vial from the sampler reservoir. Do this carefully to avoid losing the convex meniscus on each vial.

7. **To collect a VOC sample without the sampler:** Wearing gloves, submerge a capped VOC vial into the stream section; remove the cap underwater, let the vial fill to overflowing, and then firmly recap the vial underwater. Repeat this for each of the VOC vials. Check each vial for bubbles, as described in step 8.

8. Quickly cap the vial, then shake it. Invert, and check carefully for air bubbles. Discard the entire vial if bubbles are present. Three vials from the sampler set are required for one complete sample. Resample if two or more of the vials have air bubbles. If the sample is to be preserved with chemical treatment, refer to the procedure described in NFM 5.

9. Dry and label the sample vials. Place each vial into a foam sleeve, and store on ice for transport to the laboratory.

10. Clean the sampler and store it properly (see 4.0.2, "Preventing sample contamination").

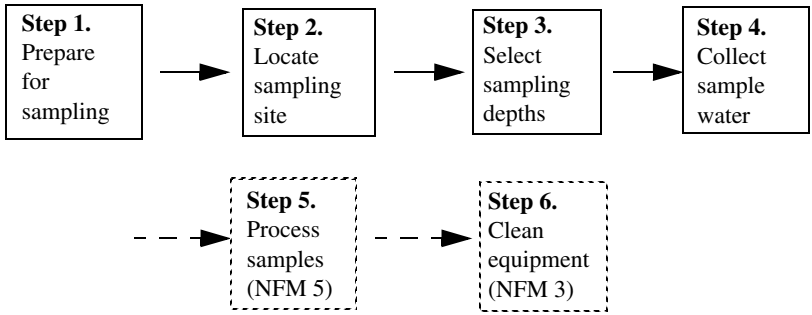
4.1.3.C Guidelines for Sampling at Still-Water Sites

In still water, samples generally are collected at multiple sites and at multiple depths. The number of sampling sites and the depths where samples will be collected should be dictated by study objectives and the physical, chemical, and biological characteristics of the water body (Ward and Harr, 1990).

Thief-type samplers usually are used to collect still-water samples; however, pumping samplers also can be used. A disadvantage of collecting a sample by pumping is that if a thin stratum of water is being sampled, water can move radially from unknown depths and distances into the pump.

- Samples must be collected at a known depth.
- Sample integrity must be maintained to the degree possible while samples are being brought to the surface for further processing.

Steps for sampling at still-water sites



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Step 1. Prepare for sampling of inorganic and organic analytes.[10]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle so as to prevent sample contamination from emissions.

b. Assemble equipment and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics other than fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- **Microbiological analyses**. Collect microbiological samples using equipment and techniques described in NFM 7.

Step 2. Locate sampling site.

a. Locate the first sampling point and maintain a sampling platform position at the site.

b. Record depth to bottom.

[10]Preparations for water sampling are described in NFM 2 and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

Step 3. Select sampling depths.

a. Make field measurements (such as specific electrical conductance, pH, temperature, and dissolved oxygen) in situ to obtain a vertical profile of field-measurement variation.

b. Measure light penetration (if applicable).

c. Select and record sampling depth(s) based on study objectives and the variation in field measurements for the vertical.

Step 4. Collect samples.

Field rinse sampling equipment first (section 4.1.3). Collect samples by using the procedures listed below under Step 4A for a thief-type sampler and under Step 4B for a pump sampler.

Step 4A. Thief-type sampler.

The instructions listed below are for samplers that operate with an open/close mechanism. If the sampler operates as a point-source bailer, follow steps a and c through g below. Pulling the bailer up will trigger the upper check valve to seal off the sample from the water overlying the targeted depth.

a. Lower opened sampler to the desired depth while minimizing disturbance of the water column.

b. Isolate the sample by activating the mechanism that closes the sampler.

c. Raise the sampler from the water body.

d. Dispense sample to sample bottle or compositing/splitting device using *CH/DH* techniques.

- If using a bailer, drain sample through the bottom-emptying device.
- If sample compositing and (or) splitting is required, ensure that all particulates in the sampler are transferred with the sample by swirling the sample gently to keep particulates suspended and pouring the sample quickly into the churn or cone splitter.

e. Repeat steps a through d if more sample is needed from the same depth for that vertical section.

f. Repeat steps a through e for each depth to be sampled in that vertical section. If a second sample from a different depth or vertical section will be composited, either (1) clean and field rinse the splitter after processing the first sample and before collecting the second sample, or (2) use another clean splitter.

g. Move to the next site if another vertical section will be sampled. Repeat steps a through f.

Step 4B. Pump sampler.

a. Lower the pump or pump-sample tubing (attached to a weighted line) to the desired sampling depth.

b. Turn on the pump and pump about three sample-tubing volumes to field rinse the pump, tubing, and other sample-collection or -processing equipment. Discard rinse water.

c. Direct sample flow into collection container(s) until sufficient sample volume has been collected.

d. Repeat Step 4B, steps a through c, if another depth and (or) vertical section is to be sampled. If a second sample from a different depth or vertical section will be composited, either (1) clean and field rinse the splitter after processing the first sample and before collecting the second sample, or (2) use another clean splitter.

Step 5. Process samples → Refer to NFM 5.

Step 6. Clean equipment → Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse the sampler components with deionized water (DIW) before they dry and place them in a plastic bag for transporting back to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling and then field-clean while at the sampling site using the prescribed procedures. Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place the cleaned sampler into a plastic bag and seal for transport to the next site.

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GROUND-WATER SAMPLING 4.2

Collecting samples of ground water that accurately represent aquifer conditions requires sampling at appropriate wells and using equipment and methods that maintain the integrity of the sample with respect to the physical, chemical, and biological characteristics of interest. This section provides guidance and protocols for (a) site reconnaissance and establishing site files, (b) avoiding collection of bad data, and (c) ground-water withdrawal up to the point of bottling or processing the sample. USGS procedures for collecting raw or filtered ground-water samples into bottles, sample preservation, and other sample-processing and handling activities are addressed in Chapter A5 (NFM 5), "Processing of Water Samples." Because ground-water sample collection is a continuous process, the information in this chapter overlaps somewhat with that of NFM 5.

For USGS studies, ground-water samples typically are collected either at monitor wells or at public or domestic water-supply wells.[11]

- **Monitor wells** are observation wells[12] that are installed principally for the collection of water samples to assess the physical, chemical, and biological characteristics of formation (aquifer) water. Samples from monitor wells are collected either with portable, low-capacity pumps or with other types of sampling devices designed for water-quality work. Sampling devices can be dedicated for use at a given well or can be installed in the well for the duration of the monitoring effort. (The terms "monitor well" and "monitoring well" are used interchangeably in this field manual.)

[11]Ground-water samples collected using passive or natural-gradient methods or direct-push or cone penetrometer systems are not addressed in this chapter.

[12]Observation wells are wells or piezometers that are installed (usually without a dedicated pump) for the purpose of collecting hydrologic data. The term generally has been applied to wells installed to observe and determine hydrologic characteristics of an aquifer (Lapham and others, 1997).

- **Water-supply wells** are wells that are installed primarily for supply of public, domestic, irrigation, commercial, or industrial water and usually are equipped with a dedicated high-capacity pump. Pumps installed in supply wells generally deliver a large volume of water that is subsampled for water quality. (Although the guidance in this manual focuses on sampling at public or domestic supply wells, similar principles and procedures apply when sampling at irrigation, commercial, or industrial wells, with the caveat that additional safety precautions need to be identified and implemented and equipment requirements reviewed.) Note that supply-well construction materials and methods and the pumps installed can have long-lasting effects on the chemistry of water entering the well from the aquifer (Lapham and others, 1997).

4.2.1 SITE INVENTORY AND SITE FILES

Information about the well and field site is compiled in the office and during site-reconnaissance visits. The information compiled is used by study personnel to help determine site suitability for conducting sampling activities. Site files are then established in the USGS National Water Information System (NWIS) electronic data base[13] and the information compiled is entered into NWIS and is used to create a file for use in the field.

[13]NWIS is the public portal to USGS water resources data (Hubbard, 1992; USGS Water Resources policy memorandum 92.59). NWISWeb displays real-time water-level data (http://waterdata.usgs.gov/nwis/gw), and real-time water-quality data for selected wells (http://waterdata.usgs.gov/nwis/qw) (website accessed June 2, 2006).

Site inventory – In an office inventory, the study team identifies existing wells or candidate sites at which to install wells, examines well-construction records, and compiles additional background information and site or well records. The field evaluation, or site reconnaissance, is used to verify well location, select or reject candidate well(s), determine the suitability of the site to meet study objectives, and become aware of equipment or other requirements needed to address specific site conditions (table 4-6). Site-reconnaissance visits also are used to identify areas of ground-water recharge and discharge; test field equipment; test well-purging and sampling procedures; conduct aquifer tests; make preliminary field measurements (see NFM 6); and identify the presence of target analytes, sources of contamination, and potential matrix interferences.

When conducting site inventories:

- Be familiar with study objectives and requirements for data collection and quality.
- Be familiar with the considerations for well selection and (or) installation (table 4-6).
- Be alert to changes over time that might affect the suitability of the well to meet study needs.
- Keep in mind the primary criteria for all water-quality studies:
  - The sample must represent the system, in time and space, intended for study.
  - Sample integrity must be maintained.

Review safety plans and procedures before leaving for the field (NFM 9).

Table 4-6. Example of ground-water site-inventory activities

Before the site visit
Review considerations for well selection and installation (section 4.2.2; Lapham and others, 1997).
Review background information collected.
Obtain permission to gain access to the site and to collect samples from the well.
Update well files: record changes in ownership and land use.
Contact utility companies (gas, water, and electric) before digging or drilling.
Determine whether the pump may or may not be removed from the well by field personnel (removal is not recommended, as personal safety could be compromised). The owner's permission is required to remove a pump—you could be liable for damage to pump or well.
Be sure that you get information needed about the site that could interfere with or interrupt sampling. For example, • Hours of pump operation and scheduled downtime. • Pumping rate or rates. • Holding tanks or chemical treatments. • Electrical service to the site. • Scheduled maintenance for pumps or related equipment. • Scheduled site maintenance, such as painting, construction, and defoliation. • Seasonal water-level declines that make the well unusable. • Times of denied access; for example, no access while the owner is out of town. • Special site-access needs; for example, clearance with a site owner or site operator, keys to unlock access to the site, animals. • Restrictions on the location.
Before and during the site visit
Record conditions that could compromise study objectives, including potential point or nonpoint sources of contamination. For example, • Nearby wells that could affect well hydraulics. • Condition of well—for example, rusting or punctured casing, poor surface seal. • Has the well been adequately developed? Could well-development artifacts compromise sample integrity? • Land use and land cover or changes in land use and land cover. • Application of salt on nearby roads during winter, or application or use of herbicides and pesticides. • Landfills or other waste-management facilities. • Industrial, commercial, and agricultural complexes and discharges.
During the site visit
Measure water level in each well. Record water-level measurements on the appropriate field form(s), and into the Ground-Water Site Inventory (GWSI) and Quality of Water Data (QWDATA) data bases.
Identify potential difficulties with the type of equipment and sample-collection methodology to be used. (Note that sampling plans will have to be modified accordingly.)
Update field folders. • Note site conditions that could affect the quality of data collected from that well. • Note change(s) in land use.
Verify well identification number and make sure that it is clearly and permanently labeled. • Check that identification corresponds with what is in the field folder and on site and location maps. • Correct any mistakes or uncertainty about well identification and well location.

Table 4-6. Example of ground-water site-inventory activities—*Continued*

During the site visit—*Continued*
Verify type of pump, well diameter, and use of holding tanks, pressure tanks, chemical treatments. • Check whether oil is floating on the water column in a well equipped with an oil-lubricated pump. • Make sure that the downhole treatment system is turned off before collecting water samples. • Determine if the intended sampling device is suitable for use.
Establish optimum pumping rate(s) for purging and sample collection and decide where to route excess discharge. • Adjust pumping rate to ensure adequate purging of the well without entrainment of atmospheric gases due to excessive drawdown. • Route water away from the well to prevent (1) creating muddy and slippery conditions and (2) damage to or defacement of the property to which you were granted access.
Check that well structure is intact. • Wells used for ground-water studies should be "sounded" annually to check whether depth to bottom corresponds with well-construction information or whether the well is filling with loose materials (U.S. Geological Survey, 1980; Lapham and others, 1997). A decrease in depth to bottom could indicate that the well casing is collapsing, or that there is a breach or corrosion of well screen or casing, or that the well is improperly designed to retain aquifer materials. • Borehole caliper and downhole-camera video logs can identify a damaged or broken well casing. A downhole camera can identify a plugged screen or accumulation of sediment in the well. • Aquifer tests, such as slug tests, can be used to check thehydraulic connection between the well and the aquifer. Aquifer tests, however, are generally beyond the scope of site reconnaissance. • The surface seal of a USGS monitoring well should be intact and the well should be capped. Concrete pad should be repaired if cracked or separated from outer casing. A tight-fitting well cap should have a small ventilation hole.
Check well access for sample-collection points. • Sample-collection points need to be near the wellhead, ahead of where water enters pressure tanks, holding tanks, or treatment systems. • At wells where an access point close to the well is not available, it might be possible to install a hose bibb or tap at the wellhead. Because it usually is not possible to control the pumping rate of a supply well, the field person may need to set up a hose-and-valve system to control the rate at which water is sampled and to reduce the likelihood of backflow of water stored in plumbing lines.
Check well access for water-level measurements. The construction of some supply wells makes water-level measurements difficult or impossible. • Although it is often possible to slip a weighted steel or electric well tape below the pump to get a water-level measurement, the pump can be damaged if the weight or tape becomes entangled in the pump. The weight should be attached so that it will snap off of the tape under stress. • Water levels can be estimated through the air line on some wells. • Sometimes field personnel are permitted to remove the pump from the well to get a measurement; however, pump removal can be difficult and time consuming, is potentially unsafe, and could damage the pump. • A note should be made in the well file if there is no access for a depth measurement.

NWIS files – USGS policy requires that specific information collected for each ground-water sampling site and event will be stored in one or more subsystems of NWIS (USGS Office of Water Quality (OWQ)/Office of Ground Water (OGW) Technical Memorandum 2006.01). In addition, paper documents (such as agreements between the well owner and the USGS for well use, access, or construction), field forms and logs, and any ancillary information that is collected are stored in well files and field folders (USGS Office of Ground Water Technical Memorandum 2003.03). Much of the information needed to set up files for existing wells can be obtained from well owners, drillers, records from state or local jurisdictions, and well-construction logs. Information needed to set up well files for new wells is compiled by field personnel as part of their responsibilities associated with well installation (Lapham and others, 1997).

- **NWIS –** Within the NWIS system, well information, ground-water levels, and water-quality data are stored in three subsystems: the Ground-Water Site Inventory (GWSI), Quality of Water Data (QWDATA), and the Automatic Data Processing System (ADAPS). Individual studies and USGS Water Science Center offices may have additional data-storage requirements.
  - GWSI primarily contains (1) descriptive information about the site and well, (2) construction information, and (3) noncontinuous water-level data. A GWSI site file (table 4-7) must be established for each well at which water-level and other data are collected (table 4-7) (Hoopes, 2004; USGS OWQ/OGW Technical Memorandum 2006.01). When creating or updating a GWSI site-file record, field personnel should fill in as much information as is available in addition to the required information. For example, the GUNIT (geologic unit) code provides important information for interpretation of ground-water data.
  - QWDATA contains (1) results of field and laboratory water-quality sample analyses and measurements, (2) non-continuous water-level data, and (3) other data related to water-quality samples or sample analyses (Gellenbeck, 2005). A subset of the information entered into GWSI is entered into QWDATA, as appropriate to meet the needs of the study (USGS OWQ/OGW Technical Memorandum 2006.01).
  - ADAPS contains continuous records of water levels and water quality (Bartholoma, 2003).

- **Field Folder –** The field folder contains information that is necessary or useful to have onsite during the field effort, and includes a well file for the well at which data will be collected (fig. 4-7).
  - — A well file is established for each well selected or installed for the study. The well file is the repository of the information compiled for the well, and it should contain documentation for site selection, well inventory, well installation, and sample collection.
  - — The field folder (fig. 4-8) is taken along on each site visit and includes site-location maps and a site sketch (fig. 4-9). Files taken to the field should not contain original data records.

To prepare location maps and site sketches:

1. Locate the ground-water site in the field on an aerial photograph, or a town plat/lot number map. Transfer the location of the site to a USGS 7.5 minute topographic quadrangle map.
2. Determine the ground-water site latitude and longitude to the nearest second using a USGS 7.5 minute latitude-longitude scale or a digitizer or Global Positioning System (GPS), and record the latitude and longitude accuracy as one second.
3. Prepare a detailed sketch map. Orient the ground-water site on the sketch map relative to north using a compass. The sketch map should contain enough detail so that the site can be found again by a person who has never visited it. All distances should be made in feet from permanent landmarks, such as buildings, bridges, culverts, road centerline, and road intersection.

RULE OF THUMB:

- **Before starting field work make sure the site file is established in NWIS.**
- **Keep field files current.**
- **After field work, update NWIS promptly.**

Table 4-7. Minimum information required for electronic storage of site and ground-water-quality data in the U.S. Geological Survey National Water Information System

[NWIS, National Water Information System; GWSI, Ground-Water Site Inventory; USGS, U.S. Geological Survey; QWDATA, Quality of Water Data]

Required information for creation of a ground-water site in NWIS[1, 2] (GWSI)		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number (Latitude/longitude/sequence no.)	C1	394224075340501
Station Name	C12	KE Be 61
Latitude	C9	394224
Longitude	C10	0753405
Country	C41	US
Lat/Long Accuracy	C11	S (seconds)
Lat/Long Method	C35	M (Map)
Lat/Long Datum	C36	NAD83
Time Zone	C813	EST
Daylight Savings Time Flag	C814	Y (Yes)
USGS Water Science Center/User	C6	24 (Maryland)
State	C7	10 (Delaware)
County	C8	003 (Sussex)
Station Type	C802	6 (Well)
Data Reliability	C3	C (Field Checked)
Site Type	C2	W (Well)
Use of site	C23	O (Observation)
Required information for storage of sample analyses in the water-quality subsystem (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	394224075340501
Sample Medium	MEDIM	6 (ground water)
Sample Type	STYPE	2 (blank sample)
Hydrologic (“Hydro”) Event	EVENT	9 (routine sample)
Hydrologic (“Hydro”) Condition	HSTAT	A (not determined)
Date (year/month/day)	DATES	20060909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields are available in GWSI and QWDATA that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether an agency other than the U.S. Geological Survey collected the data.
[2]From GWSI Schedule Form 9-1904-A, revised June 2004, NWIS 4.4.

WELL-FILE CHECKLIST, Page 1 of 2

Project name and identification number:_____
Latitude-longitude: _____ Sequence number: _____
Other site or well ID:_____ Station name: _____

Indicate use of water/site: Public Supply Irrigation
Domestic Observation
Commercial Monitoring
Industrial Other _____

Item in well file	Date item filed
Criteria for well selection or installation	_____
Station Analysis	_____
Station Description	_____
ADR (Automatic Data Recorder) Manuscript	_____
Ground-Water Site Inventory (GWSI) data entered into National Water Information System (NWIS)	_____
Paper copy of GWSI form (9-1904-A)	_____
Copies of agreement to complete activity (drilling, sampling, etc.) _____	_____
List agreements _____	_____
Copies of field forms and logs:	
Well-drilling record	_____
Driller's log	_____
Lithologic log: Cuttings	_____
Cores	_____
Aquifer tests: (list types) _____	_____
_____	
Geophysical logs: (list types) _____	_____
_____	
Well-construction record	_____
Well-development record	_____
Well-maintenance checks: (list types) _____	_____
_____	
Well-location information:	
Latitude-longitude, datum, method of determination, and any changes	_____
Well-location map(s)	_____
Site-sketch map	_____
Written description of location	_____
Well-casing elevation (elevation, and method and date of determination)	_____
Photographs of well and vicinity (with measuring/sampling points identified)	_____
Land use/land cover form (Lapham and others, 1997)	_____

Figure 4-7. Example of a checklist for a well file.

WELL-FILE CHECKLIST, Page 2 of 2

Item in well file	Date item filed
Water-quality records for each sampling event (for example, purging, field measurements, field forms, sampling history) and copies of laboratory analyses requested	_____
	_____
	_____
	_____
	_____
Water-level measurements - current:	_____
	_____
	_____
Water-level measurements - historical:	_____
	_____
	_____
Record of well leveling (survey)	_____
Datum corrections	_____
Pumping schedule/history	_____
Type of pump in well and location of intake	_____

Description of measuring point for water levels: _____
_____
_____

Description of collection point for samples from
Supply wells _____
_____
Monitoring wells_____

Other information (for example, geologic unit, aquifer name): _____
_____
_____
_____

Figure 4-7. Example of a checklist for a well file—*Continued.*

Field-folder checklist: ground-water quality		
✓	**Item**	**Comments**
	Forms (new forms and (or) examples of completed forms): • Permission forms—must be signed by proper authority. • Analytical Services Request form(s). • Ground-water field form and well-inventory form.	
	Equipment and supplies checklists.	
	Field-techniques manuals.	
	Safety information: • Nearest emergency facilities; home phone number of supervisor. • Diagram of where to park, placement of flags and cones. • Traffic conditions; location of power lines. • Environmental hazards such as weather and animals.	
	Site location and description: • Maps showing location and identification number of well(s). • Name of landowner, tenant, or other responsible party. • Site access instructions (call owner; get keys or tools needed for security gate, well house, well protective casing). • Photographs and land use/land cover form to document site conditions. • Well dimensions and construction logs.	
	Sampling schedule and instructions: • Laboratory analyses, codes, and bottle types. • Preservation requirements, including chilled samples. • Quality-control samples. • Location of sampler intake during sample collection. • Pumping rate for purging and sampling.	
	Purging instructions: • Number of well volumes. • Rate of pumping; containment and discharge of purge water. • Location of sampler intake during purging. • Field measurements and stability protocols. • Previous field-measurement and purge-volume records. • Discharge of purge water.	
	Water-level measurements: • Location of measuring point. • Previous records from well.	
	Ancillary information: • Geologic section(s). • Hydrologic section(s). • Borehole geophysical logs.	
	Shipping instructions: • Mailing labels; location of nearest post office or shipping agent. • Ice and holding time requirements.	

Figure 4-8. Checklist for contents of a field folder for ground-water sampling.

A. Example of site and well-location maps.

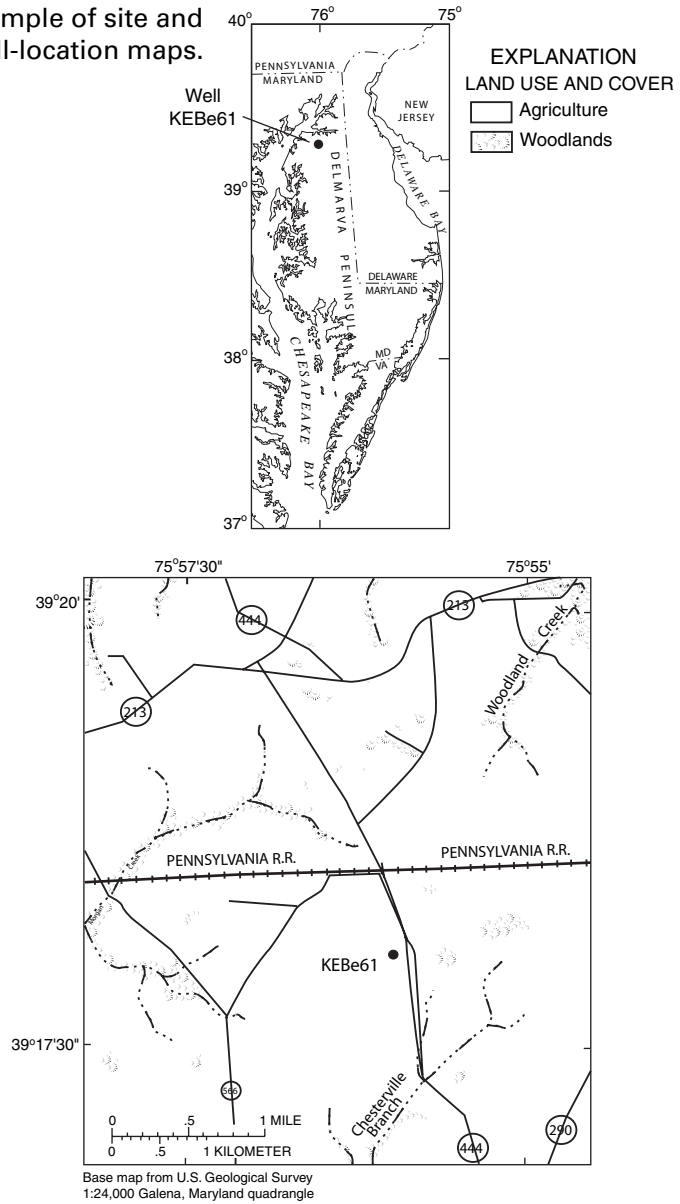
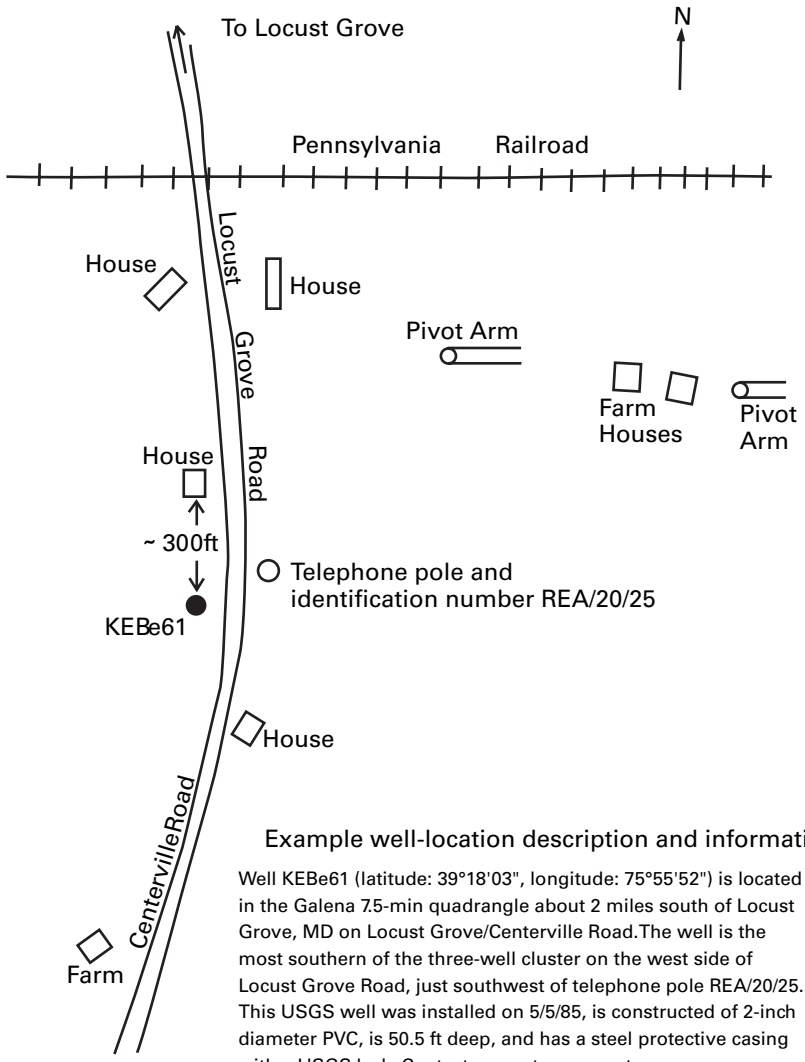


Figure 4-9. Example of (*A*) site- and well-location maps and (*B*) well-site sketch.

B. Example of well-site sketch (with well-site information).



Example well-location description and information:

Well KEBe61 (latitude: 39°18'03", longitude: 75°55'52") is located in the Galena 7.5-min quadrangle about 2 miles south of Locust Grove, MD on Locust Grove/Centerville Road.The well is the most southern of the three-well cluster on the west side of Locust Grove Road, just southwest of telephone pole REA/20/25. This USGS well was installed on 5/5/85, is constructed of 2-inch diameter PVC, is 50.5 ft deep, and has a steel protective casing with a USGS lock. Contact property owner at ( )___-____ one day before sampling.

Figure 4-9. Example of (*A*) site- and well-location maps and (*B*) well-site sketch—*Continued.*

4.2.2 CONSIDERATIONS FOR COLLECTING REPRESENTATIVE SAMPLES AT WELLS

The study team must ensure that the wells to be sampled will yield samples that accurately represent the water chemistry of the hydrogeologic system targeted for study. To help prevent data biases that could compromise study objectives, field personnel must be aware of how specific well characteristics and field activities can affect sample chemistry. These considerations are addressed as follows:

- Table 4-8 summarizes factors that can compromise sample integrity and general strategies for maintaining the integrity of ground-water samples. Table 4-9 lists considerations for selection or installation of wells at which water-quality will be monitored that relate to the quality or representativeness of the samples to be collected.
- Section 4.2.2.A discusses adverse effects on sample chemistry from introducing air and other fluids into the borehole during well construction, and the importance of monitoring the communication of the well with the aquifer for signs of deterioration.
- Section 4.2.2.B describes the effect of pumping rates, well yield, and aquifer heterogeneity and anisotropy on the sampling effort and how these factors can limit the types of sample analyses to be performed.
- Section 4.2.2.C focuses on the vulnerability of ground-water samples to contamination from atmospheric gases, standing fluids and bottom detritus in the borehole, and equipment use.

Some wells might not be suitable for water-quality monitoring. The ultimate decision as to when and if a well should be sampled rests with the study or program personnel and depends on the specific sampling and data-quality requirements of the study. Field personnel need to be alert to the conditions that might cause a change in the suitability of the well over time, whether because of well characteristics, land-use conditions, or other factors. **In general, avoid sampling:**

- Wells that cannot produce a continuously pumped sample or wells at which water-level recovery takes longer than 24 hours after being pumped.
- Wells at which purging will stir up bottom detritus that can bias analytical results. This often is the case in wells having 5 ft or less of water. Any reported interpretations of chemical analyses when sampling under such conditions must be clearly qualified and the well conditions documented.
- Wells at which field measurements have not met stabilization criteria (section 4.2.3), unless the study sampling and (or) quality-assurance plans provide for alternative protocols.
- Wells in which the water column within the sampling interval is in contact with and mixes with atmospheric gases, unless the analytes of concern will not be affected.
- Wells at which the water withdrawn must pass through holding tanks or chemical treatments.

Table 4-8. Considerations for maintaining the integrity of ground-water samples

Factors that can compromise sample integrity
• **Time.** Chemical and microbial reactions that affect target-analyte concentration can be rapid. • **Loss of pressure.** Pressure in ground water can be much greater than atmospheric pressure. As the sample is brought to land surface, depressurization of the sample can cause changes in sample chemistry. • **Leaching or sorption.** Chemical substances can be leached from or sorbed by the equipment that contacts the sample. • **Exposure to the atmosphere.** Atmospheric gases and particulates that enter the sample can affect the water chemistry. • **Temperature.** Ground-water temperature is often lower than the atmospheric temperature at land surface. As the sample is brought to land surface, an increase in temperature can increase chemical reaction rates and microbial activity and cause degassing.
Strategies to maintain sample integrity
• **Plan sampling at sites in a sequence that avoids contamination.** Start with pristine sites or those least contaminated or with lowest concentrations of dissolved solids or target analytes. End at the site with the highest concentrations of target analytes. • **Clean equipment.** Sample only with decontaminated equipment and quality assure the efficacy of the cleaning procedures (collect equipment blanks). • **Purge the well of standing water.** Purge the well to reduce artifacts from well installation or sampler deployment. If possible, pump at a rate that does not overly stress the aquifer, creating drawdown and mobilizing particulates. Protocols for purging and pumping rate can depend on well type and study objectives. • **Isolate the sample.** For example, use packers downhole and processing and preservation chambers at land surface. • **Avoid temperature changes.** Keep sample tubing as short as possible and shaded from direct sunlight. • **Avoid sample aeration.** Filter in-line; use thick, nonpermeable sample tubing; completely fill filtration assemblies and sample tubing with sample; fill sample bottles from bottom up to overflowing whenever appropriate; handle anoxic water under an inert gas atmosphere, if necessary (section 4.2.2.C). • **Collect quality-control samples.** Review the analytical results and adjust field procedures, if necessary, before the next sampling.

Table 4-9. Considerations for well selection and well installation

[Modified from Lapham and others, 1997]

Well location
• Location conforms to the study's network design for areal and depth distribution. • Land-use/land-cover characteristics, if relevant, are consistent with study objectives. • Site is accessible for equipment needed for well installation and sample collection. • Well elevation has been determined.
Hydrogeologic unit(s)
• Hydrogeologic unit(s) that contribute water to the well can be identified. • Depth and thickness of targeted hydrogeologic unit(s) are known or can be determined. • Yield of water is adequate for sampling (typically, a minimum of 1 gallon (3.785 liters) per minute).
Well records, description, design, materials, and structure
• Available records (for example, logs of well drilling, completion, and development) have sufficient information to meet the criteria established by the study. • Borehole or casing/screen diameter is adequate for equipment. • Depth to top and bottom of sample-collection (open or screened) interval is known (to determine area contributing water to well); well depth and other well-construction and well-development information is available. • Length of well screen is proportional to the vertical and areal scale of investigation. • Well has only one screened or open interval, if possible. (Packers can be used to isolate the interval of interest, but packers might not completely isolate zones in unconsolidated or highly fractured aquifers. If packers are used, materials of construction must be compatible with analytes to be studied.) • Top of well screen is several feet below mean annual low-water table to reduce chances of well going dry and to avoid sampling from unsaturated intervals. • Filter pack is of a reasonable length (a long interval compared with length of screened or open interval usually results in uncertainty as to location of the source of water to well). • Well-construction materials do not leach or sorb substances that could alter ambient target-analyte concentrations. • Well-structure integrity and communication with the aquifer are sound. (Checks include annual depth-to-bottom measurements, borehole caliper and downhole-camera video logs, and aquifer tests.)
Pump type, materials, performance, and location of sampler intake
• Supply wells have water-lubricated turbine pumps rather than oil-lubricated turbine pumps. (Avoid suction-lift, jet, or gas-contact pumps, especially for analytes affected by pressure changes, exposure to oxygen, or that partition to a gas phase.) • Pump and riser-pipe materials do not affect target-analyte concentrations. • Effects of pumping rate on measurements and analyses have been or will be evaluated. • Sampler intake is ahead of where water enters treatment systems, pressure tanks, or holding tanks.

4.2.2.A Well Construction and Structural Integrity

Lapham and others (1997) describe common well-drilling, well-completion, and well-development methods and the importance of checking the structural integrity of the well periodically. Study personnel should be aware of the effects that well installation and the potential failure of the well structure can have on the data being collected.

Effects of well construction

Well-drilling, well-completion, and well-development methods can have long-range effects on sample chemistry (Lapham and others, 1997). Field personnel should review the well-construction methods and materials used, in addition to the length and diameter of the well screen and casing and how the well was completed.

- Circulation in the borehole of air and fluids such as water, bentonite, and biochemical slurries can infiltrate the aquifer, thereby altering water chemistry or biochemistry. For example, studies indicate that samples collected for chlorofluorocarbon (CFC) and sulfur hexafluoride (SF_6) analyses at monitor wells drilled in fractured-rock aquifers using air-rotary methods can be biased for those analyses 12 months or longer after being drilled (L.N. Plummer, U.S. Geological Survey, written commun., 2006), although a three-well-volume purge protocol is used (section 4.2.3). Well development by air injection also is likely to bias CFC and SF_6 analyses and produce faulty interpretations with respect to ground-water ages (Shapiro, 2002). High-capacity, high-yielding, or frequently pumped supply wells are less likely to be affected. Claassen (1982) discusses how mud-rotary drilling, grouting, and other well-construction practices also can have a relatively long-lasting effect on major-ion compositions and chemical properties of ground water, and provides methods by which to analyze these effects.
- Mixing of waters with different quality can occur in wells with long or multiple screens because of well-bore flow. On the other hand, wells with short screens relative to the total thickness of an aquifer might be screened at intervals that miss major zones of interest, such as zones with high transmissivity or contamination.

Selection of the appropriate well design depends on study objectives. For example, if samples withdrawn from an unconfined aquifer will be analyzed for volatile organic compounds, dissolved gases, or trace metals, the top of the screened or open interval should be located far enough below the lowest anticipated position of the water table (3 ft (~1 m) or more) so that the screened interval will not be intersected by the water table during drawdown. The purpose of this design is to avoid gaseous diffusion into the sample from a partially saturated or open interval. On the other hand, the well might be designed specifically to screen across the water table to better assess the thickness of oil or other light non-aqueous phase liquids (LNAPL) floating on the water surface.

Deterioration of the well structure

The integrity of the well's construction can deteriorate or the well can "silt in" over time. The structural integrity of monitor wells and their hydraulic connection with the aquifer should be checked at least annually or as described below. Checking well integrity should be scheduled to occur during a nonsampling site visit, if possible. If the well integrity will be checked during a sampling field trip, do this only after completing sample collection to avoid stirring up particulates that could enter the sample and cause a bias in analysis of trace metals, polychlorobiphenyls (PCBs), or other analytes that tend to associate with particulate matter.

- Inspect the integrity of the surface casing and seal routinely when visiting the well.
- Inspect the subsurface casing (this can be done using a borehole televiewer).
- Note any changes in depth to the bottom of the well; this measurement should be made annually at wells with recurring water-level or water-quality data collection. In addition, the well should be tested for hydraulic connection to the aquifer every 3 to 5 years.
- Purge well water laden with particulates until turbidity values return to background or near-background levels; that is, the final turbidity value recorded after the well has been properly developed. Typically, the turbidity value measured at a properly constructed and developed well is about 10 turbidity units, although it is common for background turbidity in ground water to be 5 turbidity units (the threshold for visible turbidity). Turbidity values that cannot be improved to less than about 25 units after purging or well redevelopment can indicate failure of the well structure or that the well was improperly constructed. If possible, a different well should be selected or a new well installed.

4.2.2.B Well-Hydraulic and Aquifer Characteristics

Hydraulic characteristics of the well and the structural and material properties of the aquifer can impose specific constraints on the sampling effort and achieving results that can be interpreted within a defined measure of quality. These considerations affect the selection of the equipment and sampling methods to be used, and ultimately may result in determining that a well is unsuitable for the intended data-collection effort.

Pumping rate

The pumping-rate capability of a given well-and-pump system is related to well capacity. Compared with pumping rates at supply wells, pumping rates at domestic wells are low. Advantages and disadvantages associated with low- and high-capacity wells are described in Lapham and others (1997). When reviewing study objectives, consider the effect of the proposed pumping rate on the aquifer with respect to what the water quality of the samples to be collected will represent.

- Pumping a few tens of gallons per minute can induce substantial leakage from confining beds if drawdown is rapid (formation materials are low-yielding). By contrast, pumping at a rate of thousands of gallons per minute from high-yielding materials is not likely to induce such leakage.
- Pumping at a high rate can cause turbulence and thus turbidity in the water column, resulting in biased data.
- Pumping at a low rate (for example, 1 to 4 gal/min, or 3.8 to about 15 L/min) in deep wells might result in the sample taking several hours to reach land surface. A long residence time of water within the sample tubing may compromise sample integrity.

- Be aware that pumping at any rate draws water preferentially from the most transmissive intervals, whether in fractured rock or unconsolidated media. Since the wellbore has a much higher hydraulic conductivity than the formation, the sample collected represents a flux-weighted average of the various inflow locations and the location of the pump intake does not affect this result (A.M. Shapiro, U.S. Geological Survey, written commun., 2006; Gibs and others, 2000; Reilly and LeBlanc, 1998; Gibs and others, 1993; Reilly and Gibs, 1993).
- The rate of pumping during purging should remain constant and be maintained as the pumping rate for sample withdrawal and collection. Fluctuations in pumping rate affect sample quality (Gibs and others, 2000).

Low-yield wells

A yield of at least 1 gal (3.75 L) per minute without causing drawdown of about 2 ft or more below the top of the open or screened interval is recommended for adequate sampling at monitor wells with a diameter of 2 in. or greater (Lapham and others, 1997). Wells that yield less than 100 mL/min frequently incur substantial drawdown during well purging. **Low-yielding wells, especially those that exhibit slow recovery or are pumped dry, are not recommended for water-quality sampling.** Situations may occur, however, that necessitate use of such wells.

- Low yield may be a function of poor well construction. Try to improve the well yield by redeveloping the well. Mechanical surging methods commonly produce the best results and avoid introduction of contaminating fluids; however, such methods must be employed in a manner to avoid damage to the structure of the well (Lapham and others, 1997). Pumping or over-pumping methods usually are not as effective for increasing the well yield. It is advisable to consult with an experienced and reputable well driller
- When drawdown occurs across the open interval, contamination from atmospheric gases or other inputs can affect subsequent water chemistry; for example, VOC loss, contamination of ambient CFC and SF_6 concentrations, and increase in turbidity.

- Wells must be purged before sampling (see section 4.2.3). After purging, the water level in the well should recover to approximately 90 percent of its starting level before sampling should commence. In low-yield wells this can take several hours or longer, requiring potentially multi-day visits to complete a three-well-volume purge. The longer the recovery time, the lower the confidence that the sample to be collected can be considered representative of ambient aquifer water composition. The actual volume of well water purged needs to be documented if it is less than the standard three-volume protocol.

RULE OF THUMB:

Do not sample wells at which recovery of water level after purging to 90 percent exceeds 24 hours.

- Consider whether packers can be used to seal off the interval to be sampled; in this case, only the isolated interval needs to be purged. This assumes that the interval selected is sufficiently transmissive to yield the volume needed of formation water. **CAUTION:** installing packers within a well screen can result in drawing in water from above or (and) below the packed-off interval through the filter pack in the annular space.
- Weigh several factors when selecting the sampler to withdraw water from a low-yield well. If possible use a low-volume submersible pump (for example, a Bennett pump).
  - — Bailers may stir up particulate matter and compromise specific analyses of interest.
  - — Suction-lift pumps, such as peristaltic pumps, can operate at a very low pumping rate; however, using negative pressure to lift the sample can result in loss of volatile analytes.
  - — Operating variable-speed, electrical submersible pumps at low flow rates may result in heating of the sample as it flows around and through the pump; this also can result in sample degassing and VOC loss, in addition to changes in other temperature-sensitive analytes.

Aquifer media with defined paths of preferential flow

In order to make a relevant interpretation of the sample chemistry, it is necessary to take into account the aquifer interval or intervals that yield substantial contributions of water to the well and understand the hydraulic conditions within the well that result from (a) ambient flow in the aquifer to the well, and (b) the conditions induced by sampling (Shapiro, 2002).

- **Regardless of the pumping rate or location of the pump intake**, water will be withdrawn first from the borehole and only later in time from the aquifer. The heterogeneity and anisotropy within the (consolidated or unconsolidated) aquifer interval being sampled dictates the paths of permeability through which formation water enters the well.

- **Flow dynamics within the well must be understood to determine if and when the water being withdrawn represents fresh formation water.** Differences in head (from contributing paths of flow within the aquifer) and differences in solution density from these contributing areas of flow will result in flow within the borehole.

4.2.2.C Vulnerability of Ground-Water Samples to Contamination

Because guidance cannot account for every potential threat to data quality, the responsibility lies with the field personnel to (a) be aware of the factors that can compromise the quality of the ground-water samples collected (table 4-8), and (b) use appropriate techniques and strategies to minimize and account for bias in the resulting data (section 4.3). The most common sources of sample contamination result from improperly cleaned equipment; contact or random particulate input from the atmosphere; and sample-water contact with hands, fumes, or other extraneous matter during sample-handling activities (Horowitz and others, 1994).

- Implement "good field practices" and collect quality-control samples (section 4.0).
- Use Clean Hands/Dirty Hands sampling techniques (table 4-3).
- Use equipment-selection and equipment-cleaning procedures that are described in NFM 2 and NFM 3, respectively.
- Withdraw sample water in a manner that avoids turbulence, contact with the atmosphere, and changes in temperature and pressure.
- Avoid sampling at wells that have less than 5 ft of water column, to prevent inclusion of detritus from the bottom of the well.
- As a rule, collect, process, and preserve samples within clean, enclosed chambers.
- Review the results of equipment blanks, field blanks, and other quality-control (QC) information well in advance of sampling. Use this information to adjust sampling plans and procedures, or to otherwise prepare for field work.

Standing borehole water

The chemical composition of standing water in a borehole is affected by well-construction practices, as described above, by contact with the initial and overlying air within the borehole, by geochemical and biochemical processes occurring in the borehole water, and by the vertical as well as horizontal borehole flow. Borehole flow is partially a function of hydraulic head differences within zones of preferential flow in the aquifer; consequently, water can move up or down vertically as well as into and out of the aquifer horizontally (Shapiro, 2002).

Formation water that is stored in a filter (gravel) pack within the annular space between the well casing (screen) and aquifer is not necessarily representative of formation-water chemistry, but can take on the mineral signature of gravel materials and can cause a change in pH values. Assuming that the well has been appropriately developed, the well also should be purged of standing water each time before samples are withdrawn (see section 4.2.3).

Atmospheric and dissolved gases

Exposure of anoxic or suboxic samples to the atmosphere can increase dissolved-oxygen (DO) concentrations to a well above ambient concentrations, causing bias not only in the DO data but also in the results of analyses for particulate and dissolved metals, sulfide, VOCs, CFCs, SF_6, microorganisms, and measurements of pH and alkalinity. Minimize or isolate the sample from atmospheric contact, using the following procedures, as appropriate.

- If pumping, only use pumps that can deliver a smooth, nonturbulent flow in-line to the sample collection/processing chamber (NFM 2.1.2). The same pumping technique applies for making field-measurement determinations (NFM 6.2), whether pumping while using a multi-parameter instrument for in situ measurements or to deliver the sample to a flowthrough chamber.

- Avoid sampling at monitor wells in which the sampler intake is drawing in water that has mixed with the overlying air column. If sampling at such wells cannot be avoided, samples should not be collected for analysis of dissolved gases such as VOCs, CFCs, and SF_6. The accuracy of trace-element data from such samples also may be in question. Check the list of analytes and data-quality requirements to determine if samples of the appropriate quality can be acquired.
- Use transparent sample-delivery tubing. Avoid entraining bubbles in the tubing by filling it to capacity; if bubbles form, tap the tubing with a blunt object to dislodge them and move them out.
- Fill sample containers within a processing chamber.
  - An effective bottle-filling method is to insert the discharge end of clean sample tubing to the bottom of the bottle so that the sample fills the container from the bottom up to overflowing. Cap the bottle quickly. This method is not practical for every sample type.
  - Atmospheric oxygen can be completely removed from the processing chamber (or glove box) by filling it with a clean, inert gas, especially one that is heavier than air, such as argon. Alternatively, good results have been documented by passing inert gas over the sample bottle opening while filling the bottle or by filling the bottle (and capsule filter, if used) with the inert gas beforehand.

To fill a chamber with inert gas:

1. Insert a desiccant pack in-line between the gas tank and the processing chamber.
2. If using a processing chamber, add a "T" fitting at the top to secure the small-diameter gas delivery hose, which is then inserted through the chamber cover.
3. Seal the chamber cover closed by twisting and tightly clipping it or using some other sealing method.
4. Start the flow of inert gas into the chamber.
5. Cut slits through the top (this is not needed if using a glove box) to allow access with gloved hands. Note that the entry of gas drives air out of the chamber through the slits.

Ground-water samples with ambient concentrations of dissolved gases (for example, methane) should be collected so as to avoid degassing. Degassing can occur from an increase in water temperature as the sample is brought to the surface, or because of leaks in the sampling and pressure system.

- Effervescent waters or samples collected for dissolved-gas analysis should use a Kemmerer or other sampling device designed to maintain ambient pressure. Collect CFCs and SF_6 samples using the procedures described on the USGS Reston Chlorofluorocarbon website, http://water.usgs.gov/lab/ (accessed July, 2006).
- Check that all equipment connections and fittings are airtight.

Use of sampling equipment

The type of equipment used for well purging and sample withdrawal can affect the quality of the sample and how the data are interpreted. Samples of ground water from monitor wells generally arewithdrawn using a submersible pump, a peristaltic or valveless metering pump, or a point sampler such as a bailer, thief sampler, or syringe; supply-well pumps generally are permanently installed and should not be removed unless absolutely necessary and with the owner's permission (NFM 2). Equipment to be used for sampling – the materials of construction and the manner of operation – must be checked against the list of target analytes and the characteristics of the well in order to determine whether the equipment is appropriate to meet study requirements. Select and prepare equipment using the guidelines and protocols described in NFM 2, 3, and 6[14] and shown on figure 4-10.

- The sample-wetted parts of the equipment must be constructed of materials that will not contaminate the sample with respect to target analytes (NFM 2). Collect an equipment blank before field activities begin to test the suitability of the equipment for its intended use.

[14]NFM 2, "Equipment selection for water sampling;" NFM 3, "Equipment cleaning for water sampling;" NFM 6, "Field measurements."

- All sampling equipment must be cleaned and the efficacy of the cleaning or decontamination procedures should be confirmed with analyses from quality-control samples (NFM 3). Document in field notes the cleaning and quality-assurance procedures used, along with the analytical results for equipment-blank samples collected to test cleaning procedures.
- A flow-splitting manifold (fig. 4-10) constructed of noncontaminating materials is recommended for directing the pumped-sample flow to the point of sample collection (usually a sample-collection or sample–processing chamber).
- When setting up a pump system that requires a hydrocarbon-fueled generator, take note of the wind direction and locate the generator downwind from the sampling operation.
- Pump tubing should be kept as short as possible (to avoid changes in sample temperature) and should extend directly into a processing chamber or glove box to avoid sample contamination from the atmosphere. Set up sample chambers before beginning sample collection (a flowthrough chamber, if used for field measurements (NFM 6); and processing and preservation chambers for sample collection and filtration, and preservation, respectively).
- The sampling device should be conditioned with the well water before being used to collect samples.

To condition or field rinse a ground-water sampler:

1. Wearing disposable gloves, gently lower the sampler through the water column in the well to the selected sampling depth interval. Take care to minimize disturbance in the water column and minimize disturbance of sediments at the bottom of the well.
    - If using a pump sampler, field rinsing is accomplished with well purging, provided that the well will be purged with the same equipment to be used for sample withdrawal. Water should be pumped through the sample tubing to achieve the equivalent volume of three equipment rinses.
    - If using a point sampler, fill the sampler partially with the water to be sampled; shake or swirl it to cover all interior parts of the sampler. Drain the rinse water through the nozzle or bottom-emptying device. Repeat this procedure three times.
2. Discard or contain the well-water rinsate (including purge water) as appropriate, to comply with waste-disposal regulations; this is especially critical if the water is known or suspected to contain toxic levels of chemical substances.

Well-bottom detritus

Incorporating sediment or other detritus from the bottom of the well into the sample can result in data that do not represent the composition of native aquifer water. To avoid this:

- Lower the pump or other sampler slowly and smoothly to the desired point of sample intake; that is, without creating turbulence and without stirring up bottom detritus.
- Keep the sampler intake far enough above the bottom of the well to avoid drawing in bottom detritus.
- Maintain a pumping rate that is not so high as to draw in bottom detritus.

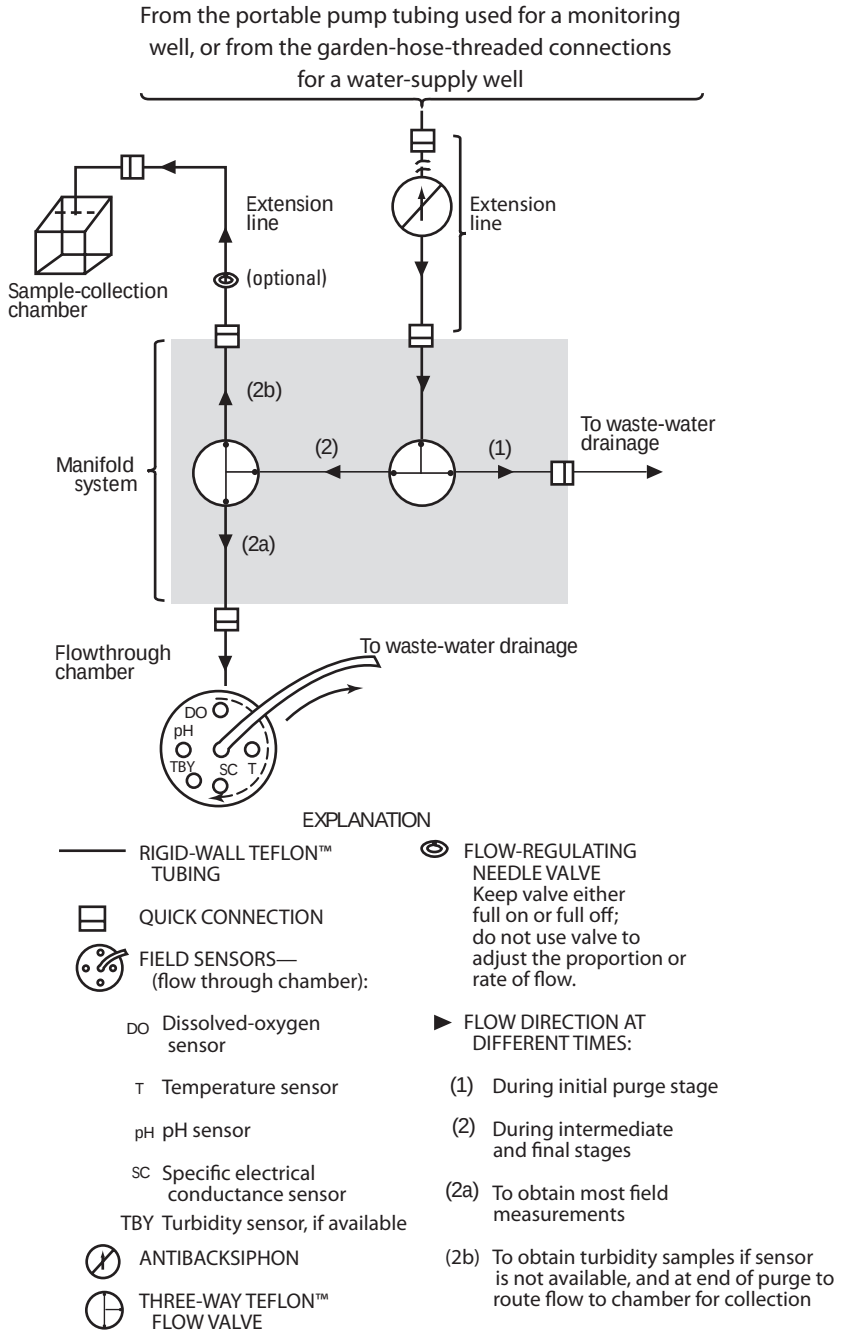


Figure 4-10. Example of a manifold used for well purging and sample collection (modified from Koterba and others, 1995).

WELL PURGING 4.2.3

Well purging removes standing water from the borehole. The purpose of purging is to reduce chemical and biochemical artifacts caused by the materials and practices used for well installation, well construction, and well development, and by reactions occurring within an open borehole or annular space between a well casing and borehole wall.[15] Purging also serves to condition the sampling equipment with well water. The purging process forms a continuum with that of sample withdrawal. Sample withdrawal is the process by which sample water is transported for collection and processing, after the well has been purged.

Standard purge procedure 4.2.3.A

As a rule of thumb, the standard USGS purge procedure removes three or more well volumes of standing water while monitoring the water level and the stabilization of routine field measurements as a function of time, pumping rate, and the volume of water being removed (figs. 4-11 and 4-12). Routine field meaurements include pH, temperature, specific electrical conductance, dissolved oxygen, and turbidity. Inherent in the purge procedure is an assumption that stabilization of field properties indicates that the discharge water represents ambient formation water. Field personnel should examine this assumption for each well, using their knowledge of the well and aquifer hydraulics. Review of the purging history, including physical and chemical data monitored, can save time and help determine how the well should be purged.

[15]Passive sampling methods may not require purging of the well prior to sample collection (Vroblesky, 2001; Powell and Puls, 1993; and Ronen and others, 1987).

- When calculating a purge volume for a cased well:
  - — Include an estimate for the volume of water stored in the annular space between the casing and borehole wall, using knowledge of the borehole diameter. It is mandatory to evacuate at least one borehole volume (that is, casing volume plus that of the annular space), whether that space has been backfilled with formation materials or with a gravel pack.
  - — Make the calculation of casing volume using the height of the water column to the bottom of the well, instead of the water column height to the top of the screen.

- The number of well volumes to be evacuated relies on confirming the time over which field measurements stabilize, using knowledge of the well and aquifer hydraulics.
  - — To the extent practical, field personnel should apply an understanding of the borehole and aquifer hydraulics for the well to determine when the water being withdrawn from the borehole will likely be dominated by formation water (Shapiro, 2002; Claassen, 1982).
  - — Values for field properties are recorded sequentially and at regular time intervals. The frequency of these measurements depends on the purging rate, which in turn is a function of well depth and diameter, and aquifer transmissivity. Field-property stabilization should be plotted as a function of a logarithmic time scale rather than a linear time scale, to best determine the point at which the contribution of aquifer water dominates pump discharge (see Shapiro, 2002). Field-measurement procedures are detailed in NFM 6.
- Purging should not cause substantial drawdown in monitor or supply wells when pumping at a rate of at least 1gal (3.75 L) per minute. Ideally, drawdown will be at a steady state, with the water level remaining above the top of the open or screened interval.
- Use of a borehole packer system or well liner is recommended for wells in fractured or low-yield media, to isolate zones of highest hydraulic conductivity or of particular interest. Transducers should be installed above and below the packers to monitor head differences.

.

Well volume = $V = 0.0408\ HD^2$ =___ gallons,
where
V is volume of water in the well, in gallons,
D is inside diameter of well, in inches, and
H is height of water column, in feet

Purge volume = (n)(V) = _____ gallons,
where
n is number of well volumes to be removed during purging

Q = estimated pumping rate = _____ gallons per minute

Approximate purge time = (purge volume)/Q = _____ minutes

Well casing diameter (D) (in inches)	Gallons per foot of casing
1.0	0.04
1.5	.09
2.0	.16
3.0	.37
4.0	.65
4.5	.83
5.0	1.02
6.0	1.47
8.0	2.61
10.0	4.08
12.0	5.88
24.0	23.50
36.0	52.90

Explanation:
Well volume: Volume of water in a borehole or cased well.

Well volumes: For cased wells, the actual number of well volumes should account for evacuation of at least one volume of water stored in the annular space between the casing and borehole wall. This can be estimated from knowledge of the drilled well diameter.

Approximate purge time: Actual purge time depends also on field-measurement stabilization (use fig. 4-12).

Figure 4-11. Estimation of purge volume and purge time.

RECORD OF WELL PURGING

Date: _____ By: _____
SITE ID _____ STATION NAME _____

HEIGHT OF WATER COLUMN_____ DEPTH OF WELL_____
PUMP INTAKE (ft or m below MP): Start_____ End _____
WELL-PURGING METHOD AND PUMP TYPE (describe):_____
_____

TIME	WATER LEVEL below *MP LS	DRAW-DOWN	TEMPER-ATURE	CONDUC-TIVITY	pH	DISSOLVED OXYGEN	TURBID-ITY	APPROX. PUMPING RATE
HR:MIN	*ft or m	*ft or m	°Celsius	µS/cm	standard units	mg/L	**	*gpm or L/min

*Circle the unit used; MP, measuring point; LS, land surface; HR:MIN, hour and minutes; ft, feet; m, meter; µS/cm, microsiemens per centimeter at 25°C; mg/L, miligrams per liter; gpm, gallons per minute; L/min, liters per minute.
**Select the appropriate turbidity unit from http://water.usgs.gov/owq/turbidity_codes.xls.

Well volume = $V = 0.0408\ HD^2$ = ____ gallons. **Purge volume** = $(n)(V)$ = ____ gallons.
V = volume of water in well, in gallons; D = inside well diameter, in inches; H = height of water column, in feet; n = number of well volumes to purge.
Well volume is 0.16 gallons per foot for a 2-in. casing diameter.

FIELD MEASUREMENT	STABILITY CRITERIA[1]
pH	± 0.1 standard units
Temperature (T) (in degrees Celsius)	± 0.2°C (thermistor thermometer) ± 0.5°C (liquid-in-glass thermometer)
Specific electrical conductance (SC)	± 5%, for SC ≤ 100 µS/cm ± 3%, for SC > 100 µS/cm
Dissolved-oxygen concentration (DO)	± 0.3 mg/L
Turbidity (TBY)[2]	± 10%, for turbidity < 100

[1]Allowable variation between 5 or more sequential field-measurement values.
[2]Select appropriate TBY unit from http://water.usgs.gov/owq/turbidity_codes.xls

Figure 4-12. Example of a field log for well purging.

Exceptions to the Standard Purge Procedure 4.2.3.B

Site characteristics, well characteristics, or study objectives could require modification of the standard purge procedure by changing the number of well volumes removed or by changing or adding types of field measurements and analyses. **Any modification to the standard well-purging procedure must be documented.** When standard purge volumes cannot be removed, (1) sufficient water must be withdrawn from the well to evacuate at least one borehole volume and to field rinse the sampler and sample tubing—alternatively, flush the pump and tubing system with the equivalent of three tubing volumes of DIW and purge the DIW from the tubing with clean nitrogen gas; and (2) field measurements should be determined before collecting samples, if possible. A lesser purge volume or other procedures may be modified, for example, when:

- A supply well to be sampled is being pumped continuously or daily at regular intervals and long enough to have removed three casing volumes of water—go directly to monitoring field properties.
- The sample-collection interval is sealed with packers (the interval to be sampled should be purged of three volumes).
- Water-level recovery from drawdown to approximately 90 percent of the original volume in the well cannot be achieved within a reasonable timeframe (not to exceed 24 hours; see the previous discussion on low-yield wells).
- The study will customize the protocol for field-determined properties or constituent analyses to address specific study objectives; however, the routine suite of field-measurement values should be determined.

> **TECHNICAL NOTE:** Target or indicator analytes may be added to the purge criteria to address study objectives. The analysis can be performed onsite using portable analytical equipment or a mobile laboratory. The acceptable variability in analyte measurements to define stabilization and minimum number of readings is defined by the study (ASTM International, 2005).

- One or more field measurement keeps drifting, and sampling at that well cannot be avoided—NFM 6 provides suggestions for poor field-measurement stabilization, including extending the purge time and purge volume. Field personnel must make a decision based on their understanding of study objectives whether to extend purge time. Such decisions should be documented in field notes.
- Use of low-flow purging techniques is a stipulated study requirement: for a detailed description of the low-flow purge technique, refer to ASTM standard procedure D6452-99 (ASTM International, 2005).

TECHNICAL NOTE: Low-flow purging procedures are designed to minimize the volume of purge water and disturbance of the water column and maximize the contribution of formation water from a given interval of interest (Puls and Barcelona, 1996; Unwin and Huis, 1983). Minimizing purge volume is especially useful when regulating authorities mandate containment of purge water.

Low-flow purging is based on the theory that water moving through the well intake is representative of formation water surrounding the intake, and assumes that pumping at a low flow rate isolates the column of standing water so that only formation water is drawn into the intake. The typical flow rates for this method are on the order of 0.1 to 0.5 L/min; however, in formations of coarse-grained materials the flow rate may be as high as 1 L/min (ASTM International, 2005).

Select a low-flow purge-and-sampling technique with caution and with an understanding of aquifer and well hydraulics. The assumption should not be made that water withdrawn using a low-flow procedure represents ambient aquifer water at the targeted (intake) interval (Varljen and others, 2006), because the conductivity of well-bore flow within the specified interval is greater than that of the aquifer (Shapiro, 2002). Even where well-bore flow does not occur, aquifer heterogeneity over the length of the specified interval results in water being drawn preferentially through zones of highest permeability.

STEPS FOR SAMPLING AT WELLS 4.2.4

Develop a systematic agenda well in advance of the field effort that follows the sampling plan and quality-assurance protocols. Offsite preparations in addition to the steps needed to carry out onsite activities need to be included in planning for field work. Review the requirements and recommendations for site inventory (reconnaissance) and site file setup (section 4.2.1) .

Field-trip preparations. Adequate time must be scheduled to plan sampling activities, review data requirements, and make field-trip preparations. Prepare a checklist of equipment and supplies that will be needed, and order what is needed well before the field effort (fig. 4-13). Refer to NFM 2, Section 2.4, for lists of equipment and supplies commonly used for ground-water field activities. Review electronic and paper site files and make sure that they are kept up to date.

Before selecting and implementing purging methods, review table 4-8 to determine how maintaining sample integrity applies to the study and site.

- Consider whether modifications of standard USGS methods might be needed to address issues specific to the field site or program or study objectives. Document any deviation from the standard protocols.
- Review the types of quality-control (QC) samples planned for the study. Certain types of blank samples are required for all USGS studies. Review the most recent analyses of blank samples collected through the equipment to be used for sampling before field work begins.
- Determine if water level and well yield are sufficient to produce a representative sample.
- Decide how to determine or constrain the interval(s) from which the sample should be collected. Consider whether packers will be used and whether screen lengths are sufficiently short or long to meet the sampling objective. Determine the major sources of flow contribution to the well, if sampling in fractured or anisotropic formation materials.

Before leaving for the field site, review reconnaissance notes from the site inventory (table 4-6), and determine the number and types of environmental and QC samples to be collected (Appendix A4-C).

- Prepare the field forms that will be needed (for example, water-level, purging, field-measurement, analytical services request, and chain-of-custody forms). Fill out as much information as possible, including the equipment to be used and numbers and types of samples to be collected.
- Check equipment requirements (NFM 2). When assembling the equipment, test that equipment is in good working condition. Take backup equipment, as appropriate.
  - **Organic-compound samples.** Use fluorocarbon polymer (Teflon), glass, or metal for equipment components that will be in contact with samples to be analyzed for organic compounds. **Exception:** if collecting CFC samples, do not use Teflon sampler components or Teflon tubing (NFM 5).
  - **Inorganic-constituent samples.** Use fluorocarbon polymer or other relatively inert and uncolored plastics or glass for any equipment components that will be in contact with samples to be analyzed for inorganic constituents. Do not use metal or rubber components for trace-element sampling. Stainless-steel sheathed pumps are generally acceptable, but can leach low concentrations of chromium, molybdenum, nickel, and vanadium to the sample. **Collect an equipment blank to be analyzed before sampling begins, to demonstrate the acceptability of the data to be collected.**
- Set up a clean workspace (usually in the water-quality field vehicle) and the sample-processing and -preservation chambers. Place the filter unit and other necessary supplies for sample collection and processing into the processing chamber. **The generator and gas tanks must not be stored or transported in the water-quality field vehicle.**

Plan ahead. Take adequate time for site recon, and to prepare sampling plans, order supplies, test equipment, and get the training needed.

✓	Checklist for ground-water site setup and well-sampling preparations[1]
	Antibacksiphon device (one-way or check valve)
	Chemical reagents (for sample preservation and field analyses) and ice
	Deionized water and blank water
	Disposable, powderless, laboratory-grade gloves
	Equipment cleaning, decontamination, and disinfectant supplies
	Field forms (for example, ground-water-quality, water-level, and chain-of-custody forms) - electronic or paper; indelible ballpoint pen (black or blue ink)
	Field manual, sampling and quality-control plan(s)
	Filtration units and supplies
	Flow-regulating valve (needle valve or pinch clamps)
	Flow-splitting valve(s) for manifold system
	Flowthrough cell or chamber and field-measurement instrument(s) (single parameter or multiparameter); standard and buffer solutions; Kimwipes (see NFM 6)
	Keys (for locked facilities)
	Microbiota sampling supplies (see NFM 7)
	Photoionization detector (PID or sniffer)
	Sample processing and preservation chambers in which samples are bottled and treated, respectively, and associated supplies
	Safety equipment
	Sample containers (precleaned)
	Sampling device(s) (precleaned, portable equipment or other, as appropriate) and power supply (if needed); spare batteries
	Sample tubing (precleaned, several lengths)
	Shipping containers and supplies
	Stopwatch and calibrated bucket to measure pumping rate
	Tarp or plastic sheeting to place around well
	Threaded fittings, male/female, such as hose-type connectors (precleaned)
	Tools (such as wrenches to remove well cap)
	Tubing to direct waste discharge offsite or into sample container
	Water-level measurement equipment

[1]See NFM 2.4 for more detailed examples of equipment and supply checklists for sampling.

Figure 4-13. Example of checklist of equipment and supplies to prepare for sampling ground water at wells.

Steps for sampling. The standard USGS procedure for collecting ground-water samples consists of the following six basic steps and the activities needed to carry them out. The procedures needed for supply wells differ somewhat from those used for monitor wells. Steps 1 through 4 are detailed in this section. Steps 5 and 6 are described in NFM 5 ("Processing of Water Samples") and NFM 3 ("Cleaning of Equipment for Water Sampling"), respectively.

Step 1. Implement safety precautions and site preparations

Act with common sense. Be aware of existing and impending environmental conditions and hazards. Field personnel must be familiar with the guidance and protocols provided in NFM 9, "Safety in Field Activities." Organized and orderly procedures for setting up a site for sampling should be routine and helps to prevent mistakes that could compromise personnel safety as well as sample integrity.

Step 2. Measure water level

Procedures for water-level measurement can differ for supply wells and monitor wells. Detailed procedures for various methods of measuring water levels are documented by the U.S. Geological Survey (1980, p. 2-8), and additional information can be obtained from the USGS Office of Ground Water (http://water.usgs.gov/ogw). Refer to Appendix A4-B for a summary of water-level-measurement methods.

- Procedures and equipment for water-level measurement can differ, depending on the type, construction, and design of a well.
- Clean well tapes after each use at a well as described in NFM 3.3.8. Document in field notes if oil is floating on the water table. Review equipment-cleaning and sample-collection strategies and revise as needed if oil is present, to prevent contamination of samples. A dual-phase sonde can be used to determine the thickness of the oil layer, as well as the depth to water.
- Record discrete water-level measurements on field forms and in GWSI (USGS Office of Water Quality Technical Memorandum 2006.01).

Step 3. Purge the well and monitor field measurements

As discussed in Section 4.2.3, purging the well of standing water is generally required to ensure that the sample water will be withdrawn directly from the aquifer. Exceptions to the well-purging protocol may apply more commonly to water-supply wells, although exceptions for some monitor wells also have been described in the previous section. Regardless of the purge procedure followed, enough water must be withdrawn from the well to field rinse sampling equipment and to make measurements of field properties (field measurements). Purging and field-measurement information must be recorded, either on electronic or paper field forms (fig. 4-12). Specific guidance for use of field-measurement instruments is described in detail in NFM 6.

Step 4. Withdraw the sample

As a rule, pumping is the preferred method for withdrawal of groundwater samples. In this case, purging and sample withdrawal form a continuous process. Field measurements are monitored during purging with sample collection following immediately after final field measurements have been recorded. Equipment is selected that channels flow in-line to a field-measurement chamber and then, without stopping, to a sample collection/processing chamber; the sample is never exposed to the atmosphere during this process (fig. 4-10).

Depending on field conditions and study objectives, samples may be withdrawn using a thief-type sampler. Lower and raise the sampler smoothly at a constant rate, keeping the suspension line clean and off the ground. A bailer or other thief-type sampler generally is not recommended for trace-element or volatile organic compound (VOC) sampling. Bailing can mobilize particulates and, unless designed for VOC sampling, can allow VOCs to escape.

- Measurements at a monitoring well
  - The standard purging procedure usually is appropriate (section 4.2.3.A). Exceptions to the standard purging procedure are described in section 4.2.3.B.
  - Either a downhole or a flowthrough-chamber system can be used for field measurements (NFM 6). If samples will be collected, use the flowthrough chamber instead of the downhole system in order to avoid bias of chemical analyses from sample contact with downhole instruments.

- Measurements at a supply well
  - The standard purging procedure may not be appropriate (see section 4.2.3.B).
  - Identify well-construction materials and any equipment permanently installed in the well (such as a pump) that can affect the logistics and quality of the field measurement or sample.
  - Use a flowthrough-chamber type of field-measurement system (NFM 6).
  - Connect the field-measurement system to the wellhead at a point before the sample would pass through holding tanks, backflow pressure tanks, flow meters, or chemical treatment systems.

If more than one well will be sampled during a field trip, each site and (or) a field vehicle must be set up for onsite cleaning of the sampling equipment. Field personnel should design the most efficient field-cleaning system, appropriate for the sites to be sampled and in accordance with the equipment-cleaning guidelines described in NFM 3.

Step 5. Process the sample

Sample processing involves, in part, sample filtration, sample collection into appropriate containers, and sample preservation. Standard USGS procedures for sample processing are described in general and according to analyte type in NFM 5.

Step 6. Clean the equipment

Standard USGS procedures for cleaning (or decontamination) and QC of specific types of equipment used for collecting and processing organic and inorganic analytes are detailed in NFM 3. Field personnel should design the most efficient field-cleaning system, appropriate for the sites to be sampled and in accordance with wastewater disposal regulations.

Practice safe sampling.

Supply Wells 4.2.4.A

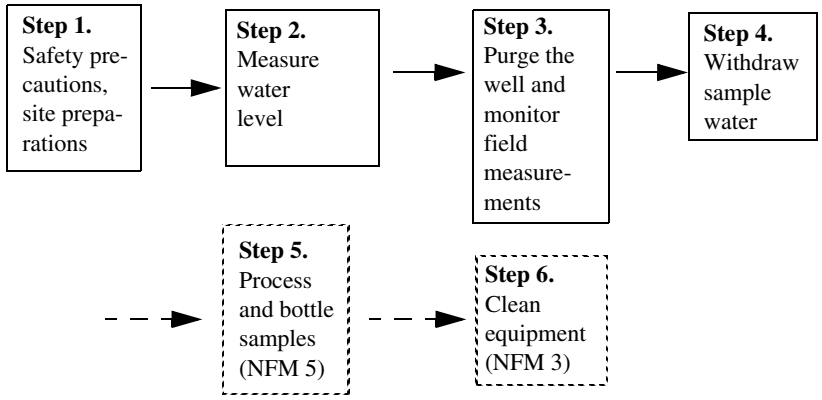
Collection of samples from water-supply wells with permanently installed pumps requires specific considerations, preparations, and precautions. Refer to NFM 9 for safety precautions. Field personnel should be aware of the potential sources of contamination to samples withdrawn from supply wells (table 4-10).

- Do not sample the well if it is not possible to bypass any holding tank or chemical treatment system.
- Document all field observations and any deviations from standard sampling procedures.
- Obtain permission for access to and collection of samples and data from the well.

Table 4-10. Advantages and disadvantages of collecting water samples from supply wells with permanently installed pumps

Advantages
• Cost of well and pump installation is not a factor. • Samples from domestic and municipal wells (for studies of the quality of potable water supplies) are collected directly from the resource being studied. • Pumps are dedicated to the site; therefore, - cross-contamination of other wells from pumping equipment is not a problem, and - field time and effort otherwise expended in operating and cleaning portable pumps can be allocated to other tasks. • In-service supply wells generally require a minimal amount of purging at the time of sampling.
Disadvantages
• The well and the open or screened intervals might not isolate the aquifer zone where water-quality information is needed. • Materials of well and pump construction may affect concentrations of the analytes targeted for study. • Pumps with high capacities can alter the water chemistry of a sample if the pump is lubricated with oil. The water chemistry of a sample also can be altered by aeration and degassing caused by high-velocity pumping, suction lift, and cavitation. • Access for water-level measurements might be unavailable; or, access might be indirect (through an air line), thus yielding less accurate measurements.

Steps for sampling from water-supply wells



Ensure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies. Implement good field practices and *CH/DH* techniques, as applicable (duties typically performed by Clean Hands (*CH*) and Dirty Hands (*DH*) are indicated in the steps that follow). Check that you have the correct site and well folders, and a document (preferably signed) granting site access and well sampling and purging permission.

Step 1. Supply-well sampling: Safety and site preparations.

a. Upon arrival, set out safety equipment such as traffic cones and signs, as needed. Park vehicle in a position to prevent sample contamination from vehicle and traffic emissions and the prevailing wind.

   - Check the well identification number and compare it with the number in the well file and in field notes (section 4.2.1).
   - Assign *CH/DH* tasks.

b. Describe well and site conditions in field notes and on field forms, as appropriate (*DH*).

c. Check site for hazardous conditions (NFM 9) (*DH*).

   - Test for toxic fumes if the well is in an enclosed structure or if there is reason to suspect the presence of organic vapors.
   - Examine the area for evidence of animal infestation and other potential safety hazards.

d. Prepare an area to be used for field cleaning of equipment *(DH)*.

e. Set up equipment and instruments for field measurements and ground-water withdrawl *(DH)*.

- Calibrate field-measurement instruments (*DH*). Refer to NFM 6 for calibration information and instructions.
- Wearing disposable gloves, set up the sample-processing and sample-preservation chambers (usually in the water-quality field vehicle). *Change gloves*. Place the filter unit and other supplies that will be needed for the first sample into their respective chambers *(CH)*.

f. Spread clean plastic sheeting (polypropylene tarp, for example) on the ground around the well to keep sampling equipment, the well tape, and sample tubing off of the ground. Prepare area to be used for field cleaning of equipment (*DH*). Take care not to trample on the sheeting.

g. Determine the location and method of tubing hookup to the well. Connect sample tubing as close as possible to the wellhead *(DH)*.

i. There must be no water-storage tanks, holding or pressurization tanks, or chemical disinfection or water-softening systems connected in-line between the pump and tap/faucet to which sample tubing will be connected. Obtain written permission to install a tap if it is necessary for bypassing a holding tank or treatment system.

ii. Select a faucet without an aerator or obtain written permission to remove the aerator (replace it after sampling). Use connectors and sample tubing that will not contaminate the sample with respect to target analytes.

- Use only precleaned sample-contacting connectors and tubing.
- Check that you have the correct size and configuration of connector fittings, as compatibility varies amont types of plumbing.
- At highly contaminated sites, sample-contacting equipment either should be dedicated for that site or should be disposable.

iii. Connect a short length of sample tubing (2 to 3 feet) between the tap/faucet fitting and the antibacksiphon valve *(DH)*.

iv. Connect sample tubing from the antibacksiphon valve to the manifold; and from manifold to theflowthrough chamber, the sample-processing chamber, and the waste outlet.

- Select transparent, nonporous sample tubing and tubing to the flowthrough chamber for field measurements to be able to check for bubbles or sediment entrained in the sample flow. Sample tubing must be clean and of the appropriate material with respect to study objectives; flowthrough-chamber tubing can be of any material if used only in connection with field measurements. Keep the discharge end of the sample tubing sealed until use.
- Tubing used solely to discharge purge water to waste can be of any material (garden hose, for example), but must be long enough to transport wastewater away from the work area.

Step 2. Measure water level *(DH)*.

Procedures and equipment for water-level measurement depend on well type and construction and the presence of nonaqueous liquid phases. Important considerations and method limitations are described in Appendix A4-B.

a. Put on gloves if chalking a steel tape. Using a weighted steel or electric tape in a nonpumping well, measure water level to the nearest 0.01 ft (for wells <200 ft to water), starting at the permanent measuring (reference) point. Repeat the measurement until precision is within 0.02 ft (U.S. Geological Survey, 1980). At wells deeper than 200 ft, calculate the compensation factor to account for streching of the tape.

- Do not allow the well tape to contact the ground before inserting it into the well.
- Care must be taken not to entangle the well tape in the pump discharge pipe or intake.
- Do not use lead weights; use stainless steel or other noncontaminating material. An unweighted tape might be necessary if the weight cannot fit past the pump apparatus.
- At some supply wells, the water level only can be estimated using the less accurate air-line method. As a last resort if no water-level measurement can be made, use the measurement recorded on the driller's well log in order to calculate an estimated purge volume.

b. Water-level measurements must be recorded on field form(s) and in GWSI forms. On the field form, note any deviations from standard water-level measuring procedures. It is useful also to record water level in QWDATA (USGS Office of Water Quality Technical Memorandum 2006.01).

c. Clean the tape after each use to avoid cross-contamination of wells (see NFM 3.3.8).

Step 3. Purge the well and monitor field measurements *(DH).*

a. Calculate or estimate the well volume (the depth to the bottom of the well and the inside casing diameter must be known):

$$\mathbf{V = 0.0408 \times H D^2}$$

where,

V is volume, in gallons
H is height of water column
$\mathbf{D^2}$ is the inside well diameter squared, in inches.

b. Begin pumping to purge the well according to study objectives. Discharge the initial well water through the waste line until sediment is cleared from the flow.

- Supply-well pumps commonly are either on or off, with no variable-speed capability. To regulate the flow, use a manifold with a needle valve, if possible.
- Open any additional valves or taps/faucets to ensure that the pump will operate continuously and reduce the possibility of backflow stored in ancillary plumbing lines; keep these open throughout purging and sample withdrawal.
- The pump should produce a smooth, solid stream of water with no air or gas bubbles and without pump cavitation during field measurements and sample withdrawal.
- **Do not halt or suddenly change the pumping or flow rate during the final phase of purging or while sampling.**
- Contain and dispose purge waters according to Federal, State, or local regulations. Do not discharge purge water from one well into another without proper authorization. Discharge purge water far enough away from the well or well cluster so as not to enter or affect water quality in the well, and to prevent muddy and slippery work conditions.

TECHNICAL NOTE: A supply well that is in regular service and that is pumping continuously or that has been operating long enough to have removed three casing volumes of water within several hours of sample collection does not require removal of three well volumes. Before withdrawing sample in this case, flush sample water through the tubing and monitor measurements.

- Field personnel could request a site operator or homeowner to start pumping the well before personnel arrive onsite.
- If the pump has been turned off but three well volumes were removed within 24 hours before sampling and samples only will be analyzed for nutrient or major-ion concentrations, additional purging is not necessary.
- Purging immediately before sampling is recommended if samples for trace elements and volatile organic compounds will be collected.

c. When the water runs clear, divert flow to the flowthrough chamber for field measurements (unless a downhole instrument is in use). Once the flow is constant (see instructions in step b), begin monitoring field measurements (refer to NFM 6 for detailed instructions); in addition, record the number of well volumes being discharged, the start and end times of purging, the pumping rate, water level, and location of the pump intake (fig. 4-12).

- To control the flow rate from the maniford, use a flow-regulating valve, such as a faucet or needle valve.
- Keep three-way valves either completely open or closed (partially open three-way valves can create a vacuum or air bubbles, and can draw in contaminating water). **Do not use a two- or three-way valve to regulate the flow.**
- **Recommended:** To ensure a representative sample, maintain the water level in the well above the screened or open interval.

d. As the final well volume (commonly the third well volume) is purged, calculate the final pumping rate and record on field forms at least five sets of field measurements determined at regularly spaced intervals while pumping at this rate. Referring to the instructions provided in NFM 6, check the field-measurement data against the measurement-stability criteria (fig. 4-12).

- To record the pumping rate of water flowing through more than one conduit, sum the rate of flow through each conduit.
- Routine field measurements for USGS studies include water temperature, conductivity, pH, dissolved oxygen, and turbidity.
- The final pumping rate, used during the final five sets of field measurements, also should be used during sample collection.

Step 4. Withdraw ground water (*CH*).

Maintain the same rate of pumping throughout sample withdrawal and collection as the rate used during withdrawal of the final purge volume.

a. Put on disposable gloves. Check that the sample tubing is properly secured within the sample-processing chamber.

b. Direct sample flow through the sample tubing to the processing chamber and channel two tubing volumes of the water to waste.

- **If samples will be collected for organic carbon analysis through equipment and tubing that previously was methanol-rinsed, flush at least five tubing volumes of sample water through the tubing (or collect the organic-carbon sample using a separate, non-methanol-rinsed sampler) before proceeding to Step 5.**
- Use the needle valve at the manifold to adjust sample flow as appropriate for the target analysis. Depending on the site-specific logistics, a second needle valve can be installed after the outlet end of the manifold and close to the sample-processing chamber. Avoid splashing or pooling water inside the chamber while processing sample and filling sample bottles.

Flow should be constant and uninterrupted while purging and sampling.

Step 5. Collect and process the sample → Refer to NFM 5, *Processing of Water Samples*, for instructions regarding the field rinse of sample bottles, sample filtration, and the collection and preservation of wholewater and filtered samples.

RULE OF THUMB: The rate of flow for filling sample bottles should not exceed

- 500 mL/min for bottles 250 mL or greater in volume,

or

- 150 mL/min for 40-mL VOC vials.

Step 6. Clean equipment→ Refer to NFM 3, *Cleaning of Equipment for Water Sampling*. Sampling equipment must be cleaned as instructed in NFM 3 before leaving the field site.

At sites at which the level of contamination is suspected or known to exceed drinking-water standards or health advisories, use sample tubing that is disposable or dedicated to that site in order to minimize the risk of cross contamination between wells. Wear gloves while cleaning and handling sampling equipment.

- Rinse sampling equipment with deionized water before the equipment dries.
- Clean equipment to be used at another well during the same field trip after rinsing it and before moving to the next site.
- Collect field blanks to assess equipment-cleaning procedures directly after the sampling equipment has been cleaned in the field or after moving to the next site and before sampling, as dictated by the data-quality requirements of the study (section 4.3).

Monitor Wells 4.2.4.B

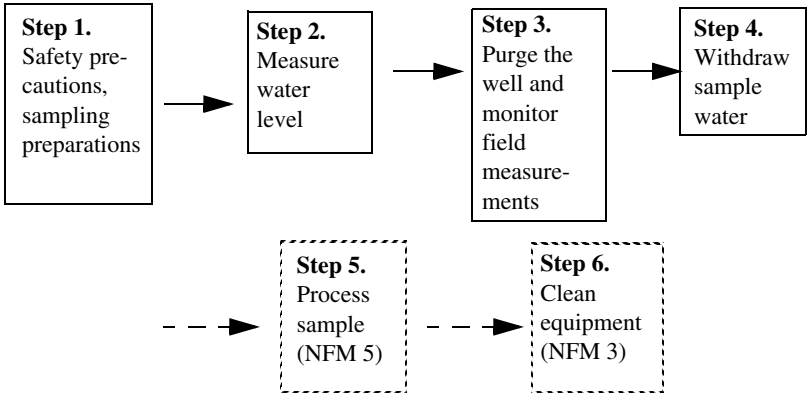
When selecting purging equipment for monitor wells, site conditions need to be considered. In general, a portable, submersible nonaerating pump that also will be used for sampling is recommended. The specific equipment and well-purging method selected, however, can depend on depth to water, length of the open interval, well construction, and site contamination. For example, to reduce the volume and time required for purging, especially in deep wells or in wells for which purge water is contaminated and must be contained, inflatable packers can be used to isolate the aquifer interval of interest.

In addition:

- When the water table is deeper than 250 ft and (or) a large volume of water must be purged, a dual-pump system can be used: position, in series, a submersible pump downhole and a centrifugal pump at the surface.
  - Water discharging from the slow-pumping submersible pump is used for field measurements and sample collection, whereas the centrifugal pump removes the required volume of purge water at a faster rate. Changes in pumping rate might increase turbidity.
  - Dissolved-oxygen concentration, Eh, or turbidity should not be measured while using a dual-pumping system. Record measurements while operating only the submersible pump.
- When the water table is less than 25 to 30 ft from land surface, a peristaltic pump can be used for small-diameter wells. A peristaltic pump or other comparable suction device can affect dissolved-oxygen concentrations and Eh measurements unless low gaseous-diffusion tubing such as Tygon® is used (NFM 2).
- An inflatable packer sometimes is set above and below the screened/open interval, with a pump intake located within the screened/open interval.
  - Packers sometimes fail to form a complete seal between aquifer intervals, and should be used with pressure transducers located directly above and below the isolated interval to indicate whether water is leaking past the packers or short circuiting in the aquifer.
  - The materials of which the packer is made also might affect sample chemistry by leaching or sorbing target analytes.

- A bailer is not recommended for purging. The plunging action of the bailer can release orstir up particulates that are not ambient in groundwater flow, resulting in biased measurements and analyses.

Steps for sampling at monitoring wells



Step 1. Monitor-well sampling: safety and site preparations.

a. Upon arrival, set out safety equipment such as traffic cones and signs, as needed. Park vehicle in a position to prevent sample contamination from vehicle and traffic emissions and prevailing wind.

   - Check well-identification number (this should be indelibly marked on the well casing) and compare it with the well file and field notes (section 4.2.1).
   - Assign *CH/DH* tasks.
   - If a gasoline-powered generator is used, locate it downwind of sample collection or elsewhere to avoid sample contamination from fumes.
   - Prepare an area to be used for field cleaning of equipment (*DH*)

b. Describe well and site conditions on field forms, as appropriate (*DH*).

c. Check site for hazardous conditions (NFM 9) (*DH*).

   - Test for toxic fumes if the well is in an enclosed structure or if there is reason to suspect the presence of organic vapors.
   - Examine the area for evidence of animal infestation and other potential safety hazards.

d. Spread a clean plastic sheeting (polypropylene tarp, for example) on the ground around the well tokeep sampling equipment, the well tape, and sample tubing clean (*DH*). Take care not to trample on the sheeting.

e. Set up equipment and instruments for field measurements and ground-water withdrawal (*DH*). Locate a power supply source, if needed.

- Set up the pump and generator (if needed) in a location to avoid sample contamination from generator fumes.
- Calibrate field-measurement instruments (*DH*). (Refer to NFM 6 for calibration information and instructions.)
- Wearing disposable gloves, set up the sample-processing and -preservation chambers (usually in the water-quality field vehicle). Keep sample tubing as short as is practical and shaded from direct sunlight (to minimize changes in the temperature of the sample). *Change gloves.* Place the filter unit and other supplies that will be needed for the first sample into their respective chambers *(CH).*

f. Remove the well cap. Verify clear access downhole by lowering a section of blank pipe through the depth interval to be sampled and raising it slowly. **Take care not to drop the pipe or otherwise stir up particulates in the process of lowering and raising the pipe** (*DH*)**.**

i. Connect the antibacksiphon valve in-line between pump and manifold (the antibacksiphon valve is a standard component of some submersible pumps).

ii. Use connectors and sample tubing that will not contaminate the sample with respect to target analytes.

- Use only precleaned sample-contacting connectors and tubing.
- At contaminated sites, sample-contacting equipment either should be dedicated for that site or should be disposable.

iii. From the manifold, connect the appropriate tubing to the flowthrough chamber, the sample-processing chamber, and the waste outlet.

- Select transparent, nonporous sample tubing and tubing to the flowthrough chamber for field measurements to be able to check for bubbles or sediment entrained in the sample flow.
- Tubing that transfers sample to the processing chamber must be clean and of noncontaminating material. Keep the discharge end of the sample tubing sealed until use.
- Flowthrough-chamber tubing can be of any material if used only in connection with field measurements.
- Tubing used solely to discharge purged water to waste can be of any material (garden hose, for example), but must be long enough to transport wastewater away from the work area.

Step 2. Measure water level (*DH*).

Procedures and equipment for water-level measurement depend on well type and construction and the presence of nonaqueous liquid phases. Important considerations and method limitations are described in Appendix A4-B-3, 4, and 5. Each well must have a designated measuring point that is indicated permanently on the well (Appendix A4-B-1).

a. Put on gloves before chalking a steel tape. Using a weighted steel or electric tape in a nonpumping well, record two or more consecutive water-level measurements to the nearest 0.01 ft (for wells of < 200 ft to water), starting at the permanent measuring (reference) point. Repeat the measurement until precision is within 0.02 ft (U.S. Geological Survey, 1980).

   - Do not allow the well tape to contact the ground before inserting it into the well. After measuring the water level, clean the tape (NFM 3.3.8) to avoid cross contaminating the next well.
   - Do not use lead weights, but weight the tape with stainless steel or another relatively noncontaminating material.
   - At wells deeper than 200 ft, calculate the compensation factor to account for stretching of the tape.

b. Record water-level measurement on field forms and in GWSI (USGS Office of Water Quality Technical Memorandum No. 2006.01). Note any deviations from standard water-level measuring procedures on field forms (fig. 4-12). It is useful also to record water-level data into QWDATA.

c. Set up a system to measure water levels throughout purging. Electrical tapes or submersible pressure transducers are recommended—repeated measurements with a steel tape can be cumbersome and can generate turbidity in the water column. If a packer system is used, installpressure transducers above and below the packer.

d. Clean the tape after each use to avoid cross contamination of wells (NFM 3.3.8).

RULE OF THUMB: The initial water-column height should be greater than 4 ft plus the length of the sampling device.

Step 3. Purge the well and monitor field measurements (*DH*)**.**

Purge monitor wells, preferably using a variable-speed pump (see the TECHNICAL NOTES listed at the end of step 6). Operate the pump in a manner that avoids or minimizes turbidity. **Do not use a bailer for purging** unless the well characteristics or other constraints exclude alternatives and the turbidity during and afterbailing is at the background level. **Recommendation:** Measure water levels throughout purging to document drawdown and the location of the water level with respect to the screened/open interval and the pump intake.

- Use the same pumping equipment for purging that will be used to collect samples, if possible.
- **Avoid refueling or changing equipment, and do not stop the pump during the final phase of purging and sample collection.** Be aware of study objectives and potential sources of contamination. For example, avoid fueling the generator on the same day that samples are collected for VOC analysis. Do not transport a generator or gas tanks in the water-quality field vehicle.
- Adjust the flow rate at the pump if using a variable-speed pump. If a constant-speed pump is used, adjust the flow rate using a needle valve.
  - — Pump at a rate that does not substantially lower the water level. Ideally, well yield should be sufficient so that the water level is maintained above the screened or open interval.
  - — Flow should not be halted or the flow rate changed suddenly during the final phases of purging and sampling.

a. Calculate the well volume. For a cased well, the depth to the bottom of the well and the inside casing diameter must be known:

V=0.0408 x HD2

where,
V is volume, in gallons
H is height of water column
D^2 is the inside well diameter squared, in inches

Note that for a cased well, the volume of water stored within the annular space between the well screen and borehole well also should be evacuated at least once.

b. Lower a submersible pump, followed by a water-level sensor, to the desired location of the pump intake. (The pump position is fixed if the monitoring well has a permanently installed sampling system.) Move the equipment slowly and smoothly through the water column to avoid stirring up particulates. The intake can be either lowered continually while purging to the final depth desired or placed immediately at its final position. **Note that the final pump intake position always is at the point of sample collection.**

   - Position the pump intake about 3 ft (about 0.9 m) below static water surface and a minimum distance above the top of the screened/open interval of 7 to 10 times the well diameter (for example, 14 to 20 in. for a 2-in. well diameter), if the sample is to represent the entire screened or open interval of aquifer. The location of the intake might be different if the study objective requires collecting the sample from a point within the screened/open interval or from wells in which packers are installed.
   - Place water-level sensor (electric tapes) a maximum of 1 ft (about 0.3 m) below the water surface.

c. Position the pump intake.

   - **If final intake position is above the screened or open interval, do not exceed 1 ft (about 0.3 m) of drawdown.**
   - **If final intake position is within the screened or open interval, do not exceed 0.5 ft (about 0.15 m) of drawdown.** The final pumping rate should be as slow as necessary to avoid causing turbidity.

d. Start the pump, channeling initial discharge to waste. Discharge the initial well water through the waste line until sediment is cleared from the flow.

   - Gradually increase and (or) adjust the pumping rate to limit drawdown to between 0.5 and 1 ft (about 0.15 to 0.3 m), if possible.
   - **If using a variable-speed pump, adjust the rate of flow at the pump.** If using a constant-speed pump, control the flow rate using a needle valve (fig. 4-10).

- **Do not use a three-way valve or flow-splitting valve to adjust flow rate.** It is necessary to keep the two- or three-way valves either completely open or completely closed (partially open three-way valves can create a vacuum or air bubbles, and can draw in contaminating water).
- **Contain and dispose of purge waters according to Federal, State, or local regulations.** Do not discharge purge water from one well into another without proper authorization. Discharge purge water far enough away from the well or well cluster so as not to enter or affect water quality in the well, and to prevent muddy and slippery work conditions.

e. When the water runs clear, divert flow through the manifold to the flowthrough chamber (unless a downhole instrument is being used for field measurements.

- **The flow should be a smooth, solid stream of water with no air or gas bubbles and without pump cavitation** during field measurements and sample withdrawal. Adjust the pumping rate to eliminate air or gas bubbles or cavitation, but do not halt or suddenly change the flow rate.
- **Record the start time of purging, the pumping rate(s), water level(s), and final location of the pump intake** (fig. 4-12). If water is flowing through more than one conduit (such as valve and manifold lines), calculate the flow rate by summing the flow rate through each conduit.
- **Begin monitoring field measurements** (refer to NFM 6 for instructions) once flow to field-measurement instruments is constant (see instructions above).
- **Do not move the pump or change the rate of pumping during field measurements or sample collection after setting the intake at its final depth location.**

f. **Purge a minimum of three well volumes or the purge volume dictated by study objectives.** (Check exceptions to the three-well-volume procedure described in section 4.2.3.B).

- Record water levels and field measurements at regular time intervals (fig. 4-12; NFM 6). Routine field measurements for USGS studies include water temperature, conductivity, pH, dissolved-oxygen concentration, and turbidity. Check for special instructions regarding field-measurement or field-analysis requirements based on study objectives.
- As the final well volume (commonly the third well volume) is purged, check the field-measurement data against the measurement-stability criteria (fig. 4-12). Record at least five sets of field measurements determined at regularly spaced intervals, which indicate that measurement values are relatively constant (have "stabilized") or that stabilization cannot be achieved in the given time interval (NFM 6).

Step 4. Withdraw the sample (*CH*).

Pumped samples—

Maintain the same rate of pumping throughout sample collection as the rate used during withdrawal of the final purge volume.

a. Put on disposable gloves. Check that the sample tubing is properly secured within the sample-processing chamber.

b. Direct sample flow through the sample tubing to the processing chamber and channel two tubing volumes of the water to waste. Use the needle valve at the manifold (fig. 4-10) to adjust sample flow as appropriate for the target analysis.

- Depending on the site-specific logistics, a second needle valve can be installed after the outlet end of the manifold and close to the sample-processing chamber.
- The flow should be smooth and non-turbulent. Avoid splashing or pooling water inside the chamber while processing sample and filling sample bottles.
- **If samples will be collected for organic carbon analysis through equipment and tubing that previously was methanol-rinsed, flush at least five tubing volumes of sample water through the tubing (or collect the organic-carbon sample using a separate, non-methanol-rinsed sampler) before proceeding to step 5.**

Remember, flow should be constant and uninterrupted while purging and sampling.

RULE OF THUMB: When using a pump, the rate of flow for filling sample bottles should not exceed

- 500 mL/min for bottles 250 mL or greater in volume,

or

- 150 mL/min for 40-mL VOC vials.

Nonpumped samples—

a. Field rinse the sampler (typically, a bailer) and sampler emptying device (and compositing device, if used) three times before collecting the sample. Deploy the sampler so as to minimize disturbance to the water column and aquifer materials.

   i. Use a reel to keep sampler line clean and untangled.

   ii. Lower sampler smoothly, entering water with as little disturbance as possible.

   iii. Allow sampler to fill, then withdraw sampler smoothly.

   iv. Shake water in sampler vigorously to rinse all interior surfaces.

   v. Attach sample-delivery tube or bottom-emptying device to sampler and drain the rinse water through the sampler.

   vi. Repeat rinse procedure at least twice.

b. Repeat steps (a) i-iii to withdraw ground water for the sample.

   TECHNICAL NOTE: When a device is lowered and raised through the water column, the disturbance to the water column can result in outgassing or degassing of ambient dissolved gases and an increase in concentrations of suspended particulates. Repeated movement of the device through the water column exacerbates these effects and can result in substantial modification of the ambient water composition and chemistry.

c. Set up the bailer in an enclosed or protected space.

Step 5. Process/collect the sample →Refer to NFM 5, *Processing of Water Samples*, for instructions regarding the field rinse of sample bottles, sample filtration, and the collection and preservation of whole-water and filtered samples.

Step 6. Clean equipment →Refer to NFM 3, *Cleaning of Equipment for Water Sampling*. Sampling equipment must be cleaned as instructed in NFM 3 before leaving the field site.

At contaminated sites, use sample tubing that is disposable or dedicated to that site in order to minimize the risk of cross contamination between wells. Wear gloves while cleaning and handling sampling equipment.

- Rinse sampling equipment with deionized water before the equipment dries.
- Clean equipment to be used at another well during the same field trip after rinsing it and before moving to the next site.
- Collect field blanks to assess equipment-cleaning procedures directly after the sampling equipment has been cleaned in the field or after moving to the next site and before sampling, as dictated by the data-quality requirements of the study (section 4.3).

QUALITY CONTROL 4.3

Collection and analysis of quality-control (QC) samples are mandated components of USGS water-quality field studies. The goal of QC sampling is to identify, quantify, and document bias and variability in data that result from the collection, processing, shipping, and handling of samples. **The bias and variability associated with environmental data must be known for the data to be interpreted properly and be scientifically defensible** (Horowitz and others, 1994; Koterba and others, 1995; Mueller and others, 1997). This section addresses quality control for aqueous samples to be analyzed for inorganic and organic analytes (see NFM 7 for quality control of microbiological sampling and analysis). Quality-assurance terminology in general, and quality-control terminology in particular, can differ within and among organizations; see "*Conversion Factors, Selected Terms, and Abbreviations*" for a glossary of definitions as used in this report.

Bias: systematic, directional error measured by the use of blank, spike, or reference-material samples.

Variability: random error measured by the use of environmental or QC sample replicates.

The types of QC samples to be collected and their temporal and spatial frequency and distribution depend on study objectives, data-quality requirements, site conditions, and management or regulatory policy. QC sampling is part of an overall strategy for quality assurance of the data collected and generally is described in the Quality Assurance Plan (QAP) or Sampling and Analysis Plan (SAP). QC samples of various types can be used to measure environmental data quality (for example, assign error bars to measurement sets), identify data-quality problems, and locate the sources or causes of data-quality problems. **Field personnel need to understand the purpose for each QC sample type (Appendix A4-C) and how the resulting QC data will be used so they can account for and accommodate QC needs that arise from unforeseen site conditions.**

- **Basic QC samples** are collected routinely to document the quality of the environmental data and to identify whether data-quality problems exist. They are designed to measure most sources of error that affect environmental samples. Basic QC samples include field blanks, field matrix spikes, and field replicates.
- **Topical QC samples** address specific QC needs or topics and commonly are designed to (1) help determine when sampling should commence; (2) locate the cause and source of data-quality problems; and (3) assess comparability among field methods. Topical QC samples include all the QC sample types not specifically designated "basic" QC samples.

Good science requires consideration of measurement errors – such as bias and variability – in data analysis.

The field team or person collecting samples should be involved in assessing the analytical results of the QC samples collected, because only they have all of the information about the site conditions and procedures that were followed. This knowledge could be crucial in understanding QC sample results. For any water-quality sampling event, USGS field personnel must:

- Be knowledgeable about and alert to potential sources of contamination (table 4-11). When in doubt, it usually is wisest to collect additional QC samples and decide later whether to have them analyzed.
- Collect field QC samples at approximately the same time as environmental samples are collected, using the same equipment.
- Document in the field log as complete a description of the sampling event as possible. Include how, when, where, and why the QC sample was collected, and observations about site or sampling conditions.
- Implement the prescribed procedures for equipment cleaning and QC sample collection and processing.

- Use chemical preservatives from the same lot number for a given set of environmental and associated QC samples. Record the preservative lot number on field forms and in field notes.
- Store QC data in an electronic database devoted to QC data. For USGS studies, this should be a QC-designated data base within NWIS.

Use Good Field Practices (table 4-2) and Clean Hands/Dirty Hands techniques (table 4-3) when collecting and processing QC samples.

Table 4-11. Common sources of contamination related to field activities

[SPMDs, semi-permeable membrane devices; DIW, deionized/distilled water of ASTM grade one or better; DEET, N,N-diethyl-meta-toluamide (the active ingredient commonly used in insect repellents)]

Contaminant source type	Examples
Sampling environment	Airborne particulates; precipitation; dust, soil, solid particles; fumes from engine exhaust, chemical preservatives, upwind industrial emissions.
Sample-collection equipment	Pumps, isokinetic samplers, bailers, sample tubing, SPMDs.
Sample-processing equipment	Filtration devices, churn splitter, cone splitter, bottles, water (DIW, tap, blank).
Sample-cleaning processes	Cleaning equipment (basins, brushes); carryover from cleaning solutions or tainted water; methanol carryover; insufficient decontamination or rinsing.
Transport and shipping	Field vehicles; coolers or other shipping containers; improperly closed or protected sample bottles.
Storage	Warehouse; refrigerator; field vehicle; office laboratory; office storage space.
Personnel	Dirty hands; sweat; sunscreen; DEET; nicotine, caffeine, and alcohol (breath); dirty gloves; gloved or ungloved contact with the sample to be analyzed; shedding clothing; hair and dandruff.

How, when, where, and why a QC sample was collected must be known to understand the sources of error measured.

4.3.1 BLANK SAMPLES

The primary purpose of a blank sample ("blank") is to measure the magnitude of contaminant concentration (for analyte(s) of specific interest) that might have been introduced into the sample as a result of sampling-related activities (table 4-11 and Appendix A4-C). Various types of blanks can be used or customized to identify the source of sample contamination (table 4-12 and Appendix A4-C). Appendix A4-D provides examples for estimating the volume of blank solution needed.

It is necessary to obtain blank water of the quality and type appropriate for the chemical analysis to be performed on the sample. Blank water is strictly defined within the USGS as specially prepared distilled/deionized water (DIW) that is laboratory produced, quality-controlled, and that carries a certificate of analyte concentrations for each grade and lot of water produced. USGS water-quality projects obtain quality-assured blank water through the One-Stop Shopping system of the National Water-Quality Laboratory (NWQL).

- I**norganic-grade blank water (IBW**) is required for blanks that will be analyzed for inorganic constituents (major and minor ions including nutrients, trace elements) and suspended sediments.
- **Pesticide-grade (PBW)** is required for blanks that will be analyzed for pesticide compounds and organic carbon.
- **VOC/Pesticide-grade (VPBW)** has been purged with nitrogen gas (N_2) and is required for blanks that will be analyzed for volatile organic compounds. VPBW is appropriate as a blank sample for analysis of pesticides, organic carbon, and suspended sediments.

Before collecting blank samples, the laboratory certification of concentration for each analyte in the blank water should be compared with the expected concentration in the environmental samples and with the detection limit of the laboratory method to be used for sample analysis**. The laboratory certificate of analysis for each lot of blank water should be kept on file with project records, and the lot number(s) used for each sample should be recorded on field forms.**

Wear clean, powderless, disposable gloves and conform meticulously to other Clean-Hands practices when working with blank solutions.

Table 4-12. Common types of blank samples and the questions they address
[QC, quality control; IBW, inorganic-grade blank water; PBW, pesticide-grade blank water; VPBW, volatile-organic-compound and pesticide-grade blank water]

Type	Targeted Source(s) of Bias[1]
Field blank	Sample-collection, -processing, -transport process ***Basic QC sample****: Was my sample contaminated as a result of field activities and exposure?*
Equipment blank	Sample-collection and processing equipment system ***Topical QC sample***: *Does an initial equipment assessment[2] confirm the suitability of the equipment to provide samples within my data-quality requirements?* ***Topical QC sample***: *Is my equipment-cleaning protocol adequate?*
Sampler blank	Sampling device (for example, the D-95 sampler, Fultz pump, or peristaltic-pump tubing) ***Topical QC sample***: *Is my sampling device the source of contamination?*
Filter blank	Filtration device (for example, the capsule filter, in-line filter holder, aluminum plate filter) ***Topical QC sample***: *Is my filtration device the source of contamination?*
Ambient blank	Exposure to atmospheric outfall or other conditions ***Topical QC sample***: *Was sample exposure to the atmosphere a contaminant source?*
Source-solution blank	The blank water used (for example, IBW, PBW, or VPBW) ***Topical QC sample***: *Was my blank water tainted with respect to my analyte(s) of interest?*

[1]The bias and variability measured includes that from laboratory handling, processing, and analysis of the sample in addition to the targeted source listed.
[2]An equipment blank is required for U.S. Geological Survey investigations to determine the equipment suitability to provide the analyte data needed to meet study objectives.

To prepare for processing blank samples:

1. Label the capped, precleaned sample bottle with the site identification number, laboratory sample designation code (NFM 5), date and time, or affix the proper bar-code label to the sample container, as appropriate. Record this information on field forms.
2. Put on gloves. Place each stock container of the blank solution to be used (IBW, PBW, and VPBW) into a clean plastic bag. If pumping blank water from a standpipe, change gloves and then rinse the precleaned standpipe three times using a small volume of blank solution of the type selected. Keep standpipe covered until use.
3. Change gloves. Place precleaned, labeled sample bottle(s) and the stock of blank solutions to be used into processing chamber (or standpipe).
    - IBW blanks—Discard the deionized water that half fills the precleaned polyethylene sample bottle. Rinse the sample bottle with a small quantity of blank solution and discard rinsate before filling with IBW.
    - PBW or VPBW blanks—Do not prerinse the sample bottle. Use glass bottles or vials as received precleaned from the laboratory.

Do not substitute DIW for IBW.

Pre-Field Blanks 4.3.1.A

The source-solution and initial equipment blanks are common types of blank samples that are collected by the study field team in preparation for environmental sampling. **Collection of an equipment blank is mandated by USGS policy before the sampling phase of the study begins**, to determine if the sample-wetted components of the equipment proposed for use could be a source of contamination by introducing the study's target analytes to a blank or environmental sample. Collection of pre-field equipment blanks is recommended annually, or as appropriate for the sampling schedule of the study.

- **Source-solution blank**. Collect in a designated clean, draft-free area of the office laboratory, such as under a laminar-flow hood or laminar-flow bench. Do not collect the source-solution blank in a fume hood. Submit the sample for analysis along with or after the equipment blank and field-collected samples, depending on study objectives and the data resulting from other blank samples.
- **Equipment blank (pre-field)**. Collect in a designated clean area of the office laboratory at least 4 weeks before using the equipment in the field to allow enough time for sample analysis and review of the resulting data.

A variety of other types of blank samples that are collected in the controlled office-laboratory environment can be designed to test some aspect of sample handling not related to the field environment. Examples of these types of blanks include the refrigerator blank, the shelf blank, and the preservation blank (Appendix A4-C).

4.3.1.B Field Blanks

Field blanks are collected and processed at the field site in the same manner and using the same equipment as the environmental sample(s). Equipment must be cleaned meticulously before field blanks are collected (NFM 3).

- A single field blank is a "basic" QC sample that represents the entire sampling system. The feld blank is collected routinely for basic quality control of the sampling process, rather than identifying the specific source of the contamination. The field blank consists of an aliquot of blank water processed sequentially through each component of the sampling system (fig. 4-14 and Appendix A4-C). The field blank provides a measure of the total contamination (bias) present in the sample.
- To address topical quality-control questions, blanks can be collected onsite that represent components of the sampling system; for example, the sampler blank (surface water), splitter blank, filter blank, or pump or bailer blank (ground water). Such topical field blanks can be used to trace the specific source of contamination.
- When collecting field blanks for inorganic and organic analyses after sampling at a site, use the following sequence and the protocols described in NFM 3 and shown in NFM 3, fig. 3-1 for equipment cleaning.
  1. Clean equipment for inorganic-constituent sampling: detergent → tapwater/DIW → acid, if needed → DIW.
  2. Rinse equipment with IBW at least three times.
  3. Collect the IBW blank sample for analysis of inorganic constituents.
  4. Resume equipment cleaning for organic-compound sampling: methanol, if needed → air-dry exposed surfaces →IBW or PBW, as appropriate. Remove methanol from pumps, tubing, and other equipment, as described in NFM 3.
  5. Rinse equipment at least three times with the appropriate organic-grade blank water (VPBW or PBW).
  6. Collect the VPBW (or PBW) blank sample for analysis of organic compounds.

The process of producing a field blank can be designed to collect simultaneously blanks for each component of the sampling system (fig. 4-14). If laboratory analysis of the analytes being quality controlled is not time dependent, the sequential blank samples representing components of the sampling system, as well as any associated source-solution and ambient blanks, normally can be stored for up to 6 months.

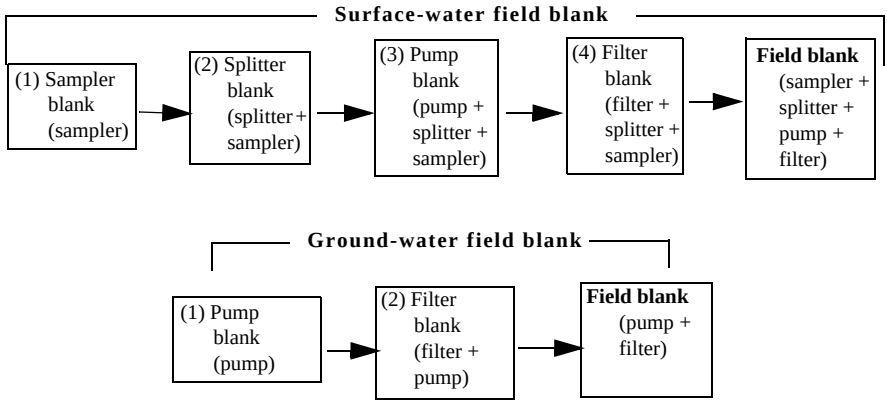
- If the field-blank data indicate constituent concentrations at acceptable levels, then the associated set of sequential blanks can be discarded. (Be sure to use appropriate means for disposing of chemically treated solutions.)
- If laboratory data indicate greater than acceptable concentrations:
  - Submit the source-solution blank, ambient blank(s), and equipment-component blank(s) (the sampler blank, splitter blank, pump blank, and so forth) to the laboratory for analysis.
  - Use the data from equipment-component blank samples to identify the source(s) of contamination detected in the field blank.
- Once the source of contamination has been identified, take the measures needed to mitigate or eliminate the contamination for future sampling efforts.

Prevent contamination of the source-solution and blank sample by capping the respective bottles immediately after decanting the volume of blank solution needed.

EXAMPLE OF FIELD-BLANK SAMPLE COLLECTION

A set of blanks can be generated that is associated with the field blank to help determine which equipment component in the system could be a source of contamination. The **field blank** is the final sample that represents all equipment components of the sampling system. After each blank sample is collected, preserve and store sample as required.

- → **Surface-water field blank: follow steps 1 through 4.** In this example, the equipment used includes a US D-95 sampler, 8-liter (L) churn splitter, peristaltic pump, and filter assembly.
- → **Ground-water field blank: follow steps 1 and 2.** In this example, the equipment used includes a submersible pump and a filter assembly.



Sampler Blank. Using the blank water selected, rinse and then fill the sampler; attach sampler cap and nozzle; pour the required volume through nozzle into sample bottle.

Splitter Blank.[1] Rinse churn splitter with blank water. Pour the blank water remaining in the sampler through the sampler nozzle and into the 8-L churn splitter. Refill sampler, repeat until churn contains 3 to 5 L of blank water. Process the required blank-sample volume through the churn spigot into the splitter-blank bottle. (If a cone splitter is used instead of a churn splitter, the blank sample is processed through the exit port tubes.)

Pump Blank.[1]

- **Surface-water example:** Using the peristaltic pump, thread the intake end of clean tubing into churn splitter through the funnel, and cap the funnel loosely. Insert the discharge end of the pump tubing into a processing chamber and pump blank water through the tubing for an initial rinse, discharging rinse water to waste. After the rinse, pump the required volume of blank water from the churn splitter into the pump-blank bottle.
- **Ground-water example:** Rinse a precleaned, noncontaminating standpipe with blank water and discard rinse water. Place submersible pump into the standpipe and pour in blank water—keep water level above the pump intake. Insert discharge end of pump tubing into a processing chamber. Circulate blank water through pump and tubing to rinse, discharging rinse water to waste. Pump the required volume of blank water from the standpipe into the pump-blank bottle.

Field Blank. The **field blank** in this example is identical to the **filter blank**[1] because the filter assembly is the final component of the equipment system through which the blank is processed. Working in the processing chamber, precondition the filter with blank water (NFM 5).

- **Surface-water example:** Pump the required volume of blank water from the churn splitter through the prerinsed filter assembly into the field-blank bottle.
- **Ground-water example:** Pump the required volume of blank water from the standpipe through the prerinsed filter assembly into the field-blank bottle.

[1]These are special cases of a splitter blank, pump blank, and filter blank, respectively, because the equipment component named is the final component but not the only component contacting the blank sample.

Figure 4-14. Example procedure for collecting a field-blank quality-control sample.

REPLICATE SAMPLES 4.3.2

The primary purpose of replicate samples is to identify and (or) quantify the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or greater multiples—are considered identical or nearly identical in composition and are analyzed for the same chemical properties. Common types of replicates are described below and summarized in Appendix A4-C. Field personnel should be careful to keep detailed notes on exactly how the replicate samples were collected and processed, to help distinguish the sources of variability that affected the samples.

Replicate samples are collected simultaneously or close in time with the associated environmental sample, using identical procedures.

Concurrent Replicates 4.3.2.A

Concurrent replicates are two or more samples of environmental water that are collected simultaneously or at approximately the same time. Concurrent replicates provide basic QC data for surface-water sampling and incorporate, for example, the total variability introduced from collection, processing, and shipping of the sample; the variability inherent in the aqueous system across a short distance in space and time; and the variability inherent in laboratory handling and analysis of the samples.

Depending on study objectives, duplicate samples can be collected concurrently by using two sampling devices of the same type or by filling separate sample-compositing containers using the same sampling device.

The following procedure, adapted from Horowitz and others (1994), is used at surface-water sites to fill two or more sample-compositing containers (usually churn splitters):

1. Complete equipment field-rinsing procedures (surface water, section 4.1.3; ground water, section 4.2.2.C), using two clean churn splitters. Label the sample bottles appropriately. Change gloves.
2. At the first vertical of an EWI or EDI section, collect a sample and pour it into the churn splitter 1 (section 4.1).
3. Using identical technique, resample at the first vertical and pour the sample into churn splitter 2.
4. Move to the second vertical, collect the sample, and pour it into churn splitter 2.
5. Using the identical technique, resample at the second vertical and pour the sample into churn splitter 1.
6. Collect and pour samples into each churn splitter in this manner for each of the remaining verticals, alternating churn splitters as described in steps 2 to 5 above.
7. Using identical technique, process and preserve a sample from churn splitter 1 and then from churn splitter 2.

4.3.2.B Sequential Replicates

Sequential replicates are samples of environmental water – commonly ground water – that are collected consecutively (one after the other) from the same sampling site and that are subjected to identical laboratory analysis. The sequential replicate can be collected, for example, as a sample pumped from a well or stream. Sequential replicates are used to assess variability among samples that result from field activities (collection, processing, and shipping procedures). Because sequential replicates are not collected simultaneously, inhomogeneities in the water resource are incorporated into the variability measured. Also included is the variability inherent in laboratory handling and analysis of the samples.

When collecting sequential replicates for whole-water samples:

1. Use identical sampling procedures and supplies, collecting the sample for each analysis one after the other.

2. Preserve the replicate-sample set in the same order as the order in which the samples were collected.

When collecting sequential replicates for filtered samples, use the procedure that best fits study objectives:

1. Trace-element samples or sample set for inorganic and nutrient analyses that includes trace metals:[16]
   a. For each replicate prepare a capsule filter unit as described in NFM 3 and NFM 5.2. Two replicates, for example, require two precleaned capsule filters.
   b. Install "Filter A" and follow filtration procedures and analyte sequence described in NFM 5.2. Trace-element (FA) samples are filtered first, passing no more than 200 mL of sample water through the capsule filter.
   c. Remove and discard Filter A. Change gloves.
   d. Install "Filter B." Use identical procedures and sampling sequence as were used for the "Filter A" sample set.
   e. Continue with this procedure for each additional replicate. This procedure helps assess the variability in sample chemistry over the time period of sample collection that results from sampling and laboratory procedures, including a potential effect from using different capsule filters. Potential effects from using different filter units is considered insignificant compared to those from particulate loading of the filter (Horowitz and others, 1994; USGS Office of Water Quality Technical Memorandums 92.13 and 93.05).

2. Pesticides and other filtered organic-compound samples:
   - If there is minor or no visible loading of particulate matter on the filter, then replicate samples can be collected one after another without changing filters.
   - If filter loading is observed, using a different filter in the manner described above for trace-element samples is recommended. The decision, however, depends on the data-quality requirements of the study and professional judgment.

[16]This method fulfills the objective to maintain the operational pore-size definition of the filtered-sample for trace-element analysis; one filter unit is designated per trace-element sample set in order to maintain comparable particulate loading on the filter.

4.3.2.C Split Replicates

Split replicates are samples obtained by dividing one sample that is designated for a specific laboratory analysis into two or more subsamples (replicates), each of which is submitted to one or more laboratories for identical analysis. Split replicates can be collected for different purposes, depending on the procedures employed and whether the purpose is to determine variability from field plus laboratory processes (the field-replicate split sample) or from laboratory procedures (the lab-replicate split sample).

When collecting split replicates, sample bottles must be labeled carefully, and the sequence of procedures used must be recorded.

- **Lab-replicate split sample**. A sample collected in a single bottle that is split into two or more replicates **after** having been processed and preserved is used to answer the question: "What is the variability associated with laboratory handling and analysis of the sample?" This type of split replicate sample typically is prepared from filtered samples; it is not appropriate, generally, for whole-water samples containing noticeable concentrations of suspended material.

  To collect a lab-replicate split sample (adapted from Horowitz and others, 1994):

  1. Wearing disposable, powderless gloves and working inside a processing chamber, start with a full bottle of sample[17] to which the appropriate chemical treatment has been added. Shake the sample thoroughly to mix.
     - For inorganic samples only, use a bottle rinsed at least twice with IBW and then field rinse the bottle with a small volume of processed sample.
     - Do not prerinse bottles for organic samples.
  2. Transfer the entire contents of the first bottle to the second bottle. Cap and shake the second bottle.
  3. Uncap the second bottle and pour its entire contents back into the first bottle. Cap and shake.
  4. Uncap the bottles and pour one-half of the sample from the first bottle into the second bottle. Cap both bottles tightly.

[17]The volume of sample collected and that of the split replicates depends on the volume of sample required by the laboratory for the analysis desired.

▶ **Field-replicate split sample.** A sample split into subsamples by use of a churn splitter, cone splitter, or T-valve (such as that used on a ground-water manifold device, fig. 4-10), for example, can be used to answer the question, "What is the variability associated with the entire sampling (including any sample collection, processing, preservation, shipping, and laboratory handling and analysis) processes?" Bottles of the replicate samples must be labeled appropriately, and the sequence of procedures used must be recorded. To split concurrent replicate samples that were processed through separate compositing devices (such as churn splitters), follow the procedure shown in steps 1-4 above and label the samples as follows:

To collect a field-replicate split sample (adapted from Horowitz and others, 1994):

Churn splitter 1: first bottle "Site (X), Sample 1, Split A"
"Site (X), Sample 1, Split B"

Churn splitter 2: first bottle "Site (X), Sample 2, Split A"
"Site (X), Sample 2, Split B"

4.3.3 SPIKE SAMPLES

A "spike" sample is an environmental sample to which target compounds (the field-matrix spike mixture) are added after the sample has been processed. Field-spike samples are used to measure bias and answer the question "What loss or gain of target analytes occurred because of degradation and water-matrix characteristics?" Bias determined from spikes is termed "recovery" and reflects the amount of analyte(s) measured expressed as a percentage of the amount spiked.

Spike samples can be customized to address the source of the bias (water matrix, degradation, laboratory method performance) in the data. To address bias from degradation, samples should be spiked in the field as soon as possible after collection. A combination of a laboratory spike, field spike, and field-spike replicate provides the most information, but may not be needed for a given study.

RULE OF THUMB:

Spike when target compounds are expected to be low; specifically, when target compounds are at least a factor of two less than the spiking level.

The numbers and types of spike samples to be selected depend on study objectives and data-quality requirements. However, **an unspiked environmental sample must accompany each spiked environmental sample to correct the data for background concentrations.** Training is required before personnel attempt to spike samples. USGS personnel obtain spike solutions, spike kits, and instructions through the NWQL One-Stop Shopping system.

Field-matrix spike mixtures are prepared in a laboratory and commonly are added to environmental samples designated for organic-compound analysis.

- Short-term use: keep matrix-spike ampoules chilled at all times. Spike compounds are unstable and degrade rapidly at room temperature.
- Long-term use: store spike mixtures in a freezer.
- Spike mixtures contain toxic compounds. Dispose of waste materials in accord with current local and State regulations and USGS Science Center guidelines.

When preparing field-spiked samples for pesticides or VOCs, follow the procedure listed below:

1. Samples should be processed, spiked, and chilled immediately after collection. If spiking is delayed, keep sample chilled until and after it is spiked. Check that the sample bottles are labeled appropriately:
   - FS = field-spiked sample
   - FSR = field-spiked replicate
   - LS = lab-spiked sample

2. Wearing disposable gloves and working in a preservation chamber, follow the laboratory instructions for spiking the sample. Be sure that the spike mixture is the one intended for the sample, in terms of analytes, volume, and concentration.
3. Chill field-spiked samples to 4°C or below without freezing, and handle in a manner identical to that of the unspiked environmental sample.
4. Record the following information related to the spike sample on field and NWQL Analytical Services Request forms: lot number of spike solution, volume of spike solution, and source of spike solution.

CAUTION: Spike mixtures can be toxic and might cause cancer or other diseases. Follow the laboratory-prescribed spiking instructions meticulously. Work in a well-ventilated area and avoid inhalation and skin and eye contact.

4.3.4 REFERENCE SAMPLES

Standard-reference-water samples (SRS) and reference-material samples that are submitted by field personnel for laboratory analysis can be used to answer questions, such as "What are the bias and variability associated with field-handling, shipping, and laboratory procedures"? Reference samples typically are submitted from the field as blind samples (section 4.3.5) and as split replicate samples (section 4.3.2.C) because the composition is known, thus eliminating guesswork regarding the accuracy of the analytical results.

Reference samples for inorganic analytes in a natural water matrix currently are available to USGS personnel from the USGS Branch of Quality Systems. The National Institute of Standards and Technology and some commercial laboratories also supply reference materials.

When preparing reference samples, follow the procedure listed below:

1. **Prepare this sample before leaving for the field site.**

    a. Relabel the reference-sample bottle with the site identification code and a field date and time. The sample should appear as if it is an environmental sample.

    b. Process SRS or reference-material samples in a clean environment in the office laboratory, under a laminar-flow hood or other protective chamber, to avoid atmospheric contamination. **Do not process these QC samples under a fume hood.**

    c. Rinse each sample bottle three times with a small volume of SRS or reference-material sample, fill the bottle with the reference solution, and cap securely.

2. Prepare an Analytical Services Request (ASR) form; record the SRS or reference-material sample identification code (from the original container) in field notes.

3. Pack the sample and the accompanying ASR form to take to the field site.

4. Ship SRS or reference-material samples in the same container with the environmental and other QC samples collected at the field site.

4.3.5 BLIND SAMPLES

For blind samples, the source and chemical composition of the samples are known to the submitter but typically not known to the analyst; therefore, blanks, SRS, or reference material often are used as blind samples. Blind samples can be designed to answer questions such as "What bias and variability are introduced by procedures used within a single laboratory or among laboratories?" Replicate or spike samples sometimes are used to answer a similar question, but with greater potential for more variability.

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CONVERSION FACTORS, SELECTED TERMS, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply By		To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
inch (in.)	25.4	millimeter
meter (m)	3.281	foot
micrometer (µm)	3.281×10^{-6}	foot
millimeter (mm)	0.03937	inch
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois
microgram (µg)	3527×10^{-5}	ounce
liter (L)	0.2642	gallon
milliliter (mL)	2.64×10^{-4}	gallon

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

SELECTED TERMS

Accuracy: The degree of agreement of a measured value with the true or expected value (Taylor, 1987).

Analyte (target analyte): "Substances being determined in an analysis" (from Bennett, 1986). The term target analyte is used in this report to refer to any chemical or biological substance for which concentrations in a sample will be determined. The definition for target analyte does not include field-measured parameters such as specific electrical conductance, pH, temperature, dissolved oxygen, Eh, alkalinity, color, or turbidity.

Aquifer: "A saturated permeable geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients" (Freeze and Cherry, 1979).

Area-weighted sample: A sample that contains an equal volume from each unit of area sampled.

Bias: Systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement, collection, or processing system; systematic directional error measured by the use of blank, spike, and reference-material samples. The error can be positive (indicating contamination) or negative (indicating loss of analyte concentration) (from Taylor, 1987).

Bag samplers: Samplers whose containers are bags that instantly transmit the ambient pressure to the interior of the sample container and do not have opening or closing valves.

Bottle samplers: A rigid sample container that does not instantly transmit the ambient pressure to the interior of the sample container and has neither pressure compensation nor opening and closing valves. Point samplers described in Edwards and Glysson (1999) use rigid bottles but have pressure compensation and opening and closing valves and are not considered bottle samplers for the purposes of this document. **The tables in Appendix A4-A were not designed for use with point samplers.**

Centroid (as used to designate a special case of stream-sampling location for the equal-discharge-increment method): The vertical in the increment at which discharge is equal on both sides of the vertical (G. Douglas Glysson, U.S. Geological Survey, written commun., 1997).

Contaminant: Biological, chemical, or physical substances or properties added to the medium of concern through human activity or natural processes and that corrupt its ambient composition.

Contamination (of water): Corruption of ambient water composition or attributes by the addition of biological, chemical, or physical substances as a result of human activity or natural processes. Addition of such substances can degrade the quality of the water resource.

Data-quality requirements: That subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the variability allowable without compromising achievement of the scientific objectives of the study.

Depth-integrated sample: A sample collected when each vertical portion of the stream depth is represented in the sample in proportion to the desired sampling scheme.

- **Depth integration.** "A method of sampling at every point throughout a given depth (the sampled depth) whereby the water-sediment mixture is collected isokinetically so that the contribution from each point is proportional to the stream velocity at the point. This process yields a sample with properties that are discharge weighted over the sampled depth" (ASTM, 1990).
- **Depth integration for a discharge-weighted sample.** "A discharge-weighted (velocity-weighted) sample of water-sediment mixture collected at one or more verticals in accordance with the technique of depth integration; the discharge of any property of the sample expressible as a concentration can be obtained as the product of the concentration and the water discharge represented by the sample" (ASTM, 1990). For a discharge-weighted sample, the water-sediment mixture is collected isokinetically so that the contribution from each point is proportional to the stream velocity at the point (that is, the sample contains an equal volume from each unit of discharge sampled).

- **Depth integration to collect an area-weighted sample.** The ASTM definition of depth integration does not accommodate the concept of an area-weighted sample. Area weighting is similar in concept to discharge weighting, except that the water-sediment mixture is collected so that the contribution from each point is proportional to the stream area at the point (that is, contains an equal volume from each unit of area sampled). Area-weighted sampling is used to obtain a sample that contains the average concentration of a property that is observed in a cross section. Averaged in situ field measurements of streams are more nearly area weighted than discharge weighted. The product of an area-weighted property concentration and the stream discharge would not yield the discharge of the property unless the stream contained the same property concentration at every point.

Discharge-weighted sample: A sample that contains an equal volume from each unit of discharge sampled.

Equal-width-increment (EWI) and **equal-discharge-increment (EDI) sample-collection methods:** Methods specifically designed to result in the collection of discharge-weighted, depth-integrated, isokinetic samples (Edwards and Glysson, 1999). When either method is used properly, the resulting samples contain the same property concentrations.

Isokinetic sampling: A sample collected in such a way that the water-sediment mixture moves with no change in velocity as it leaves the ambient flow and enters the sampler intake (ASTM, 1990).

Precision: The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions (Taylor, 1987).

Purging: Refers to removal of water standing in a cased well or borehole before water samples are collected for analysis.

Quality Assessment: Overall process of assessing the quality of the environmental data by reviewing the application of the quality-assurance elements and the analysis of the quality-control data.

Quality Assurance (QA): A system of protocols and procedures implemented to meet expected standards of quality needed to fulfill study objectives and control unmeasurable components of a study, such as sampling at the right place and (or) time using the correct equipment and techniques.

Quality Control (QC): A system of activities (such as collection of blank or replicate samples) whose purpose is to assess the quality of environmental data by generating a set of data that will be used to estimate the magnitude of the bias and variability resulting from the procedures used for obtaining the data.

Raw sample: A whole-water (unfiltered) sample that has not been processed through a filter or other phase-separation device.

Transit: To move the sampler from the stream surface to the streambed or from the streambed to the surface.

Transit rate: The rate at which the sampler is passed through the water from the stream surface to the streambed or from the streambed to the surface.

Unsampled zone: The unsampled portion of the sampling vertical, usually assumed to be the zone from the streambed to the sampler intake. Generally, sampler intakes are 4 to 7 inches above the streambed, depending on the kind of sampler used.

Variability: Random error in independent measurements as the result of repeated application of the process under specific conditions; random error measured by the use of environmental or QC-sample replicates.

Vertical: Refers to that location within the increment at which the sampler is lowered and raised through the water column.

Water Science Center: An office of the USGS, Water Resources Discipline, located in any of the States or territories of the United States.

Wholewater sample: (*see* Raw sample).

ABBREVIATIONS

~	approximately
=	equal to
>	greater than
≥	greater than or equal to
<	less than
≤	less than or equal to
+	plus
±	plus or minus
ft/s	feet per second
gal/min	gallon per minute
L	liter
L/min	liter per minute
µg/L	microgram per liter (equivalent to parts per billion)
µs/cm	microsiemens per centimeter
mg/L	milligram per liter
mL/min	milliliter per minute
ppb	parts per billion (equivalent to micrograms per liter)
ADAPS	Automatic Data Processing System
ASR	Analytical Services Request
ASTM	ASTM, International
BOD	biochemical oxygen demand
CFC	chlorofluorocarbon
CH/DH	Clean Hands/Dirty Hands
DIW	distilled, deionized water
DO	dissolved oxygen
DOC	dissolved organic carbon
EDI	equal-discharge increment
EWI	equal-width increment
FS	field-spiked sample
FSR	field-spiked replicate sample
GPS	global positioning system
GWSI	ground-water site inventory database, a subsystem within the USGS National Water Information System (NWIS)
IBW	inorganic-grade blank water
ID	identification number that is unique to a field site, station, or well

LNAPL	light non-aqueous phase liquid
LS	laborabory-spiked sample
MP	measuring point on a ground-water well
NAWQA	National Water-Quality Assessment Program (USGS)
NFM	*National Field Manual for the Collection of Water-Quality Data*
NFSS	National (USGS) Field Supplies Service (also referred to as "One-Stop Shopping")
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NWIS	National Water Information System of the USGS
NWQL	National Water Quality Laboratory
OGW	Office of Ground Water, USGS
OWQ	Office of Water Quality, USGS
PBW	pesticide-grade blank water
PCB	polychlorobiphenyls
Q	rate of discharge
QA	quality assurance
QADATA	quality-assurance database within NWIS
QAP	Quality Assurance Plan
QC	quality control
SF_6	sulfur hexafluoride
SAP	Sampling and Analysis Plan
SPMD	semi-permeable membrane device
SRS	Standard reference water sample
TBY	turbidity
TOC	total organic carbon
TU	turbidity unit
URL	Uniform Resource Locator
USGS	U.S. Geological Survey
VPBW	volatile-organic-compound and pesticide-grade blank water, purged with nitrogen gas
VCF	single vertical at centroid of flow
VOC	volatile organic compound

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TECHNICAL MEMORANDUMS OF THE U.S. GEOLOGICAL SURVEY, WATER DISCIPLINE

The following U.S. Geological Survey Branch of Quality Systems (formerly Branch of Quality Assurance), Office of Water Quality, National Water Quality Laboratory, and Water Resources Policy Memorandums are available on the World Wide Web at http://water.usgs.gov/admin/memo/.

Memo No.	Title	Date
	Branch of Quality Systems	
90.03	ADP—Storage of water-quality, quality-assurance data in NWIS	undated
92.01	ADP—Storage of water-quality, quality-assurance data in NWIS	undated
95.01	ADP—Storage of water-quality quality-assurance data in NWIS	October 28, 1994
	Office of Ground Water	
03.03	Agreement forms for gaging station and observation well installations and transfers	September 17, 2003
06.01	Storage of water-level data for ground water	February 2, 2006
	Office of Water Quality	
92.02	FIELD TECHNIQUES—Field preparation of containers for aqueous samples	December 20, 1991
92.13	Trace element contamination: findings of studies on the cleaning of membrane filters and filtration systems	July 17, 1992
93.05	Programs and Plans—Evaluation of capsule filters	January 21, 1993
94.08	Collection, handling, and analysis of environmental samples in support of regulatory projects	January 14, 1994
94.09	Revision of new Division protocol for collecting and processing surface-water samples for low-level inorganic analyses	January 28, 1994

97.06	Comparison of the suspended-sediment splitting capabilities of the churn and cone splitters	May 5, 1997
99.02	Guidance for collecting discharge-weighted samples in surface water using an isokinetic sampler	October 28, 1998
00.10	Discrete water-quality data in NWISWeb	September 15, 2000
01.02	Guidance for verifying and interpreting field blank determinations that indicate high pesticide or trace-element concentrations or that show large numbers of detections	November 14, 2000
01.03	Collection and use of total suspended-solids data	November 27, 2000
02.11	Policy for storing and reporting significant figures for chemical data	February 14, 2002
02.13	Water-quality field methods/National Field Manual for the Collection of Water-Quality Data	March 15, 2002
06.01	Storage of water-level data for ground water	February 2, 2006

National Water Quality Laboratory

02.04	Requirements for the proper shipping of samples to the National Water Quality Laboratory	September 23, 2002

Water Resources Policy Memorandums

90.34	Policy for permission to sample	March 26, 1990
92.59	Policy for management and retention of hydrologic data of the U.S. Geological Survey	undated [1992]
94.008	LEGAL—Agreement forms 9-1482, 9-1482A, and 9-1483	February 18, 1994
99.03	SAFETY—Water Resources Division hazardous waste site operations—Revised safety policy and guidance	November 17, 1998
99.32	SAFETY—Water Resources Division policy for safety associated with measurements, sampling, and related streamgaging	August 17, 1990
99.34	Quality assurance measures for serving real-time water data on the World Wide Web	February 28, 2000

APPENDIXES

APPENDIX A4-A
Transit Rate and Volume Guidelines and Filling Times for Isokinetic Samplers

The tables in Appendix A4-A apply to the first complete round-trip transit starting with an empty sampler container. **These tables are valid only if the sampler is emptied between verticals.**

Tables 1 through 5 show:

1. Isokinetic transit rates and volumes for a 1-liter bottle sampler (US DH-81, US DH-95, US D-95) with a
   a. 3/16-inch nozzle
   b. 1/4-inch nozzle
   c. 5/16-inch nozzle

   The designations in the RATE column of tables 1a, 1b, and 1c are defined as follows:

   Slowest The transit rate that fills the sampler to its maximum volume.

   Safe full volume The transit rate that will result in a volume in a bottle sampler such that, if the sampler nozzle is tipped 10 degrees down from the horizontal, no sample will spill from the nozzle.

   Fastest The transit rate that is the fastest rate to avoid compression problems in bottle samplers or to not exceed a transit rate that is more than 0.4 times the stream velocity for bag samplers.
2. Isokinetic transit rates and volumes for a US DH-2 sampler (1-liter bag) with a
   a. 3/16-inch nozzle
   b. 1/4-inch nozzle
   c. 5/16-inch nozzle
3. Isokinetic transit rates and volumes for a US D-96 sampler (3-liter bag) with a
   a. 3/16-inch nozzle
   b. 1/4-inch nozzle
   c. 5/16-inch nozzle
4. Isokinetic transit rates and volumes for a US D-99 sampler (6-liter bag) with a
   a. 1/4-inch nozzle
   b. 5/16-inch nozzle
5. Filling times, in seconds, for isokinetic samplers
   a. US DH-81
   b. US DH-95
   c. US D-95
   d. US DH-2
   e. US D-96
   f. US D-96 A-1
   g. US D-99

APPENDIX A4-A–Table 1a. Isokinetic transit rates for a 1-liter bottle sampler with a 3/16-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Volume (mL)
		1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0	
1	slowest	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.1	0.1	0.1	0.1	1,000
1	safe full volume 0	.02	0.03	0.03	0.04	0.05	0.05	0.1	0.1	0.1	0.1	0.1	0.1	800
1	fastest	0.1	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.7	130
2	slowest	0.03	0.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	1,000
2	safe full volume 0	.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	800
2	fastest	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	240
3	slowest	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	1,000
3	safe full volume 0.	1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	800
3	fastest	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	340
4	slowest	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	1,000
4	safe full volume 0.	1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	800
4	fastest	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	0.9	420
5	slowest	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	1,000
5	safe full volume 0.	1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.5	0.5	0.6	800
5	fastest	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	1.0	500
6	slowest	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	1,000
6	safe full volume 0.	1	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.7	800
6	fastest	0.2	0.2	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.1	560
7	slowest 0.	1	0.1	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	0.7	1,000
7	safe full volume 0.	1	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	800
7	fastest 0.	2	0.3	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.9	1.0	1.1	610
8	slowest 0.	1	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	1,000
8	safe full volume 0.	2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.7	0.8	0.9	1.0	800
8	fastest 0.	2	0.3	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0	1.2	670
10	slowest 0.	2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1,000
10	safe full volume 0.	2	0.3	0.3	0.4	0.5	0.5	0.6	0.7	0.8	1.0	1.1	1.2	800
10	fastest 0.	2	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.9	1.0	1.2	1.3	760
12	slowest 0.	2	0.3	0.3	0.4	0.4	0.5	0.6	0.6	0.8	0.9	1.0	1.1	1,000
12	safe full volume –		--	--	--	--	--	--	--	--	--	--	--	--
12	fastest 0.	2	0.3	0.4	0.5	0.6	0.6	0.7	0.8	0.9	1.1	1.3	1.4	830
14	slowest 0.	2	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.9	1.0	1.2	1.3	1,000
14	safe full volume –		--	--	--	--	--	--	--	--	--	--	--	--
14	fastest 0.	3	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.53	900
15	slowest 0.	2	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.1	1.2	1.4	1,000
15	safe full volume –		--	--	--	--	--	--	--	--	--	--	--	--
15	fastest 0.	3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	1.1	1.2	1.4	1.6	920

APPENDIX A4-A–Table 1b. Isokinetic transit rates for a 1-liter bottle sampler with a 1/4-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Volume (mL)
		1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0	
1	slowest	.03	0.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	1,000
1	safe full volume	.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	800
1	fastest	02	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.9	1.0	1.2	1.3	130
2	slowest	01	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	1,000
2	safe full volume	01	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.4	0.4	800
2	fastest	02	0.3	0.4	0.5	0.6	0.6	0.7	0.8	1.0	1.1	1.3	1.4	240
3	slowest	01	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	1,000
3	safe full volume	01	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	0.7	800
3	fastest	03	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.5	340
4	slowest	01	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.6	0.7	1,000
4	safe full volume	02	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	800
4	fastest	03	0.4	0.5	0.6	0.6	0.7	0.8	0.9	1.1	1.3	1.5	1.6	420
5	slowest	01	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.8	1,000
5	safe full volume	02	0.2	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.9	1.0	1.1	800
5	fastest	03	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8	500
6	slowest	02	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1,000
6	safe full volume	02	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.9	1.0	1.2	1.3	800
6	fastest	03	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.7	1.9	560
7	slowest	02	0.3	0.3	0.4	0.5	0.5	0.6	0.6	0.8	0.9	1.0	1.2	1,000
7	safe full volume	03	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.5	800
7	fastest	03	0.4	0.6	0.7	0.8	0.9	1.0	1.1	1.3	1.5	1.7	2.0	620
8	slowest	02	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.9	1.0	1.2	1.3	1,000
8	safe full volume	03	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.7	800
8	fastest	03	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8	2.1	670
10	slowest	03	0.4	0.5	0.6	0.6	0.7	0.8	0.9	1.1	1.3	1.5	1.7	1,000
10	safe full volume	04	0.5	0.6	0.7	0.9	1.0	1.1	1.2	1.5	1.7	1.9	2.2	800
10	fastest	04	0.5	0.6	0.8	0.9	1.0	1.1	1.3	1.5	1.8	2.0	2.3	760
12	slowest	03	0.4	0.6	0.7	0.8	0.9	1.0	1.1	1.3	1.6	1.8	2.0	1,000
12	safe full volume	--	--	--	--	--	--	--	--	--	--	--	--	--
12	fastest	04	0.6	0.7	0.8	1.0	1.1	1.3	1.4	1.7	1.9	2.2	2.5	840
14	slowest	04	0.5	0.6	0.8	0.9	1.0	1.2	1.3	1.6	1.8	2.1	2.3	1,000
14	safe full volume	--	--	--	--	--	--	--	--	--	--	--	--	--
14	fastest	05	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.8	2.1	2.4	2.7	900
15	slowest	04	0.6	0.7	0.8	1.0	1.1	1.2	1.4	1.7	1.9	2.2	2.5	1,000
15	safe full volume	--	--	--	--	--	--	--	--	--	--	--	--	--
15	fastest	05	0.6	0.8	0.9	1.1	1.3	1.4	1.6	1.9	2.2	2.5	2.8	930

APPENDIX A4-A–Table 1c. Isokinetic transit rates for a 1-liter bottle sampler with a 5/16-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Volume (mL)
		1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0	
1	slowest	0.04	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	1,000
1	safe full volume	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	800
1	fastest	0.3	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8	2.1	130
2	slowest	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	1,000
2	safe full volume	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.5	0.5	0.6	0.7	800
2	fastest	0.4	0.5	0.6	0.7	0.9	1.0	1.1	1.2	1.5	1.7	2.0	2.2	240
3	slowest	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.6	0.7	0.8	1,000
3	safe full volume	0.2	0.2	0.3	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0	800
3	fastest	0.4	0.5	0.7	0.8	0.9	1.1	1.2	1.3	1.6	1.9	2.1	2.4	340
4	slowest	0.2	0.2	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0	1,000
4	safe full volume	0.2	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.1	1.2	1.4	800
4	fastest	0.4	0.6	0.7	0.9	1.0	1.1	1.3	1.4	1.7	2.0	2.3	2.6	420
5	slowest	0.2	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.9	1.0	1.2	1.3	1,000
5	safe full volume	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.9	1.1	1.3	1.5	1.7	800
5	fastest	0.5	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.8	2.1	2.4	2.7	500
6	slowest	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1,000
6	safe full volume	0.3	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.4	1.6	1.8	2.0	800
6	fastest	0.5	0.6	0.8	1.0	1.1	1.3	1.5	1.6	1.9	2.3	2.6	2.9	560
7	slowest	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8	1,000
7	safe full volume	0.4	0.5	0.7	0.8	0.9	1.1	1.2	1.3	1.6	1.9	2.1	2.4	800
7	fastest	0.5	0.7	0.9	1.0	1.2	1.4	1.5	1.7	2.0	2.4	2.7	3.1	620
8	slowest	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8	2.1	1,000
8	safe full volume	0.5	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.8	2.1	2.4	2.7	800
8	fastest	0.5	0.7	0.9	1.1	1.3	1.4	1.6	1.8	2.2	2.5	2.9	3.2	670
10	slowest	0.4	0.6	0.7	0.9	1.0	1.2	1.3	1.4	1.7	2.0	2.3	2.6	1,000
10	safe full volume	0.6	0.8	0.9	1.1	1.3	1.5	1.7	1.9	2.3	2.6	3.0	3.4	800
10	fastest	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.4	2.8	3.2	3.6	760
11	slowest	0.5	0.6	0.8	1.0	1.1	1.3	1.4	1.6	1.9	2.2	2.5	2.9	1,000
11	safe full volume	--	--	--	--	--	--	--	--	--	--	--	--	--
11	fastest	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.4	2.8	3.2	3.6	830
12	slowest	0.5	0.7	0.9	1.0	1.2	1.4	1.6	1.7	2.1	2.4	2.8	3.1	1,000
12	safe full volume	--	--	--	--	--	--	--	--	--	--	--	--	--
12	fastest	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.4	2.8	3.2	3.6	910
13	slowest	0.6	0.8	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.6	3.0	3.4	1,000
13	safe full volume	--	--	--	--	--	--	--	--	--	--	--	--	--
13	fastest	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.4	2.8	3.2	3.6	980

APPENDIX A4-A–Table 2a. Isokinetic transit rates for a DH-2 sampler (1-liter bag) with a 3/16-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)										Volume (mL)
		2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	
2	slowest	0.04	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1,000
2	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	50
4	slowest	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	1,000
4	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	110
6	slowest	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	1,000
6	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	160
8	slowest	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.6	1,000
8	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	220
10	slowest	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.7	1,000
10	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	270
12	slowest	0.3	0.3	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.8	1,000
12	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	330
14	slowest	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.8	0.9	1.0	1,000
14	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	380
16	slowest	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.0	1.1	1,000
16	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	440
18	slowest	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1,000
18	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	490
20	slowest	0.4	0.5	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1,000
20	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	540
22	slowest	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3	1.4	1.6	1,000
22	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	600
24	slowest	0.5	0.7	0.8	0.9	1.0	1.2	1.3	1.4	1.6	1.7	1,000
24	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	650
26	slowest	0.6	0.7	0.8	1.0	1.1	1.3	1.4	1.6	1.7	1.8	1,000
26	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	710
28	slowest	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.7	1.8	2.0	1,000
28	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	760
30	slowest	0.7	0.8	1.0	1.1	1.3	1.5	1.6	1.8	2.0	2.1	1,000
30	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	820
32	slowest	0.7	0.9	1.0	1.2	1.4	1.6	1.7	1.9	2.1	2.3	1,000
32	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	870
34	slowest	0.7	0.9	1.1	1.3	1.5	1.7	1.8	2.0	2.2	2.4	1,000
34	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	920
36	slowest	0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.3	2.5	1,000
36	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	980
37	slowest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	1,000
37	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	1,000

APPENDIX A4-A–Table 2b. Isokinetic transit rates for a DH-2 sampler (1-liter bag) with a 1/4-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)										Volume (mL)
		2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	
2	slowest	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	1,000
2	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	100
4	slowest	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.5	1,000
4	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	190
6	slowest	0.2	0.3	0.3	0.4	0.5	0.5	0.6	0.6	0.7	0.8	1,000
6	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	290
8	slowest	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.8	0.9	1.0	1,000
8	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	390
10	slowest	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1,000
10	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	480
12	slowest	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.3	1.4	1.5	1,000
12	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	580
14	slowest	0.5	0.7	0.8	0.9	1.1	1.2	1.3	1.5	1.6	1.8	1,000
14	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	680
16	slowest	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.7	1.9	2.0	1,000
16	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	770
18	slowest	0.7	0.9	1.0	1.2	1.4	1.6	1.7	1.9	2.1	2.3	1,000
18	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	870
20	slowest	0.8	1.0	1.2	1.4	1.5	1.7	1.9	2.1	2.3	2.5	1,000
20	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	970

APPENDIX A4-A–Table 2c. Isokinetic transit rates for a DH-2 sampler (1-liter bag) with a 5/16-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)										Volume (mL)
		2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	
2	slowest	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	1,000
2	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	150
4	slowest	0.2	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.7	0.8	1,000
4	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	300
6	slowest	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1,000
6	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	450
8	slowest	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3	1.4	1.6	1,000
8	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	600
10	slowest	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.7	1.8	2.0	1,000
10	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	750
12	slowest	0.7	0.9	1.1	1.3	1.4	1.6	1.8	2.0	2.2	2.4	1,000
12	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	900
13	slowest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.5	1,000
13	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	980

APPENDIX A4-A–Table 3a. Isokinetic transit rates for a D-96 sampler (3-liter bag) with a 3/16-inch nozzle.
[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)																				Volume (mL)
		2.0	2.5	3.0	3.5	4.0	4.5	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	
2	slowest	0.01	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	3,000
2	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	50
4	slowest	0.03	0.04	0.04	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	3,000
4	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	110
6	slowest	0.04	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	3,000
6	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	160
8	slowest	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4	3,000
8	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	220
10	slowest	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.5	3,000
10	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	270
12	slowest	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5	3,000
12	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	330
14	slowest	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	3,000
14	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	380
16	slowest	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.7	0.7	0.7	3,000
16	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	440
18	slowest	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.7	0.8	0.8	3,000
18	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	490
20	slowest	0.1	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	3,000
20	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	540
24	slowest	0.2	0.2	0.3	0.3	0.3	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.0	1.1	3,000
24	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	650

APPENDIX A4-A–Table 3a. Isokinetic transit rates for a D-96 sampler (3-liter bag) with a 3/16-inch nozzle.—*continued*

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

26	slowest	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	3,000
26	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	710
28	slowest	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	3,000
28	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	760
30	slowest	0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.4	3,000
30	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	820
35	slowest	0.3	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.1	1.2	1.3	1.3	1.4	1.5	1.5	1.6	3,000
35	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	950
40	slowest	0.3	0.4	0.4	0.5	0.6	0.7	0.8	0.9	0.9	1.0	1.1	1.2	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.7	1.8	3,000
40	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,090
50	slowest	0.4	0.5	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	3,000
50	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,360
60	slowest	0.4	0.5	0.7	0.8	0.9	1.0	1.2	1.3	1.4	1.5	1.6	1.7	1.8	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3,000
60	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,630
70	slowest	0.5	0.6	0.8	0.9	1.0	1.1	1.4	1.5	1.6	1.8	1.9	2.0	2.2	2.3	2.4	2.5	2.7	2.8	2.9	3.0	3.2	3,000
70	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,900
80	slowest	0.6	0.7	0.9	1.0	1.2	1.3	1.6	1.7	1.9	2.0	2.2	2.3	2.5	2.6	2.8	2.9	3.0	3.2	3.3	3.5	3.6	3,000
80	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,200
90	slowest	0.7	0.8	1.0	1.1	1.3	1.5	1.8	2.0	2.1	2.3	2.4	2.6	2.8	2.9	3.1	3.3	3.4	3.6	3.7	3.9	4.1	3,000
90	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,400
100	slowest	0.7	0.9	1.1	1.3	1.4	1.6	2.0	2.2	2.4	2.5	2.7	2.9	3.1	3.3	3.4	3.6	3.8	4.0	4.2	4.3	4.5	3,000
100	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,700
110	slowest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	3,000
110	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	3,000

APPENDIX A4-A–Table 3b. Isokinetic transit rates for a D-96 sampler (3-liter bag) with a 1/4-inch nozzle.
[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)																					Volume (mL)
		2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	
2	slowest	0.03	0.03	0.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	3,000
2	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	100
4	slowest	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	3,000
4	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	190
6	slowest	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.5	3,000
6	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	290
8	slowest	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	3,000
8	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	390
10	slowest	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.8	0.8	3,000
10	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	480
12	slowest	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	3,000
12	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	580
14	slowest	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	0.9	1.0	1.0	1.1	1.1	3,000
14	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	680
16	slowest	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	3,000
16	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	770
18	slowest	0.2	0.3	0.3	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.2	1.2	1.3	1.3	1.4	1.4	3,000
18	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	870
20	slowest	0.3	0.3	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.2	1.2	1.3	1.4	1.4	1.5	1.5	1.6	3,000
20	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	970
24	slowest	0.3	0.4	0.5	0.5	0.6	0.7	0.8	0.8	0.9	1.0	1.1	1.2	1.2	1.3	1.4	1.5	1.5	1.6	1.7	1.8	1.9	1.9	3,000
24	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,160
26	slowest	0.3	0.4	0.5	0.6	0.7	0.8	0.8	0.9	1.0	1.1	1.2	1.3	1.3	1.4	1.5	1.6	1.7	1.8	1.8	1.9	2.0	2.1	3,000
26	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,250
28	slowest	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	3,000
28	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,350
30	slowest	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	3,000
30	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,450
35	slowest	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.3	2.4	2.5	2.6	2.7	2.8	3,000
35	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,690
40	slowest	0.5	0.6	0.8	0.9	1.0	1.2	1.3	1.4	1.5	1.7	1.8	1.9	2.1	2.2	2.3	2.4	2.6	2.7	2.8	3.0	3.1	3.2	3,000
40	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,930
50	slowest	0.6	0.8	1.0	1.1	1.3	1.4	1.6	1.8	1.9	2.1	2.3	2.4	2.6	2.7	2.9	3.1	3.2	3.4	3.5	3.7	3.9	4.0	3,000
50	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,410
60	slowest	0.8	1.0	1.2	1.4	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.2	4.4	4.6	4.8	3,000
60	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,900

APPENDIX A4-A–Table 3c. Isokinetic transit rates for a D-96 sampler (3-liter bag) with a 5/16-inch nozzle.

[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)																						Volume (mL)
		2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	
2	slowest	0.04	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	3,000
2	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	150
4	slowest	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5	3,000
4	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	300
6	slowest	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.8	3,000
6	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	450
8	slowest	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	1.0	3,000
8	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	600
10	slowest	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	3,000
10	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	750
12	slowest	0.2	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.1	1.2	1.3	1.3	1.4	1.4	1.5	3,000
12	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	900
14	slowest	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.8	0.8	0.9	1.0	1.1	1.1	1.2	1.3	1.3	1.4	1.5	1.5	1.6	1.7	1.8	3,000
14	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,060
16	slowest	0.3	0.4	0.5	0.6	0.6	0.7	0.8	0.9	1.0	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	1.9	2.0	3,000
16	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,210
18	slowest	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	3,000
18	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,360
20	slowest	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	3,000
20	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,510
24	slowest	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3	1.4	1.6	1.7	1.8	1.9	2.1	2.2	2.3	2.4	2.5	2.7	2.8	2.9	3.0	3,000
24	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,810
26	slowest	0.5	0.7	0.8	0.9	1.0	1.2	1.3	1.4	1.6	1.7	1.8	2.0	2.1	2.2	2.4	2.5	2.6	2.7	2.9	3.0	3.1	3.3	3,000
26	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	1,960
28	slowest	0.6	0.7	0.8	1.0	1.1	1.3	1.4	1.5	1.7	1.8	2.0	2.1	2.3	2.4	2.5	2.7	2.8	3.0	3.1	3.2	3.4	3.5	3,000
28	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,110
30	slowest	0.6	0.8	0.9	1.1	1.2	1.4	1.5	1.7	1.8	2.0	2.1	2.3	2.4	2.6	2.7	2.9	3.0	3.2	3.3	3.5	3.6	3.8	3,000
30	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,260
35	slowest	0.7	0.9	1.1	1.2	1.4	1.6	1.8	1.9	2.1	2.3	2.5	2.6	2.8	3.0	3.2	3.3	3.5	3.7	3.9	4.0	4.2	4.4	3,000
35	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,640
39	slowest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.3	4.5	4.7	4.9	3,000
39	fastest	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	2,940

APPENDIX A4-A–Table 4a. Isokinetic transit rates for a D-99 sampler (6-liter bag) with a 1/4-inch nozzle.
[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)																								Volume (mL)
		3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0	
2	slowest	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	6,000
2	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	100
4	slowest	0.04	0.05	0.05	0.06	0.06	0.07	0.08	0.08	0.09	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	6,000
4	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	200
6	slowest	0.06	0.07	0.08	0.09	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	6,000
6	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	300
8	slowest	0.08	0.09	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	6,000
8	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	400
10	slowest	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5	6,000
10	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	500
12	slowest	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5	0.6	0.6	6,000
12	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	600
14	slowest	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.7	0.7	6,000
14	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	700
16	slowest	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.7	0.7	0.7	0.7	0.8	6,000
16	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	800
18	slowest	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.9	6,000
18	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	900
20	slowest	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	0.9	1.0	6,000
20	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,000
24	slowest	0.2	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	1.0	1.0	1.1	1.1	1.2	6,000
24	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,200
26	slowest	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	1.0	1.0	1.1	1.1	1.2	1.2	1.3	6,000
26	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,300

APPENDIX A4-A–Table 4a. Isokinetic transit rates for a D-99 sampler (6-liter bag) with a 1/4-inch nozzle.—*continued*
[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

28	slowest	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.4	6,000
28	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,400
30	slowest	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.4	1.4	1.4	6,000
30	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,500
35	slowest	0.3	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.4	1.4	1.5	1.5	1.6	1.6	1.7	6,000
35	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,700
40	slowest	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.2	1.2	1.3	1.4	1.4	1.5	1.5	1.6	1.7	1.7	1.8	1.9	1.9	6,000
40	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,900
50	slowest	0.5	0.6	0.6	0.7	0.8	0.9	1.0	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	1.9	2.0	2.1	2.2	2.3	2.3	2.4	6,000
50	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	2,400
60	slowest	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	6,000
60	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	2,900
70	slowest	0.7	0.8	0.9	1.0	1.1	1.2	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.2	3.3	3.4	6,000
70	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	3,400
80	slowest	0.8	0.9	1.0	1.2	1.3	1.4	1.5	1.7	1.8	1.9	2.1	2.2	2.3	2.4	2.6	2.7	2.8	3.0	3.1	3.2	3.3	3.5	3.6	3.7	3.9	6,000
80	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	3,900
90	slowest	0.9	1.0	1.2	1.3	1.5	1.6	1.7	1.9	2.0	2.2	2.3	2.5	2.6	2.8	2.9	3.0	3.2	3.3	3.5	3.6	3.8	3.9	4.1	4.2	4.3	6,000
90	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	4,300
100	slowest	1.0	1.1	1.3	1.4	1.6	1.8	1.9	2.1	2.3	2.4	2.6	2.7	2.9	3.1	3.2	3.4	3.5	3.7	3.9	4.0	4.2	4.3	4.5	4.7	4.8	6,000
100	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	4,800
120	slowest	1.2	1.4	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6,000
120	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	5,800

APPENDIX A4-A–Table 4b. Isokinetic transit rates for a D-99 sampler (6-liter bag) with a 5/16-inch nozzle.
[Transit rates in feet per second; Depth is (water depth) – (unsampled zone); mL, milliliter]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)																								Volume (mL)
		3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0	
2	slowest	0.03	0.04	0.04	0.05	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	6,000
2	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	150
4	slowest	0.06	0.07	0.08	0.09	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	6,000
4	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	300
6	slowest	0.09	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.5	6,000
6	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	450
8	slowest	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.6	6,000
8	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	600
10	slowest	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.7	0.7	0.7	0.7	0.8	6,000
10	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	750
12	slowest	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.9	0.9	6,000
12	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	900
14	slowest	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	1.0	1.0	1.1	6,000
14	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,100
16	slowest	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1.0	1.0	1.0	1.1	1.1	1.2	1.2	6,000
16	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,200
18	slowest	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.4	6,000
18	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,400
20	slowest	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.4	1.4	1.5	1.5	6,000
20	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,500
24	slowest	0.4	0.4	0.5	0.5	0.6	0.7	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.1	1.2	1.3	1.3	1.4	1.4	1.5	1.6	1.6	1.7	1.7	1.8	6,000
24	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	1,800
26	slowest	0.4	0.5	0.5	0.6	0.7	0.7	0.8	0.8	0.9	1.0	1.0	1.1	1.2	1.2	1.3	1.4	1.4	1.5	1.6	1.6	1.7	1.8	1.8	1.9	2.0	6,000
26	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	2,000
28	slowest	0.4	0.5	0.6	0.6	0.7	0.8	0.8	0.9	1.0	1.1	1.1	1.2	1.3	1.3	1.4	1.5	1.5	1.6	1.7	1.8	1.8	1.9	2.0	2.0	2.1	6,000
28	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	2,100
30	slowest	0.5	0.5	0.6	0.7	0.8	0.8	0.9	1.0	1.1	1.1	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.7	1.8	1.9	2.0	2.0	2.1	2.2	2.3	6,000
30	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	2,300
35	slowest	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.6	6,000
35	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	2,600
40	slowest	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	6,000
40	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	3,000
50	slowest	0.8	0.9	1.0	1.1	1.3	1.4	1.5	1.6	1.8	1.9	2.0	2.1	2.3	2.4	2.5	2.6	2.8	2.9	3.0	3.1	3.3	3.4	3.5	3.6	3.8	6,000
50	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	3,800
60	slowest	0.9	1.1	1.2	1.4	1.5	1.7	1.8	2.0	2.1	2.3	2.4	2.6	2.7	2.9	3.0	3.2	3.3	3.5	3.6	3.8	3.9	4.1	4.2	4.4	4.5	6,000
60	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	4,500
70	slowest	1.1	1.2	1.4	1.6	1.8	1.9	2.1	2.3	2.5	2.6	2.8	3.0	3.2	3.3	3.5	3.7	3.9	4.0	4.2	4.4	4.6	4.8	4.9	5.1	5.3	6,000
70	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	5,300
78	slowest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.3	4.5	4.7	4.9	5.1	5.3	5.5	5.7	5.9	6,000
78	fastest	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	5,900

Appendix A4-A–Table 5. Filling times for isokinetic samplers. [To determine the transit rate, in feet per second, multiply the depth at the sampling vertical by 2 and divide by the sampling time.]

Appendix A4-A–Table 5a. Filling times for DH-81 sampler

DH-81 filling times, in seconds, to collect **800 milliliters**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
1.8	4	6	
2.0	74	41	27
2.2	67	38	24
2.4	61	35	22
2.6	57	32	20
2.8	53	30	19
3.0	49	28	18
3.2	46	26	17
3.4	43	24	16
3.6	41	23	15
3.8	39	22	14
4.0	37	21	13
4.2	35	20	13
4.4	33	19	12
4.6	32	18	12
4.8	31	17	11
5.0	29	17	11
5.2	28	16	10
5.4	27	15	10
5.6	26	15	9
5.8	25	14	9
6.0	25	14	9
6.2	24	13	9
6.4	1	3	8
6.6	1	3	8
6.8	1	2	8
7.0	1	2	8
7.2	1	2	
7.4	1	1	
7.6	1	1	

Appendix A4-A–Table 5b. Filling times for DH-95 sampler

DH-95 filling times, in seconds, to collect **800 milliliters**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
1.6	92	52	33
1.8	82	46	29
2.0	74	41	27
2.2	67	38	24
2.4	61	35	22
2.6	57	32	20
2.8	53	30	19
3.0	49	28	18
3.2	46	26	17
3.4	43	24	16
3.6	41	23	15
3.8	39	22	14
4.0	37	21	13
4.2	35	20	13
4.4	33	19	12
4.6	32	18	12
4.8	31	17	11
5.0	29	17	11
5.2	28	16	10
5.4	27	15	10
5.6	26	15	9
5.8	25	14	9
6.0	25	14	9
6.2	24	13	9
6.4	23	13	8
6.6	22	13	8
6.8	22	12	8
7.0	21	12	8
7.2	20	12	7
7.4	20	11	7
7.6	19	11	7

Appendix A4-A–Table 5c.
Filling times for D-95 sampler

D-95 filling times, in seconds, to collect **800 milliliters**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
1.4	105	59	38
1.6	92	52	33
1.8	82	46	29
2.0	74	41	27
2.2	67	38	24
2.4	61	35	22
2.6	57	32	20
2.8	53	30	19
3.0	49	28	18
3.2	46	26	17
3.4	43	24	16
3.6	41	23	15
3.8	39	22	14
4.0	37	21	13
4.2	35	20	13
4.4	33	19	12
4.6	32	18	12
4.8	31	17	11
5.0	29	17	11
5.2	28	16	10
5.4	27	15	10
5.6	26	15	9
5.8	25	14	9
6.0	25	14	9
6.2	24	13	9
6.4	23	13	8
6.6	22	13	8
6.8	22	12	8
7.0	21	12	8
7.2	20	12	7
7.4	20	11	7
7.6	19	11	7

Appendix A4-A–Table 5d.
Filling times for DH-2 sampler

DH-2 filling times, in seconds, to collect **1 liter**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
2.0	92	52	33
2.5	74	41	27
3.0	61	35	22
3.5	53	30	19
4.0	46	26	17
4.5	41	23	15
5.0	37	21	13
5.5	33	19	12
6.0	31	17	11

Appendix A4-A–Table 5e.
Filling times for D-96 sampler

D-96 filling times, in seconds, to collect **3 liters**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
2.0	276	155	99
2.5	221	124	80
3.0	184	104	66
3.5	158	89	57
4.0	138	78	50
4.5	123	69	44
5.0	110	62	40
5.5	100	57	36
6.0	92	52	33
6.5	85	48	31
7.0	79	44	28
7.5	74	41	27
8.0	69	39	25
8.5	65	37	23
9.0	61	35	22
9.5	58	33	21
10.0	55	31	20
10.5	53	30	19
11.0	50	28	18
11.5	48	27	17
12.0	46	26	17
12.5	44	25	16
13.0	42	24	15
13.5	41	23	15
14.0	39	22	14
14.5	38	21	14
15.0	37	21	13

Appendix A4-A–Table 5f.
Filling times for D-96 A-1 sampler

D96 A-1 filling times, in seconds, to collect **3 liters**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
2.0	277	156	99
2.2	251	141	90
2.4	231	130	83
2.6	213	120	76
2.8	198	111	71
3.0	185	104	66
3.2	173	97	62
3.4	163	91	58
3.6	154	86	55
3.8	146	82	52
4.0	137	77	50
4.2	132	74	47
4.4	126	71	45
4.6	120	68	43
4.8	115	65	41
5.0	111	62	40
5.2	106	60	38
5.4	102	58	37
5.6	99	56	35
5.8	95	54	34
6.0	92	52	33

Appendix A4-A–Table 5g.
Filling times for D-99 sampler

D-99 filling times, in seconds, to collect **6 liters**			
stream velocity (ft/sec)	nozzle diameter (in.)		
	3/16	1/4	5/16
3.0	368	207	133
3.5	316	178	114
4.0	276	155	99
4.5	245	138	88
5.0	221	124	80
5.5	201	113	72
6.0	184	104	66
6.5	170	96	61
7.0	158	89	57
7.5	147	83	53
8.0	138	78	50
8.5	130	73	47
9.0	123	69	44
9.5	116	65	42
10.0	110	62	40
10.5	105	59	38
11.0	100	57	36
11.5	96	54	35
12.0	92	52	33
12.5	88	50	32
13.0	85	48	31
13.5	82	46	29
14.0	79	44	28
14.5	76	43	27
15.0	74	41	27

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APPENDIX A4-B
Instructions Related to Measuring Water Levels at Wells and a Sample USGS Ground-Water-Quality Field Form

All USGS personnel who sample or make water-level or water-quality measurements at wells must comply with requirements and be familiar with the guidelines provided by the USGS Office of Ground Water. Guidelines established by the Office of Ground Water related to measurement of well depth and water level have been adapted for water-quality work and are summarized in this appendix.

Appendix A4-B

Equipment and Supplies All sections of appendix A4-B – common supplies A4-B-1 – Establishing a permanent measuring point on wells A4-B-2 – Well-depth measurement.	
All sections	GWSI site schedule, Form 9-1904-A
	Ground-water-level measurement field form and/or other field forms and/or handheld or field computer for data entry
	Pens, ballpoint with non-erasable blue or black ink, for writing on field forms and in equipment log books
	Field folder and well file
	Two wrenches with adjustable jaws and other tools for removing the well cap
	Clean rag
	Key(s) for opening locks
	Equipment-cleaning supplies (NFM 3). Tape-cleaning supplies: refer to NFM 3.3.8 for soap-and-water wash guidance and disinfection. If disinfecting, use either (a) commercially available hypochlorite wipes; or (b) prepare a dilute chlorine solution adding 1 mL of common household bleach to 900 mL of water (0.005-percent solution)
A4-B-1	**Establishing a permanent measuring point (MP)**
	Steel tape, graduated in feet, tenths, and hundredths of feet; calibrated for making field measurements
	Reference steel tape, graduated in feet, tenths, and hundredths of feet; designated for calibration of field steel and electric tapes
	Calibration and maintenance log book for each steel tape
	Spray paint (bright color) or casing-notching tool
A4-B-2	**Well-depth measurement with steel tape**
	Steel tape, graduated in feet, tenths, and hundredths of feet; calibrated for making measurements. A black tape is better than a chromium-plated tape. If a chromium-plated tape has to be used, paint the back of the tape with a flat black paint to make it easier to read the wetted chalk mark
	Reference steel tape, graduated in feet, tenths, and hundredths of feet; designated for calibration of field steel and electric tapes
	Steel-tape calibration and maintenance log book (one for each steel tape)
	Weight (stainless steel, iron, or other noncontaminating material) – not lead
	Strong ring and wire, for attaching weight to end of tape. Wire should be strong enough to hold weight securely, but not as strong as the tape, so that if the weight becomes lodged in the well the tape can still be pulled free
	Carpenters' chalk (blue)

Appendix A4-B-1
Establishing a permanent measuring point on wells at which water level will be measured[1]

A permanent measuring point (MP) from which all water levels for a given well are measured must be established for each well at which USGS data are collected. The MP should be established when a monitor well is installed or an existing well is inventoried. The accuracy with which the MP is established depends on the accuracy of the water-level measurement being made. **For water level measured in hundredths of a foot, the MP is to be established to an accuracy of 0.01 foot.** This guidance assumes that:

- All water-level measurements from a given well must be referenced to the same datum to ensure data comparability.
- Land-surface datum (LSD) at the well was established by the person who made the initial water-level measurement at the well. LSD is an arbitrary plane chosen to be approximately equivalent to the average altitude of the ground around thewell. Because LSD around a well may change over time, the distance between the MP and LSD should be checked every 3 to 5 years, or more frequently because of land development or other changes.
- Measuring points can change from time to time, especially on privately-owned wells. Such changes must be documented and dated in field notes and in the data base(s) into which the water-level data are entered.

To establish a permanent measuring point:

1. Establish the location of the MP at a specific point within the top of the casing. The MP is measured in reference to LSD. If possible, position the MP at a point on the casing where a leveling rod could be set on it directly over the well and the measuring tape can hang freely when it is in contact with the MP. Locate the MP at the most convenient place from which to measure the water level.

[1]From the USGS Office of Ground Water, Ground-Water Procedure Document 3.

2. Clearly mark the MP, either with an arrow sprayed with bright-colored paint or with a notch cut into the top of the casing. The MP must be as permanent as possible and be clearly visible and easily located. Location of the MP must be described in the well file.
3. Measure the height of the MP in feet above or below LSD. For USGS studies, record the following information into GWSI (figure B1):
   - Height and detailed description of the MP. Note that values for measuring point below land surface should be preceded by a minus sign (-).
   - Date the MP was established.
4. For most water-quality studies, the LSD and MP should be surveyed in.
5. Establish at least one clearly displayed reference mark (RM) in a location near the well; for example, a lag bolt set into a nearby telephone pole. The RM is an arbitrary datum established by permanent marks and is used to check the MP or to re-establish an MP should the original MP be destroyed or need to be changed.
6. Clearly locate the MP and RM on a detailed site sketch that goes into the well folder; the sketch commonly is made on the back of the paper GWSI form. If possible, photograph the site, including the RM and MP locations; draw an arrow to the RM and MP on the photograph(s) using an indelible marker, and place the photos in the well file.

Appendix A4-B-2
Well-depth measurement[2]

This method uses a graduated steel tape to measure the total depth of a well below land-surface datum. Select a graduated steel tape that is accurate to 0.01 foot. The steel tape should be calibrated against a reference steel tape. A reference steel tape is one that is maintained in the office and designated solely for tape calibration.

- If the well casing is angled, instead of vertical, the well depth will have to be corrected.
- When measuring wells of depth greater than 200 feet (deep wells), expansion and stretch of the steel tape must be considered and accounted for (see Garber and Koopman, 1968).
- Use of a steel tape is **not** recommended for measuring the depth of pumping wells.
- A weight usually is attached to the end of a steel tape to allow it to hang plumb. The weight should not be constructed of lead or other material that potentially could contaminate water in the well.
- Well obstructions could cause errors in the measurement if the steel tape cannot hang plumb.

To measure well depth:

1. Using a clean, calibrated steel tape, measure from the zero point on the tape to the bottom of the weight. Record this number as the length of the weight interval.
2. Lower the weight and tape into the well until the weight reaches the bottom of the well and the tape slackens.
3. Partially withdraw the tape from the well until the weight is standing in a vertical position, but still touching the bottom of the well. A slight jerking motion will be felt as the weight moves from the horizontal to the vertical position.
4. Repeat step 3 several times by lowering and withdrawing the tape to obtain a consistent reading.
5. Record the tape reading held at the measuring point (MP).

[2]From the USGS Office of Ground Water, Ground-Water Procedure Document 11.

6. Withdraw the tape from the well 1 to 2 feet, so that the weight will hang freely above the bottom of the well. Repeat steps 2-4 until two consistent depth readings are obtained.
7. Calculate total well depth below land-surface datum (LSD) as follows:

a. Tape reading held at the MP	84.3 feet
b. Length of the weight interval	+ 1.2 feet
c. Sum of a + b	85.5 feet
d. MP correction	- 3.5 feet
e. Total well depth below LSD	82.0 feet

8. After completing the well-depth measurement, clean the exposed portion of the tape using the procedures described in NFM 3.3.8. To prevent microbial cross-contamination of other wells, disinfect the tape using commercially available hypochlorite wipes or a dilute (0.005-percent) chlorine solution.
9. Record depth data to the nearest 0.01 foot. USGS well-depth data should be recorded in GWSI and on the Ground-Water Level Notes (fig. B1) and other field forms that are kept in the field folder.

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USGS science for a changing world

FIELD ID _____

GROUND-WATER LEVEL NOTES

Station No._____ Field ID _____

Station Name _____

Project No. _____ Proj Name_____

Measurement made by: _____

Signature _____ Date _____

WELL___ SPRING___ MONITOR___ SUPPLY___ OTHER_____

SUPPLY WELL PRIMARY USE: DOMESTIC__ PUBLIC SUPPLY__ IRRIGATION __ OTHER_____

Casing Material: _____ Altitiude (land surface) _____ ft abv MSL

Measuring Point: _____ ft abv blw LSD MSL MP Well Depth _____ ft abv blw LSD MSL MP

Sampling condition (72006) pumping (8) flowing (4) static (n/a)

[see QWDATA User Manual for additional fixed-value codes]

Water Level: _____ ft blw LSD (72019) ft blw MP (61055)

ft abv MSL (NGVD 29) (62610) ft abv MSL (NAVD 88) (62611)

Comments:

Depth to Water and Well Depth

	1ST	2ND	3RD (optional)
Time			
Hold (for DTW)			
- Cut			
= DTW from MP			
– Measuring point (MP)			
= DTW from LSD			
Hold (for well depth)			
+ Length of tape leader			
= Well depth below MP			
– MP			
= Well depth below LSD			

WATER-LEVEL DATA FOR GWSI

DATE WATER LEVEL MEASURED (C235) __ __-__ __-__ __ __ __ (Month Day Year)

TIME (C709) __ __ __ __

WATER LEVEL TYPE CODE (C243): L (below land surface) M (below meas. pt.) S (sea level)

WATER LEVEL (C237/241/242) __ __ __ __.__ __

MP SEQUENCE NO. (C248) __ __ __ (Mandatory if WL type=M)

WATER LEVEL DATUM (C245) (Mandatory if WL type=S): NGVD 29 (National Geodetic Vertical Datum 0f 1929) NAVD 88 (North American Vertical Datum 0f 1988) | | | | | | | | | | (Other (See GWSI manual for codes))

SITE STATUS FOR WATER LEVEL (C238): A atmos. pressure; B tide stage; C ice; D dry; E recently flowing; F flowing; G nearby flowing; H nearby recently flowing; I injector site; J injector site monitor; M plugged; N measurement discontinued; O obstruction; P pumping; R recently pumped; S nearby pumping; T nearby recently pumped; V foreign substance; W well destroyed; X affected by surface water; Z other

METHOD OF WATER-LEVEL MEASUREMENT(C239): A airline; B analog; C calibrated airline; E estimated; F transducer; G pressure gage; H calibrated pres. gage; L geophysical logs; M manometer; N non-rec. gage; O observed; R reported; S steel tape; T electric tape; V calibrated elec. tape; Z other

WATER LEVEL ACCURACY (C276): 0 foot; 1 tenth; 2 hundreth; 9 not to nearest foot

SOURCE OF WATER-LEVEL DATA (C244): A other gov't; D driller's log; G geologist; L geophysical logs; M memory; O owner; R other reported; S reporting agency; Z other

PERSON MAKING MEASUREMENT (C246) (WATER-LEVEL PARTY) | | | | | |

MEASURING AGENCY (C247) (SOURCE) | | | | | |

RECORD READY FOR WEB (C858): Y checked; ready for web display; C not checked; no web display; P proprietary; no web display; L local use only; no web display

COMPILED BY :_____ DATE _____ ENTERED INTO GWSI BY: _____ DATE _____

CHECKED BY :_____ DATE _____ ENTERED INTO QWDATA BY: _____ DATE _____

GW Water Level Form ver. 1

Figure B1. Example of a USGS field form for ground-water-level measurements.

Appendixes A4-B-3(a) and (b) Water-level measurement by (a) steel tape, or (b) electric tape

A4-B-3: Equipment and Supplies A4-B-3(a) – Water-level measurement by graduated steel tape A4-B-3(b) – Water-level measurement by electric tape	
A4-B-3(a + b)[1]	Steel tape, graduated in feet, tenths, and hundredths of feet; calibrated for making water-level measurements
A4-B-3(a) [1]	Reference steel tape, graduated in feet, tenths, and hundredths of feet. A reference steel tape is one that is maintained in the office and designated solely for tape calibration
A4-B-3(a)	Steel-tape calibration and maintenance log book (one for each steel tape). Field forms, paper and/or electronic; ballpoint pens (blue or black, non-erasable) for recording information in the log book and on paper field forms
A4-B-3(a)	Weight (stainless steel, iron, or other noncontaminating material – do not use lead)
A4-B-3(a)	Strong ring and wire, for attaching weight to end of tape. Wire should be strong enough to hold weight securely, but not as strong as the tape, so that if the weight becomes lodged in the well the tape can still be pulled free
A4-B-3(a)	Carpenters' chalk (blue)
A4-B-3(a + b)	Tape-cleaning supplies: refer to NFM 3.3.8 for soap-and-water wash guidance and disinfection. Disinfect using either commercially available hypochlorite wipes or a dilute (0.005-percent solution) chlorine solution
A4-B-3(b)[2]	An electric tape, double-wired and graduated in feet, tenths, and hundredths of feet, accurate to 0.01 ft. Electric tapes commonly are mounted on a hand-cranked and powered supply reel that contains space for the batteries and some device ("indicator") for signaling when the circuit is closed
A4-B-3(b)	Electric-tape calibration and maintenance log book; manufacturer's instructions. Field forms, paper and/or electronic; ballpoint pens (non-erasable blue or black ink) for recording information in the log book and on paper field forms
A4-B-3(b)	Replacement batteries, charged
A4-B-3(a + b)	Clean rag
A4-B-3(a + b)	Two wrenches with adjustable jaws or other tools for removing the well cap

[1]A black tape is better than a chromium-plated tape. If a chromium-plated tape has to be used, paint the back of the tape with a flat black paint to make it easier to read the wetted chalk mark.

[2]An older model electric tape, also known as an "M-scope", marked at 5-foot intervals with clamped-on metal bands has been replaced by newer, more accurate models.

A4-B-3(a) Steel tape[3]

The graduated steel-tape (wetted-tape) procedure is considered to be the most accurate method for measuring a depth to the water surface at nonflowing wells. A graduated steel tape is commonly accurate to 0.01 foot. When measuring deep water levels, however, tape expansion and stretch is a necessary consideration (Garber and Koopman, 1968). The method is most accurate for water levels less than 200 feet below land surface. This method is **not** recommended for measuring pumping levels in wells.

- May be impossible to get reliable results if water is dripping into the well or condensing on the well casing.
- If the well casing is angled, instead of vertical, the depth to water will have to be corrected.
- The steel tape should be calibrated against a reference steel tape. A reference steel tape is one that is maintained, in the office, for use only for calibrating steel tapes.
- Check that the well is free of obstructions that can affect the plumbness of the steel tape. An accurate measurement cannot be made if the tape does not hang plumb.

Before making a measurement:

1. Ensure that the steel tape for field use has been calibrated, using a reference steel tape (see the Equipment and Supplies table for Appendix A4-B-3, above). Check the equipment log book for the designated steel tape for calibration information.
2. Maintain the tape in good working condition by periodically checking the tape for rust, breaks, kinks, and possible stretch. Record all calibration and maintenance data associated with the steel tape in its calibration and maintenance log book.
3. If the steel tape is new, be sure that the black sheen on the tape has been dulled so that the tape will retain the chalk.
4. Attach a weight to the tape that is constructed of stainless steel or other noncontaminating material to protect ground-water quality in the event that the weight is lost in the well.
5. Place any previous measured water-level data for the well into the field folder.

[3]From the USGS Office of Ground Water, Ground-Water Procedure Document 1.

6. Check that the measuring point (MP) is clearly marked on the well and accurately described in the well file or field folder. If a new measuring point needs to be established, follow the procedures in Appendix A4-B-1 but do not use paint or create casing-material filings until after sampling has been completed for the day.
7. Prepare the Ground-Water Level Notes and Water-Level Data for GWSI field forms (fig. B1). The measurement process will be repeated at least twice and recorded in the respective column (refer to the unshaded portion of the box at the upper right of fig. B1). Record the time of measurement, using the column headed "1st" for the initial set of measurements. Water-level data are to be recorded to the appropriate accuracy for the depth being measured.
8. Spread clean plastic sheeting around the well to prevent the well tape from contacting the ground and introducing dirt into the well.

To measure water level using a steel tape:

1. Chalk the lower few feet of the tape by pulling the tape across a piece of blue carpenter's chalk (the wetted chalk mark identifies that part of the tape that was submerged).
2. If water level was measured previously at the well, use the previous measurement(s) to estimate the length of tape that should be lowered into the well.
3. Slowly lower the weight and tape into the well until the bottom end of the tape is submerged below the water. Work carefully to avoid splashing. Continue to lower the end of the tape into the well until the next graduation (a whole foot mark) is opposite the MP and record this number on the field form (fig. B1) next to "Hold (for DTW)" as illustrated on fig. B2.
4. Rapidly bring the tape to the surface before the wetted chalk mark dries and becomes difficult to read. Record the number as the "Cut."
5. Subtract the "Cut" from the "Hold" and record the difference as "DTW from MP" (Depth To Water from MP). The difference between these two readings is the depth to water below the MP.
6. Record the MP correction, subtract it from "DTW from MP," and record the result as "DTW from LSD" (depth to water from land-surface datum).

- To obtain the depth to water below land surface if the MP is above land surface: the distance between the MP and land surface datum is subtracted from the depth to water from the MP.
- To obtain the depth to water below land surface if the MP is below land surface: precede the MP correction value with a minus (-) sign and subtract the distance between the MP and land surface datum from the depth to water from the MP.
- If the water level is above LSD, record the depth to water in feet above land surface as a negative number.

7. Make a check measurement by repeating steps 2 through 6, recording check measurements in the second ("2nd") column (fig. B1).
   - The check measurement should be made using a different MP hold value than that used for the original measurement.
   - If the check measurement does not agree with the original measurement within 0.01 or 0.02 of a foot, make a third check measurement, recording this measurement in the third column. Make repeated check measurements until the reason for the lack of agreement is determined or until the results are shown to be reliable.
   - If more than two readings are taken, record the average of all readings.
8. In some pumped wells, a layer of oil may float on the water surface.
   - If the oil layer is a foot thick, read the tape at the top of the oil mark and use this data for the water-level measurement instead of the wetted chalk mark. The measurement will differ slightly from the water level that would be measured were the oil not present.
   - If several feet of oil are present in the well,or if it is necessary to know the thickness of the oil layer, a commercially available water-detector paste can be used that will detect the presence of water in the oil. Apply the paste to the lower end of the tape. The top of the oil shows as a wet line, and the top of the water shows as a distinct color change. Since oil density is about three-quarters that of water, the water level can be estimated by adding the thickness of the oil layer times its density to the oil-water interface elevation.
9. Record water-level data to the nearest 0.01 foot. Record USGS water-level data on field forms (kept in the field folder) and in GWSI, using the appropriate method code(s) (fig. B1).

10. After completing the water-level measurement, clean the exposed portion of the tape using the procedures described in NFM 3.3.8. To prevent microbial cross-contamination of other wells, disinfect the tape using commercially available hypochlorite wipes or a dilute chlorine solution (1 mL of bleach added to 900 mL water) (NFM 3.3.8). Rinse with DIW and dry the tape after each use. Do not store a steel tape while dirty or wet.

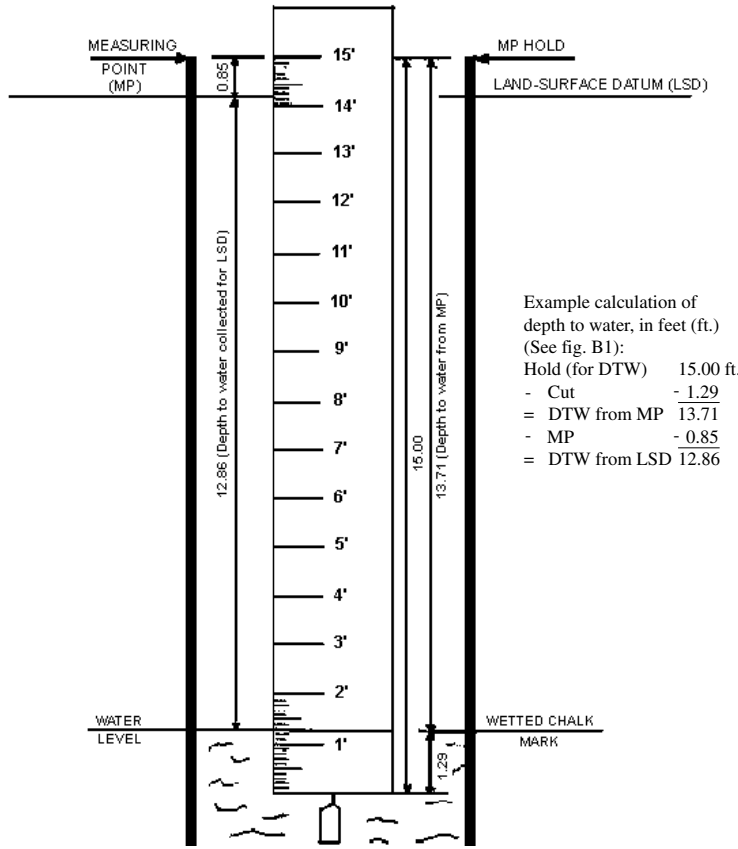


Figure B2. Example of a water-level measurement using a graduated steel tape.

A4-B-3(b) Electric tape[4]

The electric-tape procedure for measuring depth to the water surface in a nonflowing well is especially useful in wells that are being pumped with large-discharge pumps, when making a series of measurements in rapid succession (for example, during purging or aquifer tests), and in wells with condensation or dripping water. Use of an electric tape minimizes the danger of tape entanglement in the pump impellers because the probe signals when the water surface is reached.

The accuracy of electric-tape measurements depends on the type of tape used and whether or not the tape has been stretched out of calibration after use. Tapes that are marked the entire length with feet, tenths, and hundredths of a foot can be considered accurate to ± 0.01 ft and are most accurate for water levels less than 200 ft below land surface. Electric tapes are harder to keep calibrated than are steel tapes. When measuring deep water levels, tape expansion and stretch is an additional consideration (see Garber and Koopman, 1968). The electric tape should be calibrated against a reference steel tape (see the Equipment and Supplies table above for Appendix A4-B-3.

- If the water in the well has very low specific conductance, the tape may not give an accurate reading.
- Material on the water surface, such as oil, may interfere with obtaining consistent readings.
- If the well casing is angled, instead of vertical, the depth to water will have to be corrected.
- **The electric tape should be recalibrated annually or more frequently** if it is used often or if the tape has been subjected to abnormal stress that may have caused it to stretch.

Before measuring water level with the electric tape:

1. The electric steel tape requires an initial calibration before using it in the field. Calibrate the electric tape against a reference steel tape as follows:
   a. Check the distance from the probe's sensor to the nearest foot marker on the tape, to ensure that this distance puts the sensor at the zero foot point for the tape. If it does not, a correction must be applied to all depth-to-water measurements. Record this in the equipment log book and on the field form.

[4]From the USGS Office of Ground Water, Ground-Water Procedure Document 4, version 2007.1.

b. Compare length marks on the electric tape to those on the reference tape with the tapes laid out straight on the ground, or compare the electric tape against the known distance between fixed points on the ground.

c. Compare water-level measurements made with the electric tape to those made with the reference steel tape (or one that has recently been calibrated against it) in several wells that span the range of depths to water that are anticipated. For water levels of less than 500 ft below the MP, measurements should agree to within +/- 0.01 ft. For water levels greater than 500 ft below the MP, measurements should agree to within 1 part in 1000. If these accuracies are not met, then a correction factor based on a regression analysis should be developed.

d. Record all calibration and maintenance data in the calibration and maintenance log book for the electric tape.

2. Check the circuitry of the electric tape before lowering the probe into the well. To determine proper functioning of the tape mechanism, dip the probe into tap water and observe whether the indicator needle, light, and/or beeper (collectively termed the "indicator" in this document) indicate a closed circuit. For an electric tape with multiple indicators (sound and light, for instance), confirm that the indicators operate simultaneously. If they do not operate simultaneously, determine which is the most accurate and use that one.

3. Inspect the electric tape before using it in the field.

   a. Check the tape for wear, kinks, frayed electrical connections and possible stretch; the cable jacket tends to be subject to wear and tear.

   b. Test that the battery and replacement batteries are fully charged.

4. Place any previous measured water-level data for the well into the field folder.

5. After reaching the field site, check that the measuring point (MP) is clearly marked on the well and is accurately described in the well file or field folder. If a new measuring point needs to be established, follow the procedures in Appendix A4-B-1, but do not use paint or create casing-material filings until after sampling has been completed to avoid sample contamination.

6. Prepare the Gound-Water Level Notes and Water-Level Data for GWSI field forms (fig. B1). The measurement process will be repeated at least twice and recorded in the respective column (refer to the unshaded portion of the box at the upper right of fig. B1). Record the time of measurement, using the column headed "1st" for the initial set of measurements. Data are to be recorded to the appropriate accuracy for the depth being measured.
7. Prevent the well tape from contacting the ground and introducing dirt into the well by spreading a clean plastic sheet around the well.

To measure water level using an electric tape:

1. Lower the electrode probe slowly into the well until the indicator shows that the circuit is closed and contact with the water surface is made. Avoid letting the tape rub across the top of the well casing. Place the tip or nail of the index finger on the insulated wire at the MP and read the depth to water.
   - Record the depth to water measurement in the first data-entry column, as "DTW from MP."
   - Record the date and time of the measurement.
   - Make all readings using the same deflection point on the indicator scale, light intensity, or sound so that water levels will be consistent between measurements.
   - If the tape has been repaired and spliced go to the section on using a repaired/spliced tape (step 6).
2. Apply the MP correction to get the depth to water in feet below or above LSD. If the MP is below land surface, precede the MP correction value with a minus (-) sign to obtain the MP height. In all cases, subtract the MP height from the water level to obtain the depth to water (DTW from LSD). Referring to the non-shaded section of the Ground-Water Level Notes field form (fig. B1) in the "Depth to Water and Well Depth" table, record this value in the first (1st) data-entry column as "DTW from LSD." If the water level is above LSD, enter the water level as feet above land surface preceded by a minus sign (-).
3. Make a check measurement by repeating steps 1 and 2 and record the measurement in the second data column of fig. B1. If the check measurement does not agree with the original measurement within 0.01 or 0.02 of a foot, make a third check measurement, recording this measurement in the third (3rd) column. Make repeated check measurements until the reason for the lack of agreement is determined or until the results are shown to be reliable. If more than two readings are taken, record the average of all readings.

4. Water-level data are recorded to the nearest 0.01 foot. Record USGS water-level data on field forms and in GWSI, using the appropriate method code(s) (fig. B1).
5. After completing the well measurement, wipe down the section of the tape that was submerged in the well water, using the cleaning and/or disinfection method of choice (NFM 3.3.8). If disinfecting the tape, rinse the tape thoroughly with deionized or tap water after disinfection Dry the tape and rewind it onto the tape reel. Do not rewind or otherwise store a dirty or wet tape.
6. **Using a repaired/spliced tape:** If the tape has been repaired by cutting off a section of tape that was defective and splicing the sensor to the remaining section of the tape, then the depth to water reading at the MP will not be correct. To obtain the correct depth to water, apply the following steps, which is similar to the procedure for using a steel tape and chalk.
    a. Ensure that the splice is completely insulated from any moisture and that the electrical connection is complete.
    b. Measure the distance from the sensing point on the probe to the nearest foot marker above the spliced section of tape. Subtract that distance from the nearest foot marker above the spliced section of tape. That point then becomes the "tape correction." For example, if the nearest foot marker above the splice is 20 feet, and the distance to the probe sensor is 0.85 ft, then the tape correction will be 19.15 feet. Record the tape correction on a field form. Periodically recheck the tape-correction factor by measuring the spliced electric tape with a reference steel tape.
    c. Lower the electrode probe slowly into the well until the indicator shows that the circuit is closed and contact with the water surface is made. Place the tip or nail of the index finger on the insulated wire at the MP and read the depth to water. Record the depth-to-water measurement and the date and time of the measurement on the field form.
    d. Subtract the "Tape Correction" value from the "Hold" value and record the result as DTW from LSD (fig. B1).
    e. Return to Step 2.

Appendix A4-B-4
Water-level measurement by the air-line method[5]

The submerged air-line method for measuring a depth to the water surface in a nonflowing well requires installation of the air line and associated equipment. This method is especially useful in pumped wells where water turbulence may preclude using a more precise (steel-tape or electric-tape) method and can be used while the well is being pumped.

The air-line method is less accurate than the graduated steel-tape or the electric-tape method. Bends or spirals in the air line do not influence the accuracy of this method as long as the position of the tubing is not appreciably changed.

- Water-level measurements using an altitude gage should be accurate to 0.1 foot.
- Water-level measurements using a pressure gage are approximate and should notbe considered accurate to more than the nearest one foot.
- When measuring deep water levels, corrections for fluid temperatures and vertical differences in air density are additional considerations (see Garber and Koopman, 1968).

Equipment and Supplies Appendix A4-B-4 – Air-line method for water-level measurement	
	1/8 or 1/4-inch diameter, seamless copper tubing, brass tubing, or galvanized pipe with a suitable pipe tee for connecting an altitude or pressure gage. (Flexible plastic tubing can be used but is less desirable).
	Altitude or pressure gage, and spare gages
	Tire valve stem and tire pump
	Small open-end wrench
	Wire or electrician's tape
	Steel tape (see Appendix A4-B-3)
	Carpenters' chalk
	Equipment calibration and maintenance log books, for each altitude or pressure gage and steel tape.
	Tape-cleaning supplies (refer to the list for well depth and steel- and electric-tape water-level measurement)

[5]From the USGS Office of Ground Water, Ground-Water Procedure Document 13

To measure water level using the air-line method:

1. Install an air-line pipe or tube in the well. Figure B3 shows a typical installation for measuring water levels by the air-line method.
   - The air line can be installed by either lowering it into the annular space between the pump column and casing after the pump has been installed in the well, or by securing it to sections of the pump and pump column with wire or tape as it is lowered into the well.
   - The air line must extend far enough below the water level that the lower end remains submerged during pumping of the well.
2. Attach a pipe tee to the top end of the air line. On the opposite end of the pipe tee, attach a tire valve stem.
3. Using a wrench, connect to the fitting on top of the pipe tee either (a) an altitude gage that reads in feet, or (b) a pressure gage, that reads pressure in pounds per square inch (lb/in^2 or psi).
4. Connect a tire pump to the tire valve stem fitting on the pipe tee.
   - As the water level in the well changes, **h** and **d** (fig. B3) must change in a manner such that their sum remains the same.
   - Their sum is a constant (**k**), which is determined at the same time as a simultaneous wetted-steel tape and air gage measurement is made.
5. To calibrate the air line and gage, make an initial depth to water level (**d**) measurement with a wetted-steel tape, and an initial air gage reading (**h**). Add **d** and **h** to determine the constant value for **k**. Use a tire pump to pump compressed air into the air line until all the water is expelled from the line. Once all water is displaced from the air line, record the maximum gage reading.
   - *Example (a)* – using an altitude gage: given an initial measured depth to the water level, **d,** of 25.86 ft, the initial altitude gage reading, **h**, is 75.5 ft. Then the constant **k** = 25.9 ft + 75.5 ft = 101.4 ft).
   - *Example (b)* – using a pressure gage: given an initial measured depth to the water level, **d,** of 85.85 ft, the initial pressure gage reading, **h**, is 28 psi. Then the constant **k** = 86 ft + (2.3 ft/psi x 28 psi) = 86 ft + 64 ft = 150 ft.
6. Calibrate the air line and gage as described in step 5 above.

7. To measure the water level depth in a well with an air line, subsequent air line readings are subtracted from the constant **k** to determine the depth to the water level below the MP. Use a tire pump to pump compressed air into the air line until all the water is expelled from the line, and record the maximum gage reading.
   - *Example (a)* – depth to the water level in a well using an altitude gage with a constant **k** of 101.4 ft. During a later pumping period, the maximum altitude gage **h** reads 50.0 ft; therefore, the water level, **d** = 101.4 ft - 50.0 ft = 51.4 ft.
   - *Example (b)* – depth to the water level in a well using a pressure gage with a constant **k** of 150 ft. During a later pumping period, the maximum pressure gage **h** reads 18 psi; therefore, the water level, **d** = 150 ft - (2.3 ft/psi x 18 psi) = 150 ft - 41 ft = 109 ft.
8. Measure the water-level depth as described above in step 7.
9. Apply the MP correction to get the depth to water below or above land-surface datum.
10. Record USGS water-level data on a field form and in GWSI, using the appropriate method code(s).

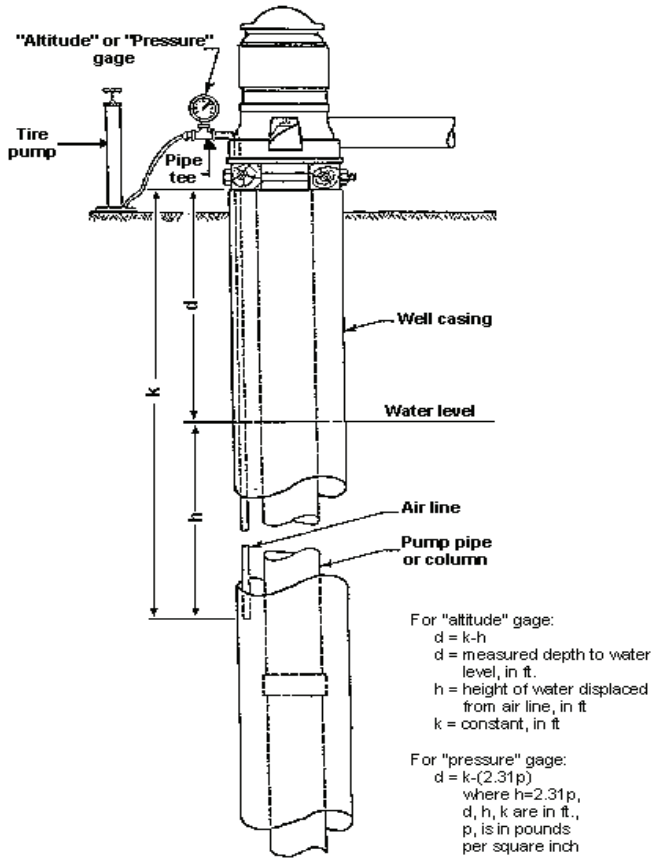


Figure B3. Typical installation for measuring water level by the air-line method. Modified from Driscoll, 1986.

Appendix A4-B-5
Water-level measurement at flowing wells using low-pressure and high-pressure methods[6]

Head can be measured at flowing wells under low-pressure and high-pressure conditions, but require training and experience to be executed correctly. The low-pressure head-measurement method is more accurate, simpler, faster, and safer than the high-pressure head-measurement method.

- Use the low-pressure head-measurement method at wells with heads lower than 5 to 6 feet above land surface (the low-pressure method is impractical at wells with heads greater than 5 to 6 feet above land surface).
- Use the high-pressure method at wells with heads greater than 5 to 6 feet above land surface. Be aware that implementing the high-pressure method is more complex, takes more time, and can be dangerous.
- The accuracy of the head measurement depends on the method and equipment used, and on the experience and care of the field person:
  - Low-pressure head measurements can be measured to an accuracy of 0.1 foot.
  - High-pressure head measurements using a pressure-gage probably are not accurate to within less than 0.1 foot, although they may be read to 0.01 foot.

[6]From the USGS Office of Ground Water, Ground-Water Procedure Document 12.

Equipment and Supplies Appendix A4-B-5 – Flowing-well water-level measurements	
Low pressure	Short length of transparent plastic tubing
	Hose clamps
	Measuring scale
High pressure	Flexible hose with a 3-way valve
	Hose clamps
	Altitude or pressure gage, and spare gages
	Small open end wrench
	Altitude or pressure gage calibration and maintenance log book(s)
	Soil-pipe test plug ("sanitary seal") to fit 2 to 10-inch diameter pipes (available at plumbing supply stores).[1]

[1] Soil-pipe test plugs consist of a length of small-diameter pipe, generally 0.75 inch, surrounded by a rubber packer. The packer can be expanded by an attached wingnut to fit tightly against the inside of the well casing or discharge pipe. The small-diameter pipe is threaded so that it can be attached to a valve, hose, or altitude/pressure gage.

When preparing for measuring the head at a flowing well:

1. **If using the high-pressure method, handle the pressure gage appropriately and with care**. Altitude/pressure gages are delicate, easily broken and subject to erroneous readings if dropped or mistreated.
   - The middle third of the range of the pressure gage provides the most accurate reading.
   - **Never let the well pressure exceed the altitude/pressure gage limits.**
   - Never connect a gage to a well that uses a booster pump in the system – the pump could start automatically and the resulting pressure surge may ruin the gage.
   - Altitude/pressure gages must be calibrated with a dead-weight tester. Record the calibration in the instrument log book for the gage that is being used.
2. When a flowing well is closed or opened by a valve or test plug, it should be done gradually. If pressure is applied or released suddenly, the well could be permanently damaged by the "water-hammer effect" by caving of the aquifer material, breakage of the well casing, or damage to the distribution lines or gages. To reduce the possibility of a "water-hammer effect", install a "pressure-snubber" ahead of the altitude/pressure gage.

3. If possible, shut down all flow from the well so that a static water-level measurement can be made; however, shut down may not be possible because of well owner objections or system leaks. Wells without a shut-down valve, can be shut-in by installing a soil-pipe test plug on the well or discharge line.
4. If a well has to be shut down, the time required to reach static pressure after shut-in may range from hours to days. Since it may be impractical or impossible to reach true static conditions, record the shut-in time for each gage reading. During return visits to a particular well, it is desirable to duplicate the previously used shut-in time before making an altitude/pressure gage reading.
5. Check that the measuring point (MP) is clearly marked on the well and accurately described in the well file or field folder. If a new measuring point needs to be established, follow the procedures in Appendix A4-B-1 but do not use paint or create casing-material filings until after sampling has been completed for the day.

To measure water level at a flowing well:

Low-pressure head-measurement (direct measurement) method:

1. Connect a short length of transparent plastic tubing tightly to the well with hose clamps.
2. Raise the free end of the tubing until the flow stops.
3. Rest the measuring scale on the measuring point (MP).
4. Read the water level directly, by placing the hose against the measuring scale.
5. Apply the MP correction to get the depth to water above land-surface datum.
6. Repeat steps 2 through 5 for a second check reading.

High-pressure head-measurement (indirect measurement) method:

1. Make sure that all well valves are closed except the one to the altitude/pressure gage. This will prevent use of the well during the measurement period and ensure an accurate water-level reading. Record the original position of each valve that is closed (full open, half open, closed, etc.), so that the well can be restored to its original operating condition.

2. Connect a flexible hose with a 3-way valve to the well with hose clamps.
3. Select a gage where the water pressure in the well will fall in the middle third of the gage range. If in doubt, use a pressure gage having a 100-pound per square inch (psi) range to make an initial measurement, then select the gage with the proper range for more accurate measurements.
4. Attach the altitude/pressure gage to one of the two "open" valve positions using a wrench. Never tighten or loosen the gage by twisting the case because the strain will disturb the calibration and give erroneous readings.
5. Bleed air from the hose, using the other "open" valve position.
6. Open the altitude/pressure gage valve slowly to reduce the risk of damage by the "water-hammer effect" to the well, distribution lines and gages. Once the needle stops moving, tap the glass face of the gage lightly with a finger to make sure that the needle is not stuck.
7. Make sure that the well is not being used by checking to see that there are no fluctuations in pressure.
8. Hold the altitude/pressure gage in a vertical position, with the center of the gage at the exact height of the MP. If using an altitude gage, read the gage to the nearest 0.1 foot. For pressure gages with psi units, read the gage to the nearest psi or 0.1 psi and multiply by 2.31 to convert to feet of water.
9. Apply the MP correction to get the depth to water above land-surface datum.
10. Shut off the well pressure and repeat steps e-i for a second check reading.
11. Record the identification number of the altitude/pressure gage with each water-level measurement so that the reading can be back referenced to the calibration record, if necessary.
12. Record USGS water-level data on field forms and in GWSI, using the appropriate method code(s).

Appendix A4-B-6
Sample of the U.S. Geological Survey Ground-Water Quality Notes field form[7]

[7]This form was developed for U.S. Geological Survey personnel and is included for informational use only.

February 2006

USGS science for a changing world

U. S. GEOLOGICAL SURVEY GROUND-WATER QUALITY NOTES

FIELD ID _____

NWIS RECORD NO _____

Station No._____ Station Name _____ Field ID _____

Sample Date _____ Mean Sample Time (watch) _____ Time Datum _____ (eg. EST, EDT, UTC)

Sample Medium _____ Sample Type _____ Sample Purpose (71999) _____ Purpose of Site Visit (50280) _____ QC Samples Collected? Y N

Project No. _____ Proj Name_____ Project No. _____ Proj Name_____

Sampling Team _____ Team Lead Signature _____ Date _____

Comments:

Sample Set ID _____

LABORATORY INFORMATION

Samples Collected: NUTRIENTS ____ MAJOR IONS ____ TRACE ELEMENTS: filtered ____ unfiltered ____ MERCURY: filtered ____ unfiltered ____ MICROBIOLOGY ____

ORGANICS: filtered ____ unfiltered ____ PEST ____ VOC ____ RADIOCHEMICALS: filtered ____ unfiltered ____ RADON ____ (Radon samp coll time:_____)

ISOTOPES ____ DOC ____ TPC ___ (vol filtered ____mL) PIC ___ (vol filtered ____mL) TPC (QC) ___ (vol filtered ____ mL) OTHER _____ _____

Lab Schedule: _____ _____ _____ _____ _____ _____ _____ _____ _____

Lab Codes: _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE

COMMENTS _____ Date Shipped _____

****Notify the NWQL in advance of shipment of potentially hazardous samples—phone 1-866-ASK-NWQL or email LabLogin@usgs.gov**

FIELD MEASUREMENTS

Water Level _____

ft blw lsd (72019) ft blw mp (61055)

ft abv msl (NGVD 1929) (62610)

ft abv msl (NAVD 1988) (62611)

Flow Rate (00059) _____ gal/min

Sampling Depth (78890) _____ ft blw msl

Sampling Depth (TBD) _____ ft blw lsd

Depth to top of sampling interval (72015) _____ ft blw lsd

Depth to bottom of sampling interval (72016) _____ ft blw lsd

Temp, Air (00020) _____ °C

Temp, Water (00010) _____ °C

pH (00400) _____ units

Sp. Cond (00095) _____ µS/cm@25 °C

Dis. Oxygen (00300) _____mg/L

DO sat. (00301) _____ %

Barometric pres. (00025) _____ mm Hg

Eh (00090) _____ mvolts

Turbidity ( ) _____ Method code ___

Units: FNU NTU FNMU FBU

ANC ( ) _____ mg/L

Alkalinity ( ) _____ mg/L

Bicarbonate ( ) _____ mg/L

Carbonate ( ) _____ mg/L

Hydroxide ( ) _____ mg/L

Hydrogen sulfide odor detected? (71875) yes no

Sample acidified beforehand? yes no

[see p. 7 for NWIS coding info]

Hyd. sulfide, unfltd, measured (99119) _____mg/L

Method: Hach Chemetrics Electrode

Other: _____ _____

SAMPLING INFORMATION

Sampler Type (84164) _____ Sampler/Pump Type (make/model) _____ Pump/Sampler ID _____

Sampling Method (82398) _____ Sampling Condition (72006) _____ Filter Type(s): Capsule Disc 142mm 47mm 25mm GFF Membrane

Sampler Material: STAINLESS STEEL PVC TEFLON OTHER _____ Tubing Material: TEFLON PLASTIC TYGON COPPER OTHER _____

Aquifer name _____ Depth pump set at: _____ft blw LSD MSL

Sampling point description _____

GW Color _____ GW Clarity _____ GW Odor _____ Sample in contact with: ATMOSPHERE OXYGEN NITROGEN OTHER _____

Weather : ***SKY-*** CLEAR PARTLY CLOUDY CLOUDY ***PRECIPITATION-*** NONE LIGHT MEDIUM HEAVY SNOW SLEET RAIN MIST _____

WIND- CALM LIGHT BREEZE GUSTY WINDY EST. WIND SPEED _____ MPH ***TEMPERATURE-*** VERY COLD COOL WARM HOT

OBSERVATIONS:

COMPILED BY :_____ **DATE** _____ **CHECKED BY :**_____ **DATE** _____ **LOGGED INTO NWIS BY:** _____ **DATE** _____

Calibrated by:_____ STN NO_____
Date:_____ Time:_____ Location: _____

METER CALIBRATIONS/FIELD MEASUREMENTS

TEMPERATURE Meter make/model _____ S/N _____ Thermister S/N _____ Thermometer ID _____

Calibration criteria: ± 1 percent or ± 0.5 ℃ for liquid-filled thermometers ± 0.2 ℃ for thermisters

Lab Tested against NIST Thermometer/Thermister? Y N Date: _____ ±_____ °C

Measurement Location : FLOW-THRU CHAMBER SINGLE POINT AT _____ ft blw LSD VERTICAL AVG. OF ____ POINTS

Field Readings # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN**:_____ **ºC** Remark ___ ___ Qualifier __ __

pH Meter make/model _____ S/N _____ Electrode No. _____ Type: GEL LIQUID OTHER _____

Sample: FILTERED UNFILTERED FLOW-THRU CHAMBER SINGLE POINT AT _____ ft blw LSD VERTICAL AVG. OF ____ POINTS

pH Buffer	Buffer Temp	Theoretical pH from table	pH Before Adj.	pH After Adj.	Slope	Millivolts
pH 7						
pH 7						
pH 7						
pH ___						
pH ___						
pH ___						
CHECK pH ___						

Temperature correction factors for buffers applied? Y N

BUFFER LOT NUMBERS : pH 7: _____
pH ____: _____
CHECK pH ____: _____
BUFFER EXP. DATES: pH 7: _____
pH ____ : _____
CHECK pH ____: _____

Calibration Criteria: ± 0.2 pH units

Field Readings # 1 _____ # 2 _____ # 3 _____ # 4_____ # 5 _____ **MEDIAN: _____ units** Remark __ __ Qualifier __ __

SPECIFIC CONDUCTANCE Meter make/model _____ S/N _____ Sensor Type: Dip Flow-thru Other _____

Sample: Flow-thru chamber Single point at _____ ft blw lsd Vertical avg. of _____ points

Std Value µS/cm	Std Temp	SC Before Adj.	SC After Adj.	Std Lot No.	Std type (KCl; NaCl)	Std Exp. Date

Calibration Criteria: the greater of 5 µS/cm or 3% of measured value

AUTO TEMP COMPENSATED METER ___
MANUAL TEMP COMPENSATED METER ___
CORRECTION FACTOR APPLIED? Y N
CORRECTION FACTOR= _____

Field Readings # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:_____ µs/cm** Remark ___ ___ Qualifier ___ ___

DISSOLVED OXYGEN Meter make/model _____ S/N _____
Sensor Type: Polarographic Luminescent Probe No. _____
Sample: Flow-thru chamber Single point at _____ ft blw lsd Vertical avg. of _____ points BOD bottle Stirrer Used? Y N
Water-Saturated Air Air-Saturated Water Air Calibration Chamber in Water Air Calibration Chamber in Air Winkler Titration Other _____

Calibration Temp ºC	Barometric Pressure mm Hg	DO Table Reading mg/L	Salinity Correc-tion Factor	DO Before Adjust-ment	DO After Adjust-ment

Calibration Criteria: ± 0.3 mg/L

Zero DO Check _____mg/L Adj. to _____ mg/L Date: _____
Zero DO Solution Date_____ Thermister Check? Y N Date_____
Membrane Changed? N Y N/A Date: _____ Time: _____
Barometer Calibrated? N Y Date: _____ Time: _____
Battery Check: REDLINE _____ RANGE _____

Field Readings # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN: _____ mg/L** Remark___ ___ Qualifier___ ___

STN NO_____

TURBIDITY Meter make/model _____ S/N _____ Type: turbidimeter submersible spectrophotometer

Sample: pump discharge line flow-thru chamber single point at _____ ft blw LSD MSL MP Sensor ID _____

Sample: Collection Time: _____ Measurement Time: _____ Measurement: In-situ/On-site Vehicle Office lab NWQL Other _____

Sample diluted? Y N Vol. of dilution water _____ mL Sample volume _____ mL

Calibration Criteria: ± 0.5 TU or ± 5%	Lot Number or Date Prepared	Expiration Date	Concentration _____ (units)	Calibration Temperature °C	Initial instrument reading	Reading after adjustment
Stock Turbidity Standard						
Zero Standard *(DIW)*						
Standard 1						
Standard 2						
Standard 3						

TURBIDITY VALUE = ***A*** x (***B***+***C***) / ***C***

where:

A= TURBIDITY VALUE IN DILUTED SAMPLE

B= VOLUME OF DILUTION WATER, mL

C= SAMPLE VOLUME, mL

Comments/Calculations:

Field Readings #1 _____ #2 _____ #3 _____ #4 _____ #5 _____

MEDIAN _____ **Parameter Code** _____ FNU NTRU FNMU FBU **METHOD CODE** ___ **Remark Codes(s)** ___ ___ **Qualifier(s)** ___ ___

WELL and WATER-LEVEL INFORMATION

WELL___ SPRING___ MONITOR___ SUPPLY___ OTHER_____

SUPPLY WELL PRIMARY USE: DOMESTIC__ PUBLIC SUPPLY__ IRRIGATION __ OTHER_____

Casing Material: _____ Altitude (land surface) _____ ft abv MSL

Measuring Point: _____ ft abv blw LSD MSL MP

Well Depth _____ ft abv blw LSD MSL MP

Sampling condition (72006) pumping (8) flowing (4) static (n/a)

[see reference list for additional fixed-value codes]

Water Level: _____ ft blw LSD (72019) ft blw MP (61055)

ft abv MSL (NGVD 29) (62610) ft abv MSL (NAVD 88) (62611)

Comments:

Depth to Water and Well Depth

	1ST	2ND	3RD (optional)
Time			
Hold (for DTW)			
- Cut			
= DTW from MP			
– Measuring point (MP)			
= DTW from LSD			
Hold (for well depth)			
+ Length of tape leader			
= Well depth below MP			
– MP			
= Well depth below LSD			

WATER-LEVEL DATA FOR GWSI

DATE WATER LEVEL MEASURED (C235) __ __ - __ __ - __ __ __ __ (Month - Day - Year) TIME (C709) __ __ __ __

WATER LEVEL TYPE CODE (C243): **L** (below land surface) **M** (below meas. pt.) **S** (sea level)

WATER LEVEL (C237/241/242) ___ ___ ___ ___.___ ___

MP SEQUENCE NO. (C248) (Mandatory if WL type=M) ___ ___ ___

WATER LEVEL DATUM (C245) (Mandatory if WL type=S): **NGVD 29** (National Geodetic Vertical Datum 0f 1929) **NAVD 88** (North American Vertical Datum 0f 1988) Other (See GWSI manual for codes)

SITE STATUS FOR WATER LEVEL (C238): A atmos. pressure; B tide stage; C ice; D dry; E recently flowing; F flowing; G nearby flowing; H nearby recently flowing; I injector site; J injector site monitor; K plugged; L measure-ment discontinued; M obstruct-tion; N pumping; O recently pumped; P nearby pumping; R nearby recently pumped; S foreign sub-stance; T well des-troyed; V affected by surface water; W other; X; Z

METHOD OF WATER-LEVEL MEASUREMENT(C239): A airline; B analog; C calibrated airline; E esti-mated; F trans-ducer; G pressure gage; H calibrated pres. gage; L geophysi-cal logs; M manometer; N non-rec. gage; O observed; R reported; S steel tape; T electric tape; V calibrated elec. tape; Z other

WATER LEVEL ACCURACY (C276): **0** foot; **1** tenth; **2** hun-dreth; **9** not to nearest foot

SOURCE OF WATER-LEVEL DATA (C244): A other gov't; D driller's log; G geol-ist; L geophysi-cal logs; M memory; O owner; R other reported; S reporting agency; Z other

PERSON MAKING MEASUREMENT (C246) (WATER-LEVEL PARTY)

MEASURING AGENCY (C247) (SOURCE)

RECORD READY FOR WEB (C858): **Y** checked; ready for web display; **C** not checked; no web display; **P** proprietary; no web display; **L** local use only; no web display

WELL PURGE LOG STN NO_____

Allowable Drawdown: _____ *ft* **Purge method:** STANDARD LOW-FLOW OTHER _____

Time	Water Level blw MP LSD	Draw-down ft	Well Yield gpm	Pumping Rate gpm	Water Temp ºC	Conduc-tivity µs/cm	pH units	Dis-solved oxygen	Turbidity _____ _____	Comments [clarity, etc.]
										MEDIAN VALUES
										QUIESCENT PH
										FINAL FIELD MEASUREMENTS

Well Volume (gal) = *V* = 0.0408 *HD*² or **Well Volume = *H* x *F***

where:
V is volume of water in the well, in gallons
H is height of water column, in feet
D is inside Diameter of well, in inches
F is casing Volume Factor (see table)

H = Well depth - Static water level = _____ feet

Diameter, inside (***D***) = _____ inches

1 well volume (***V***) = _____ gallons

Parameter	Stability Criteria*
pH	± 0.1 units (± 0.05 units if instrument display 2 or more digits to the right of the decimal)
Temperature (T)	± 0.2° C (thermistor)
Specific Conductivity (SC)	± 5%, of SC < 100 µS/cm ± 3%, for SC > 100 µS/cm
Dissolved Oxygen (DO)	± 0.3 mg/L
Turbidity (TU)	± 10%, for TU< 100: ambient TU is < 5 or most ground-water systems (visible TU > 5)

*allowable variation between 5 or more sequential field-measurement values

Purge Volume = (*n*)(*V*) = _____ gallons [Actual =_____ gal]

where:
n is number of well volumes to be removed during purging
V is volume of water in the well, in gallons
Q = estimated pumping rate = _____ gallons per minute
Approximate purge time = (purge volume)/***Q*** = _____ minutes

	VOLUME FACTORS												
DIAMETER (in.)	1.0	1.5	2.0	3.0	4.0	4.5	5.0	6.0	8.0	10.0	12.0	24.0	36.0
CASING VOL.	0.04	0.09	0.16	0.37	0.65	0.83	1.02	1.47	2.61	4.08	5.88	23.5	52.9

Screened/Open Interval: TOP _____.____ ft blw LSD MSL

Bottom _____.____ ft blw LSD MSL

Depth to Top of Sampling Interval _____.____ft blw LSD MSL

Depth to Bottom of Sampling Interval _____.____ ft blw LSD MSL

Depth to set pump from MP (all units in feet) **:**

Distance to top of screen from LSD	
+ MP	
– (7 to 10 x diameter (ft) of the well)	
= Depth to pump intake from MP	

Depth to pump from LSD (all units in feet) **:**

– MP	
= Depth pump set from LSD MSL	

Notes/Calculations:

STN NO_____

ALKALINITY/ANC CALCULATIONS

BEGINNING H_2O TEMP. _____ °C

pH	ΔpH	VOL ACID DC OR mL	ΔVOL ACID DC OR mL	ΔpH / ΔVOL ACID

END H_2O TEMP. _____ °C

BEGINNING H_2O TEMP. _____ °C

pH	ΔpH	VOL ACID DC OR mL	ΔVOL ACID DC OR mL	ΔpH / ΔVOL ACID

END H_2O TEMP. _____ °C

FIRST TITRATION RESULTS

DATE _____

BEGIN TIME _____ END TIME_____

ALKALINITY/ANC _____ meq/L

ALKALINITY/ANC _____ mg/L AS $CaCO_3$

BICARBONATE_____mg/L _____meq/L AS HCO_3^-

CARBONATE_____mg/L _____ meq /L AS CO_3^{2-}

ACID: 1.6N 0.16N 0.01639N

OTHER:_____

ACID LOT NO. _____

ACID EXPIRATION DATE _____

SAMPLE VOLUME: _____mL

FILTERED UNFILTERED

METHOD: INFLECTION POINT GRAN

FIXED ENDPOINT

STIRRING METHOD: MAGNETIC MANUAL

SECOND TITRATION RESULTS

DATE _____

BEGIN TIME _____ END TIME_____

ALKALINITY/ANC _____ meq/L

ALKALINITY/ANC _____ mg/L AS $CaCO_3$

BICARBONATE _____mg/L _____meq/L AS HCO_3^-

CARBONATE _____mg/L _____ meq /L AS CO_3^{2-}

ACID: 1.6N 0.16N 0.01639N

OTHER:_____

ACID LOT NO. _____

ACID EXPIRATION DATE _____

SAMPLE VOLUME: _____mL

FILTERED UNFILTERED

METHOD: INFLECTION POINT GRAN

FIXED ENDPOINT

STIRRING METHOD: MAGNETIC MANUAL

CALCULATIONS

ALKALINITY OR ANC (meq/L) = 1000 (B) (C_a) (CF) / V_s

ALKALINITY (mg/L AS $CaCO_3$) = 50044 (B) (C_a) (CF) / V_s

where:

B = volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts)

C_a = concentration of acid titrant, in milliequivalents per milliliter (same as equivalents per liter, or *N*)

CF = correction factor (obtain from OWQRL for Hach acid cartridges of certain lot numbers — default value is 1.00)

V_s = volume of sample, in milliliters

For samples with pH ≤ 9.2:

BICARBONATE (meq/L) = 1000 (B-2A) (C_a) (CF) / V_s

BICARBONATE (mg/L) = 61017 (B-2A) (C_a) (CF) / V_s

CARBONATE (meq/L) = 2000 (A) (C_a) (CF) / V_s

CARBONATE (mg/L) = 60009 (A) (C_a) (CF) / V_s

where:

A = volume of acid titrant added from the initial pH to the carbonate equivalence point (near pH 8.3), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts)

NOTE: For samples with pH > 9.2, these equations for bicarbonate and carbonate will fail to give accurate results. Use the Alkalinity Calculator at http://oregon.usgs.gov/alk or PCFF.

HACH CARTRIDGE CORRECTION FACTOR _____

[See OWQ WaQI Note 2005.02 for info]

pH meter calibration	Meter make/model:		S/N	
Electrode No.		Type: gel liquid other	Slope	Milli-volts
pH buffer	**Buffer temp**	**Theoretical pH from table**	**pH before adj.**	**pH After adj.**
pH 7				
pH __				
Check pH ___				

Comments/Calculations:

STN NO_____

QUALITY-CONTROL INFORMATION

PRESERVATIVE LOT NUMBERS

7.5N HNO_3 _____ (METALS&CATIONS) 6N HCl _____ (Hg) 4.5N H_2SO_4 _____ (NUTRIENTS&DOC) Conc. H_2SO_4 _____ (COD, PHENOL, O&G) NaOH _____ (CYANIDE)

OTHER _____ 1:1 HCl _____ (VOC) Number of drops of HCL added to lower pH to ≤ 2 _____ (**NOTE:** Maximum number of drops = 5)

BLANK WATER LOT NUMBERS

Inorganic (99200) _____ 2nd Inorganic (99201) _____

Pesticide (99202) _____ 2nd Pesticide (99203) _____ Spike vials (99104) _____

VOC/Pesticide (99204) _____ 2nd VOC/Pesticide (99205) _____ Surrogate vials _____

FILTER LOT NUMBERS

capsule_____ pore size _____ type _____

disc_____ pore size _____ type _____

142mm GFF _____ (organics) pore size _____ type _____

47mm GFF _____ (organics) pore size _____ type _____

25mm GFF _____ (organic carbon) pore size _____ type _____

142mm membrane _____ (inorganics) pore size _____ type _____

other _____ pore size _____ type _____

QC SAMPLES

Starting date for set of samples (99109) (YMMDD) _____ **Ending date for set of samples** (99110) (YMMDD) _____

Sample Type	NWIS Record No.	Sample Type	NWIS Record No.	Sample Type	NWIS Record No.
Equip Blank _____	_____	Sequential _____	_____	Trip Blank _____	_____
Field Blank _____	_____	Spike _____	_____	Other _____	_____
Split _____	_____	Concurrent _____	_____	Other _____	_____

NWQL Schedules/lab codes (QC Samples) _____ _____ _____ _____ _____ _____

_____ _____ _____ _____ _____ _____ _____ _____ _____

COMMENTS_____

(Circle appropriate selections)

99100 Blank-solution type
10 Inorganic grade (distilled/deionized)
40 Pesticide grade (OK for organic carbon)
50 Volatile-organic grade (OK for inorganic, organic, and organic carbon)
80 Universal blank water
200 Other

99101 Source of blank water
10 NWQL
40 NIST
55 Wisconsin District Mercury Lab
200 Other

99105 Replicate-sample type
10 Concurrent
20 Sequential
30 Split
40 Split-Concurrent
50 Split-Sequential
200 Other

99102 Blank-sample type
1 Source Solution
30 Trip
60 Filter
70 Preservation
80 Equipment (done in non-field environment)
90 Ambient
100 Field
200 Other

99111 QC sample associated with this environmental sample
1 No associated QA data
10 Blank
30 Replicate Sample
40 Spike sample
100 More than one type of QA sample
200 Other

99108 Spike-solution volume, mL _____

99106 Spike-sample type
10 Field

99107 Spike-solution source
10 NWQL

99112 Purpose, Topical QC data
1 Routine QC (non-topical)
10 Topical for high bias (contamination)
20 Topical for low bias (recovery)
100 Topical for variability (field equip)
110 Topical for variability (field collection)
120 Topical for variability (field personnel)
130 Topical for variability (field processing)
140 Topical for variability (shipping&handling)
200 Topical for variability (lab)
900 Other topical QC purpose

REFERENCE LIST FOR CODES USED ON THIS FORM

Sample Medium Codes
6 Regular Ground water
S Quality-control sample (associated environmental sample –6 (GW))
For replicates and spikes
Q Artificial

71999 Sample purpose
10 Routine
15 NAWQA
50 GW Network
110 Seepage Study
120 Irrigation Effects
130 Recharge
140 Injection

A complete set of fixed-value codes can be found online at:
http://wwwnwis.er.usgs.gov/currentdocs/index.html

Time Datum Codes

Time Zone	Std Time Code	UTC Offset (hours)	Daylight Time Code	UTC Offset (hours)
Hawaii-Aleutian	HST	-10	HDT	-9
Alaska	AKST	-9	AKDT	-8
Pacific	PST	-8	PDT	-7
Mountain	MST	-7	MDT	-6
Central	CST	-6	CDT	-5
Eastern	EST	-5	EDT	-4
Atlantic	AST	-4	ADT	-3

Value Qualifiers
e see field comment
f sample field preparation problem
k counts outside the acceptable range

Sample Type Code
9 Regular
7 Replicate
2 Blank
1 Spike

00003 Sampling depth, ft blw LSD
00059 Sampling flow rate, GPM
72004 Pump or flow period prior to sampling, minutes
72019 Water level, ft blw LSD

Null-value Qualifiers
e required equipment not functional or available
f sample discarded; improper filter used
o insufficient amount of water

82398 Sampling method
4010 Thief sampler
4020 Open-top bailer
4025 Double-valve bailer
4030 Suction pump
4040 Submersible pump
4045 Submersible multiple impeller (turbine) pump
4050 Squeeze pump
4060 Gas reciprocating pump
4070 Gas lift
4080 Peristaltic pump
4090 Jet pump
4100 Flowing well
4110 Resin trap collector
8010 Other

84164 Sampler type
4010 Thief Sampler
4020 Open-top Bailer
4025 Double-valve Bailer
4030 Suction Pump
4035 Submersible Centrifugal Pump
4040 Submersible Positive-pressure Pump
4041 Submersible Helical Rotor Pump
4045 Submersible Gear Pump
4050 Bladder Pump
4060 Gas Reciprocating Pump
4070 Gas Lift
4075 Submersible Piston Pump
4080 Peristaltic Pump
4090 Jet pump
4095 Line-Shaft Turbine Pump
4100 Flowing Well
8010 Other

50280 Purpose of site visit
2001 Primary (primary samples should not exist for a site for more than one date per HIP, and the primary sampling date generally has the highest number of NAWQA analytes)
2002 Supplemental (to fill in missing schedules not sampled or lost)
2003 Temporal characterization (for previously sampled schedules; includes LIP and seasonal samples)
2004 Resample (to verify questionable concentrations in primary sample)
2098 Ground-water quality control
2099 Other (ground-water related samples with medium code other than "6", such as soil samples or core material)

72006 Sampling Condition
0.01 The site was dry (no water level is recorded)
0.02 The site had been flowing recently
0.03 The site was flowing, head could not be measured
0.04 A nearby site that taps the Aquifer was flowing
0.05 Nearby site tapping same Aquifer had been flowing recently
0.06 Injector site
0.07 Injector site monitor
0.08 Measurement discontinued
0.09 Obstruction encountered in well above water surface
0.10 The site was being pumped
0.11 The site had been pumped recently
0.12 Nearby site tapping the same Aquifer was being pumped
0.13 Nearby site tapping the Same Aquifer was pumped recently
0.14 Foreign substance present on the surface of the water
0.16 Water level affected by stage in nearby site
0.17 Other conditions affecting the measured water level
2 Undesignated
4 Flowing
6 Flowing on gas lift
8 Pumping
10 Open hole
18 Producing
19 Circulating
22 Lifting
23 Flowing to Pit
24 Water Flooding
25 Jetting
30 Seeping
31 Nearby well pumping
32 Nearby well taking water
33 Well taking water

Alkalinity/ANC Parameter Codes
39086 Alkalinity, water, filtered, incremental titration, mg/L
00418 Alkalinity, water, filtered, fixed endpoint, mg/L
29802 Alkalinity, water, filtered, Gran titration, mg/L
00419 ANC, water, unfiltered, incremental titration
00410 ANC, water, unfiltered, fixed endpoint, mg/L
29813 ANC, water, unfiltered, Gran titration, mg/L
29804 Bicarbonate, water, filtered, fixed endpoint, mg/L
63786 Bicarbonate, water, filtered, Gran, mg/L
00453 Bicarbonate, water, filtered, incremental, mg/L
00440 Bicarbonate, water, unfiltered, fixed endpoint, mg/L
00450 Bicarbonate, water, unfiltered, incremental, mg/L
29807 Carbonate, water, filtered, fixed endpoint, mg/L
63788 Carbonate, water, filtered, Gran, mg/L
00452 Carbonate, water, filtered, incremental, mg/L
00445 Carbonate, water, unfiltered, fixed endpoint, mg/L
00447 Carbonate, water, unfiltered, incremental, mg/L
29810 Hydroxide, water, filtered, fixed endpoint, mg/L
71834 Hydroxide, water, filtered, incremental, mg/L
71830 Hydroxide, water, unfiltered, fixed endpoint, mg/L
71832Hydroxide, water, unfiltered, incremental, mg/L

71825 Hydrogen Sulfide Odor
Value
none entered (null)

Remark Code	Method Code
M detect	U un-acidified sample
U non-detect	V acidified sample

APPENDIX A4-C
Quality-control samples collected by field personnel for water-quality studies

Page

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

BLANK SAMPLES[2]		
Sample type	**General description[3]**	**Purpose[3]**
Field blank	Blank water that is passed through the entire sampling equipment system **onsite** and subjected to identical collection, processing, preservation, transportation, and storage procedures and laboratory handling as for environmental samples. • The field blank is processed onsite through clean equipment on the same day as, and along with, the environmental samples, either, (*a*) directly after the equipment has been field cleaned and before leaving for the next site (NFM 3), ***or***, (*b*) at the next site, just before environmental samples for that site are processed. • A set of blanks can be processed and associated with the field blank (fig. 4-14).	Determine the concentrations of target analyte(s) present in the environmental sample that could be attributed to field procedures for equipment cleaning and sample handling. Results include effects from laboratory handling. Examples related to (*a*) and (*b*) (see "General description"): (*a*) Check the adequacy of field-cleaning procedures (demonstrate that equipment was adequately decontaminated after previous use); (*b*) Identify contamination of sampling equipment while in transport from office to field site or between field sites, and ambient field conditions at the field site.
Equipment blank	Blank water that is passed sequentially through each component of the equipment system to be used for collecting and processing environmental samples and resulting in a single final blank sample. • Differs from a field blank in that the equipment blank is processed under controlled conditions in an office laboratory and before equipment will be used for field work. Standard USGS procedure is to collect an annual equipment blank if the equipment is not in active use. • Can result in collecting a series of blank samples sequentially, each sample of which represents a different component or components of the equipment system; for example, sampler-equipment blank, splitter-equipment blank, filter-equipment blank.	• Identify effects of the equipment system used to collect and process samples on analyte concentrations. • Verify adequacy of equipment-cleaning procedures (NFM 3). • Relating to components of the equipment system, assess potential of sample contamination and adequacy of equipment-cleaning procedures associated with each component of the equipment system to be used for field work. • Can be used to help identify or eliminate source(s) of contamination.

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

BLANK SAMPLES[2]		
Sample type	**General description[3]**	**Purpose[3]**
Ambient blank	Blank water that is exposed to the identical collection and processing areas and time period as environmental samples. The blank water is transferred from the stock-solution container to the same type of bottle used for an environmental sample. The specific mode of exposure to the atmosphere is determined by the QC objective. **Examples:** (*a*) The blank water is transferred to a sample bottle while in the sample-processing chamber used for environmental samples. (*b*) Container such as a sample bottle is prefilled with blank water, opened while in the processing chamber, and exposed to the chamber atmosphere throughout the processing of environmental samples.	Determine analyte concentrations present in the environmental sample that could be attributed to exposure of sample to the ambient atmosphere in which samples are collected, processed, and analyzed. Referring to the general description: • Example (*a*) is used to assess concentrations after processing the blank in a manner that mimics collection of the environmental sample. • Example (*b*) is used to indicate the maximum analyte concentration that would result from prolonged sample exposure to ambient conditions.
Source-solution blank	Stock solution of PBW, VPBW, or IBW that is transferred to a sample bottle in an area of the office laboratory within a controlled atmosphere that is relatively clean and protected with respect to target analytes.	Determine the source of water used for blanks and the degree to which the composition of blank solution could have changed (with respect to target analytes) from time of laboratory certification to time of use.
Sampler blank	Blank water processed through the same sampler used for environmental samples after the sampler has been cleaned. (Blanks processed through pump samplers usually are designated pump blanks).	• Identify effects of sampler components on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Splitter blank	Blank water processed through the same sample-splitting device used to collect or to process environmental samples (such as a churn splitter, cone splitter, or manifold system), after the splitter has been cleaned.	• Identify effects of splitter components on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC control samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

BLANK SAMPLES[2]		
Sample type	**General description[3]**	**Purpose[3]**
Pump blank	Blank water processed through the pump-and-tubing system used for environmental samples, after pump and tubing have been cleaned.	• Identify effects of pump components and tubing on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Filter blank	Blank water processed through the filter assembly used for environmental samples, after the filter unit or assembly has been cleaned.	• Identify effects of filtration assembly on analyte concentrations. • Verify adequacy of cleaning procedures, if a plate or cartridge assembly is used—see NFM 3. • If the filter blank is to represent the same filter media, the blank is processed prior to the environmental samples.
Preservation blank	Blank water that is transferred to a sample bottle and chemically treated with a preservative in an area protected from atmospheric contamination (usually under a clean hood environment in the office laboratory). The preservative used is from the same lot number used for the other QC and environmental samples.	Determine the potential for, and magnitude of, sample contamination from the chemical treatment to be used to preserve the environmental sample.
Shelf blank ("Hold" blank)	Blank water that is transferred into the same type of bottle used for an environmental sample (usually in a protected environment in the office laboratory) and stored adjacent to stored environmental samples for the same length of time.	Determine the potential for and magnitude of sample contamination from sample storage in a designated area for a designated length of time.
Refrigerator blank	Blank water that is transferred to a sample bottle (usually in a protected environment in the office laboratory) and stored adjacent to environmental samples in a refrigerated area for the same length of time.	Determine the potential for, and magnitude of, sample contamination from refrigeration of the sample for a designated length of time.

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

	REPLICATE SAMPLES	
Sample type	**General description[3]**	**Purpose[3]**
Replicates (duplicates, triplicates, etc. of sequential, split, concurrent, or other type of replicate sample)	A set of samples that is collected close in time and space and in a manner so that the samples are thought to represent virtually the same physical, chemical, and biological properties.	Depending upon its type, a replicate is used to determine variability in some part of the sample collection, processing, and analysis system.
Concurrent replicates	Samples obtained simultaneously using two or more samplers or by using one sampler and alternating collection of samples into two or more compositing containers (Horowitz and others, 1994).	Identify and (or) quantify the variability in the system being sampled.
Sequential replicates	Samples that are collected one after the other and considered virtually identical in composition.	• Identify and (or) quantify the variability introduced from collection, processing, shipping, and laboratory handling and analysis. • Can be designed to indicate temporal variability resulting from consecutive collection of samples.
Split replicates	Samples obtained by dividing one sample into two or more subsamples either before or after sample processing and preservation. **Each of the subsamples is to be analyzed for concentrations of the same constituents or compounds**. Examples: (*a*) A processed and treated sample in a sample bottle is split into two or more aliquots and subjected to identical handling and analysis. (*b*) Environmental water is passed through a splitting device (such as a cone splitter or T-valve) from which subsamples are collected simultaneously and subjected to identical handling and analysis. (*c*) Environmental water is collected into a compositing device from which subsamples are collected sequentially and subjected to identical handling and analysis.	• Assess variability for a given sample matrix. • Compare differences in analyses obtained from the same or separate laboratories.

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

	REFERENCE, SPIKE, AND BLIND SAMPLES	
Sample type	**General description[3]**	**Purpose[3]**
Reference sample	A laboratory-prepared solution or material whose composition is certified for one or more properties so that it can be used to assess a measurement method or for assigning concentration values of specific analytes.	Tests for bias and variability of the laboratory measurement process.
Spike sample	Environmental ("field-matrix spikes") or reference-material sample to which a spike solution has been added in known concentrations and in a manner that does not substantially change the original sample matrix. **Spike solution** is a solution having laboratory-certified concentrations of selected analytes and that are added in known quantities to a sample.[4]	Assess the recovery of target analytes relative to the actual conditions to which samples have been exposed; quantify effects of sample-matrix interferences and analyte degradation on analyte recovery.
Blind sample	A sample (typically, reference material) submitted for laboratory analysis with composition known to the submitter but unknown (blind) to the analyst. Every blind sample analyzed should have an associated reference to the source and preparation procedure.	Test for bias and variability of the laboratory measurement process.

[1]Blank water is a solution that is free of analyte(s) of interest at a specified detection limit and that is used to develop specific types of QC samples.USGS personnel are required to use blank water that has been analyzed and certified to be of a specific grade.

[2]Blank samples (blanks) for trace-element analysis have a unique NWQL schedule of analysis, different from that of the environmental sample.

[3]The description of a QC sample depends to some extent on the purpose for which it is collected. The purpose for the QC sample can govern the mode of its collection, processing, and treatment, and the equipment to which it is exposed. Purposes for a specific type of QC sample are varied. Analysis of all QC samples includes the bias and variability introduced from shipping and laboratory handling and analysis of the sample.

[4]For USGS studies, obtain spike solutions in spike kits for pesticide and volatile organic compound analyses from the USGS National Field Supplies Service (NFSS) through One-Stop Shopping.

APPENDIX A4-D
Examples from the National Water-Quality Assessment Program Related to Protocols for Collecting Blank Samples at Ground-Water Sampling Sites

Modified from Koterba and others, 1995

Table 1. Example of procedure to estimate and collect field volumes of blank solutions.

Table 2. Example of procedure to collect blank samples with a submersible water-quality pump.

APPENDIX A4-D—Table 1. Example of procedure to estimate and collect field volumes of blank solutions.

[Modified from Koterba and others, 1995, and based on protocols of the National Water-Quality Assessment Program. DIW, District deionized water with specific electrical conductance less than 1.0 microsiemens per liter; VPBW, volatile-organic-compound and pesticide-grade blank water; PBW, pesticide-grade blank water; IBW, inorganic-grade blank water; DOC, dissolved (filtered) organic carbon; gal, gallons; L, liters; ~, approximately; NWQL, National Water Quality Laboratory]

Assumptions: Submersible pump was used to collect the ground-water samples. Equipment just used to collect ground-water samples has been decontaminated, and, except for the pump intake being in a standpipe, is set up on site in the same manner as it was for the collection of ground-water samples.

Blank-Solution Types and Estimate of Volumes Required[1]

Field blank(s) desired	Required blank-solution type	Minimum volume in gal (L)	Comments
Major ions and nutrients	IBW	1.0 (~4)	Waste 0.5 gal, then collect field blanks; can use DIW to force last of the IBW needed through the system.
Trace elements	IBW	1.0 (~4)	
Major ions and nutrients and trace elements	IBW	1.5 (~6)	Waste 0.5 gal, then collect field blanks; if necessary, use DIW to force last of the IBW needed through the system.
VOCs and DOC[1]	VPBW	1.5 (~6)	Waste 0.5 gal, then collect field blanks; can use DIW to force last of VPBW (or PBW) through the system.
Pesticides and DOC	PBW[1]	1.5 (~6)	
VOCs, DOC[1] and pesticides	VPBW	2.0 (~8)	Waste 0.5 gal, then collect field blanks; can use DIW to force last of VPBW or PBW through the system.

[1]Use VPBW for VOC field blanks. PBW can not be used. Select VPBW or PBW for DOC field blanks only after reviewing certification forms of the lot numbers available. A solution-blank sample of water from the same lot of NWQL water is poured directly into the DOC 125-mL amber sample bottle and is required for every DOC field blank. Record the lot number of the water used for the solution blank on the ASR form.

APPENDIX A4-D—Table 2. Example of procedure to collect blank samples with a submersible water-quality pump.

[Modified from Koterba and others (1995). DIW, deionized water; VPBW, volatile-organic-compound and pesticide-grade blank water; PBW, pesticide-grade blank water; IBW, inorganic-grade blank water; VOC, volatile organic compound; QC, quality control]

General Field-Blank Collection Procedure[1]

1. Divide field team duties—Three-person team recommended—Two people collect samples in a manner similar to that used to collect ground-water samples; the third person adds blank water to standpipe and controls flow through system, as needed, to facilitate field blank collection.

2. Check flow set-up—From standpipe to sample collection/processing chamber, ensure that adequate volumes of DIW and the required blank water are within easy reach of person stationed at standpipe andarranged in order of cdlection: IBW first, and PBW or VPBW last.[2]

3. Set low flow rate—Once pumping is initiated, set flow (on basis of measurement at chamber outflow) to about 0.1 gal. (500 mL) per minute orless to avoid wasting excessive amounts of blank water (to avoid air bubbles, 150 mL/min or less is recommended for filling VOC vials).

4. Collect blank solutions in prescribed sequence, collecting the IBW before the equipment is exposed to methanol and PBW or VPBW—As solutions are changed, pump operator should change to clean gloves, empty residual solution from standpipe, rinse pump intake and standpipe, individually, at least three times each, with the next solution.

   • Use an air segment to mark the end of one solution and the beginning of the next; alternatively, determine the change in solutions on the basis of the storage volume in the line divided by the pumping rate to estimate the time it takes for the solution to travel from the standpipe to the collection/processing chamber.

   • Pass about 0.5 gallons (approximately 2 L) of blank solution to waste before collecting the QC sample, regardless of whether air segments or timed flow or both are used to assess when the solution arrives at the collection chamber.

   • Use one type of water toforce the last of another type from the sample tubingafter all samples that require that blank-water type have been collected, in order to limit the amount of blank water left in the sample tubing.

[1]**Assumptions:** Submersible pump w as used to collect the ground-w ater samples. Organic and inorganic field blanks will be collected. Equipment just used to collect ground-water samples has been cleaned, and, except for the pump intake being in a standpipe instead of a we ll, is set up on site in the same manner as it was for the collection of ground-water samples. Standpipe has just been cleaned and subsequently rinsed with VPBW . If only inor ganic field bla nks will be collected, rinse cle aned standpipe with IBW and modify steps 2 to 4 accordingly.

[2]Referring to NFM 3, follow the cleaning sequence shown on fig. 3-1 for the inorganic and organic cleaning procedure.

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A5. PROCESSING OF WATER SAMPLES

Franceska D. Wilde
Managing Editor

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

For additional information write to:

Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

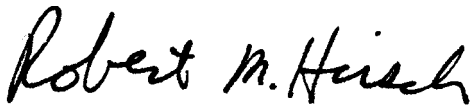
Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

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PROCESSING OF WATER SAMPLES

A5.

National Field Manual for the Collection of Water-Quality Data

Chapter A5.

[1] Section 5.2.2.C (revised 1/2002) was rewritten to reflect changes in methodology. The original version of 5/99, with minor changes, appears as Appendix A5-D.

[2] Section 5.3.2 was revised, see Chapter 5 HTML page.

Illustrations

Tables

Chapter A5. PROCESSING OF WATER SAMPLES

Edited by **Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and

bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to nfm-owq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, J.H. Eychaner, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, R.W. Lee, D.K. Mueller, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. These scientists contributed significantly to the accuracy, quality, and usability of this report. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

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PROCESSING OF WATER SAMPLES A5.

Edited by **Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo**

Sample processing forms a continuum with sample collection (NFM 4) and involves the compositing, subsampling (splitting), filtration, solid-phase extraction, preservation, and shipment of samples. Samples are most vulnerable to sampling artifacts, contamination, incorrect chemical treatment, and mislabeling during sample processing. Samples must be processed as soon as possible after collection.[3]

Sample processing: the measures taken to prepare and preserve a water sample as or after it is collected and shipped for laboratory analysis.

GENERAL INFORMATION 5.0

By **D.B. Radtke and F.D. Wilde**

How samples are processed depends on the targeted analytes and the intended use of the data. Processing procedures for some analytes might require modification of standard processing procedures, as described in section 5.6. **Equipment components must be made of materials that (1) will not contribute or sorb target analytes to or from the water sample, and (2) can withstand cleaning solutions**.

[3]Consult NFM 4 for collection of water samples, and in addition, NFM 1 for field preparations, NFM 2 for equipment selection, NFM 3 for equipment cleaning, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material samples, and NFM 9 for field safety.

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PREPARATORY PROCEDURES 5.0.1

Use of the procedures described in this section will help to avoid mistakes and preserve sample integrity. Protocols that are applicable to most sampling efforts for surface water are described in detail in Horowitz and others (1994). Koterba and others (1995) describe the protocols for ground-water sampling that were designed for the National Water-Quality Assessment (NAWQA) Program; these protocols are generally applicable to the routine collection of ground-water samples. Field personnel are responsible for being familiar with any specific sampling protocols that might be required for their studies and programs, especially those that differ from the routine procedures covered by this field manual. For example, field procedures, bottle type, and sample preservation requirements differ for samples collected as part of the USEPA Drinking Water Program (National Water Quality Laboratory Technical Memorandum 97.05[4]).

- To minimize delays in sample processing, calibrate field instruments (NFM 6), and set up processing equipment and supplies in the work area before collecting the sample.
- Clean-sampling procedures are recommended as a general practice when processing raw samples, particularly those for analysis of trace levels of inorganic and organic analytes.
- **Clean-sampling procedures such as Clean Hands/ Dirty Hands techniques (NFM 4) are required when collecting samples to be filtered for analysis of trace elements** (Office of Water Quality Technical Memorandum 94.09; Horowitz and others, 1994; Koterba and others, 1995).

[4]The technical memorandums referenced in this manual are available on the World Wide Web; see "Selected References and Internal Documents" for memorandum titles, dates, and the Web Site address.

- **When using Clean Hands/Dirty Hands techniques:**
  - Designate the Clean Hands (CH) person and the Dirty Hands (DH) person before field work begins (table 4-2 in NFM 4).
  - **CH duties**: Has the only contact with the sample bottle; transfers sample from sampler to splitter; filters, extracts, and preserves sample.
  - **DH duties**: Operates sampling equipment and manages any contact with potential sources of contamination (for example, the churn carrier and pumps).
  - **CH and DH**: Both must wear appropriate disposable, powderless gloves (vinyl, latex, or nitrile for inorganic work; latex or nitrile for organic work).
- **Check sample-designation codes and processing requirements for each sample.** Requirements depend on program and laboratory protocols, study objectives, and data-quality requirements. Laboratory codes and processing requirements are summarized in Appendixes A5-A, B, and C.
  - **Organic analytes**. Identify the bottle requirement by checking the sample designation code (see in-text table below and Appendix A5-A). Use only containers that arrive clean, baked, and capped. **Discard any bottles that arrive uncapped**.
  - **Inorganic and radiochemical analytes**. Identify the bottle requirement by checking the sample designation code (see in-text table below and Appendixes A5-B and A5-C). For example, samples to be acidified must be collected in bottles that arrive from the laboratory acid rinsed and capped; **discard any acid-rinsed bottles that arrive uncapped**. Prerinse all bottles used for nutrients, major-ion, and trace-element samples with deionized water (DIW) before sampling. Field rinse bottles with the water to be sampled, if a field rinse is specified (section 5.0.3 and Appendixes A5-B and A5-C).

Common organic-compound sample-designation codes for the National Water Quality Laboratory of the U.S. Geological Survey

[Refer also to Appendix A5-A. ml, milliliters; °C, degrees Celsius]

Sample designation code	Bottle description and sample preservation
VOC	40-mL amber glass vials, laboratory cleaned and baked, for analysis of volatile organic compound sample (VOC or VOA); sample chilled to or below 4°C without freezing. Some programs require chemical treatment.
GCC	1-L amber, glass bottle, laboratory cleaned and baked, for various types of pesticides and organic-compound samples other than VOCs; sample chilled to or below 4°C without freezing.
TOC, DOC	125-mL amber glass bottle, laboratory cleaned and baked, for total (TOC) or dissolved (DOC) organic carbon; sample chilled to 4°C or below without freezing.

Common inorganic-constituent sample-designation codes of the National Water Quality Laboratory of the U.S. Geological Survey

[Refer also to Appendix A5-B and A5-C. mL, milliliter; <, less than; °C, degrees Celsius; L, liter]

Sample designation code	Bottle description and sample preservation
RA, FA	250-, 500-, or 1,000-mL polyethylene bottles, acid-rinsed, capped, to be filled with raw (RA) or filtered (FA) samples and acidified with nitric acid to pH <2.
RU, FU	250-, 500-, or 1,000-mL polyethylene bottles, uncapped, to be filled with untreated raw (RU) and filtered (FU) samples.
FCC	125-mL polyethylene bottles, uncapped, to be filled with filtered (FCC, brown bottle) sample for nutrient analysis and chilled to or below 4°C without freezing.
WCA, FCA	125-mL polyethylene bottles, uncapped; to be filled with raw (WCA, uncolored bottle) or filtered (FCA, brown bottle) sample for nutrient analysis, treated with sulfuric acid, and chilled to or below 4°C without freezing.
RAM, FAM	250-mL glass bottles, ~~acid-rinsed,~~ capped, to be filled with raw (RAM) or filtered (FAM) sample for mercury analysis, and treated with 6 N hydrochloric acid, ultrapure. Acid rinsed was deleted 02/17/2011.
FAR	1-L polyethylene bottles, acid rinsed, capped, to be filled with filtered (FAR) samples for radiochemical analysis and treated with nitric acid to pH <2.

- **Clean equipment and supplies as directed in NFM 3.**
  - **Organic analytes.** All containers arrive precleaned and baked from the laboratory. **Do not prerinse or field rinse these glass bottles or vials.** Samples to be analyzed for organic compounds are hereafter referred to as organic-compound samples.
  - **Inorganic analytes.** Prerinse bottles with DIW and store half filled with DIW. This procedure is required for all FA samples with target analytes at parts-per-billion (ppb) concentrations, and is recommended for all samples to be analyzed for inorganic constituents (hereafter referred to as inorganic-constituent samples) that also require field-rinsed bottles.
- **Set up a clean work area** at the field site for sample processing. (An appropriate area includes, for example, a mobile laboratory, a water-quality field vehicle (NFM 2), or clean space in a building near the sampling site.)
  - Protect the area from airborne sources of contamination such as dust, vehicle emissions, and vapors from inorganic chemicals and organic solvents.
  - Spread sheeting over the area where samples are to be processed. For inorganic-constituent samples, use plastic sheeting. For organic-compound samples, use aluminum foil.
- **Prevent direct contact with potential source(s) of contamination.**
  - Exclude airborne particulates by processing samples onsite in processing and preservation chambers.
  - Handle anoxic samples rapidly and under an inert gas atmosphere (NFM 4.0.3).
  - Keep hands gloved and away from potential sources of contamination while processing samples. While filling the sample bottle, the sample must not come in contact with gloved hands.
- **Keep sample-processing equipment covered** with a clean, noncontaminating material when not in use; keep sample bottles capped and covered or bagged.

SEQUENCE FOR PROCESSING SAMPLES 5.0.2

The order of sample collection, processing, and preservation for specific analytes should be determined before beginning field work and adhered to consistently. The recommended sequence for sample collection and processing is based on logistics for maintaining sample integrity and differs for ground-water and surface-water sampling. The recommended sequence can be modified, depending on the types of samples to be collected and on data objectives. In general, process samples in the order indicated on table 5-1.

- For ground-water sampling, the amount of well purging might affect concentrations of VOCs measured in the ground-water samples (Gibs and Imbrigiotta, 1990). Therefore, VOC samples are collected first.
- When sampling either surface water or ground water for inorganic analyses,
  - Filter trace-element samples first, as prescribed and explained in section 5.2 and in Horowitz and others (1994).
  - Next, filter nutrient, major ion, and other inorganic-constituent samples having concentrations that will not be appreciably affected as nominal pore size of the filter media decreases.
  - Filter the alkalinity sample (NFM 6) with the other anions.
- When composite samples of surface water are processed, samples for analysis of organic compounds usually are processed first and are taken from a noncontaminating compositing device separate from that for inorganic-constituent samples, unless a cone splitter is used (section 5.1).

Table 5-1. Recommended sequence for processing samples

1. Organic compounds—Raw (wholewater or unfiltered) samples first, followed by filtered samples. **Do not field rinse bottles.** Chill. a. Volatile organic compounds (VOCs). b. Pesticides, herbicides, polychlorinated biphenyls (PCBs) and other agricultural and industrial organic compounds.
2. Organic carbon[1]. Chill. See step 4 for capsule-filtered dissolved organic carbon (DOC).
3. Inorganic constituents, nutrients, radiochemicals, isotopes: **For ground water,** filtered samples first, followed by raw samples. **For surface water,** raw samples first, followed by filtered samples. (Field rinse each bottle, as required.) a. Trace and major element cations. b. Separate-treatment constituents (such as mercury, arsenic, selenium). c. Nutrients, major anions, and alkalinity. Chill nutrients. d. Radiochemicals and isotopes. (Bottle-rinse, filtration, and preservation requirements depend on analysis to be performed (section 5.6 and Appendix A5-C.)[2])
4. Capsule-filtered DOC (5.2.2.C), followed by radon and chlorofluorocarbons.[2] (Do not rinse bottles.)
5. Microorganisms (NFM 7).

1(Footnote deleted.)

[2]Radon and chlorofluorocarbon and most isotope samples are collected outside of the processing chamber.

5.0.3 FIELD RINSING OF BOTTLES USED TO CONTAIN SAMPLES FOR ANALYSIS OF INORGANIC CONSTITUENTS

Most polyethylene sample bottles and only those glass sample bottles that are designated for analysis of inorganic constituents (inorganics bottles) are field rinsed as described in table 5-2. Check Horowitz and others (1994) and the laboratory requirements (summarized in Appendixes A5-B and A5-C) for more detailed discussions of field rinsing. **The field-rinse water normally is the same as the water that will fill the sample bottle: use wholewater sample for raw (unfiltered) samples and filtrate for filtered samples.**

Page revised 2/27/2009.

- If the volume of sample obtained for processing is limited, DIW of the appropriate quality may be substituted as the rinse solution for the first two of the three required rinses.
- Wear disposable, powderless gloves while processing samples.

Check analyte requirements before field rinsing bottles. For example, DO NOT field rinse glass bottles that are designated for analysis of organic compounds.

Table 5-2. Directions for field rinse of bottles used to contain samples for inorganic-constituent analysis

[DIW, deionized water; mL, milliliters]

Bottle Preparation
• If bottles were previously rinsed and half-filled with DIW[1], discard DIW and rinse once only with the water to be sampled. Use filtrate for filtered samples and wholewater for raw samples.
• If bottles were not prerinsed with DIW, rinse twice with DIW onsite, followed by one field rinse with the water to be sampled (use only 25-mL filtrate for bottle rinse for the filtered sample[1,2]).
Field-Rinse Technique
1. Put on disposable, powderless gloves.
2. Fill sample bottle about 1/10 full of rinse water. Cap bottle.
3. Shake the bottle vigorously to rinse all interior surfaces.
4. Discard rinse water by swirling the solution out of the bottle.
5. Shake off adhering droplets.

[1]Required for filtered trace-element samples (Horowitz and others, 1994).
[2]Refer to section 5.2.1.A for detailed guidance relating to surface-water and ground-water samples.

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RAW SAMPLES 5.1

By **D.B. Radtke, A.J. Horowitz, Jacob Gibs, and F.D. Wilde**

Raw samples, commonly referred to as wholewater or unfiltered samples, are collected directly into the appropriate type of sample bottle from the sampling device (such as a submersible pump, sample-compositing device, peristaltic pump, or cone splitter). It is recommended that this sample collection take place within a processing chamber, especially if analyte concentrations are expected to be near the detection limit, to prevent contamination from airborne sources.

- Equipment must be clean before samples are collected and processed.
- Disposable, powderless gloves must be worn throughout sample collection and processing. In order to withstand the solvents or chemicals that could be contacted, vinyl gloves are adequate for inorganic work, but use of organic solvents for organic work requires latex or nitrile gloves.

COMPOSITES AND SUBSAMPLES 5.1.1

Surface-water samples normally are composited and processed through sample splitting (subsampling) devices (NFM 2). Ground-water samples are not composited but are pumped either directly through a splitter or through a filtration assembly (filter assembly) into sample bottles, unless a bailer or other thief-type sampler is used to collect the sample. Inorganic-constituent samples usually are composited in the plastic or fluoropolymer churn splitter; organic-compound samples commonly are composited in a fluoropolymer churn splitter or metal container, or are processed through a fluorocarbon polymer cone splitter.

Only the Clean Hands person fills sample bottles with water withdrawn from the churn or cone splitter (NFM 4).

Two types of water-sample splitters commonly used by the USGS are the polypropylene churn splitter (churn) and the fluorocarbon polymer cone splitter (cone).[5] Each splitter has specific advantages and disadvantages (NFM 2.2.1). By convention, the churn usually is used only for inorganic-constituent (and possibly for suspended organic carbon) samples. The churn is constructed of plastic materials that can potentially affect concentrations of other organic compounds. The cone is constructed of fluorocarbon polymer material and can be used for either inorganic-constituent or organic-compound samples. **Program or study protocols might dictate which equipment to use.**

- Either the churn or cone splitter can be used for splitting raw samples with suspended-sediment concentrations up to 1,000 mg/L.
- Only the cone splitter can be used for splitting raw samples with suspended-sediment concentrations up to 10,000 mg/L (Office of Water Quality Technical Memorandum 97.06).
- The splitting accuracy of the cone splitter is unknown for suspended-sediment concentrations between 10,000 to 100,000 mg/L (Office of Water Quality Technical Memorandum 97.06), but data are available that indicate the splitting accuracy of the cone is unacceptable at concentrations of 100,000 mg/L or more.

5.1.1.A Churn-Splitter Procedure

Subsamples collected from the composite sample in a churn splitter must be processed according to the specific procedures described below, using Clean Hands/Dirty Hands (CH/DH) techniques as applicable.

1. Assemble sample-processing equipment and supplies on a clean work surface.
   - Put on appropriate, disposable, powderless gloves (gloves). (Wearing multiple pairs of gloves at one time provides an efficient means of changing gloves quickly.)

[5]Consult the following references for more detailed information about the churn and cone splitters: Office of Water Quality Technical Memorandums 76.24-T, 80.17, 94.13, and 97.06; Capel and others (1995); and Capel and Larson (1996).

- If hand contact is made with a potential contaminant, remove the outer (contaminated) gloves before continuing with sample processing.
- For CH/DH techniques: Remove churn splitter and inner bag from churn carrier. Leave the churn carrier and outer bag outside the processing area (vehicle or building).

2. Place all prelabeled wholewater or suspended-material bottles within easy reach of the churn spigot.
3. Churn the composite sample at a uniform rate by raising and lowering the disk inside the churn splitter with smooth, even strokes.
   - When churning, the disk should touch bottom on every stroke, and the stroke length should be as long as possible without breaking water surface. **Do not break the surface of the water**.
   - **The churning rate should be about 9 inches per second (in/s).** If the churning rate is significantly greater than 9 in/s, or if the disk breaks the surface of the water, excessive air is introduced into the sample and could affect dissolved gases, bicarbonate, pH, and other characteristics of the sample.
   - Inadequate churning can result in withdrawal of nonrepresentative wholewater or suspended-material samples.
4. Pre-mix the composite sample by churning for about 10 strokes to uniformly disperse suspended material before subsampling.
5. **Raw subsample.** Withdraw the raw subsamples for wholewater or suspended-materials analyses first.
   - Withdraw an adequate volume of sample water for the field rinse while continuing to churn.
   - **Withdraw the first subsample.** The first subsample withdrawn from the churn should be the largest volume required (usually a 1-L sample).
   - Do not interrupt the churning/subsampling process, if possible. If an interruption occurs, reestablish the churning rate and remix the sample by churning ten strokes before resuming subsampling.
   - As the volume of composite sample in the churn decreases, adjust the stroke length to maintain a churning rate of about 9 in/s and avoid breaking the surface of the water being sampled.

6. Check requirements for sample preservation. **For raw samples that require chemical treatment ⇨ Go to section 5.4.**
   - For raw samples that require chilling without chemical treatment(s)—Pack samples in ice or refrigerate as quickly as possible. Maintain at or below 4°C without freezing (section 5.4).
   - For raw samples that do not require chilling or chemical treatment—Set samples aside in a clean area for shipping to the laboratory (section 5.5).
7. **Filtered samples ⇨ Go to section 5.2.** After wholewater or suspended-material subsampling is complete, use the remainder of the composite sample in the churn for filtered samples.
8. Empty the churn after the required number of samples has been processed.
   - If the churn will be reused during the field trip, disassemble and field clean onsite while still wet, as described in NFM 3.
   - If the churn will not be reused during that trip, rinse with DIW before it dries out, place it in a plastic bag and in the churn carrier to be transported back to the office laboratory for cleaning.
9. Document on field forms and in field notes the types of samples collected and the splitting procedures used.

A field blank might be required after all sampling and processing equipment has been field cleaned (NFM 4.3).

TECHNICAL NOTES: Subsamples totaling 10 L and 5 L can be withdrawn from the 14-L and 8-L churn, respectively, for samples for wholewater analysis. The sample volume remaining in either churn may be used for filtered samples.

The churn splitter is used to split samples with particle sizes ≤ 250 µm and suspended-sediment concentrations ≤1,000 mg/L. Splitting accuracy becomes unacceptable at particle sizes > 250 µm and concentrations > 1,000 mg/L.

Cone-Splitter Procedure 5.1.1.B

Inorganic-constituent and organic-compound samples can be split using a fluorocarbon polymer (Teflon™) cone splitter. Although the cone splitter is used primarily for simultaneous distribution of surface-water samples into bottles, the cone also can be used similarly for a bailed or composited ground-water sample. The sample is poured into the splitter from the sampling device or transferred from a noncontaminating compositing container. If used for splitting pumped ground-water samples, the sample is pumped directly into the cone splitter.

1. Put on appropriate, disposable, powderless gloves (gloves). Remove cone splitter from protective covering.
2. Prepare a processing area that is protected from dust and fumes. Preferably, the cone splitter is installed in a processing chamber or covered with a large plastic bag.
3. Install cone splitter (see NFM 2, fig. 2-10, for a labeled diagram). **The cone splitter is built to close tolerances to achieve accurate and reliable operation and requires the following:**
   - **Use a bull's-eye level to level the cone splitter: this is critical for accurate performance.**
   - All tubes exiting the cone splitter must be the same length, as short as possible, and precleaned. Organic-compound samples require fluorocarbon polymer tubing. Carry a separate set of tubes for each site, and clean all sets on return to the office laboratory. If extra tubes are not available, do not reuse tubes for multiple sites without first cleaning them.
   - Push tubes as far as possible into the fittings on the splitter.

Minimize atmospheric contamination—Cover the cone splitter and sample bottles during the sample splitting process and when not in use.

4. Field rinse cone splitter and the appropriate sample bottles with the water to be sampled. **Do not field rinse laboratory-cleaned and baked glass bottles.**
   a. Open cover to access cone-splitter reservoir. (Flap or access slots for hands can be cut into the plastic bag covering the splitter.)
   b. Transfer 2 to 4 L of the sample into the cone-splitter reservoir. Some splitter reservoirs may be retrofitted with a funnel to ease pouring.
   c. Close cover and lightly tap splitting system to dislodge adhering water drops. Discard rinse water.
   d. Field rinse bottles for raw samples (RA, RU, and so on) with wholewater sample. Do not use the water sample previously processed through the cone splitter; follow directions in table 5-2.
5. Place bottles for raw samples under outlet tubes. Complete splitting procedure first with bottles for organic-compound samples, next with bottles for inorganic-constituent samples.
   - Place outlet tubes into sample bottles to prevent spilling. **Outlet tubes should not extend beyond the neck of the sample bottle. Do not submerge the ends of outlet tubes in the sample.**
   - Outlet tubes can be combined to collect various combinations of volumes of the original sample. Make sure no back pressure results from restrictions of water and air flow if combining outlet tubes into a single bottle.
   - Direct sample discharge from unused outlet tubes to waste.
6. Pour (or pump) sample into cone splitter. If hand contact is made with a potential contaminant while using CH/DH techniques, remove outer contaminated glove(s) or put on a new pair of gloves before transferring sample to cone splitter.
   a. Gently shake or agitate sample for at least 10–15 seconds to resuspend any particulate matter present in sampler bottle or discrete sampler (such as a bailer).

b. Transfer sample to cone-splitter reservoir (some splitter reservoirs may be retrofitted with a funnel to ease filling).

- Open cone-splitter cover and invert sampler or compositor containing sample over splitter reservoir. (If using a bailer, empty through bottom-emptying device. If using a pump, hold sample line over the cone-splitter reservoir and pump sample directly into the cone splitter.)
- First, collect organic-compound samples into clean, baked glass bottles (Appendix A5-A).
- Next, collect inorganic-constituent samples into cleaned and field-rinsed polyethylene bottles or as designated (Appendix A5-B or A5-C).

c. Maintain a head of water above the splitter standpipe to prevent air from entering the splitting block while rapidly transferring the sample. **Do not spill any of the sample when pouring or pumping it into the cone splitter.**

d. For proper operation, the splitter standpipe must be discharging at full-flowing capacity.

- **Never overfill sample bottle.**
- **Always transfer the entire composite sample into cone splitter** for thorough distribution into the sample bottles.

7. **When splitting the samples, avoid exposing samples to direct sunlight or freezing conditions.** During sample splitting, the temperature of samples from the cone splitter should remain constant.
8. Close cone-splitter cover.
9. After flow has stopped, lightly tap the cone splitter to dislodge adhering drops.
10. Remove sample bottles and cap them immediately.
11. **To obtain smaller subsample volumes**, position bottles at cone outlet ports and pour a sample from the preceding set of split samples into the cone splitter. **For inorganics only, remember to rinse each new set of polyethylene sample bottles with DIW and sample as previously directed** (sections 5.0.1 and 5.0.3).

12. If multiple passes through the cone are required, randomize the ports selected. This minimizes bias from differences in ports caused by manufacturing processes.
13. Check requirements for sample preservation. **For samples that require chemical treatment ⇨ Go to section 5.4.**
    - For raw samples that require chilling without chemical treatment(s)—Pack samples in ice or refrigerate as quickly as possible. Maintain samples at or below 4°C without freezing (section 5.4).
    - For raw samples that do not require chilling or chemical treatment—Set samples aside in a clean area for shipping to the laboratory (section 5.5).
14. **Filtered samples ⇨ Go to section 5.2.** Remember to use only sample filtrate for the bottle field rinse.
15. Clean cone splitter, following instructions in NFM 3.
    - Disassemble and clean in the field before reusing. Field cleaning between sites must be done onsite while the cone splitter is still wet.
    - If the cone splitter will not be reused immediately, rinse with DIW and place in a plastic bag for transporting back to the office laboratory for cleaning.
16. Document on field forms and in field notes the types of samples collected and the splitting procedures used.

A field blank might be required after sampling and processing equipment has been field cleaned (NFM 4.3).

GROUND WATER: PUMPED AND BAILED SAMPLES 5.1.2

Steps for filling bottles with raw sample pumped from water-supply wells and monitoring wells are described in this section (refer also to section 5.6 and Appendixes A5-A, A5-B, and A5-C). The equipment needed and the procedures required to purge a well and withdraw the sample are described in NFM 2 and NFM 4, respectively, and are only briefly described below.

The recommended method for withdrawing ground-water samples from conventional supply or monitoring wells is to use a submersible or peristaltic pump and to pump the sample directly to a processing chamber (or to a glove box filled with inert gas).[6] Ground-water samples collected using a bailer or other discrete sampling device can be processed either as described under 5.1.1 (composites and subsamples) or within a processing chamber (or glove box), as described later in this section.

Only the Clean Hands person fills the sample bottle inside of the sample processing chamber (NFM 4).

Collect/process equipment blanks, field blanks, replicates, and other types of quality-control (QC) samples periodically (NFM 4.3 and Appendix A4-B of NFM 4). The frequency, number, types, and distribution of QC samples are determined ahead of time according to the study workplan. Nevertheless, in the event of unforeseeable field conditions (for example, dust storms, new point source(s) of contamination, or application of agricultural or other chemicals), **field personnel must judge whether to process additional QC samples**.

- Replicates of environmental samples—Fill bottles one after the other (NFM 4.3).
- Field blanks—Process according to the study quality-assurance plan or as needed (NFM 4.3).

[6]Wells or devices constructed to obtain samples under natural flow gradient (passive) conditions are not addressed in this report.

Processing of samples

The steps listed below for processing raw ground-water samples are based on the assumption that both organic-compound and inorganic-constituent samples will be collected. Before proceeding, check section 5.6 for analyte requirements.

- Prelabel bottles with site identification, sample designation, date, and time (section 5.5 and NFM 1).
- Process samples in the order recommended for sample collection listed on table 5-1. This helps to limit overpurging of volatile compounds, reduce airborne contamination and cross contamination among samples and sites, and minimize discrepancies in the ionic mass balance.
- When pumping the sample, do not stop the pump or interrupt flow to the processing chamber during sampling. The rate of flow during sampling should remain constant throughout processing and be the same as the rate of flow while making final field measurements at the end of purging (NFM 4, NFM 6).

To process ground-water samples for organic-compound analyses:

1. Put on appropriate (latex or nitrile), disposable, powderless gloves (gloves). Cover bench or table with a sheet of aluminum foil to make a clean work surface.
2. Assemble necessary equipment and supplies on the clean work surface, and remove aluminum foil wrapping from precleaned equipment. Attach processing chamber cover. (Processing of organic-compound samples within a chamber is not mandatory but is recommended.)
3. Check requirements for treatment of the sample(s) collected.
   - If collecting a VOC sample that will be acidified—Test for the number of drops of HCl needed to lower sample pH to ≤ 2 using 40 mL of the final purge water. Dispense the HCl from a dropper bottle.
   - All samples processed for organic-compound analysis are to be chilled to 4°C or below without freezing.
4. Place bottles and other equipment needed for processing raw samples into processing chamber. If collecting samples for VOCs, place only VOC vials and VOC equipment in the chamber.

5. Withdraw samples from the well.

If using a pump—

a. Purge wells first, preferably with the same pump to be used for withdrawing the samples. Consult NFM 4.2 for purging procedures.

b. Check that the discharge end of sample line from the pump or manifold is secured in the processing chamber.

c. Direct sample flow through the sample line into the processing chamber (NFM 4.2).

- Waste initial sample through chamber drain for the sample-line rinse; do not let sample spray onto chamber cover—change chamber cover if this happens.
- Check for air bubbles in the sample line; tap the line or make adjustments to remove any air from the line.
- Flow should appear smooth and uniform (with no splashing) and should not exceed 150 mL/min when filling 40-mL VOC vials or 500 mL/min for larger bottles.

If using a bailer—

a. Purge wells first, using a pump (NFM 4.2). Do not purge wells with a bailer unless absolutely necessary.

b. Set up holding stand, as appropriate.

c. Lower the sampler (after field rinse) smoothly into the well; cause as little disturbance to the water column as possible. Follow analogous directions as those for sampler field rinsing (NFM 4.0.2.A).

d. After reaching the sampling depth within the screened or open interval, collect sample by raising the sampler smoothly (minimizing disturbance to water column). Keep the deployment line clean and untangled as sampler is lowered and raised.

e. Place sampler into holding stand and insert sample-delivery tube/device.

> TECHNICAL NOTE: Sampling from wells with a bailer or other discrete sampling device is not recommended if target analytes (such as trace elements and hydrophobic organic compounds) are those that typically associate or partition to particulates because deployment of bailers or other point-source samplers usually stirs up or otherwise mobilizes particulates. Fine-grained and colloidal-sized particulates can persist in the water column, causing a potential for bias.

6. Collect all raw organic-compound samples into designated bottles.
   a. Fill VOC vial from bottom of vial to overflowing without entraining air bubbles. Leave a convex meniscus. If sample will not be acidified, cap vial securely, invert, and check for air bubbles. **Follow directions in section 5.6.1.A.**
   b. If acidification of the sample is required,
      - The preservative can be added to VOC samples while samples are inside the processing chamber as long as the chemical treatment will not affect any subsequent samples to be collected for analysis of organic compounds. Otherwise, acidify VOC samples in a preservation chamber.
      - Add 1 to 5 drops of HCl to the sample (sections 5.4 and 5.6). Usually two drops of HCl are sufficient to lower the pH of the VOC sample to ≤ 2. Cap vial securely, invert, and check for air bubbles. If air bubbles are present, discard the vial and start again.
      - Change cover of processing chamber and change gloves.
   c. Place remaining raw organic-compound sample bottles into processing chamber. Fill bottles directly from the sample line to the shoulder of each bottle (section 5.6.1.B).
7. For filtered organic-compound samples:
   a. Place aluminum plate-filter assembly into chamber for pesticides and other filtered organic-compound samples. Change gloves.
   b. Load the filter, connect the plate-filter assembly, and field rinse the filter as directed in section 5.2.2.A.
   c. After following filtration directions in section 5.2.2.A, pass bottles out of chamber for DH handling.
8. After processing raw and filtered organic-compound samples:
   a. Fill sample bottle with DIW and label "temperature-check sample" to accompany chilled organic-compound samples.
   b. Remove the equipment used to process the samples and pass to DH.
   c. Discard chamber cover.
   d. Remove aluminum foil covering from work bench.
9. **Sample preservation ⇨ Go to section 5.4.**

Process ground-water samples for inorganic-constituent and remaining analyses:

1. Direct flow of pumped sample away from the processing chamber. Change to vinyl or latex, disposable, powderless gloves (gloves).
2. Cover bench or table with a plastic sheet to make a clean work surface. Change processing chamber cover. Assemble equipment and supplies needed on the clean work surface. Remove plastic wrapping from pre-cleaned equipment. Change gloves.
3. **For filtered inorganic-constituent, nutrient, radiochemical, and isotope samples**:
   a. Place filtration equipment, sample bottles (prelabeled), and other supplies and equipment for filtered inorganic-constituent samples into processing chamber. Change gloves.
   b. Connect filtration equipment as directed in section 5.2.1.
   c. Resume sample flow to the chamber.
      - Check for air bubbles in the sample line; tap line or make adjustments to remove air from the line.
      - Flow should be smooth and uniform—about 500 mL/min to fill sample bottles without splashing.
   d. Collect all filtered inorganic-constituent samples first, as directed in section 5.2.1.
4. Disconnect the filter assembly. Change gloves.
5. **Raw inorganic-constituent, nutrient, radiochemical, and isotope samples:**
   a. Place prelabeled bottles for raw samples into the processing chamber. Change gloves.
   b. Field rinse bottles with raw sample (section 5.1, table 5-1).
   c. Collect samples into designated bottles.
   d. Place bottles outside of chamber. Change gloves.
6. Remove equipment, discarding chamber cover appropriately.
7. **Sample preservation ⇨ Go to section 5.4.**
8. **Radon and CFC samples ⇨ Go to section 5.6.**

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FILTERED SAMPLES 5.2

By **D.B. Radtke, A.J. Horowitz, and M.W. Sandstrom**

Filtration is the physical process used to separate the particulate and aqueous fractions of a water sample. Samples are filtered for several purposes; for example, to remove microorganisms in order to help preserve ambient analyte concentrations, to remove suspended materials that interfere with specified analytical procedures, and to determine chemical speciation and fractionation of trace elements for geochemical studies.

Study objectives and the analytes targeted for study dictate the filtration method and equipment to be used. Ambient concentrations of filtered analytes typically can be near the limit of detection; therefore, field personnel must pay strict attention to possible sources of contamination from sampling and processing equipment, construction material of the chamber frame and of the filtration equipment, and the way the equipment is handled. (Equipment and supplies used to filter water samples are described in detail in NFM 2.)

- Check the composition and pore size of the filter medium and the effective filtration area of the filter; these can affect the quality and accuracy of the data and can compromise data-quality requirements.
- To minimize airborne contamination,
  - Filter samples within a processing chamber.
  - Add chemical treatments to samples within a separate preservation chamber.

Filter samples during or immediately after sample collection.

5.2.1 INORGANIC CONSTITUENTS

Most filtration systems currently used by the USGS are appropriate for filtering wholewater samples, if the limitations of each system are taken into account. **Standard USGS procedure is to filter inorganic-constituent wholewater samples through a 0.45-micrometer (µm) pore-size disposable capsule filter.** Filtration through media with pore sizes other than 0.45 µm or with other equipment (such as tangential-flow devices) depends on the use and interpretation of the data and can yield substantially different results for trace-element concentrations.

Data-quality requirements for interpretive studies of ground-water and surface-water chemistry can dictate filtering the sample through a nominal pore size of ≤ 0.2 µm. The quality-assurance procedures used for samples filtered through the 0.45-µm nominal-pore-size capsule, plate, or other filtration equipment also are required for the ≤ 0.2-µm filters. If concentrations of target analytes are analyzed at sub-parts-per-billion levels, more stringent QA/QC measures are needed. Such samples can be filtered through a plate filter or other filtration equipment (for example, a 47-mm-diameter vacuum-filter unit) as long as the equipment used is approved by the study or program, data-quality requirements are met, and additional quality-control samples are collected. For additional information on filtration artifacts, procedures, and equipment, see Kennedy and others (1976), Salonen (1979), McCarthy (1988), McCarthy and Zachara (1989), Puls and Barcelona (1989), Ward and Harr (1990), Horowitz and others (1992, 1994), Williams and others (1993), Robards and others (1994), and Koterba and others (1995).

Cleaning and conditioning of various filter media used for inorganic constituents are summarized in table 5-3. Contamination during sample filtration can be reduced by following the instructions given for cleaning, conditioning, and handling of the filter media.

Table 5-3. Field cleaning and conditioning procedures for media used to filter samples for inorganic-constituent analysis

[µm, micrometer; mL, milliliter; sample, the water to be sampled; µg/L, microgram per liter; mm, millimeter; HNO_3, 1 molar solution of ultrapure-grade nitric acid; HCl, 1 molar solution of ultrapure-grade hydrochloric acid; nutrients, nitrogen and phosphorus species; DIW, District- or laboratory-produced deionized water of known quality, ASTM Type-1 grade or better; IBW, laboratory-produced inorganic-grade blank water; *N*, normal; >, greater than]

Description	Filter media	Field cleaning/ conditioning	Application
Disposable capsule filter[1] (Polypropylene)	Polysulfone, pleated membrane, 0.45-µm or 0.2-µm pore size	Clean with 1,000 mL DIW and remove residual DIW[2] Condition with 25 mL sample	Major ions and nutrients; trace elements with concentrations > 1 µg/L; radio-chemicals and isotopes
Plate filter — 142 mm (Polycarbonate or acrylic)	Cellulose nitrate, tortuous path (0.45 and 0.1 µm are most commonly used pore sizes)	Clean with 500 mL DIW and extract residual DIW Condition with 100 mL sample	Major ions and nutrients; trace elements if concentrations > about 100 µg/L
Cartridge or hand-pressure filter assembly—47 mm (Polypropylene or fluorocarbon polymer)	Cellulose nitrate, tortuous path (0.45, 0.2, and 0.1 µm are most commonly used pore sizes)	Clean with 100 mL DIW and remove residual DIW Condition with 20 mL IBW or 10 mL sample	Major ions and nutrients; trace elements with concentrations at about 1 µg/L or greater
Cartridge or hand-pressure filter assembly—47 mm (Fluorocarbon polymer)	Polycarbonate (such as Nuclepore), direct path (0.40 and 0.1 µm are most commonly used pore sizes)	Soak in HNO_3 rinse with IBW.[3] Remove residual IBW Condition with 20 mL IBW or 10 mL sample	Major ions and nutrients; trace elements with concentrations at about 1 µg/L or greater

[1]Example: Gelman Sciences 12175 (0.45 µm); 600 square-centimeter filtration area. Other disposable capsule filters are available that have different effective filtration area, media type, and media pore size.

[2]For trace-metal analyses at nanogram-per-liter concentration levels, first acid rinse with 500 mL of 1-*N* HCl (polysulfone membranes cannot withstand HNO_3).

[3]Substitute HCI for HNO_3 if sampling includes nutrients.

- Before filtering, designate one member of the processing team as Clean Hands (CH) and another member as Dirty Hands (DH) if using the CH/DH method (NFM 4).
- Wear appropriate, disposable, powderless gloves throughout the process. Vinyl gloves are adequate for inorganic-constituent sampling.
- Filter the samples within a processing chamber to minimize the possibility of contamination.

5.2.1.A Capsule-Filter Procedure

The capsule filter is a disposable, self-contained unit composed of a pleated filter medium encased in a plastic housing that can be connected in-line to a sample-delivery system (such as a submersible or peristaltic pump) that generates sufficient pressure (positive or negative) to force water through the filter. Filter media are available in several other pore sizes, but 0.45 µm is the pore size used routinely for most studies at this time. The capsule filter is required for most studies when filtering samples for trace-element analysis and is recommended when filtering samples for major-ion or other inorganic-constituent analyses.

The following instructions implement Clean Hands/Dirty Hands (CH/DH) techniques and the other QA procedures that are required for trace-element samples with analyte concentrations at the parts-per-billion (ppb) level and that are recommended as good field practice for all samples.

- The DH team member performs operations that are outside of the processing chamber and the CH team member performs operations inside the chamber. DH and CH must wear appropriate disposable, powderless gloves (gloves).
- Preclean capsule filters (step 5 below) before leaving for the field to save field time.

Fill bottles for filtered samples in this sequence: FA (trace elements) ➜ FAM (mercury) ➜ FA and FU (major ions) ➜ FCC or FCA (nutrients) ➜ FAR and all other samples.

Revise the above sequence to: FA (trace elements and cations) -> FAM (mercury) -> FCC or FCA (nutrients) -> FU (anions) -> FAR -> DOC and all other samples.

Capsule Filter requires 2-L rinse of IBW or DIW

To prepare the work space, sample bottles, and capsule filter:

1. CH/DH: Put on one or several layers of gloves.
2. *CH*: Assemble processing chamber, attach chamber cover, and change gloves. Place capsule filter and sample bottles into chamber, and run discharge end of peristaltic pump tubing into the chamber. Open DIW[7] container and cover it with a plastic bag to prevent contamination from airborne particulates.
3. *CH*/*DH*: (*CH*) Insert intake end of peristaltic pump tubing through the plastic covering and into a l-L container of DIW.
   a. (*DH*): Attach tubing to peristaltic pump head and pump DIW to fill tubing.
   b. Discharge waste rinse water through a sink funnel or a toss (waste) bottle.
4. Discard DIW stored in DIW-prerinsed sample bottles. If sample bottles were not DIW-prerinsed by field personnel:
   a. Wearing gloves, rinse off exterior of each bottle.
   b. Pour DIW into bottle until about one-tenth full.
   c. Cap bottle and shake vigorously about five times.
   d. Uncap and empty bottle.
   e. Repeat b–d of step 4 twice (for a total of three times).
   f. Recap bottles until ready to field rinse.

[7]Office of Water Quality Technical Memorandum 92.01 describes the quality required of the deionized water.

5. **Clean the capsule filter.** If the capsule filter was precleaned, go to the sections that follow on "To filter a composite sample" or "To filter a pumped sample," as appropriate. The steps below comprise sufficient precleaning of the filter for inorganic analytes at the parts-per-billion (ppb) concentration level. More rigorous precleaning procedures that include rinsing with trace-metal-grade hydrochloric acid are required for samples containing ppb concentrations of target analytes (table 5-3). **Only CH touches those portions of tubing that will be in direct contact with the DIW or capsule filter.**

   a. *CH*: In the processing chamber, remove capsule filter from protective bags.

      - Attach pump tubing to inlet connector of capsule filter, keeping tubing as short as possible. **Make sure direction of flow through capsule filter matches the direction-of-flow arrow on the side of the capsule.**
      - To help minimize aeration of the sample (usually for ground-water samples), secure a short length of clean fluorocarbon polymer tubing onto capsule filter outlet to extend into the sample bottle so the bottle can be filled from the bottom up.

   b. *CH/DH*: Pump 1 L [illegible] DIW through capsule filter; discharge waste rinse water through a sink funnel or to a toss bottle.

      - *DH* operates the pump at a low speed.
      - *CH* inverts the capsule filter so the arrow on the housing is pointing up. (This expels trapped air from the capsule during initial filling; do not allow water to spray onto the chamber walls.)

   c. *DH*: Remove tubing from DIW reservoir and continue to operate pump in forward mid-range speed position to drain as much of the DIW that remains in the capsule filter as possible. While pump is operating, shake capsule filter to help remove any entrained DIW.

   d. *CH*: Detach capsule filter from peristaltic pump tubing, put it into a clean, sealable plastic bag, and place in a corner of the processing chamber until ready for use.

Filtration procedures differ somewhat, depending on how the sample is collected. If the sample is collected using discrete collection equipment, such as the surface-water bag or bottle sampler or ground-water bailer, use the procedures described below in "To filter a composite sample." If the sample is collected by pumping it directly from the source, use the procedures described below in "To filter a pumped sample." Ground-water samples usually are not collected as a composite. If samples are to be withdrawn from

Capsule Filter requires 2-L rinse of IBW or DIW

a well using a bailer, consider using a bailer to which the capsule filter or other filtration device can be connected inline to the bailer bottom-emptying device. Pouring a sample from the top of the bailer into another receptacle aerates the sample and therefore is not a generally recommended procedure for processing ground-water samples.

To filter a composite sample (generally for surface water):

1. Field rinse peristaltic pump tubing with the water to be sampled.
   a. *CH:* Rinse the outside of each end of the peristaltic pump tubing.
   b. *CH*: Transfer intake end of peristaltic pump tubing into composite sample. If a churn splitter is used, transfer intake end of peristaltic pump tubing through churn funnel and reseal plastic bag around the tubing.
   c. *DH*: Start peristaltic pump to slowly pump sufficient sample to completely fill pump tubing.
   d. *CH*: Discard rinse water through the sink funnel or into a toss bottle or other receptacle and dispose of appropriately. Prevent water from ponding in the processing chamber.
   e. *DH*: Stop peristaltic pump after tubing is field rinsed.
2. Field rinse capsule filter:
   a. *CH*: Remove cleaned capsule filter from plastic bag and attach discharge end of the peristaltic pump tubing to the inlet connector on the capsule filter.
      - A clean, small plastic hose clamp may be used to secure the discharge end of the tubing to the capsule filter inlet connector.
      - Check that the direction of sample flow through the capsule filter matches the direction of the arrow on the capsule.
   b. *DH:* Operating the pump at low speed, pump sample through the tubing to the capsule filter.
   c. *CH:* Turn capsule filter so that the outlet is pointing up (arrow on capsule housing is pointing up) and flow of the sample forces trapped air out of the capsule filter while it is filling. **Do not let sample spray onto chamber cover.**
      - The chamber cover must be changed if sample has sprayed onto it.
      - If some water that sprayed onto the chamber cover has dripped into the sample bottle, discard the bottle, change the cover, and collect a new sample.

d. *DH:* Stop the peristaltic pump as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.

TECHNICAL NOTE: The goal is to minimize clogging the filter medium with suspended materials by minimizing the volume of sample that will be used to field-rinse the filter.

~~1~~3. Collect sample filtrate.

a. *CH*: Check that there is a tight connection between the pump tubing and the capsule filter.

DH: Check that the intake tube is properly inserted in the sample and start the pump.

CH: Collect a maximum of 25 mL of the water to be sampled as it discharges through the filter. **Do not exceed 25 mL**.

CH: Field rinse a precleaned 250-mL FA bottle for trace-element sample only with sample filtrate.

DH: Stop the pump in time to prevent losing filtrate to waste.

CH: Cap bottle, shake vigorously, and then discard rinse water into appropriate receptacle.

b. *DH:* Start pump and resume flow from pump to the filter.

CH: **Filter only the next 200 mL of the sample** into the trace-element FA bottle (fill to top of upper lip of standard 250-mL polyethylene bottle). Cap bottle securely and set aside for chemical treatment.

c. *DH:* Stop the pump after the trace-element/major ion FA bottle is filled.

d. If a filtered mercury sample is required, restart pump and repeat steps 3a–c, substituting a FAM bottle for the FA bottle.

e. *CH:* Field rinse any remaining sample bottles for inorganic analyses. **Use no more than a total of 100 mL of filtrate per capsule filter to field rinse any remaining bottles for filtered sample. Do not rinse the DOC bottle.**

f. Fill remaining bottles in the following order: (1) nutrients and major anions (including alkalinity), (2) radiochemicals (Appendix A5-A), and (3) stable isotopes. Cap each bottle immediately after filling. Collect capsule-filtered dissolved organic carbon (DOC) last.

Note: Page revised 2/27/2009.

To filter a pumped sample (usually ground water):

Ground-water samples usually are withdrawn from a well by means of a submersible pump. Note that this method might be appropriate for some surface-water samples. The capsule filter or other filter assembly is connected inline with the sample tubing in order to collect samples directly from the well.

- When sampling ground water, DH should check that the turbidity values recorded at the end of purging have remained stable. Equipment changes or adjustments that disrupt sample flow can affect sample turbidity and should be avoided. If sample flow is disrupted, pump for several minutes until ambient turbidity values are reestablished.
- **Maintain a smooth, uniform flow.** Do not stop pump or divert flow from capsule filter or other filter assembly during bottle field rinse or filtration, if possible.

  TECHNICAL NOTE: If using a three-way valve, changing the setting to divert the flow of sample being pumped to the filter with a submersible pump can cause air bubbles to form, can air-block the filtration equipment, and can cause changes in pumping rate that could result in increased turbidity. These effects should be avoided to preserve sample integrity; therefore, flow to the filter should not be stopped until all filtration is complete.

1. Field rinse the capsule filter with sample water:
   a. *CH:* Ensure that the sample line is full of sample and free of bubbles; then attach the discharge end of the sample line to the inlet connector on the capsule filter.
      - Practice your technique for attaching the capsule filter to the tubing carrying flowing water so that water does not spray onto chamber walls.
      - Check that the direction of flow matches the direction of the arrow on the capsule.

   b. *DH:* Adjust the sample flow through the sample line to the capsule filter, keeping a slow rate of flow.

   c. *CH*: Turn the capsule filter so the outlet is pointing up (arrow on capsule housing is pointing up) and the flow of sample forces trapped air out while the capsule filter is filling.
      - Do not allow water to spray onto chamber walls.
      - The capsule filter should be full of sample. No air should be left in the capsule filter.

d. Field rinse bottles for inorganic-constituent filtered samples with sample filtrate (section 5.0.3). Use bottles that were already rinsed three times with DIW. Determine whether the potential clogging of pores in the filter medium is of concern for your samples (see TECHNICAL NOTE below).

CH: Fill a 250-mL FA bottle for trace elements with 25 mL of sample filtrate; cap, shake vigorously, and discard rinse water into appropriate receptacle.

CH: Fill a FA bottle for trace elements with about 200 mL of sample filtrate (to top of upper lip of 250 mL bottle). Cap bottle and set aside for chemical treatment.

CH: If a mercury sample is required, field rinse and fill a FAM bottle using the same procedure as for the 250-mL FA bottle.

CH: Field rinse remaining bottles, trying to use no more than an additional 100 mL of sample filtrate. Do not rinse the DOC bottle.

> TECHNICAL NOTE: Depending on sample turbidity and composition, the nominal pore size of filter media tends to decrease as the volume of sample passed through the filter increases because pores are clogged by sediment loading or mineral precipitation on the filter (Horowitz and others, 1994). Ground water with turbidity ≤5 NTU should not affect filter pore size appreciably. To minimize the chance of filter clogging, limit the volume of sample passed through the filter by eliminating the field rinse—be sure that you use clean bottles and fill them one after the other. For ground-water sampling, do not stop the pump during the field-rinse and sampling process.

e. *CH:* Collect sample filtrate immediately into any remaining bottles in the following sequence (flow rate should be slow enough to avoid splashing sample out of the bottle): (1) nutrients and major anions (including alkalinity sample for field titration), (2) radiochemicals (check Appendix A5-A for bottle-rinse and filtration requirements, (3) stable isotopes, (4) capsule-filtered dissolved organic carbon (DOC).

f. *CH*: Cap each bottle immediately.

Rinse FA, FU, FAM, FCA, and FCC bottles with filtered sample—not with raw sample.

Note: Page revised 2/27/2009.

After collecting filtered samples:

1. *CH*: If samples require chemical treatment, place FA bottles in the preservation chamber and go to section 5.4.
2. For filtered samples that do not require chemical treatment:
   a. *CH*: Set samples outside processing chamber.
   b. *DH*: Check that information on the bottle label is correct and complete.
   c. *DH:* Pack samples that require chilling in ice or refrigerate immediately.
   d. *DH:* Pack remaining samples for shipping (section 5.5).
3. Rinse all reusable equipment with DIW immediately—before equipment dries.
   - *CH*: If equipment will be reused at another site before returning to the office, rinse immediately with DIW and field clean tubing and other sample-wetted parts of the equipment using the prescribed cleaning procedures (NFM 3).
   - *CH*: If equipment or tubing will not be reused before returning to the office, rinse immediately with DIW and store rinsed tubing and equipment in plastic bags for office or laboratory cleaning.
4. **Discard the capsule filter after filtering each sample—do not reuse.**
5. Document the filtration procedures used on field forms and in field notes.

Use of the 0.45-µm disposable capsule filter for trace-element samples is required for many USGS programs.

5.2.1.B Plate-Filter Procedure

The filtering procedure using a 142-mm-diameter plastic plate-filter assembly is described below. The procedure remains basically the same for plate-filter assemblies of different diameters.

Prepare and precondition plate-filter assembly:

The following instructions pertain to either a 142-mm-diameter or a 47-mm-diameter plastic plate-filter assembly and require that the assembly components have been rigorously cleaned (NFM 3). To avoid recleaning in the field, prepare a set of filtration equipment for each well or surface-water sampling station. (Ignore Step 3 below if plate-filter assembly has been rinsed in the office.)

1. *CH*: Put on gloves. In a processing chamber, open a clean plate-filter assembly and load with the filter.
   a. Using nonmetallic forceps, place the bottom retaining screen on the base of the filter assembly. **Do not interchange bottom and top retaining screens.**
   b. Place the filter on top of bottom retaining screen using clean, blunt plastic or ceramic forceps. Do not touch the filter with hands (gloved or ungloved).
      - Be sure that only one filter is transferred from its original container directly to the plate of the filter assembly. Take care not to transfer the paper liner that separates each filter.
      - The filter should never be removed from the original container until each is transferred to the plate-filter assembly for use. (Exception: polycarbonate (Nuclepore) filter medium is precleaned with acid solution. If transferring one of these, hold the filter with forceps and rinse off acid with inorganic blank water (IBW) dispensed from wash bottle.)
   c. Using forceps, place the top retaining screen on top of the filter.

      TECHNICAL NOTE: If filtering sediment-laden water, a prefilter can be placed between the filter and the top retaining screen.

   d. Dispense 10 to 20 mL of DIW from a wash bottle onto the filter.

e. Close the plate-filter assembly by aligning the top and bottom plates and lightly tightening the plastic bolts, followed by finger tightening opposite pairs of bolts. **Overtightening can cause the plate-filter assembly to warp and leak.** Check that O-rings are in place before closing the assembly. Change gloves.

2. *DH/CH*: Pass the discharge end of the pump tubing through the hole in the side or top of the processing chamber. **Only the CH team member touches sections of tubing that will be in direct contact with the plate-filter assembly.**
   - Keep tubing as short as practical.
   - Attach a short piece of clean tubing to outlet connector of plate-filter assembly.
3. *DH/CH*: Rinse the plate-filter assembly with DIW, using a peristaltic pump, as follows **(rinsing must be repeated each time a clogged filter is replaced with a new filter)**:
   a. *CH*/*DH*: Place intake end of peristaltic pump tubing into a 500-mL container of DIW. Turn pump on low speed.
   b. *CH*: Open the air-vent valve on top of the plate-filter assembly. Tilt the filter assembly slightly to the side and squeeze the outlet tube closed to force trapped air out through the vent. Release the outlet tube. (Venting trapped air is necessary because air bubbles will reduce the effective filtering area by preventing sample from passing through the filter.)
   c. *CH*: Close valve when top is filled with sample.
   d. *CH*: Pump sample through the plate-filter assembly and discard this field-rinse water through the sink funnel or into the toss bottle to prevent the water from ponding in the bottom of the processing chamber.
   e. *CH*/*DH*: Remove intake end of the pump tubing from the DIW container and continue to pump, draining as much of the remaining DIW from the plate-filter assembly as possible.
4. If using a peristaltic pump to transfer the sample to the processing chamber (go to step 5 if sample delivery is with a submersible ground-water pump):
   a. *CH*: Rinse intake end of the peristaltic pump tubing with the water to be sampled.
   b. *CH*: Transfer intake end of the peristaltic pump tubing into the container of sample. If a churn splitter is used, transfer the intake end through the churn funnel and reseal the plastic bag around the tubing.

c. *CH*: Remove peristaltic pump tubing from the inlet connector of the plate-filter assembly and hold the end of the tubing over the sink funnel or toss bottle.

d. *DH/CH*: Start the peristaltic pump in the forward position at slow speed and pump sufficient sample to fill and rinse all pump tubing. Stop the pump after the tubing is rinsed.

5. *CH*: Attach the discharge end of the peristaltic-pump or submersible pump tubing to the inlet connector of the plate-filter assembly.
   - Keep tubing as short as practical.
   - A clean, small, plastic hose clamp can be used to secure the discharge tubing to the inlet connector.
6. *DH*: Start sample flow to the plate-filter assembly.
7. *CH*: Vent trapped air and rinse plate-filter assembly as instructed in steps 3 b–d above.
   - If using a peristaltic pump, turn pump on low speed.
   - If using a submersible pump, maintain a slow and steady flow rate.
8. *CH*: Rinse appropriate sample bottles once with filtrate. Filter no more than 100 mL of sample for the final rinse of all sample bottles that require rinsing.
9. Filter samples, filling bottles in the following order, as applicable to study objectives and sample designation:
   a. Trace elements/major cations

      TECHNICAL NOTE: Study objectives and data-quality requirements govern procedures to be used if the filtered trace-element sample is to reflect concentrations of analytes in true solution (the dissolved fraction). Such interpretive studies of ground-water or surface-water chemistry commonly use ≤0.1-µm filter media and plate-filter assembly or a tangential flow method of phase separation. Note that any deviation from the standard procedure for collecting filtered trace-element samples through the 0.45-µm capsule filter must be documented and reported with the analytical results.

   b. Nutrients, major anions, and alkalinity sample
   c. Radiochemicals
   d. Isotopes

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Note: Page revised 2/27/2009.

10. *CH*: If the filter medium clogs before the needed volume of water is filtered, carefully remove the filter and replace with a new filter. Repeat steps 1 through 7. Cap each bottle immediately after filling.
11. **If samples require chemical treatment ⇨Go to section 5.4.**
12. *DH*: After filtration,
    a. Check that information on the bottle label is complete and set the samples aside for shipping (section 5.5). Samples that must be chilled need to be refrigerated or packed in ice as quickly as possible and maintained at 4°C without freezing.
    b. Disconnect and disassemble the plate-filter assembly. **Discard the used filter.**
    c. Rinse all equipment with DIW immediately after use and before it dries. Equipment that has dried after sampling without being rinsed or cleaned needs to be cleaned vigorously with a detergent and rinsed with DIW before the next use. Nonmetallic equipment must also be acid rinsed.
    d. Put rinsed tubing in a plastic bag for cleaning at the office laboratory.
    e. If equipment is to be used at the next site, field clean all the equipment using the procedures described in NFM 3. Field cleaning between sampling sites is carried out while still at the sampling site.
13. Document on field forms and in field notes any modifications to the filtration procedures used.

ORGANIC COMPOUNDS 5.2.2

Standard procedure for phase separation of general trace-organic compounds involves the use of a stainless steel or aluminum 142- (or 293-) mm-diameter plate-filter assembly with glass-fiber filter media and a valveless piston or fluorocarbon polymer diaphragm-head metering pump (section 5.2.2.A). Equipment and procedures differ when filtering samples for dissolved and suspended organic carbon (section 5.2.2.C) and optionally for organonitrogen herbicide analyses (section 5.2.2.B). Required conditioning for filter media is discussed below and summarized in table 5-4.

Table 5-4. Field conditioning requirements for media used to filter samples for organic-compound analysis

[mm, millimeter; mL, milliliter; PBW, pesticide-grade blank water; sample, the water to be sampled; methanol, pesticide-grade methanol; DIW, deionized water]

Filtration equipment *Application*	Construction materials	Filter media	Filter cleaning and conditioning[1]
Plate-filter assemblies: 142 or 293 mm *General trace organic compounds*	Stainless steel or aluminum	Glass-fiber filter[2]	Wet with PBW: 10-20 mL (142 mm) or 50-75 mL (293 mm) Condition with 100-125 mL sample
Disposable capsule filter: 25 mm *Organonitrogen herbicides*	Polypropylene	Nylon	Rinse with 10 mL of methanol No conditioning
Pressure filter apparatus: 47 mm *Dissolved and suspended organic carbon*	Stainless steel or fluorocarbon polymer	Silver metal	Rinse with 100 mL PBW or District-prepared organic-grade DIW Condition with 10-15 mL sample

[1]Do not reuse filters.

[2]Use only glass-fiber filters that have been adequately baked.

The procedures for filtering samples for analysis of trace-organic compounds, including volatile organic compounds, pesticides, and base-neutral compounds, are summarized from Sandstrom (1995). CH/DH techniques and associated QA procedures for inorganic analytes with parts-per-billion concentrations are not required for organic analytes but are recommended as good field practices to maintain the integrity of sample chemistry. Field personnel must wear disposable, powderless gloves (gloves). These gloves must be able to withstand any solvents or other chemicals that will be used during sample processing and equipment cleaning. Equipment and supplies used to filter different types of organic compounds are described in NFM 2. Additional information about organic-compound filtration can be found in Ward and Harr (1990), Manning and others (1994), Shelton (1994), and Koterba and others (1995).

For revised procedures for dissolved organic carbon (DOC) refer to section 5.2.2.C.

Plate-Filter Procedure 5.2.2.A

Read through the procedures described in Sandstrom (1995) and presented in tables 5-4 and 5-5 and in figure 5-1. Obtain the equipment needed (table 5-5), test equipment operation, and collect an equipment blank if needed. Filtering samples for organic-compound analysis inside a processing chamber and using Clean Hands (CH)/Dirty Hands (DH) techniques is not mandatory but is recommended.

Table 5-5. Equipment for filtration of water-sediment samples for determination of organic compounds

[Modified from Sandstrom (1995); FEP, fluorinated ethylene-propylene; mm, millimeter; mL/min, milliliter per minute; L, liter; µm, micrometer; °C, degree Celsius]

Item	Description of equipment
	Container for unfiltered sample. Clean, laboratory-grade glass bottles with fluorocarbon polymer-FEP-lined lids.
	Fluorocarbon polymer-FEP tubing, 6.35-mm outside diameter.
	Union, 6.35-mm tube (Swagelok Company, Solon, Ohio, No. SS-400-6 or equivalent).
	Fluorocarbon polymer-FEP convoluted tubing, 6.35-mm outside diameter (Cole-Parmer Instrument Company, Chicago, Ill., No. L-06486-02 or equivalent).
	Tube fitting, 6.35-mm diameter tube to 6.35-mm diameter pipe thread (Swagelok Company, Solon, Ohio, No. SS-400-1-4 or equivalent).
	Pump, ceramic-piston, valveless, with 12-volt direct current motor, capable of pumping from 0 to 500 mL/min (Fluid Metering, Inc., Oyster Bay, N.Y., Model QB-1 CSC or equivalent).
	Battery, 12-volt direct current.
	Tube fitting, 6.35-mm diameter tube to 9.53-mm diameter pipe thread (Swagelok Company, Solon, Ohio, No. SS-400-1-6 or equivalent).
	In-line plate-filter assembly, aluminum (or stainless steel), 142-mm diameter (Geotech Environmental Equipment Inc., Denver, Colo., No. 0860 or equivalent).
	Glass-microfiber filter media, binder-free, 142-mm diameter, 0.7-µm nominal pore size (Whatman Inc., Clifton, N.J., GF/F grade, No. 1825C142 or equivalent). Note: The filters must be baked at 400°C for at least 2 hours and kept wrapped in aluminum foil before use.
	Bottle for filtered samples, amber borosilicate glass, 1 L with fluorocarbon polymer-FEP-lined cap.
	Fluorocarbon polymer-FEP squeeze (wash) bottle for organic-grade blank water.
	Stainless-steel forceps for handling the filters.

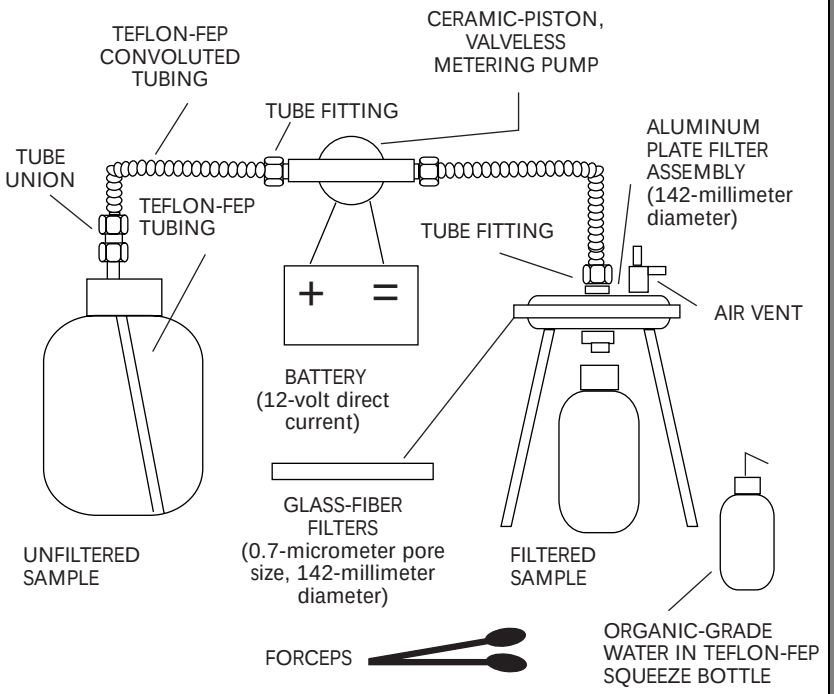

Figure 5–1. An equipment system suitable for filtering samples for analysis of organic compounds (from Sandstrom, 1995).

To filter sample for analysis of general trace-organic compounds in solution:

1. *CH/DH*: Wear appropriate (latex or nitrile) gloves throughout sample processing. Change gloves after setting up equipment. (Wearing several layers of gloves can save time.)
2. *CH*: Load the filter onto the plate-filter assembly within the processing chamber.
   a. Open precleaned plate-filter assembly.
   b. Place one stainless steel support screen on the base of the plate-filter assembly—Use stainless steel forceps.
   c. Place one clean 0.7-µm pore-size glass microfiber filter on top of the screen. **Do not touch the filter with fingers; use stainless steel forceps.**
   d. Wet the filter with a few drops of pesticide-grade blank water (PBW) from a fluorocarbon polymer wash bottle to help keep the filter in place as the unit is assembled.

e. Close plate-filter assembly—Align top and bottom plates. **Lightly tighten** the locking bolts or locking ring. Attach a short length of fluorocarbon polymer tubing to the outlet of the plate-filter assembly to channel filtrate to a toss bottle, sink funnel, or drain.

f. Add 10 to 20 mL of PBW rinse water through the inlet in the upper plate to wet the filter completely before tightening the clamps. (This rinse also helps prevent damage to the filter: a dry filter might rupture when the plate-filter assembly is tightened.)

g. Tighten the locking bolts or ring by hand. **Overtightening can cause the plate-filter assembly to warp and leak and the filter to rupture.**

3. *CH/DH*: Rinse the pump tubing (from a metering pump) or the sample tubing (from a submersible ground-water pump) with the water to be sampled. Discard rinse water into a sink funnel or toss bottle.

4. Set up the pump for filtration.

- *CH*: If using a metering pump, place intake end of tubing into the container holding the sample. Attach discharge end of pump tubing to the inlet connector of the plate-filter assembly. Use a stainless steel compression fitting of the appropriate size to secure the discharge hose to the inlet connector.
- *CH*: If using a submersible pump, attach discharge end of the sample tubing from the pump to the plate-filter assembly, keeping tubing as short as practical. Use a stainless steel compression fitting of the appropriate size to secure the discharge hose to the inlet connector.

5. *CH*: Rinse and condition the filter. The total volume of sample passed through the filter, including rinse water, needs to be accurately determined to ±1 mL and recorded in the field notes.

a. Turn on the metering pump at low speed or open the sample tubing from the submersible pump and operate at a low flow rate.

b. Open the air-vent valve located on top of the plate-filter assembly. Tilt the assembly slightly to the side to allow all trapped air to escape (vent).

c. Close the air-vent valve when water discharges through the valve.

d. Pass 100 mL of sample through the filter to remove any residual liquids from the cleaning or prewetting procedures. If concentration of organic compounds in suspended-material phase is to be determined:

   i. Capture the rinse water in a dry, clean, graduated cylinder.

   ii. Measure and record the actual volume of sample passed through the filter.

e. Discard rinse water to a sink funnel or toss bottle.

6. *DH*: Tare the weight of a clean, baked, glass sample bottle. (First check to see if this is required for the analytical procedures to be used.)
   a. Set up, level, zero, and check the accuracy of the balance with a reference weight. Record accuracy in field notes.
   b. Tare the weight of a dry, clean, capped 1-L amber bottle, and record the weight. Remove the bottle cap.
7. Filter and weigh each sample. (Do not field rinse baked, glass sample bottles.)
   a. *CH*: Resume the flow of sample through the plate-filter assembly.
   b. *CH*: Place the appropriate sample bottle under the outlet of the plate-filter assembly.
   c. *CH*: Collect approximately 1 L of filtered sample for each analytical schedule, but leave headspace in each bottle. If the filter medium becomes too clogged to proceed, go to step 13 below.
   d. *DH*: Cap the bottle(s) and pass sample(s) out of chamber. Wipe the bottle dry with a lint-free laboratory tissue, such as Kimwipe™, to remove any condensation from the outside of the sample bottle.
   e. *DH*: Weigh and record the amount of sample filtered (total weight minus tare weight of bottle).
   f. Chill samples immediately and maintain at or below 4°C without freezing for shipment to the laboratory (section 5.5).

8. *CH*: Remove as much water as possible from the inside of the plate-filter assembly by using the metering pump to pump air through the sample tubing, or by pulling water out through the outlet nozzle with a peristaltic pump, or by using a syringe to apply positive air pressure to the inlet connector. This removes any residual sample and prevents spilling the water-sediment slurry when the plate-filter assembly is disassembled.
9. *CH*: If sediment collected on the filter is to be analyzed for organic compounds:
   a. Carefully disassemble the top of the plate-filter assembly.
   b. Using metal forceps, carefully fold the filter in half and then in half again (quarters).
   c. Transfer the filter to a baked, wide-mouth glass jar with a fluorocarbon-polymer-lined cap.
   d. Record on the jar label and on field forms the total volume of sample that passed through the filter.
   e. Chill and maintain the sediment sample at or below 4°C for shipment to the laboratory (section 5.5)
10. *DH/CH*: If sediment on the filter will not be analyzed, disassemble the top of the plate-filter assembly and remove the filter with forceps. Discard the filter appropriately. Rinse the plate-filter assembly components and tubing immediately after the filter has been removed.
11. *DH/CH*: **If the equipment is to be used at a subsequent site, field clean all equipment while equipment is still wet and before going to the next site.** Clean with detergent solution, rinse with DIW, and final rinse with methanol—do not use methanol on equipment used for TOC, DOC, or SOC samples (NFM 3). If the plate-filter assembly will not be reused before returning to the office, rinse all components with DIW. Put rinsed components and tubing in a resealable bag for cleaning at the office laboratory.
12. Document on field forms and in field notes the filtration procedures used.

13. **If the filter medium becomes clogged before the required volume of sample has been collected,** stop the metering pump or divert the sample flow from the submersible pump (see TECHNICAL NOTE below) and replace the filter with a new filter as indicated in steps a through f below.

> TECHNICAL NOTE: Diverting the flow of sample being pumped with a submersible pump by use of a three-way valve can result in a temporary increase in turbidity (NFM 4). Allow turbidity to clear after reestablishing flow through the sample tubing and to the plate-filter assembly.

a. Remove as much water as possible from inside the plate-filter assembly. The stainless-steel or aluminum plate-filter assembly does not have an upper support screen, so the filter cannot be backflushed. Remove the inlet tubing to the metering pump from the sample and either attach tubing from a peristaltic pump to the outlet and pull residual water out, or use a syringe to apply positive air pressure to the inlet connector.

b. Remove the clogged filter with forceps. **If sediment collected on a filter is to be analyzed for organic compounds, follow directions in step 9**.

c. Load the plate-filter assembly with a new filter and reassemble the unit as described in step 2.

d. Prepare the filter as described in steps 2f and 5a–d, allowing the first 125 mL of sample to remove any sediment particles that may have moved below the filter during the replacement procedure. Use a graduated cylinder to measure volume.

e. Record the volume of sample rinsed through the plate-filter assembly if sediment collected on the filter is to be analyzed for organic compounds. Volume accuracy should be ± 1 mL.

f. Place a tared sample bottle under the plate-filter assembly outlet, resume the flow of sample through the filter, and continue to collect the sample filtrate.

Capsule-Filter Procedure for Processing Samples for Analysis of Organonitrogen Herbicides (Optional) 5.2.2.B

The capsule-filter procedure for filtering samples for organonitrogen-herbicide analysis described below is provided if the option to process these samples onsite is selected. The steps that follow are taken from Sandstrom (1995), which includes more detailed instructions and description of the equipment, including the 25-mm-diameter disposable nylon-media filter capsule (nylon filter):

1. Before leaving for the field site, clean the nylon filter.
   a. Put on appropriate, disposable, powderless gloves (gloves).
   b. Place intake end of the metering pump tubing into the methanol.
   c. Pump about 10 mL through the nylon filter to a used-methanol disposal container.

CAUTION: Do the following if using methanol or other organic solvent:

- **Work under a fume hood or in a well-ventilated area, NOT in the field vehicle.**
- **Wear protection against skin and eye contact and do not inhale fumes.**
- **Collect methanol rinse waste into proper disposal containers and dispose of according to local regulations.**

The guidance in this section, 5.2.2.B, has been replaced, refer to new 5.2.2.B at end of chapter 5.

This section of 5.2.2.B will be replaced when the next revision of chapter 5 has been completed; see the August 15,2014 post in the comments and errata for clarification. http://water.usgs.gov/owq/FieldManual/mastererrata.html#Chapter 5

2. At the field site, cover the field bench or table with a sheet of aluminum foil or Teflon™ to prepare a clean work surface.
3. Place equipment and supplies on the clean work surface. Remove foil or other wrapping from precleaned equipment. Change gloves.
4. Remove the nylon filter from the plastic bag. Rinse the discharge end of the pump tubing with methanol. Discard used methanol to a proper waste container. Attach the metering-pump tubing to the capsule inlet; keep tubing as short as possible.
5. If filtering with a metering pump, transfer the intake end of the pump tubing to the sample. If using a submersible pump to collect the ground-water sample, redirect the sample flow to and from the nylon filter as needed, using a manifold flow-valve system.
6. Purge air from the sample tubing. Before connecting the nylon filter, allow ground-water sample to flow through the tubing at a very low rate. This will require just a few milliliters of sample if a metering pump is used. With sample flowing, connect tubing to the nylon filter. (Use a Luer™ connector of appropriate size to secure the discharge hose to the inlet connector.)
7. Collect at least 100 mL of filtrate in a 125-mL baked amber glass sample bottle. Do not completely fill the bottle. Allow 2–3 cm of headspace. The headspace leaves space for matrix spike standards to be added (if required) and prevents sample loss if the sample freezes.
8. If the nylon filter medium becomes clogged before a sufficient amount of sample has been filtered, replace it with a new nylon filter and repeat steps 6 and 7 until at least 100 mL have been collected.
9. When filtering is complete, cap the bottle firmly. Chill and maintain the sample at or below 4°C without freezing during storage and shipment to the laboratory (section 5.5).
10. Discard the nylon filter. Field clean the pump and tubing as described in NFM 3 before using the equipment at the next site.
11. Document on field forms and in field notes the filtration procedures used.

The guidance in this section, 5.2.2.B, has been replaced, refer to new 5.2.2.B at end of chapter 5.

This section of 5.2.2.B will be replaced when the next revision of chapter 5 has been completed; see the August 15,2014 post in the comments and errata for clarification.
http://water.usgs.gov/owq/FieldManual/mastererrata.html#Chapter 5

Procedures for Processing Samples for Carbon Analysis 5.2.2.C

Standard methods are described in this section for processing a sample for analysis of (1) total particulate carbon (TPC), particulate inorganic carbon (PIC), and particulate organic carbon (POC)[1]; and (2) dissolved organic carbon (DOC). The specific method to be used depends on the target analyte and the choice of filter type and filtration equipment, which are to be documented on field forms and in field notes.

- **TPC (Total Particulate Carbon), PIC (Particulate Inorganic Carbon), and POC (Particulate Organic Carbon).** Filtration of the sample requires a 25-mm glass-microfiber filter (see *UPDATE* below). Particulate organic carbon is determined by subtracting the laboratory-analyzed concentrations of particulate inorganic carbon from total particulate carbon; that is, POC = TPC - PIC.

- **DOC (Dissolved Organic Carbon).** Filtration of the sample requires either a quality-controlled disposable disc filter (i.e., Pall Aquaprep filter) or a 25-mm glass-microfiber filter (GF/F) (see *UPDATES* below).

For Aquaprep, One Stop item Q460FLD; For GF/F, Q441FLD

UPDATE: The NFM-5/99 version of this section (5.2.2.C) entitled "Gas-Pressurized Filter Procedures for Processing Samples for Analysis of Dissolved and Suspended Organic Carbon," which was based on a field method using silver filters, has been moved to Appendix A5-D. That method is no longer used in USGS studies as a standard procedure because of the decreasing availability of the silver filters (Office of Water Quality Technical Memorandum 2000.08).

UPDATE: Use of the Whatman large-capacity Supor capsule filter, beginning with lot # T873, was discontinued for filtration of samples for DOC analysis as of August 6, 2008, because of systematic failure in quality-control testing.

[1]POC, determined by a calculation, is distinguished from the suspended organic carbon (SOC) analysis, which is determined by direct analysis of organic carbon residue on a silver filter. USEPA method 440.0 is used for laboratory analysis of the TPC and PIC samples and also provides direct determination of total particulate nitrogen (TPN) concentration.

Replacement page 8/11/2008

Equipment and equipment-cleaning procedures

The equipment needed to process samples for analysis of TPC and PIC depends on whether the pressure-filtration method (table 5-6a) or the vacuum-filtration method (table 5-6b) will be used. The equipment options for processing samples for analysis of DOC are given in table 5-6c. (Refer to Appendix A5-D if the silver-filter method will be used to process samples for analysis of TOC, SOC (suspended organic carbon), or DOC.)

Equipment should be cleaned while still wet from sampling, preferably before leaving the field site. Immediately after each use, rinse the carbon-processing equipment at least three times with DIW and store it in a plastic bag until sampling is complete and there is time to clean the equipment using USGS standard procedures.

- Clean the carbon-collection and carbon-processing equipment according to the standard procedures described in NFM 3.3.4.C. **Do not use methanol or any other organic solvent to clean this equipment** (see TECHNICAL NOTE).
- If it is necessary to return to the office before cleaning the equipment, be sure to field rinse the equipment onsite immediately after use and then place it in a clean plastic bag for transport.
- After the equipment has been cleaned, double-wrap all apertures and the filter apparatus with aluminum foil and store them inside a sealable plastic bag for transport to the next site or storage in the office.

> TECHNICAL NOTE: Periodically check the NFM Comments and Errata page (http://water.usgs.gov/owq/FieldManual/mastererrata.html)under Chapters A3 and A5 for an update or any changes in equipment-cleaning procedures. If a circumstance arises in which methanol-cleaned equipment must be used to collect samples for DOC analysis, it is necessary to (1) record and report the total volume of water that has passed through the equipment before the DOC sample is collected, (2) collect a field blank sample for laboratory analysis by passing organic-grade blank water through the equipment, (3) collect a source-water blank for laboratory analysis, and (4) compare the laboratory results of carbon concentrations for the environmental and quality-control samples and document the results in field notes and in any report in which the DOC data are presented.

Table 5-6a. Equipment and supplies used to process samples for analysis of total particulate carbon and particulate inorganic carbon using the pressure-filtration method

[FEP, fluorinated ethylene-propylene; DOC, dissolved organic carbon; mm, millimeter; µm, micrometer; °C, degrees Celsius; mL, milliliter; in, inch; oz, ounce; lbs/in^2, pounds per square inch; mg/L, milligrams per liter; VOC, volatile organic compound]

Item	Description/Comments	Supplier or USGS One Stop Shopping Item Number[1]
FEP pressure-filtration apparatus (DOC-25)	Holds a 25-mm filter	Q444FLD
Ring stand and clamp	Holds the DOC-25 filtration unit	Open market
Filter, in-line vent, 50 mm	0.2-µm pore size; pre-filter to remove airborne particulates	Q445FLD
Peristaltic pump	Adjustable flow rate	Open market
C-Flex tubing	For use with pump	Open market
Precombusted (baked) glass-microfiber filters (GF/F)	25 mm, 0.7-µm pore size, laboratory-baked at 400°C (3 filters are required)	Q441FLD
Metal forceps, two pair	Standard metal forceps for handling filter media.	Open market
Glass cylinder	100-mL graduated cylinder, cleaned	Open market
Aluminum foil squares	6 in x 6 in	Q443FLD
Whirl-Pak bags	6 oz	Open market
Whirl-Pak bags	18 oz	Open market
Aluminum foil	Heavy duty	Open market
Cooler and ice	Standard; check with shipper for size and weight restrictions	Open market
Replacement filter-support screen	25 mm, either stainless steel or polysulfone	Pall Gelman Laboratory Part nos. 79791 or 87265
Pressure gage (optional)	Glycerin-filled, 0-30 lb/in^2, to be inverted into side of a plastic tee that is positioned in-line between the peristaltic pump and the DOC-25 filtration unit.	Cole Parmer catalog no. P-07370-70 or equivalent
Organic grade water (if using this method for DOC processing)	Laboratory analysis of the water must certify a concentration of organic carbon that is less than the long-term laboratory reporting limit for DOC (currently <0.16 mg/L). Check the laboratory analysis for the lot number to confirm that it can be used.	N1600 (Pesticide-grade blank water) or N1570 (VOC/Pesticide grade blank water)

[1]The equipment designated by the letters Q or N preceding a unique number is supplied exclusively for USGS studies through the USGS internal One Stop Shopping. The USGS performs quality-control checks for such equipment. Such equipment can be obtained for non-USGS studies on the open market or other source specified by the user. "Open market" designates equipment to be obtained from a retail or other vendor.

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Table 5-6b. Equipment and supplies used to process samples for analysis of total particulate carbon and particulate inorganic carbon using the vacuum-filtration method

[mL, milliliter; mm, millimeter; µm, micrometer; °C, degrees Celsius; in, inch; oz, ounce; FEP, florinated ethylene-propylene]

Item	Description/Comments	Supplier or USGS One Stop Shopping Item Number[1]
Filtration flask	Polypropylene, 500 or 1,000 mL	Open market
Filter funnel	Polysulfone, 25 mm with 200-mL reservoir[2]	Open market
Peristaltic pump or hand pump	Adjustable flow rate	Open market
C-Flex tubing	For use with pump	Open market
Baked glass-microfiber filters (GF/F)	25 mm, 0.7-µm pore size, laboratory-baked at 400°C (3 filters are required)	Q441FLD
Metal forceps, 2 pair	Standard metal forceps for handling filter media	Open market
Glass cylinder	100-mL graduated cylinder	Open market
Aluminum foil squares	6 in x 6 in	Q433FLD
Whirl-Pak bags	6 oz	Open market
Whirl-Pak bags	18 oz	Open market
Aluminum foil	Heavy duty	Open market
Cooler and ice	Standard: check with shipper for size and weight restrictions	Open market

[1]The equipment designated by the letters Q or N preceding a unique number is supplied exclusively for USGS studies through the USGS internal One Stop Shopping. The USGS performs quality-control checks for such equipment. Such equipment can be obtained for non-USGS studies on the open market or other source specified by the user. "Open market" designates equipment to be obtained from a retail or other vendor.

[2]The filter-support screen can be replaced with a stainless-steel screen like the one used in the FEP pressure-filtration apparatus. Contact Pall Gelman Laboratory, 600 Wagner Road, Ann Arbor, MI, 48103-9019; phone (734) 665-0651.

Do not use methanol or any other solvent to clean TPC or DOC equipment (NFM 3).

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Table 5-6c. Equipment and supplies used to process samples for analysis of dissolved organic carbon

[µm, micrometer; GF/F, glass microfiber filter; mm, millimeter; °C, degrees Celsius; FEP, fluorinated ethylene-propylene; oz, ounce; mL, milliliter; DOC, dissolved organic carbon; <, less than; mg/L, milligrams per liter; *N*, normal; VOC, volatile organic compound]

Item	Description and Comments	Supplier or USGS One Stop Shopping Item Number[1]
Disposable disc filter	Pall Apuaprep disc filter, in disposable polypropylene casing, 0.45-µm pore size; for sample size < 1 liter	Q460FLD
----------or----------	----------or----------	----------or----------
Precombusted (baked) glass microfiber filters (GF/F)	25-mm diameter, 0.7-µm nominal pore size, laboratory baked at 400°C FEP pressure-filtration apparatus or filtration flask with funnel and associated equipment is required, as indicated in table 5-6a and table 5-6b, respectively	Q441FLD
4-oz amber glass bottle, baked	Bottles (125 mL) supplied for DOC samples have been pre-cleaned and baked at 400°C and quality-controlled to meet a detection limit criterion for organic carbon of <0.1 mg/L	Q28FLD
Sulfuric acid (H_2SO_4) preservative	4.5*N*-H_2SO_4, supplied in 1-mL vials	Q438FLD
Organic-grade water	Laboratory analysis of the water must certify a concentration of organic carbon that is less than the long-term laboratory reporting limit for DOC (currently <0.16 mg/L). Check the laboratory analysis for the lot number to confirm that it can be used.	N1600 (Pesticide-grade blank water) or N1570 (VOC/Pesticide grade blank water)
Aluminum foil	Heavy duty	Open market
Cooler and ice	Standard; check with shipper for size and weight restrictions	Open market
Foam bottle sleeve	Individual bottles are slipped into foam sleeves to protect from breakage.	Q137FLD

[1]The equipment designated by the letters Q or N preceding a unique number is supplied exclusively for USGS studies through the USGS internal One Stop Shopping. The USGS performs quality-control checks for such equipment. Such equipment can be obtained for non-USGS studies on the open market or other source specified by the user. "Open market" designates equipment to be obtained from a retail or other vendor.

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TPC, PIC, and POC sample processing

The sample-processing options described below involve use of either the pressure-filtration or vacuum-filtration method. The equipment and supplies needed are listed in tables 5-6a and 5-6b, respectively. Particulate analytes (TPC, PIC, POC, SOC) are reported in units of mass per volume (milligrams per liter), and therefore **the volume of sample passed through each filter must be measured accurately and recorded on the field form and the Analytical Services Request (ASR) form**.

- The amount of water to be filtered to obtain a sufficient quantity of material for the analysis depends on the suspended-sediment concentration and/or on the concentration of humic and other substances (such as organic and inorganic colloids).
- A graph of the historical stream stage plotted against suspended-materials concentration can aid in estimating concentrations of suspended materials. Suspended-material concentrations can be used to help select the volume of sample to be filtered for a POC determination (table 5-6d).
- Record the filtrate volume passed through each filter used for particulate analysis. **This is critical for calculation of POC concentrations.**

Table 5-6d. Guidelines for selecting the volume needed for filtration of samples for analysis of suspended and particulate organic carbon
[Guidelines are based on sand-sized materials; other physical property factors and chemical composition were not taken into account; mg/L, milligrams per liter; mL, milliliters; >, greater than]

Approximate concentration of suspended materials (mg/L)	Volume of sample to be filtered (mL)
1 - 30	250
30 - 300	100
300 - 1,000	30
> 1,000	10

For TPC and PIC samples, be sure to record the total volume of water that passed through each GF/F filter.

To process samples for analysis of TPC and PIC:

1. **Sampling location and collection:** Study objectives and site characteristics determine where the sample will be collected. Follow guidelines for (1) preventing sample contamination as described in NFM 4.0, (2) using the appropriate isokinetic or nonisokinetic method as described in NFM 4.1, and (3) preparing composites and subsamples or discrete samples as described in NFM 5.0 through 5.1.1.[2] Avoid the use of methanol-rinsed equipment.

2. Select one of the following three options. (Note that the actual volume of sample needed is determined by the concentration of particulates for the specific site and not by the bottle volume.)

   - **Collect a discrete sample with a weighted bottle sampler at centroid of flow** (see NFM 4, section 4.1.1.A, VCF method)—Load the sampler with baked 125-mL DOC bottles or a 1-L baked pesticide bottle, depending on the type of sampler being used. Cap all bottles securely after they are filled with sample.

   - **Collect, composite, and process the sample through a cone splitter**—Using procedures described in 5.1.1.B, collect the TPC/PIC subsample from the methanol-free cone splitter into a baked, 1-L pesticide bottle or into three to four baked 125-mL DOC bottles. Cap all bottles securely.

   - **Collect, composite, and process the sample through a churn splitter**—Using procedures described in 5.1.1.A, collect the TPC/PIC subsample from the churn splitter into a baked, 1-L pesticide bottle or into three to four baked 125-mL DOC bottles. Cap all bottles securely.

     TECHNICAL NOTE: An experiment to test the effect of sand in the polyethylene churn splitter on particulate carbon concentrations showed that, under most sampling conditions, the abrasion of material from the churn by sand particles will result in negligible bias in the analytical results. Caution is recommended in situations where very large concentrations of sand particles coincide with carbon concentrations that are close to the analytical minimum reporting limit (MRL).

[2]The guidelines described were designed for stream sampling. These procedures can be adapted for the collection of TPC, PIC, and TPN in ground-water samples, if necessary.

ALERT! Do not field rinse the baked DOC or pesticide bottles.

3. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Put on disposable, powderless gloves. Assemble necessary equipment and supplies on the clean work surface.

   a. Fold into thirds the aluminum foil square(s) into which the filters will be placed.

   b. To remove airborne particulates, attach an in-line, 0.2-µm pore-size filter to the inlet side of a dry pump hose between the filtration apparatus and the peristaltic or hand pump.

   c. Attach pump tubing to pump.

   d. Remove the aluminum foil wrapping from the equipment.

   e. Change gloves.

4. Prepare the filtration apparatus.

   • **Pressure-filtration method:**

      a. Open the bottom of the DOC-25 filtration unit.

      b. Using metal forceps, place a 25-mm, 0.7-µm pore size, GF/F onto the support screen in the base of the DOC-25 apparatus.

      c. Push the bottom white ring that holds the filter base up against the filter unit and screw it onto the base of the filtration-apparatus barrel by screwing the blue top ring down onto the bottom white ring.

         – Finger-tighten only. Turning the bottom white ring will cause the outer edge of the filter to be cut off, making removal of the filter difficult.
         – Take care not to wrinkle or tear the GF/F.

      d. Place the DOC-25 apparatus into the ring-stand clamp. Place a bottle or beaker under the DOC-25 filtration unit.

      e. Shake the sample vigorously to suspend all particulate matter and immediately pour an aliquot of the sample into the barrel of the DOC-25 apparatus. While pouring, ensure that the particulates remain suspended.

      f. Screw the top part of the DOC-25 apparatus onto the barrel and attach the peristaltic pump tubing.

- **Vacuum-filtration method:**

  a. Place the filter funnel on the filter flask.

  b. Lift the top part of the filter funnel.

  c. Using metal forceps, place the GF/F onto the base of the filter funnel. **Make sure the filter is not wrinkled or torn.**

  d. Place the top part of the filter funnel back on the base.

  e. Shake the sample vigorously to suspend all particulate matter and immediately pour an aliquot of the sample into the filter funnel. While pouring, swirl sample to ensure that the particulates remain suspended (top of filter flask can be covered with aluminum foil while swirling sample).

  f. Attach the pump tubing from the peristaltic pump or hand pump to the vacuum flask.

5. Apply pressure (pressure filtration) or suction (vacuum filtration) to start the flow of sample water through the filtration apparatus.

   - If using a peristaltic pump to pressurize the DOC-25, install a pressure gage in the line.

     a. Do not exceed about 15 lbs. of pressure.

     b. During pumping, a drop in pressure will signal when the last of the sample water has passed through the filter.

6. After an aliquot of sample has been filtered, tap the bottom of the filter apparatus and increase the pressure slightly to dislodge the remaining drops of sample water. When no more filtrate comes out:

   a. Depressurize the filtration apparatus carefully.

      – **Pressure-filtration method**: Remove the tubing to release the pressure and then remove the top of the DOC-25 apparatus. Check that there is no water on the filter and that the filter is covered with particulates. The particulate cake should not be extremely thick.

      – **Vacuum-filtration method**: Remove the foil cover and look into the top of the filter funnel. Check that there is water on the filter and that the filter is covered with particulates.

   b. If the filter is dry but not covered with particulates, add another aliquot of sample by repeating steps 4e-f, 5, and 6a until the filter is loaded to capacity. **It is important that all the water in the barrel be passed through the GF/F, leaving the filter "dry."**

   c. After the filter is dry and covered with particulates, go to step 7.

7. Pour the filtrate into a graduated cylinder and measure and record the volume on the field form and on the "Comments to NWQL" line of the ASR form.

8. Using organic-grade water, rinse any remaining particles from the sides of the DOC-25 barrel or the sides of the filtration funnel. **Do not include the rinse water in the measured volume.**

9. Discard filtrate. **Do not send this filtrate to the laboratory for analysis of DOC.**

10. After all the organic-grade water filtrate has passed through the DOC-25 filtration unit:

    a. Remove the DOC-25 apparatus from the ring stand.

    b. Continue pumping, rotating the DOC-25 apparatus at a slight angle while tapping the side of the filtration unit to evacuate any remaining water droplets that are clinging to the sides of the filtration unit. This procedure moves droplets toward the center of the filter surface for final passage through the filter.

    c. The procedure is complete when filtrate droplets are entirely evacuated and have passed through the filter-holder funnel.

11. After completing the rinse, depressurize the filtration apparatus. Change gloves.

12. Lift the top off the filter funnel to check that the filter is dry before proceeding to carefully remove the bottom of the DOC-25 apparatus.

    a. Open the previously folded aluminum foil square and place it on the clean work surface.

    b. Gently remove the filter from the filter holder with metal forceps. Do not touch the filter with your fingers. Using two metal forceps:

        i. Place the filter so that it is centered on one of the creases in the aluminum foil square; start the fold with the forceps, then press the foil down on top of the filter to complete the fold.

        ii. Fold it in half with suspended material on the inside. Do not lose any suspended material.

Wear safety glasses when pressurizing or depressurizing a filter apparatus.

13. Repeat steps 4-12 two more times until a total of three filters (two for TPC and one for PIC) have been processed.

    - **If the same volume of sample water was filtered through all three filters,** place them all, side by side, into one aluminum-foil envelope.
    - **If different volumes have been filtered,** use either three separate, properly labeled aluminum foil envelopes or use a single packet and write the volume for each filter on the outside of the foil in which each of the filters is located.

14. Close the other flap of the aluminum foil, turning the ends up carefully.

    i. Label the aluminum foil envelope(s) with site identification, date and time, total filtered volume of sample, laboratory sample-designation code, and the laboratory schedule requested.

    ii. Do not use tape and, if a preprinted label is used, do not let it wrap around the ends of the envelope. (The envelope will be opened and used at the laboratory when drying the filters.)

15. Place labeled aluminum foil envelope(s) into small (6 oz) Whirl-Pak bag(s) and seal the bag(s).

16. Place the 6-oz Whirl-Pak bag(s) inside a large (18 oz) Whirl-Pak bag and seal the large bag.

17. Place the 18-oz Whirl-Pak package into an ice-filled cooler and maintain the samples at or below 4°C during storage and shipment to the laboratory.

For TPC and PIC analyses, record the TOTAL volume of sample that passed through each filter.

DOC sample processing

The sample-processing options described below involve filtering the sample either through a GF/F and pressure-filtration apparatus (the pressure-filtration method), or through a disposable disc filter (the disc-filter method). The pressure-filtration and disc-filter methods are described below and the equipment needed for each method is listed in tables 5-6a and 5-6c, respectively. The silver-filter method and equipment are described in Appendix A5-D.

- Use organic-grade water when collecting an equipment blank or field blank for quality control. Organic-grade water is deionized water that has been certified by laboratory analysis of the lot to have an organic-carbon concentration that is less than the laboratory reporting limit (currently at 0.16 mg/L for DOC).
- Each equipment or field blank designated for carbon analysis should be accompanied by a source blank collected from the same lot of organic-grade water as is used for the equipment and field blanks.

  The small-capacity disc filter that is in current use and quality controlled at the NWQL (One Stop item Q460FLD) has a 19.6 cm_2 effective filter area and should be rinsed with ~~100~~ 50 mL of VPBW followed by 10 mL of sample water before use. Because of its small capacity, clogging of pores in the filter media may occur rapidly and the disc filter may need to be replaced repeatedly.

- USGS designations and preservation treatment for various filtered samples are listed below. The general order of preservation is to acidify all samples requiring HCl treatment first, followed by those for H_2SO_4 treatment if nutrient samples are to be acidified, and then those for HNO_3 treatment. Wholewater samples are preserved along with their filtered counterparts. The chamber cover is changed with each change in the acid treatment.

  - FAM: filtered, acidified with HCl, for mercury analysis.
  - FCC: filtered and chilled to ≤ 4 ˚C for nitrogen and phosphorus nutrient analysis.
  - FCA: filtered, acidified with H_2SO_4, and chilled to ≤ 4 ˚C for nitrogen and phosphorus nutrient analysis.
  - DOC: filtered, acidified with H_2SO_4, for dissolved organic carbon analysis.
  - FA: filtered, acidified with HNO_3, for trace-element and major-cation analysis.
  - FAR: filtered, acidified with HNO_3, for radiochemical analysis.

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Disc-filter method:

1. Collect samples within a protective chamber that has been set up with a clean disc filter and laboratory-cleaned DOC sample bottle(s).

   a. **Surface Water:** Follow guidelines for (1) preventing sample contamination as described in NFM 4.0, (2) using the appropriate isokinetic or nonisokinetic method as described in NFM 4.1, (3) preparing composites and (or) subsamples or discrete samples as described in NFM 5.0 through 5.1.1, and (4) equipment selection and quality control as described in the TECHNICAL NOTE below.

   b. **Ground Water:** Follow standard guidelines for (1) well purging (NFM 4.2), (2) sampling (NFM 4.0, 4.2, 5.0, and 5.1.2), and (3) equipment selection and quality control as described in the TECHNICAL NOTE below. Use a clean bailer that has not contacted methanol if other sampling equipment has been methanol-rinsed. Sample collection and filtration can be conducted in the same protective chamber.

   TECHNICAL NOTE: Process the DOC sample after other filtered samples have been processed. To prevent methanol contamination of the sample, do not use methanol-rinsed collection and processing equipment, and use a fresh disc filter. Collection and analysis of field-blank and source-blank samples is recommended. If methanol-rinsed equipment must be used, collection of these blanks to correlate with each DOC sample is required, regardless of the volume of water passed through the system before DOC sample collection. Taking these quality-control measures does not remove the possibility of methanol contamination of the sample, however.

2. Change gloves. Place a 125-mL baked glass amber bottle under the disc filter outlet.

   - Do not field rinse the DOC bottle.
   - Do not splash sample water.
   - Pass ~~100~~ 50 mL of **organic-grade water** (VPBW or certified for organic-carbon concentration of less than the laboratory reporting limit) through the disc filter. If collecting a quality-control sample, go to step 3.
   - Pass at least 10 mL of **sample water** through the disc filter before collecting the DOC sample. If the filter shows signs of clogging, replace with a new disc unit.

3. Fill the bottle to its shoulder.

4. Cap the bottle and transfer it to the preservation chamber.

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5. Change gloves. Open the DOC bottle in the preservation chamber. Add the contents of a 1-mL H_2SO_4 vial to the DOC sample.
6. Cap the DOC bottle securely. Shake the sample bottle vigorously to mix the sample and H_2SO_4.
7. Remove the DOC bottle from the preservation chamber.
8. Check that the bottle is labeled correctly and completely. Place the bottle in a foam sleeve and then into an ice-filled shipping container.
9. Maintain the sample at or below 4°C without freezing (NFM 5.5).

Pressure-filtration method:

1. Collect sample(s).
   a. **Surface Water:** Follow guidelines for (1) preventing sample contamination as described in NFM 4.0, (2) using the appropriate isokinetic or nonisokinetic method as described in NFM 4.1, (3) preparing composites and (or) subsamples or discrete samples as described in NFM 5.0 through 5.1.1, and (4) equipment selection and quality control as described in the TECHNICAL NOTE below.
   b. **Ground Water:** Follow standard guidelines for (1) well purging (NFM 4.2), (2) sampling (NFM 4.0, 5.0, and 5.1.2), and (3) equipment selection and quality control as described in the TECHNICAL NOTE below.

TECHNICAL NOTE: To prevent methanol contamination of the sample, avoid using methanol-rinsed collection and processing equipment. If methanol residue is a concern, process the DOC sample either before introduction of any methanol-rinsed equipment or well after the work area has been cleared of methanol-rinsed equipment and methanol fumes. Collection and analysis of field-blank and source-blank samples is recommended. If methanol-rinsed equipment must be used, collection of these blanks to correlate with each DOC sample is required, recording the volume of water passed through the system before DOC sample collection. Taking these quality-control measures does not remove the possibility of methanol contamination of the sample, however.

2. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Assemble the necessary equipment on the clean work surface, wearing disposable powderless gloves.

   a. When using the DOC-25 filtration apparatus, remove airborne particulates as follows: attach an in-line, 0.2-µm pore-size filter (table 5-6a) to the inlet side of a dry pump hose or to the outlet between the peristaltic pump and the DOC-25 unit. If attaching the DOC-25 on the inlet side, be sure to dedicate a piece of tubing for the sole purpose of channeling air flow.

   b. Remove the aluminum foil wrapping from the precleaned equipment.

   c. Change gloves.

3. Prepare the filtration apparatus:

   a. Remove the bottom barrel of the filtration apparatus.

   b. With metal forceps, place a clean GF/F filter onto the support screen in the base of the filtration apparatus. **Make sure that the filter medium is not wrinkled or torn.**

   c. Push the bottom white ring that holds the filter base up against the filter unit and screw it onto the base of the filtration-apparatus barrel by screwing the blue top ring down onto the bottom white ring.

      – Finger-tighten only. Turning the bottom white ring will cause the outer edge of the filter to be cut off, making removal of the filter difficult.
      – Take care not to wrinkle or tear the GF/F.

   d. Open the top of the filtration-apparatus barrel and fill with approximately 100 mL of wholewater sample.

      – **For water with high concentrations of suspended materials** (usually in surface water), collect the sample into a clean baked glass bottle, cap it securely, place it on ice, and allow the suspended materials to settle; then, pour 100 mL of the clear supernatant into the filter barrel.
      – **For surface water,** the 100-mL wholewater sample can be either a subsample collected from the churn or cone splitter or the supernatant from the bottle(s) used in the weighted-bottle sampler.
      – **For ground water,** the 100-mL wholewater sample is collected directly from the pump discharge unless turbidity is high. For turbid samples, follow the procedure described above for water with high concentrations of suspended materials.
      – **For a quality-control sample,** use organic-grade blank water.

e. Screw the top part of the filter apparatus onto the barrel and attach the pump tubing.

f. Apply pressure, regulated to less than 15 lb/in^2, to start the flow of sample water through the filter apparatus.

g. Place a 125-mL clean, baked glass bottle under the discharge tube of the filtration apparatus. **Do not field rinse the DOC bottle.**

h. Fill the DOC bottle to the shoulder with sample filtrate.

- If the filter clogs before 100 mL of sample for DOC analysis can be filtered, depressurize the filtration unit, empty the remaining volume of wholewater sample from the barrel, and remove the clogged GF/F filter.
- Using clean metal forceps, replace the old filter with a new GF/F filter, following the directions from steps 3b-g above for a pressure-filtered DOC sample.

4. After the DOC sample bottle has been filled to the shoulder, cap the bottle and transfer it to the preservation chamber.

5. Depressurize and dismantle the filtration apparatus, discarding the used GF/F filter(s). Clean the apparatus immediately (while still wet), following the USGS procedures prescribed in NFM 3.3.4.C. If the apparatus cannot be field-cleaned immediately, it must be cleaned the same day it is used and before being reused—rinse it copiously with DIW and place it into a plastic bag so that it will not dry before being cleaned.

6. Change gloves before working in the preservation chamber.

7. In the preservation chamber, open the DOC bottle. Add the contents of a 1-mL vial containing 4.5*N* H_2SO_4 preservative.

8. Cap the DOC bottle securely and shake vigorously to mix the sample. Remove the DOC sample bottle from the preservation chamber.

9. Check that the bottle is labeled correctly and completely. Place the bottle into a foam sleeve and into an ice-filled shipping container (see NFM 5.5 for correct shipping procedures).

10. Maintain the sample at or below 4°C without freezing (NFM 5.5).

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

11. To collect a QC sample:

    a. Use the same carbon-processing equipment after it has been cleaned (see step 5, above).

    b. Label bottles.

    c. Change gloves.

    d. Working in a clean processing chamber, process a sample of organic-grade water through the cleaned carbon-sampling and carbon-processing equipment, following the steps prescribed in steps 2-4 above. Cap securely and pass the bottle to the preservation chamber.

    e. Follow steps 6-10 above for sample preservation, handling, and shipping.

    f. Depressurize and dismantle the filtration apparatus, discarding the used filter(s). Allow the apparatus components to air dry in a clean chamber. Cover the apertures of the dry apparatus with aluminum foil and place in a clean, sealable plastic bag for storage.

Never increase the pressure in a filter apparatus to greater than 15 lb/in^2 in order to increase the rate of filtration.

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5.3 SOLID-PHASE EXTRACTION OF PESTICIDES

By **M.W. Sandstrom**

Samples collected for analysis of dissolved pesticides can be processed at the laboratory or onsite through a column containing pesticide-specific sorbents. Onsite solid-phase extraction (SPE) is useful, especially at remote sites, because pesticides isolated on the sorbent are less susceptible to degradation than when in water. Also, the SPE cartridges are less expensive to ship than water samples. However, onsite SPE is not required, and in some situations, laboratory SPE might be preferred.

All SPE methods require that the water sample be filtered (section 5.2.2.A) as soon as possible after collection. General equipment and supply needs for SPE for a broad-spectrum analysis of pesticides are listed in table 5-7 and general instructions are given in sections 5.3.1 and 5.3.2. More detailed information on SPE methods and procedures can be found in Sandstrom and others (1992), Sandstrom (1995), Zaugg and others (1995), Lindley and others (1996), and Werner and others (1996).

- Filter the environmental sample (section 5.2.2.A): this is necessary to prevent blockage of the SPE column by particulate material.
- Process the pesticide sample through an SPE column within 4 days of collection.
- Determine the reagents needed for the SPE method to be used (for example, conditioning solution, surrogate solution, and field-matrix spike solution).

Table 5-7. Checklist of general equipment and supplies required for broad-spectrum pesticide analysis by onsite solid-phase extraction

[SPE, solid-phase extraction; mm, millimeter; µL, microliter; µm, micrometer; mL, milliliter; NWQL, National Water Quality Laboratory]

✓	General equipment and supplies[1]	Description	Number required
	Aluminum foil	Heavy duty	1 box
	Blank water[2]	Pesticide grade (One-Stop Shopping)	4 L
	Filter media	Glass microfiber, 147-mm diameter, 0.7-µm pore diameter, precleaned[3]	1 per sample
	Detergent, nonphosphate laboratory	0.2-percent solution	4 L
	Glass bores	Disposable, for 100-µL micropipet	ample
	Gloves, disposable	Powderless, latex or nitrile, assorted sizes	supply ample
	Graduated cylinder or beaker	50 mL, glass	supply 2
	Luer™ connector, Tefzel™ male	P-625	1 or more
	Metering pump, valveless, piston-type	FMI Model RHB OCKC	1
	Methanol	Pesticide grade (One-Stop Shopping)	4 L
	Micropipet	Fixed volume (100 µL)	1 or more
	Nut and union, Tefzel™	P-623	1 or more
	Plastic beaker	1 L, for collecting extracted water	1 or more
	Plate-filter assembly	147-mm diameter, aluminum or stainless steel	1
	Portable balance	(Check method for weight requirements.)	1
	Sample bottles and vials (40 mL)[2]	Amber glass, precleaned	1 per sample
	SPE column adapter	(Check method requirements)	1 or more
	SPE columns, precleaned[2]	C-18: Analyticum™ C-18, 500 mg; Carbopak-B™, 500 mg; Other: as required	1 or more of each, as required
	SPE solutions[2]	(Check method requirements for conditioning, surrogate, and spike solutions)	as required by method
	Stopwatch	Standard	1
	Wash bottle, fluorocarbon polymer	250 mL, for methanol	1
	Wash bottle, fluorocarbon polymer	250 mL, for pesticide-grade water	1

[1]Filtration equipment and supplies are described in section 5.2.2.A, table 5-5, and figure 5-1.

[2]Supplies are ordered by USGS personnel from USGS One-Stop Shopping.

Replacement page 11/24/2004

SOLID-PHASE EXTRACTION BY C-18 COLUMN 5.3.1

The C-18 SPE column is used for samples that will be analyzed by capillary column gas chromatography/mass spectrophotometry with selected ion monitoring using NWQL schedule 2010 for a broad spectrum of pesticides.[8] Detailed descriptions of the method and laboratory and field extraction procedures are found in Zaugg and others (1995). For C-18 SPE processing, obtain a precleaned Analytichem™ SPE column (500 mg) and the other supplies and equipment described in the spike kit available from the NWQL (table 5-7).

Quality-control samples are required as an integral part of the sampling program.

- Process an initial field blank and then after about every 10 to 20 samples.
  - Use pesticide-grade blank water (PBW, obtained from the laboratory).
  - Process the blank in the same manner as you process the environmental water sample.
- Process a field matrix spike about every 20 samples. When processing a field matrix spike:
  - Collect duplicate samples.
  - Use a 100-µL micropipet to add the spike solution (mixture) to one of the duplicate samples. The concentration of spike solution can vary, depending on availability and the needs of the study (1 ng/µL concentration is commonly used at this time). Follow the instructions provided with the spike kit.
  - Add the surrogate to every spiked sample and an associated unspiked sample.
  - Record lot number and concentration of spike mixture on the NWQL Schedule 2010 Reporting Form (worksheet) (fig. 5-2).

[8]C-18 solid-phase extraction method is used for isolation and concentration of 41 pesticides and pesticide metabolites with concentrations of 4 mg/L or less in natural water samples (atrazine, alachlor, cyanazine, and metolachlor have upper concentration limits of 20 mg/L) (Zaugg and others, 1995).

Schedule 2010 Field Extraction Checklist and Reporting Form
U.S. Geological Survey/National Water Quality Laboratory
Solid-Phase Extraction and GC/MS Analysis Filtered Water

Station ID or Unique Number:_____ Station Name_____
Date: _____ Time:_____ Collector: _____
Telephone Number of Collector: _____
Comments: _____

NWQL INFORMATION

❑ SPE Column Brand or Type: _____
Lot #: _____
Dry weight (wt.): _____ grams (g)

ON-SITE INFORMATION

❑ Filter Sample (0.7-µm glass fiber filter)
Prior to filtration record bottle tare wt.:_____g
❑ SPE column Conditioning
Methanol (2 mL):_____milliliters (mL)
Pesticide-grade water (2 mL):_____mL

(DO NOT LET COLUMN GO DRY ONCE CONDITIONING STARTED)

❑ Sample Sample + bottle wt: _____ g
– Bottle tare wt: _____ g
= Sample wt:_____ g
Add methanol conditioner (1% of sample wt.): _____ mL
Sample + bottle + methanol: _____ g
❑ Surrogate Solution ID:_____
Volume added (100 µL): _____ µL
❑ QA Samples – Spike Mixture
Solution ID:_____
Volume added (100 µL): _____ µL
❑ Sample through column _____g
Sample + plastic beaker_____ g
Plastic beaker_____ g
❑ Flow Rate (= Sample wt. extracted/Time) _____ g
Start time _____ hr:min
Finish time_____ hr:min
❑ Remove excess water. Write station ID,date,time, on column. Store in 40-mL vial @ 4°C.

NWQL INFORMATION

Lab ID:_____ Set#:_____ Date Received_____
❑ Dry Column with N_2 or CO_2: Date:
Pressure: _____ lb/in^2
Time: _____ min
Dry SPE column wt.:_____ g
❑ SPE Elution_____ Date: _____
Add 1.8 mL elution solvent _____ mL
❑ Internal Standard (PAH-dn mixture in toluene keeper)
Solution ID:_____
Volume added (100mL): _____ mL
❑ Evaporate solvent - nitrogen
Pressure: _____ lb/in^2
Time: _____ min

Analysis: Instrument ID:_____ Date:_____
Comments:

Figure 5-2. Worksheet for C-18 solid-phase extraction of pesticides.

Prepare to process samples onsite using the C-18 SPE column:

1. Cover a bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves.
2. Collect and split samples using the appropriate procedures (NFM 4; NFM 5.1; Sandstrom and others, 1995). Filter the samples as instructed in section 5.2.2. Wear gloves (usually latex or nitrile) during sample collection and processing.
3. Set up the necessary equipment and supplies and assemble them on the clean work surface. Remove the aluminum foil wrapping from the precleaned equipment.
4. Record the sampling site information, the lot number and dry weight of the C-18 SPE column, and the surrogate solution identification number on the Schedule 2010 worksheet (fig. 5-2).
5. Change gloves.
6. Tare the weight of a clean amber glass 1-L sample bottle and a 1-L plastic beaker to the nearest gram using an analytical balance and record the weights on the Schedule 2010 worksheet.

Extract the sample:

Use the appropriate surrogate solution mixture supplied by the NWQL for the C-18 SPE method with each environmental sample.

SAMPLE EXTRACTION SHOULD BE COMPLETED ONSITE, IF POSSIBLE. If onsite extraction is not possible, extract the sample within 4 calendar days of collecting the sample.

1. Condition the SPE column:
   a. Pipet 2 mL of pesticide-grade methanol into the C-18 SPE column and allow it to flow through the column by gravity. Collect the methanol rinse in a proper container for disposal.
   b. Remove any excess methanol by rinsing approximately 2 mL of PBW, by gravity, through the column. The rinse water/ methanol mixture must be disposed of according to local, State, or Federal regulations.

c. **Do not allow the SPE column to go dry once the conditioning has started.**

- If the column goes dry, repeat the conditioning process.
- To keep the column from drying out once the conditioning has started, maintain water in the C-18 SPE column by replacing water that drained through the column. Alternatively, attach an on/off valve-to-column outlet to prevent complete draining before the sample is extracted.

2. Following the filtration instructions for general organic compounds (5.2.2.A or Sandstrom, 1995), pass about 1 L of sample through the a glass microfiber filter into the tared bottle, leaving about 2 cm of headspace.
3. Weigh the filled bottle and record the weight on the worksheet (fig. 5-2).
4. Add about 10 mL of methanol to the filtered sample using the bottle-top dispenser or a volumetric pipet. Weigh and record the sample-plus-methanol weight on the worksheet.
5. Add the surrogate solution contained in the 2-mL amber screw-cap vial to the filtered sample as follows (refer to Spike Kit Instruction Manual for detailed information and instructions on use of a micropipet):
   a. Withdraw the surrogate solution from the 2-mL amber screw-cap vial using a clean 100-µL micropipet and a clean glass bore.
   b. Insert the tip of the glass bore into the sample bottle below the surface of the sample, and depress the plunger to deliver the surrogate to the sample. (Tip the bottle on its side, if necessary, to reach below the surface of the sample with the glass bore.)
   c. Keeping the plunger depressed, swirl pipetor in water several times and then withdraw the micropipet from the bottle. Release the plunger, then remove the used glass bore from the micropipet and discard properly.
   d. Rinse the fluorocarbon polymer tip of the micropipet with methanol.
   e. Add the field-matrix spike as dictated by the study's quality-assurance plan, as required.
   f. Cap and swirl the sample to mix the sample + surrogate. (For spiked samples, mix sample + surrogate + spike solution.)
   g. If a duplicate will be submitted for analysis, repeat steps 5a–f on the duplicate sample.

6. Extract the sample through the SPE column using a metering pump fitted with 3.18 mm (1/8 in.) fluorocarbon polymer tubing with appropriate connectors (Sandstrom, 1995; NFM 2).
   a. Insert clean tubing from the inlet side of the pump into the sample bottle.
   b. Turn on the pump, flush air from the tubing (be careful to minimize any sample discharge from the end of the tubing), and then attach the outlet side of the tubing to the small end of the SPE column.
   c. Invert the SPE column to drain any remaining conditioning water left in the SPE column reservoir.
   d. Begin extraction by pumping the sample through the column at a rate of 20 to 25 mL/min and collect the extracted water into the tared 1-L plastic beaker.
7. After the sample has been pumped through the SPE column, turn the pump off and disconnect the column.
8. Remove excess sample from the SPE column using a syringe with 10 to 20 mL of air to push excess sample into a plastic beaker.
9. Weigh the beaker containing the volume of sample extracted through the SPE column. Subtract the tare weight of the beaker from the weight of the beaker plus the extracted sample and record this weight on the worksheet.
10. Write the sample identification number and the sampling date and time on the side of the SPE column. Place the SPE column into a 40-mL glass or plastic shipping ampoule and wrap it in aluminum foil.
11. Finish filling out the worksheet (fig. 5-2). Wrap the completed worksheet around the shipping ampoule and secure it with a rubber band or tape. Place in a sealable plastic bag.
12. Chill the SPE column immediately and maintain between 4°C and 25°C during storage and shipping.
13. Keep a copy of the worksheet for the field folder.

14. Field clean all equipment, including the pump and tubing, immediately after use and before going to the next site (NFM 3).
    a. Rinse thoroughly with about 50 mL of a 0.2-percent solution of a phosphate-free laboratory detergent, followed by about 50 mL of tap water (or DIW) to remove the detergent.
    b. Final rinse with about 30 to 50 mL of methanol. Collect used methanol into an appropriate container for disposal.
15. After cleaning, wrap all the equipment apertures with aluminum foil.

Ship the SPE column to the laboratory immediately. Elution from the SPE column must be completed within 7 days of extraction.

5.3.2 INSTRUCTIONS FOR FIELD USE OF SPIKE SOLUTIONS FOR ORGANIC-ANALYTE SAMPLES

-This section replaces Solid-Phase Extraction by Carbopak-B™ Column (no longer in use by the USGS NWQL).

.To view the Instructions for Field Use of Spike Solutions for Organic-Analyte .Samples, see Section 5.3.2 in the Chapter 5 html page.

. (Page revised 8/10/2009.)

SAMPLE PRESERVATION 5.4

By **D.B. Radtke**

Sample preservation is the measure or measures taken to prevent reduction or loss of target analytes. Analyte loss can occur between sample collection and laboratory analysis because of physical, chemical, and biological processes that result in chemical precipitation, adsorption, oxidation, reduction, ion exchange, degassing, or degradation. Preservation stabilizes analyte concentrations for a limited period of time. Some samples have a very short holding time. **Verify that time-dependent samples were received in proper condition, at the correct temperature, and that holding times were not exceeded by contacting the laboratory.**

Some samples must be preserved by filtration (section 5.3) and (or) chilling and (or) chemical treatment (Appendixes A5-A through A5-C). The preservation required for a given sample is described by the analyzing laboratory; for the NWQL, consult the laboratory for sample-preservation instructions.

- Before going to the field site and again at the field site:
  - Check the sample-designation code required for each sample.
  - Check sample requirements for chilling and chemical treatment.
  - Check with the laboratory and make note of holding time restrictions.

CHILLING 5.4.1

Immediately following sample collection and processing, samples that require chilling must be packed in ice or placed in a refrigerator and maintained at 4°C or less, without freezing, until analyzed.

- Check that there is sufficient headspace in the sample bottle to allow for sample expansion.
- Put foam sleeves around samples in glass bottles before packing them in ice.

- **Include a temperature check sample in the shipping container.**
  - Fill a polyethylene bottle with tap water, cap it securely, and label it "Temperature Check Sample," along with the site identification and the date(s) and time(s) of sampling and shipping.
  - Prepare a self-addressed, stamped postcard that is labeled "Temperature Check Sample report." The postcard should include the site information, date(s) and time(s) of sampling and shipping, and a space for the laboratory to record the arrival temperature of the check sample.
  - Put the postcard into the sealable plastic bag with the ASR form. The laboratory will record the temperature of the check sample upon arrival and will complete the card and return it to the sender.
  - Use this information to document that samples were maintained at 4°C or less.

Pack a temperature check sample with other chilled samples.

Chilled Samples

[This list of samples that require chilling is not comprehensive—check with the analyzing laboratory. These samples must be refrigerated or placed on ice immediately and maintained at or below 4 degrees Celsius without freezing.]

Chemical classification	USGS sample-designation codes[1]
Organic compounds	VOC, GCC, TOC, DOC, SOC, RCB, LC0052, SH 2010, SH 2051, SH 2001, SH 2050
Nutrients	WCA, FCA, FCC
Chemical Oxygen Demand (COD)	LC 2144
Cyanide	LC 0880, LC 0023
$^{15}N/^{14}N$	RUS; LC 1717, LC 1718
^{14}C	RUR/RUS; LC 1199

[1]These sample-designation codes are unique to the USGS and are subject to change.

CHEMICAL TREATMENT 5.4.2

Chemicals used for sample preservation depend on the target analyte (Appendixes A5-A, A5-B, and A5-C). The most frequently used chemical preservatives by the USGS are provided in individual ampoules and contain one of the following: ultrapure nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), or phosphoric acid/copper sulfate ($H_3PO_4/CuSO_4$). The National Water Quality Laboratory can provide a complete list of sample treatments, along with sample designations and container requirements. The preservatives are procured from One-Stop and come with a quality-control certificate of analysis for selected constituents. Keep the certificate of analysis in the study data file to help with future interpretation of quality-control and environmental data.

Take steps to minimize sample contamination and maximize safety during the preservation process (Horowitz and others, 1994; Shelton, 1994; Koterba and others, 1995; Timme, 1995). Note that a chemical preservative for one sample may be a source of contamination for another. To help reduce contamination during the preservation process and ensure proper handling of chemicals:

- Work inside a preservation chamber (only the Clean Hands person works inside the chamber). **Change gloves and the cover of the portable preservation chamber each time a different type of chemical treatment is used**. Clean Hands/Dirty Hands techniques must be used for parts-per-billion levels of trace elements and are recommended for use in general and as appropriate for the study.
- Use preservatives packaged in individual ampoules for routine preservation. Be aware that preservatives dispersed from dropper-type bottles or automatic pipets could become contaminated and could result in the contamination of subsequent samples.
- Use the grade of preservative appropriate to meet data-quality requirements. (Check the certificate of analysis for the method detection limit and the concentration of the target analytes of interest.)

Replacement page 11/23/2004. (In the first paragraph, the preservatives are procured from the USGS One-Stop Shopping in place of QWSU.

- Always store preservatives in separate, sealed containers, preferably away from each other, and away from environmental and quality-control samples.
- Store spent preservative ampoules, containers, and supplies separately in closed and labeled containers (such as screw-cap bottles) until they can be disposed of properly.
  - Use a separate ampoule-waste container for each type of chemical preservative.
  - Store used gloves and chamber covers in a closed container, such as a pail with a lid, until proper disposal can be arranged.
- Follow a prescribed order in which samples are to be preserved (the recommended order is described in the steps below).

CAUTION: Before handling any chemical, refer to the Material Safety Data Sheet (MSDS) for safety precautions. Wear appropriate gloves, safety glasses, and apron when working with corrosive or oxidizing solutions.

For chemical treatment and handling of samples, follow the recommended sequence and procedure described in the steps that follow:

1. Put on appropriate disposable, powderless gloves.
2. Set up preservation chambers and assemble equipment and solutions in the order in which they will be used. If nitric acid is the only chemical preservative being used, the processing chamber can be used as a preservation chamber after all the filtered samples have been removed from the chamber.
3. Rinse the outside of each preservative ampoule with DIW and dry with a laboratory-grade, lint-free paper towel (for example, Kimwipe™).
4. For organic-compound samples:
   a. Change gloves.

Note: This section is being revised. Change the order of preservation described on pages 93-94 to the following:
1. Nutrients (4.5-N H2SO4)
2. Organic carbon (4.5-N H2SO4)
3. Trace elements and major cations (HNO3)
4. Mercury (6-N HCL) followed by other samples that require HCL
5. Remaining samples that require chemical treatment.

b. Place inside the preservation chamber the required organic-compound samples, chemical preservatives (treatments), and ampoule-waste containers. Common treatments include hydrochloric acid, sulfuric acid, or phosphoric acid/copper sulfate. **(VOC samples that are to be chemically treated can have the acid preservative added to the sample within the processing chamber as long as subsequent samples are not contaminated (section 5.1.2 and Appendix A5-A).**

c. Change gloves.

d. Uncap the sample bottle and dispense the appropriate chemical treatment into the sample. Place any spent ampoule into the appropriate ampoule-waste container.

e. Immediately recap the sample bottle and invert the bottle about five times to mix. **Vials with septum-lined caps for VOC must have no headspace.**

f. Repeat steps b, c, and d for each type of chemical treatment, if necessary, changing gloves and chamber cover each time. Make sure there is headspace in all glass bottles except for the vials for volatile organic compounds (VOC).

g. Chill all organic samples (treated and untreated) immediately and maintain them at 4°C during storage and shipment to the laboratory (section 5.5).

5. For inorganic-constituent samples:

a. Change gloves.

b. Change the chamber cover. Set up additional preservation chambers, if practical. (For example, one chamber for nitric acid treatments and a separate one for potassium dichromate treatment.)

- Transfer samples requiring chemical treatment to the preservation chamber.
- Place the first preservative and its waste container inside the chamber.
- Change gloves.

c. Add chemical treatments to samples as follows:

i. Major, minor, and trace cation samples: Add contents of the vial containing 1-mL HN03 to the samples designated RA or FA (Appendix A5-B). Place the spent vial into the HNO3-vial waste container.

ii. Mercury sample(s): Add contents of the vial containing 2 mL of 6N ultrapure HCl to the sample(s) designated RAM or FAM (Appendix A5-B). Place spent vial into the HCl-vial waste container .

The correct (9/2004) order of sample treatment: (1) nutrients, (2) organic carbon, (3) trace elements, (4) major ions, (5) mercury, (6) other acid-preserved samples, HCL first, (7) other.

iii. Change chamber cover and change gloves.

iv. Nutrient samples designated WCA or FCA (Water Quality Technical Memorandum 99.04):

- Place sample bottles into chamber.
- Add contents of the 1-mL 4.5-normal H_2SO_4 ampoule to 125-mL samples designated as WCA or FCA (Appendix A5-B). Place the spent ampoule into the H_2SO_4 ampoule waste container.
- Chill samples to 4°C or below without freezing immediately after adding the sulfuric acid.

v. Change chamber cover and gloves. Place bottles requiring other acid treatments into the chamber, along with the necessary chemicals and chemical-waste containers. Add the hydrochloric or other acid treatments to the samples. Place spent ampoules in appropriate waste containers.

vi. Remaining samples (Appendixes A5-B and A5-C): Change the chamber cover and change gloves for each type of treatment (for example, zinc acetate, sodium hydroxide, copper sulfate).

d. Tighten the cap on the bottle immediately after adding the chemical treatment and invert about five times to mix.

- Chilled samples must be put on ice and shipped to the laboratory immediately.
- Emptied ampoules must be stored in designated waste or recycle containers.

6. Disassemble and clean the chamber frame.
   a. Remove the disposable cover from the chamber and the work area.
      - Collapse the plastic cover while outside of the field vehicle.
      - Tie a knot in the cover to close it.
      - Dispose of the cover as regulations require.
   b. Clean the chamber frame, if necessary.
7. Document in field notes the preservation procedures and chemical treatments used.
8. Spent ampoules should be collected and, at the end of each field trip, disposed of according to Federal, State, and local regulations. (The District safety officer and water-quality specialists can be consulted for proper ampoule-disposal methods.)

HANDLING AND SHIPPING OF SAMPLES 5.5

By **D.B. Radtke**

Samples should be packaged and shipped to the laboratory for analysis as soon as possible. Generally, the shorter the time between sample collection/processing and sample analysis, the more reliable the analytical results will be. Before shipping samples to the laboratory:

- Check that sample bottles are labeled correctly.
- Complete an Analytical Services Request (ASR) form.
- Pack samples carefully in the shipping container to prevent bottle breakage, shipping container leakage, and sample degradation. Check that the bottle caps are securely fastened.

Protocols for labeling, documenting, and packaging samples established by the receiving laboratory must be followed. **Obtain authorization from the laboratory before shipping highly contaminated or potentially hazardous samples for analysis.** A summary of procedures for shipping samples to the NWQL is outlined below. Office of Water Quality Technical Memorandum 92.06 and National Water Quality Laboratory Technical Memorandum 95.04 give detailed instructions on shipping procedures.

LABELING SAMPLE BOTTLES 5.5.1

Each sample bottle must be correctly labeled with the station identification number, date, time, and sample designation. Sample designation is established by the laboratory. Laboratory codes that are added or deleted from the analytical schedule requested should be recorded on the ASR forms that accompany the samples—**not on the sample bottles.**

1. Label each bottle with a permanent, waterproof marker, or use preprinted labels that will remain securely attached to the bottles, even if they become wet.

2. Write legibly and include as a minimum the following information:
   - Station identification number.
   - Date and time of sample collection.
   - Sample designation code (Appendixes A5-A through A5-C).

A bottle with an unreadable label or no label is a wasted sample.

5.5.2 FILLING OUT AN ANALYTICAL SERVICES REQUEST FORM

Each set of samples must include an Analytical Services Request (ASR) form. To ensure correct processing of samples, the information recorded on the ASR form must correspond to each sample in the shipment.

- **Never send a sample to the NWQL without an ASR form** (forms are available through DENSUPPL).
- **Information recorded on ASR forms must be legible** and completed in permanent ink or by computer.

Fill out the ASR form as follows, including as much information about the sample(s) as possible:

1. Record mandatory information:
   - Station identification number and (or) unique number
   - Telephone number at which field personnel who collected the samples can be reached
   - Name of study chief and (or) field personnel
   - State and District user codes
   - Project account number
   - Date and time at beginning of field trip
   - Schedules and laboratory codes of the analytical work requested for submitted samples

2. Record the Sample Medium, Analysis Status, Analysis Source, Hydrologic Condition, Sample Type, and Hydrologic Event information. This information is mandatory if the analytical results are to be stored in the USGS National Water Information System (NWIS) data base.
3. Record the field-measurement values of specific electrical conductance (conductivity), pH, and field alkalinity (or acid neutralizing capacity).
4. In the comments section of the form, add information that needs to be brought to the laboratory's attention. **Be sure to note if the samples are potentially hazardous or highly contaminated so that proper precautions can be taken by laboratory personnel.**
5. At the bottom of the ASR form, list the total number of sample bottles for each sample-designation code.
6. To prevent water damage to paperwork accompanying samples to the laboratory (such as the ASR form and the temperature-check postcard), place all paperwork inside two sealable plastic bags. In coolers, tape the bags containing the paperwork to the underside of the lid.
7. Keep a copy of the completed ASR forms in the study files.

Add a bold cautionary note to the ASR form if samples could contain hazardous concentrations of contaminants.

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5.5.3 PACKAGING SAMPLES

When packaging samples for shipment to the laboratory, remember that all bottles must be protected from breaking (especially glass bottles) and (or) leaking. The laboratory usually will return with the cooler reusable packing materials such as mesh bags, foam sleeves, and bubble wrap. Plastic bags and cardboard boxes will not be returned. **Do not use foam peanuts or vermiculite.**

When packaging samples:

1. Make sure bottle labels are waterproof and that information is legible.
2. Tighten all bottle caps to prevent leakage.
3. Line all shipping containers, including those without ice, with doubled heavy-duty plastic bags.
4. Use adequate packing material to prevent bottle breakage.
   - Ship all glass bottles in foam sleeves or wrap them with bubble wrap.
   - Enclose each sleeved FAM and RAM bottle in two sealable plastic bags.
   - Pack bottles so that they do not touch each other.

Sample integrity must be maintained. Ship samples with enough ice to keep chilled at 4°C or below without freezing until the sample is logged in at the laboratory.

5. Pack samples designated for chilling in coolers.
   a. Use insulated ice chests (coolers) (1- to 5-gallon sizes are recommended). Larger volumes of chilled samples can be sent in coolers as long as the carrier's maximum weight and size restrictions are not exceeded. **Do not use broken or leaky coolers.**
   b. Pack samples designated for chilling with ice.
      - The volume of ice should be equal to or greater than the volume occupied by samples (twice the volume of ice to samples is recommended during warm temperatures).
      - The amount of ice necessary will vary depending on the length of time in transit and ambient air temperature. Chilling the cooler and samples prior to shipment is recommended in hot weather.
      - **Do not use blue ice or other types of commercial refreezing containers that have freezing points below 0°C.** This can cause bottles to freeze and result in ruined samples or broken bottles.
      - Enclose ice and samples in doubled plastic bags. **Do not mix ice with water-absorbent packing materials.**
   c. Seal cooler spouts or drains, preferably with silicone or epoxy.
6. Samples not requiring chilling can be shipped in heavy-duty cardboard boxes but may also be shipped in coolers.

DO NOT USE

— foam peanuts or vermiculite as packing material.

— dry ice to keep samples chilled.

7. When shipping multiple sets of samples in the same container, label each set of sample bottles with a different letter of the alphabet (A, B, C) so that bottles of each sample set will have the same letter.
   - Print the letter in the upper right-hand corner of the ASR form for that particular sample set.
   - Place all bottles from a sample set into a separate bag (such as plastic or mesh) or bind with a rubber band to keep them together.

8. All bottles for a particular schedule should be sent in the same shipping container, with some exceptions. Samples that do not need to be chilled can be packed and shipped in the cooler with chilled samples, provided the following exceptions do not apply. The ASR form must list only those samples that are being shipped with that form. On the ASR form, delete laboratory codes of any sample bottles not included in the same shipping container.
   - **Exception: Do not ship nutrient samples with samples that were treated with HNO_3.**
   - **Exception:** Do not ship FAM and RAM samples in the same container as FA or RA samples when requesting sample analysis for potassium and (or) chromium concentrations.
9. After samples and ice (if required) are placed in doubled plastic bags, close each bag separately with a knot.
10. Inside coolers:
   - Include a return address shipping label with the ASR form. This label must include a street address (not a post office box number), an account number, and the USGS District User Code (to bill return-shipping charges).
   - Label the inside of each cooler and cooler lid with a current return address and telephone number, using a permanent waterproof marker.
11. Include the ASR form for each sample set shipped in each cooler or box.
   - Remember to place the ASR form and temperature-check postcard into two sealable plastic bags to prevent water damage.
   - Tape the plastic bag containing the ASR form(s) and temperature-check card to the underside of the cooler lid, or place the sealed paperwork on top of samples packed in a cardboard box.

SHIPPING SAMPLES 5.5.4

Whenever possible, ship samples to the laboratory on the day of collection. Check laboratory hours of operation—keep in mind that the laboratory might not receive samples on Saturdays, Sundays, or holidays. The integrity of chilled samples sent late on a Thursday or on a Friday could be compromised if not received by the laboratory in time to be unpacked and refrigerated. Check planned arrival time before selecting the carrier service.

- No carrier service will accept or deliver leaky boxes or coolers. Securely tape the outside of shipping containers to prevent leaking and to maintain container integrity.
- Do not exceed maximum weight and size restrictions set by the carrier service.
- When shipping a single set of samples in multiple containers, mark the outside shipping label with the number of containers being shipped (such as 1 of 2, 2 of 2).
- Comply with the carrier service's requirements for meeting U.S. Department of Transportation regulations for transporting hazardous substances.
- **Identify samples that require special shipping procedures:**
  - Send chilled samples to the laboratory by the fastest means possible.
  - Some samples require special handling and shipping (such as radon and CFC samples). Contact the laboratory for specific instructions.
  - Obtain authorization from the laboratory before sending any highly contaminated or potentially hazardous samples to the laboratory for analysis.

Document date of sample shipment on the copy of each ASR form. Keep a copy in study files.

5.6 SUMMARY OF SAMPLE-COLLECTION AND SAMPLE-PROCESSING PROCEDURES FOR SPECIFIC ANALYTES

By **F.D. Wilde and Jacob Gibs**

Collection methods, equipment needs, and preservation requirements for specific analytes can change over time, owing to advancements in knowledge and technology. Any major changes to sample collection and processing procedures will be announced on the USGS Office of Water Quality Web site (http://water.usgs.gov/lookup/get?owq/) or as a technical memorandum (http://water.usgs.gov/lookup/get?techmemo/). Consult NWQL or the District water-quality specialist for instructions related to the collection, processing, or analysis of solid materials, gases, biota, and any other analytes not described in this manual. Chemical formulas used in this section are spelled out in "Conversion Factors, Selected Terms, Abbreviations, and Chemical Formulas."

5.6.1 COMMON ORGANIC COMPOUNDS

Sample bottles for organic-compound analyses are precleaned and baked at the laboratory and should be received capped. Collect and process samples within processing and preservation chambers, as appropriate, and while wearing disposable, powderless latex or nitrile gloves. In general, change gloves between each collection and processing step and with each new sample type. After collection and processing, check that the information is correct on the bottle label. Place the filled glass sample bottle in a foam sleeve and chill sample to 4◦C or below without freezing.

- Most samples for organic-compound analysis are collected in 1-L amber glass bottles, leaving headspace in case of sample expansion (Appendix A5-A).

Note: Section 5.6.1.F, "Wastewater, Pharmaceuticals, and Antibiotic Compounds" must be accessed as a separate file (see Contents page for Chapter A5).

- Samples for glyphosphate analysis are collected in 40-mL vials, leaving headspace in case of sample expansion.
- Volatile organic compounds are collected in 40 mL baked glass vials without headspace.

Do not field rinse bottles prepared for organic-compound samples.

5.6.1.A Volatile Organic Compounds (VOCs)

Label baked 40-mL amber glass vials as "VOC." Collect three vials per sample for ground water and four vials per sample for surface water.

- **Do not use tape on the vials.** Tape causes the autosampler to jam.
- **Do not aerate the sample.** Samples with air bubbles must be discarded.

TECHNICAL NOTE: **Some programs, such as NPDES and NAWQA, require treatment of VOC samples by adding HCl.** To determine the number of HCl drops needed to lower sample pH to ≤2 before collecting the sample, collect a test sample toward the end of purging and pour 40 mL of the sample into a beaker or spare VOC vial. Check the pH (use narrow-range pH indicator strips such as pHydrion™) after each addition of 2, 3, and 4 drops. Do not use pH indicator strips that are old or expired.

To collect VOC samples:

1. Insert the fluorocarbon polymer discharge line from the pump or the bailer emptying device to the bottom of the vial; flow should be smooth and uniform (between 100 and 150 mL/min).
   - If the vial was supplied with chemical treatment, do not fill vial to overflowing.
   - If no chemical treatment will be added or if the treatment will be added after the vial is filled, allow sample to overflow the vial in order to help purge air from the sample.
2. Slowly withdraw the discharge line from the bottle; slide the discharge line to the side of the vial as the line is about to clear the vial so as to avoid breaking the water surface. Leave a convex meniscus.

3. Add chemical treatment (HCl) to sample if required by the program and if the HCl is not already in the vial. Add 2 to 5 drops (see TECHNICAL NOTE above) of 1:1 HCl:H_2O, drop by drop, to the filled vial to lower the pH to ≤2. Dispense the HCl from a fluorocarbon polymer dropper bottle. **Do not add more than 5 drops of HCl**.
4. If residual chlorine is present, add 25 mg of ascorbic acid to the vial in addition to the HCl.
5. Replace the vial cap immediately. Do not allow the samples to degas. The fluorocarbon polymer (white) side of the septum in the cap should contact the sample.
6. Invert the vial and tap the vial to release any bubbles. Check carefully for gas bubbles in the sample. If gas bubbles are present, discard the sample vial and resample. If degassing of the samples makes excluding bubbles impossible, record this on the field forms and the laboratory ASR form and report an estimate of the relative volume of bubble(s) in the sample.
7. Protect the sample from sunlight. Chill and maintain at 4°C or below without freezing.

Semivolatile Organic Compounds (Base-Neutral Acids), Pesticides, Organonitrogen Herbicides, Polychlorinated Biphenyls (PCBs) 5.6.1.B

Label 1-L baked glass bottles as "GCC." Add the laboratory code, if required. Certain analytical schedules require a filtered sample (check with the laboratory for processing and bottle requirements).

1. Fill to the shoulder of the bottle directly from the sampling, splitting, or filtering device.
2. Be sure to leave headspace in the bottle.
3. Chill and maintain at 4°C or below without freezing.

Instructions for field solid-phase extraction (SPE) of pesticides are provided in section 5.3. Field SPE is an alternative method for processing samples for pesticide analysis and should be considered in situations where transporting glass bottles, shipping weight, or holding/shipping times pose a problem. Field SPE samples usually are extracted after most other onsite activities are completed or by a third team member because equipment setup, sample extraction, and equipment cleaning can be quite time consuming.

REPLACEMENT PAGE

5.6.1.C Phenols (Modified 4/2004)

Label two 500-L baked amber glass phenol bottles as "LC2322" -NWQL TechMemo 99.03

1. Fill two 500-mL baked amber glass bottles with raw sample directly from the sampling or splitting device.
2. Leave a small headspace in the bottle.
3. Add 1 mL H_2SO_4 to the sample to achieve pH <2. If chlorine is suspected in the sample water, add 0.5 mL of a 100 g/L (or 1 mL of a 50 g/L) $FeSO_4$ solution.
4. Chill and maintain at or below 4°C without freezing.

5.6.1.D Carbon

Particulate organic and inorganic carbon[10]***:***

1. Label the samples for Total Particulate Carbon (TPC) as "LC2606" and for Particulate Inorganic Carbon (PIC) as "LC2608." Note that the concentration of Particulate Organic Carbon (POC, LC2611) is calculated as the difference between TPC and PIC.
2. Refer to the detailed instructions given in section 5.2.2.C for processing the TPC and PIC samples.

Raw (TOC) sample:

1. Use 125-mL baked glass bottles. Label the sample for total organic carbon "LC114."
2. Pour, discharge, or pump the raw sample directly into the sample bottle, up to the shoulder of the bottle (leave headspace).

[10]The analysis for total particulate nitrogen (TPN), LC2607, is performed on the TPC sample upon request.

Filtered (DOC) and suspended (SOC) samples:

1. Label the DOC sample as follows: (a) "LC2612" if processed through a disposable disc filter; (b) "LC2613" if processed through a GF/F; and (c) "LC113" if processed through a silver filter.
2. Refer to the detailed instructions given in section 5.2.2.C for processing DOC using either the disc or GF/F filtration procedures. Fill the 125-mL baked glass bottle to the shoulder—allow enough heasdspace for the addition of 4.5*N* H_2SO_4 and the expansion of the chilled sample. Refer to the instructions given in Appendix A5-D if using the silver-filter procedure.
3. Label the SOC sample as "LC305." Refer to the detailed instructions given in Appendix A5-D for the silver-filter procedure. LC305 is available only as a custom analysis.

Methylene Blue Active Substances (MBAS) and Oil and Grease 5.6.1.E

MBAS:

1. Label a 250-mL polyethylene bottle as "RCB."
2. Field rinse the bottle and fill with raw sample.
3. Chill and maintain at 4°C or below without freezing.

Oil and grease:

1. Label a 1-L baked amber glass bottle as "LC0127."
2. Do not field rinse; fill with raw sample, leaving a small headspace.
3. Add approximately 2 mL of sulfuric acid to reach a pH <2.
4. Chill and maintain at 4°C or below, without freezing.

MAJOR IONS AND TRACE ELEMENTS 5.6.2

Bottles (including acid-rinsed polyethylene and glass bottles) used to collect samples for analysis of major ions and trace elements should be rinsed and partially filled with DIW before they are used at the field site, as instructed in NFM 3. Exceptions apply when collecting samples for analysis of isotopes or radiochemicals—consult the isotope laboratory. Collect and process samples within processing and preservation chambers, as appropriate, and while wearing appropriate (for example, vinyl) disposable, powderless gloves. In general, change gloves between each collection and processing step. After collection and processing, check the bottle label for correct information and place glass bottles into foam sleeves.

Replacement page 8/11/2008

- Use acid-rinsed bottles (for cations) only if they arrive capped with colorless translucent caps. Do not use any acid-rinsed bottles that are received uncapped.
- Before going to the field, first rinse and then half fill each bottle with DIW as described in NFM 3.
- Discard DIW from bottles at the field site before field rinsing and (or) sampling.
- **Field rinse the inside of sample bottles and bottle caps with sample** (table 5-2; Appendix A5-B). Use filtrate to rinse the bottles that will contain filtered sample.

5.6.2.A Major and Minor Cations and Trace Elements

Use of Clean Hands/Dirty Hands techniques and good field practices are required for samples with parts-per-billion concentrations of trace elements and are recommended for all samples.

Raw samples:

1. Label acid-rinsed polyethylene bottles as "RA" for major and minor cations and most trace-element samples. Label bottles with the laboratory schedule, as appropriate.
   - Arsenic, antimony, and selenium analyses—Label bottles as "RAH." (Some samples are designated "USEPA"—check with the laboratory.)
   - Mercury samples—Label glass bottles as "RAM."
   - USEPA drinking water samples—Label bottles as described in NWQL Technical Memorandum 97.05 or as directed.
2. Field rinse and fill sample bottles directly from the sample-collection or processing device.
3. Add chemical treatment, as specified by the analyzing laboratory.
   - Major and minor cations and trace elements: Add HNO_3 to lower sample pH to <2.
   - Mercury: Add contents of vial containing 2 mL of 6*N* ultrapure HCl.

Filtered samples:

1. Label acid-rinsed polyethylene bottles as "FA" for most trace-element samples, including arsenic, antimony, and selenium. Check NWQL Technical Memorandum 97.05 for requirements for USEPA drinking water samples.
   Exception: Mercury—Label the ~~acid-rinsed~~ 250-mL glass bottles as "FAM." Acid rinsed was deleted 02/17/2011.
2. Field rinse and fill sample bottles directly from the filter assembly. Refer to section 5.2 for filtration instructions.

3. Add chemical treatment, if specified by the analyzing laboratory.
   - Major and minor cations and trace elements: Add HNO_3 to lower sample pH to <2.
   - Mercury: Add contents of vial containing 2 mL of 6*N* ultrapure HCl.

Nutrients (Nitrogen and Phosphorus) 5.6.2.B

Refer to Office of Water Quality Technical Memorandums 94.16, 99.04 and 2000.08 for the most recent changes to collecting and processing nutrient samples. See 5.6.1.D and 5.2.2.C for processing of a Total Particulate Nitrogen (TPN) sample, LC2607.

Raw samples:

1. Label bottles as follows:
   - "WCA" for raw samples to be treated with H_2SO_4 (125-mL translucent bottles are preferable).
   - "ERC" for raw samples collected for the USEPA Drinking Water Program (refer to National Water Quality Laboratory Technical Memorandum 97.05 or contact the laboratory for instructions).

   A clean, graduated cylinder may be used when the volume of sample to be filtered is less than 64 mL.
2. Field rinse and fill the sample bottles directly from the sampler or sample splitting device.
3. Add a chemical treatment to WCA and ERC samples, as appropriate.
4. Chill WCA and ERC samples immediately and maintain at 4°C or below without freezing.

Filtered samples:

1. Label bottles as follows:
   - FCC" for filtered samples (125-mL brown bottles).
   - FCA" for filtered samples to be treated with H_2SO_4 (125-mL brown bottles).
2. Field rinse and fill sample bottles directly from the capsule filter or other filter assembly.

- **Use of 0.45-µm pore-size filter media is the standard to date for State or Federal programs that regulate drinking water and for routine water-quality studies for which consistency with historical nutrient data is necessary.** +
- Use of 0.2-µm pore-size filter media is recommended for studies for which exclusion of bacteria from the sample is desirable, and inconsistency with historical data is not an issue. Prefilter sediment-laden samples through 0.45-µm filter media. Record the filter pore size used, if other than 0.45 µm, under the comments section on the field form and ASR forms.

3. Add chemical treatment to FCA samples. (FCC samples do not require chemical treatment.)
4. Chill FCC and FCA samples immediately and maintain at 4°C or below without freezing.

5.6.2.C Anions

Label polyethylene bottles as "FU" (filtered untreated). Process alkalinity samples for field titration using the same steps as for other anions (with the exception of ANC samples) (NFM 6).

1. Refer to section 5.2 for filtration instructions. +
2. Field rinse and fill sample bottles directly from the capsule filter (or filter assembly).
3. Do not add chemical treatment.

Exceptions:

- **Cyanide**—Label the 250-mL polyethylene bottle as "LC0880" for filtered sample and as "LC0023" for raw sample. **Cyanide requires addition of NaOH to raise the pH to >12.**
- **ANC** (acid neutralizing capacity)—Do not filter the ANC sample. Label sample bottle as "RU" (NFM 6).

+

TABLE ISOTOPES AND RADIOCHEMICALS 5.6.3

Isotopes and radiochemicals generally are not processed in a processing or preservation chamber, unless samples are being handled in a glove box. Wear appropriate, disposable, powderless gloves when collecting and processing samples.

Leave enough air space (at least 2 cubic centimeters) if glass bottles are used and the sample will be chilled to allow for the expansion of water samples unless instructed otherwise (Appendix A5-C). Close the polyseal cap tightly and seal with wax or plastic tape, or as directed below for the specific isotope or radiochemical.

Carbon ($^{13}C/^{12}C$ and ^{14}C) 5.6.3.A

Do not let the sample contact air. Filter the sample along with other inorganic-constituent samples if particulates are visible. **Samples without particulates do not require filtration or chemical treatment** (NWQL Technical Memorandum 96.05). If ^{13}C will be collected by direct precipitation in the field using ammoniacal $SrCl_2$, then the precipitates must be submitted as washed, dried, homogenized powders. **The laboratory will not accept bottles with ammoniacal $SrCl_2$ in solution.**

Samples for $^{13}C/^{12}C$ analysis:

1. Label a 1-L glass bottle as "$^{13}C/^{12}C$, RUS," and the laboratory code or schedule number (as requested by the laboratory).
2. Filter the sample if particulates are visible. Establish a closed path from the sample source through the filter and to the bottle to exclude air from the collection system.
3. When filling the bottle, fill from the bottom of the bottle and allow an overflow of two to three bottle volumes. Cap the sample immediately.

Samples for ^{14}C analysis:

The sample must provide a minimum of 5 mg dissolved inorganic carbon (DIC) per sample container.

1. Label bottles as "^{14}C, RUS/RUR," and the appropriate laboratory schedule number. Check with the laboratory and refer to NWQL Technical Memorandum 96.05 for bottling and other field requirements for samples to be analyzed for ^{14}C.
2. Collect sample in duplicate. Filter the sample if particulates are visible. Establish a closed path from the sample source, through the filter, to the bottle to ensure that air is excluded from the collection system.
3. Fill sample container.
   - For samples with ^{14}C content greater than or equal to 5-percent modern carbon, fill the bottle from the bottom of the bottle, allowing an overflow of 2 to 3 bottle volumes. This helps to purge air from the sample. Cap the bottle immediately. For potentially low ^{14}C concentrations, (<10 percent modern carbon) or if relatively long filtration time is required, flush the headspace above the water sample with nitrogen while filling the bottle.
   - For samples with ^{14}C content less than 5-percent modern carbon, use a stainless steel collection vessel, such as a Whitey™ Sample cylinder No. 304L-HDF4, with stainless steel valves on each end. Flush with several liters of filtrate from the bottom of the cylinder up and close the cylinder, leaving no headspace.
4. Archive a duplicate sample and store in the dark, chilled to 4°C or below without freezing.
   - Secure container caps with electrical tape.
   - Record the sample pH and alkalinity on the sample bottle.

Hydrogen ($^{2}H/^{1}H$) and Oxygen ($^{18}O/^{16}O$) 5.6.3.B

Hydrogen and oxygen isotope samples can be collected together in one bottle. Use either a 60-mL clean glass bottle or a 250-mL polyethylene bottle. Label the bottles as "RUS, SH 1142." Use caps with polyseal conical inserts. **To request bottles with appropriate caps, send E-mail to isotopes@usgs.gov.**

- Do not field rinse bottles.
- Do not add chemical treatment.
- Samples may be either raw or filtered.

1. Fill bottle to overflowing directly from the sampler or sample splitting device (raw sample) or from the capsule filter or other filter assembly (filtered sample).
2. If filling a glass bottle, fill to overflowing and then decant the sample until the water level is at the bottle shoulder. Cap the bottle immediately
3. If filling a polyethylene bottle, fill to overflowing and cap the bottle immediately, leaving no headspace. Do not use polyethylene bottles if the sample will be held or archived.

5.6.3.C Nitrogen ($^{15}N/^{14}N$)

Collect filtered, untreated sample **(do not use mercuric chloride)** in a 1-L amber or foil-wrapped glass or high-density polyethylene bottle. Use a polyseal bottle cap. Refer to National Water Quality Technical Memorandum 95.05.

1. Label the bottles as "RUS" and with the appropriate laboratory code (LC 1717, for $^{15}N/^{14}N$ as ammonia; LC 1718, for $^{15}N/^{14}N$ as nitrate; or LC 1921, for $^{15}N/^{14}N$ as nitrate plus ammonia).
2. Fill the bottle to the shoulder directly from the capsule filter or other filter assembly.
3. Put the glass sample bottle into a foam sleeve and keep it chilled at or below 4°C without freezing. Ship overnight, per shipping instructions in NWQL Technical Memorandum 95.04.

5.6.3.D Sulfur ($^{34}S/^{32}S$)

Dissolved sulfide and sulfate are collected and processed separately, according to the directions given in Carmody and others (1998).

1. Label the bottles as "RUS" and with the appropriate laboratory code or schedule number.
2. Send questions to the following E-mail address: <isotopes@usgs.gov>. Special equipment, chemical reagents, and training are needed in order to collect these samples properly.
   Sulfate: Procedures and equipment differ for processing the sulfate sample, depending on whether sulfate concentrations are less than 20 mg/L or equal to or greater than 20 mg/L. Onsite estimation of sulfate concentration is described in Carmody and others (1998).
   - When a water sample from which dissolved sulfate will be collected for isotopic analysis also contains dissolved sulfide (greater than 0.01 mg/L), the sulfide should be removed by nitrogen stripping to avoid contamination of the sulfate sulfur by oxidized sulfide sulfur with very different isotopic composition.

- Sulfate in water with concentrations of greater than 20 mg/L sulfate is collected by precipitating $BaSO_4$ from an acidified sample (up to 2-L volume). $BaSO_4$ can be precipitated and filtered in the laboratory or in the field.
- Anion exchange resin can be used to collect sulfate from samples in which sulfate concentrations are less than 20 mg/L.

Sulfide: Determine if dissolved sulfide (H_2S) is present by its distinctive rotten-egg odor. Measure H_2S concentration with a field spectrophotometer.

- Measurement of dissolved sulfide concentrations greater than 0.6 mg/L with a field spectrophotometer has been problematic.
- An alternative method for samples with dissolved sulfide concentration greater than about 0.5 mg/L is to collect the dissolved sulfide by direct precipitation of Ag_2S by adding $AgNO_3$ to the sample. Care must be taken to add sufficient $AgNO_3$ to precipitate all the sulfide present, or the sulfide sample will be fractionated.
- A method for collection of dissolved sulfide by nitrogen stripping and precipitation of Ag_2S in an $AgNO_3$ trap has been tested and found to cause a small fractionation of the isotopic composition of the sulfide. Two approaches are recommended to minimize this fractionation: (1) collect sulfide by nitrogen stripping for 3 hours or more to minimize the amount of sulfide left in the carboy and, thus, the fractionation produced; and (2) determine the kinetic fractionation factor (α) for the collection apparatus and use this α to calculate the original sulfur isotopic composition of the dissolved sulfide in the ground water from Ag_2S collected for a short time (about 30 minutes).

5.6.3.E Radium 226 and Radium 228

Label acid-rinsed polyethylene bottle(s) as "FAR" and add the appropriate laboratory code ("LC 794" for radium-226 and "LC 1364" for radium-228). Bottle-size requirements depend on analytical method or schedule.

1. Filter the sample using the procedures for inorganic-constituent samples, and fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
2. Add reagent-grade HNO_3 to preserve sample to pH <2. **Do not substitute HCl for HNO_3.**

5.6.3.F Uranium (U-234, U-235, U-238)

Label 1-L acid-rinsed polyethylene bottle(s) as "FAR, SH 1130." Check with the laboratory for bottle requirements for the analysis requested.

1. Filter the sample and fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
2. Add reagent-grade HNO_3 to preserve the sample to pH <2. **Do not substitute HCl for HNO_3.**

5.6.3.G Gross Radioactivity

Label 1-L acid-rinsed polyethylene bottle(s) as "FAR" (filtered sample) for the gross alpha and the gross beta analyses and with the appropriate laboratory schedule number. The laboratory schedule requested depends on the concentration of total dissolved solids in the sample.

1. Filter the sample.
2. Fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
3. Add reagent-grade HNO_3 to preserve the sample to pH <2. **Do not substitute HCl for HNO_3.**

Tritium 5.6.3.H

Label a 1-L bottle as "RUR" and add the appropriate laboratory code. (High density polyethylene bottles are preferred; a glass bottle with a polyseal cap may be used. Refer to National Water Quality Technical Memorandum 92.04.)

- Do not place tritium samples near watches or other devices with luminescent dials. Do not store sample near tritium sources (for example, glowing clocks, watches, signs).
- **Do not field rinse sample bottles.**

1. Fill bottle with raw, untreated sample. The bottle should be dry before being filled. It might be desirable to flush the bottle with a filtered, inert gas such as argon or nitrogen before leaving for the field—consult with the laboratory.
2. Do not allow the bottle to overflow when filling with sample.
3. Leave a slight headspace in the bottle to allow for expansion of the sample.
4. Cap the bottle securely and tape the cap to prevent it from working loose during shipping.
5. Record the date and time of sampling on the bottle label and ASR form.

For tritium samples—Keep luminescent devices far from sample collection, handling, or storage areas.

5.6.3.I Radon-222

Modify the sample collection setup to collect raw samples for radon analysis. Sample is collected in a glass vial containing liquid-scintillation solution (obtain radon kit from NWQL). Label radon-222 samples as "RURCV" and add the laboratory code.

Do not write on or put any labels on the side of the radon vial.

Precautions are needed when collecting samples for radon analyses to prevent introducing gas bubbles into the sample and to prevent the sample from degassing.

- Use insulated sample tubing to prevent warming of the sample.
- Inspect sample tubing to determine whether gas bubbles are forming inside the tubing or whether any air is being drawn into the sample at any connection.
- Dislodge bubbles in sample tubing by striking the tubing firmly with a blunt object.
- Tighten connections to help prevent entrainment of air.
- To reduce degassing during sample collection, create back pressure by partially closing the valve on the radon-collection unit.

1. Collect the radon sample into a syringe directly from the pump discharge or other sampling device.
2. Rinse the syringe as follows: Insert the glass syringe needle through the septum port with the collection-unit valve partially closed. Close the valve further until there is sufficient back pressure to create an almost effortless withdrawal of sample into the syringe. Fill the syringe partially, withdraw it from the septum and invert (needle up). Eject the water to waste. Repeat at least once.
3. With the syringe plunger completely depressed (no air or water in the syringe barrel) and after the final rinse, reinsert the needle through the septum. Withdraw about 15 mL of sample into the syringe barrel slowly; avoid suction and degassing.

4. Withdraw the needle, invert the syringe (needle up), and eject the sample slowly until 10 mL remain in the syringe.
5. Tip the syringe needle downward, and insert the needle tip into the mineral oil and down to the bottom of the radon sample vial.
6. Inject the entire sample slowly. Remove the syringe and cap the vial firmly. Record the date and the exact time of sample collection on the top of the cap (do not write on or put a label on the vial).
7. Shake the vial for 30 seconds after injecting the sample. Repack it in the shipping tube and cap the tube. Complete the ASR form, wrap it around the tube, secure with a rubber band, and place the tube into a sealable plastic bag. **Ship to the NWQL immediately by overnight delivery. Do not ship samples on a Friday. Do not ship radon-222 samples in coolers.**

Do not allow air to contact samples for radon analysis.

Tritium/Helium-3 ($^3H/^3He$) 5.6.3.J

This section has been updated and now includes Chlorofluorocarbons (formerly section 5.6.3.K). See the next page for the updated section.

5.6.3.J Chlorofluorocarbons (CFCs), Sulfur Hexafluoride (SF_6), Dissolved Gases, and Tritium/Helium-3 ($^3H/^3He$)

The Reston Chlorofluorocarbon Laboratory provides analytical services for CFCs, sulfur hexafluoride, and dissolved gases, and administers the USGS contract for tritium/helium-3 dating. The data generated by the Reston Chlorofluorocarbon Laboratory are being used in hydrologic studies to trace the flow of young water and to determine the time elapsed since recharge.

Guidance and detailed directions in collecting and processing samples for these analyses, is provided at to the USGS Chlorofluorocarbon Laboratory website: http://water.usgs.gov/lab/, at which is located also a sample submission form. The links shown below allow access to information specific to the analyte shown:

CFCs: http://water.usgs.gov/lab/chlorofluorocarbons/

Dissolved Gas: http://water.usgs.gov/lab/dissolved-gas/

SF_6: http://water.usgs.gov/lab/sf6/

SF_5CF_3 and CFC-13: http://water.usgs.gov/lab/sf5cf3/

$^3H/^3He$: http://water.usgs.gov/lab/3h3he/

Section 5.6.4 - CONSTITUENT SPECIES

5.6.4.A - Arsenic Speciation
(Access as a separate file)

5.6.4.B - Low-level Mercury
(Access as a separate file)

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CONVERSION FACTORS, SELECTED TERMS, ABBREVIATIONS, AND CHEMICAL FORMULAS

CONVERSION FACTORS

Multiply	By	To obtain
micrometer (µm)	0.00003937	inch
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
microliter (µL)	0.0000338	ounce, fluid
milliliter (mL)	0.0338	ounce, fluid
	0.000264	gallon
liter (L)	0.2642	gallon
nanogram (ng)	3.53×10^{-11}	ounce
microgram (µg)	3.53×10^{-8}	ounce
milligram (mg)	0.0000353	ounce
gram (g)	0.03527	ounce, avoirdupois
kilopascal	0.1450	pound per square inch
picocurie (pCi)	0.037	Becquerle (Bq)

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

Selected Terms

Editors and authors of the *National Field Manual* have attempted to use terms common in the water-quality community. Some of the terms used have restricted meanings within the context of this report. The following terms either are used in a context familiar primarily to USGS personnel, or in a format that is more succinct, or that is considered to be more specific than a common usage:

Accuracy: The degree of agreement of a measured value with the true or expected value (from Taylor, 1987).

Analyte (target analyte): "Substances being determined in an analysis" (from Bennett, 1986). The term target analyte is used in this report to refer to any chemical or biological substance for which concentrations in a sample will be determined. The definition for target analyte does not include field-measured parameters such as temperature, specific electrical conductance, pH, dissolved oxygen, Eh, alkalinity, color, or turbidity.

Bias: Systematic error inherent in a method or caused by some artifact or idiosyncrasy of the sample measurement, collection, or processing system. The error can be positive (indicating contamination) or negative (indicating loss of analyte concentration) (from Taylor, 1987).

Contaminant: Biological or chemical substances added to the medium of concern, commonly through human activity.

Contamination (of water): Change of ambient water composition by the addition of biological or chemical substances as a result of human activity or natural processes. Addition of such substances can be detrimental to the quality of the water resource.

Data-quality requirements: The subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the variability allowable to fulfill the scientific objectives of the study.

Quality Assurance (QA): The systematic management of data-collection systems by using prescribed guidelines and criteria for implementing technically approved methods and policies. Quality assurance incorporates a comprehensive plan that outlines the overall process for providing a product or service that will satisfy the given requirements for quality.

Quality Control (QC): The specific operational techniques and activities used to obtain the required quality of data. Quality control consists of the application of technical procedures to achieve prescribed standards of performance and to document the quality of collected data. Quality-control data are used to identify and evaluate any corrective actions necessary to improve performance or data interpretation to acceptable levels.

Trace element(s): For the purpose of this report and to maintain consistency with common usage, the term trace element(s) is used to refer to metal and nonmetal inorganic elements such as arsenic, antimony, selenium, and tellurium that usually are present in natural surface-water and ground-water systems in concentrations less than 1 mg/L (modified from Hem, 1985). Common usage of this term, as defined above, is inexact and not rigorous with respect to aqueous chemistry.

Abbreviations

cc	cubic centimeter
lb/in^2	pounds per square inch
min	minute
mg/L	milligram per liter

µg/L	microgram per liter (equivalent to parts per billion (ppb))
mL/min	milliliters per minute
+ ng/L	nanogram per liter
ng/µL	nanogram per microliter
pCi	picocuries
ppb	parts per billion (see µg/L)
ANC	acid neutralizing capacity
ASR	Analytical Services Request
BNA	base-neutral acids
CFC	chlorofluorocarbon
CH	Clean Hands
DH	Dirty Hands
DIC	dissolved inorganic carbon
DIW	distilled/deionized water
DOC	dissolved organic carbon
FA	filtered, acidified sample
FAM	filtered, acidified sample for analysis of mercury
FAR	filtered, acidified sample for analyses of selected radiochemicals
FCA	filtered, chilled, acidified sample
+ FCC	filtered, chilled sample
FEP	fluorinated ethylene-propylene
FU	filtered, untreated sample
GCC	glass, chilled sample for analysis of nonvolatile organic compounds
GC/MS	gas chromatograph/mass spectrophotometer
IBW	inorganic-grade blank water (water with certified analysis of trace elements and other inorganic constituents and used for blank QC samples for analysis of inorganic constituents)
MBAS	methylene blue active substances
NAWQA	National Water-Quality Assessment Program
NFM	*National Field Manual for the Collection of Water-Quality Data*
NPDES	National Pollutant Discharge Elimination System
NWQL	National Water Quality Laboratory of the U.S. Geological Survey (Denver, Colo.)
OWQ	Office of Water Quality of the U.S. Geological Survey (Reston, Va.)
PBW	pesticide-grade blank water (water certified free of pesticide compounds)
PCB	polychlorinated biphenyl
+ QA	quality assurance
QC	quality control

QW	quality of water
QWSU	Quality of Water Service Unit of the U.S. Geological Survey (Ocala, Fla.)
RA	raw, acidified sample
RAH	raw, acidified sample for analysis of antimony, arsenic, and (or) selenium
RAM	raw, acidified sample for analysis of mercury
RCB	raw, chilled sample
RU	raw, untreated sample
RUR	raw, untreated sample for analysis of selected radiochemicals
RUS	raw, untreated sample for analysis of stable isotopes
SOC	suspended organic carbon
SPE	solid-phase extraction
TOC	total organic carbon
URL	Uniform Resource Locator
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VBW	volatile-organic-compounds-grade blank water (water certified free of VOCs)
VOC	volatile organic compounds
WCA	raw, chilled, acidified nutrient sample

Chemical Formulas

Ag_2S	silver sulfide
$AgNO_3$	silver nitrate
$BaSO_4$	barium sulfate
$^{13}C/^{12}C$	carbon-13/carbon-12 isotope ratio
^{14}C	carbon-14
$CuSO_4$	copper sulfate
$^{2}H/^{1}H$	deuterium/protium isotope ratio
$^{3}H/^{3}He$	tritium/helium-3 isotope ratio
HCl	hydrochloric acid

H_2O	water
H_2S	hydrogen sulfide
H_2SO_4	sulfuric acid
H_3PO_4	phosphoric acid
HNO_3	nitric acid
$HNO_3/K_2Cr_2O_7$	nitric acid/potassium dichromate
NaCl	sodium chloride
NaOH	sodium hydroxide
$^{15}N/^{14}N$	nitrogen-15/nitrogen-14 isotope ratio
$^{18}O/^{16}O$	oxygen-18/oxygen-16 isotope ratio
$^{34}S/^{32}S$	sulfur-34/sulfur-32 isotope ratio
$SrCl_2$	strontium chloride

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Memo No.	Title	Date
	Water Quality	

qw92.01	Distilled/Deionized Water for District Operations	December 20, 1991
qw92.02	FIELD TECHNIQUES--Field Preparation of Containers for Aqueous Samples	December 20, 1991
qw92.06	Report of Committee on Sample Shipping Integrity and Cost	March 20, 1992
qw92.11	Deleted - out of date.	
qw94.09	Revision of New Division Protocol for Collecting and Processing Surface-Water Samples for Low-Level Inorganic Analyses	January 28, 1994
qw94.16	New Preservation Techniques for Nutrient Samples	August 5, 1994
qw95.02*	Establishment of U.S. Geological Survey (USGS) Laboratory for Determination of Chlorofluorocarbons (CFCs) in Air and Water Samples	December 29, 1994
qw97.03	Protocols for Cleaning a Teflon Cone Splitter to Produce Contaminant-Free Subsamples for Subsequent Determinations of Trace Elements	February 7, 1997
qw97.06	Comparison of the Suspended-Sediment Splitting Capabilities of the Churn and Cone Splitters	May 5, 1997
qw99.04	Changes in Field Treatment Protocols and Bottle Types for Whole-Water Samples Collected for Total Ammonium Plus Organic Nitrogen and Total Phosphorus Determinations	November 25, 1998

*95.02 was prepared jointly by the Office of Water Quality and the Office of Ground Water.

Memo No.	Title	Date
	National Water Quality Laboratory	
92.01	Technology Transfer. Availability of Equipment Blank Water for Inorganic & Organic Analyses	March 25, 1992
92.04	Bottles for Tritium Analyses	August 12, 1992
93.01	Identification of Low Levels of Sodium Contamination in Nitric Acid Samples	October 5, 1992
93.09	Radon—Discontinuance of Duplicate Samples for Radon-In-Water	August 24, 1993
95.04	Shipping Samples to the National Water Quality Laboratory	December 2, 1994
95.05	Nitrogen Isotope Sample Preservation for Water Samples	March 8, 1995
96.05	Collection, Processing, and Analysis of Carbon Isotope Samples	April 5, 1996
97.01 97.01S	Use of Syringes to Add Volatile Organic Compounds to Water Samples for Use as Matrix Spike Samples (97.01S is supplementary)	November 5, 1996
97.04S	Collection, Processing, and Analysis of Ground-Water Samples for Tritium/Helium-3 Dating	April 7, 1997
97.05	Using the National Water Quality Laboratory for the Analysis of Drinking Water Samples	February 28, 1997

PUBLICATIONS ON TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further divided into sections and chapters. For example, Section A of Book 9 (Handbooks for Water-Resources Investigations) pertains to collection of water-quality data. The chapter, which is the unit of publication, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises.

The Techniques of Water-Resources Investigations (TWRI) reports listed below are for sale by the U.S. Geological Survey, Branch of Information Services, Box 25286, Federal Center, Denver, CO 80225 (authorized agent of the Superintendent of Documents, Government Printing Office). Prepayment is required. Remittance should be sent by check or money order payable to the U.S. Geological Survey. Prices are not included because they are subject to change. Current prices can be obtained by writing to the above address. When ordering or inquiring about prices for any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations." An updated list of TWRI reports can be found by accessing the World Wide Web url: http://water.usgs.gov/lookup/get?TWRI.

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Book 6. Modeling Techniques

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Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water

[NWQL, National Water Quality Laboratory of the U.S. Geological Survey; mL, milliliters; °C, degrees Celsius; HCl, hydrochloric acid; mg, milligram; L, liter; LC, laboratory code; %, percent; H_3PO_4, phosphoric acid; $CuSO_4$, copper sulfate; g/L, grams per liter; µm, micrometer; GF/F, baked glass fiber filter media; SH, schedule number; mm, millimeter; SPE, solid-phase extraction; <, less than; oz, ounce; in, inch]

Organic compound[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
Volatile or purgeable organic compounds (VOCs or POCs)	40-mL baked glass septum vial. Replicates are required and numbered in the order filled. Fill 3 vials for ground water, 4 vials for surface water. **No field rinse.**	VOC	Raw sample. Do not let sample degas. Chill/maintain at 4°C. • For treated sample[4]: Add two drops of 1:1 HCl from Teflon™ dropper bottle • If residual chlorine is present, add 25 mL ascorbic acid to vial before filling.
Methylene-chloride-extractable compounds (BNAs)	500-mL baked glass bottle. **No field rinse.**	GCC	Fill bottle to shoulder. Add 1 mL concentrated sulfuric acid to adjust to pH <2. If chlorine is suspected in the sample, add 100 mg ferrous sulfate. Mix, chill, and maintain at 4°C.
Phenols	1-L baked amber glass bottle. **No field rinse.**	LC0052	Raw sample. Add 2 mL of 8.5% H_3PO_4 to 1 L sample to pH 4. Add 10 mL $CuSO_4$ (100 g/L). Fill to shoulder. Chill/maintain at 4°C.
Polychlorinated biphenyls (PCBs)	1-L baked glass bottle. **No field rinse.**	GCC	Raw, untreated sample. Chill/maintain at 4°C.
Pesticides (raw)	1-L baked amber glass bottle. **No field rinse.**	GCC	Raw, untreated sample. Chill/maintain at 4°C.
• Organo-nitrogen herbicides	1-L baked amber glass bottle. **No field rinse**.	GCC	Raw sample, untreated. Chill/maintain at 4°C.
Pesticides (filtered)	1-L baked amber glass bottle. **No field rinse.**	GCC	Filtered sample (0.7-µm GF/F). Chill/maintain at 4°C.
• Organo-nitrogen herbicides	125-mL baked amber glass bottle. **No field rinse**.	GCC (SH1379)	Filtered sample, untreated. Optional: use 25-mm nylon filter capsule. Chill/maintain at 4°C.

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water—*Continued*

Organic compound[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
• Broad spectrum pesticides by C-18 SPE	C-18 SPE column.	SH2010	Filtered sample (0.7-µm GF/F), pass through SPE column and treat as described in text. Chill/maintain at 4°C.
• Broad spectrum pesticides by Carbopak-B™ SPE	Carbopak-B™ SPE column.	SH2051	Filtered sample (0.7-µm GF/F), pass through SPE column and treat as described in text. Chill/maintain at 4°C
Total particulate carbon (TPC)[5]	6-oz and 18-oz Whirl-Pak bags	TPC (LC2606)	Retain particulate material on 25-mm baked glass microfiber filters (GF/F). Fold filters into 6-in x 6-in aluminum foil squares, as described in the text, label, and place into 6-oz bag and then into 18-oz bag. Chill/maintain at 4°C.
Total organic carbon (TOC)	125-mL baked glass bottle. **No field rinse.**	TOC (LC0114)	Raw sample, untreated. Fill to shoulder. Chill/maintain at 4°C.
Dissolved (filtered) organic carbon (DOC)	125-mL baked glass bottle. **No field rinse.**	DOC (LC0113)	Filtered sample (silver filter media) , untreated. Fill to shoulder. Chill/ maintain at 4°C.
Suspended organic carbon (SOC)	Petri dish, plastic. No field rinse.	SOC (LC0305)	Retain suspended materials on silver filter, untreated. Chill/maintain at 4°C.
Methylene blue active substances (MBAS)	250-mL polyethylene bottle. **Field rinse.**	RCB	Raw sample, untreated. Fill to shoulder. Chill/maintain at 4°C.
Oil and grease	1-L baked glass bottle. **No field rinse.**	GCC (LC2125)	Raw sample. Leave small headspace. Add about 2 mL H_2SO_4 to lower pH to <2. Chill/maintain at 4°C.

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water—*Continued*

Explosives	1-L baked amber glass bottle. **No field rinse.**	GCC (SH 1377)	Filtered sample (0.7 µm GF/F), untreated. Chill/maintain at 4°C.
Total petroleum hydrocarbons	1-L baked glass bottle. **No field rinse.**	GCC (LC2126)	Raw sample. Leave small headspace. Add about 2 mL H_2SO_4 to lower pH to <2. Chill/maintain at 4°C.
Ultraviolet-absorbing substances			

[1]This table is not complete or comprehensive. Check with NWQL for the most current information on analytical schedules, laboratory codes, parameter codes, sample requirements, prices, and associated information.

[2]Container size is subject to sample-volume and analytical-method requirements. Glass bottles must be received from the laboratory baked, capped, and ready for use. **Do not use glass bottles that arrive uncapped.**

[3]Procedures for sample treatment and preservation are also described in Shelton and others (1994), Koterba and others (1995), Timme (l995), Sandstrom (1995), Zaugg and others (1995), and Werner and others (1996).

[4]Acidification of VOC samples is mandatory for NPDES and NAWQA programs, but normally is optional (unless study objectives dictate acidified samples).

[5]The summary for particulate inorganic carbon (PIC), sample designation code LC2608, is identical for that of TPC.

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Appendix A5-B. Sample-designation codes and a summary of field-processing requirements for analyses of inorganic constituents in water

[NWQL, National Water Quality Laboratory of the U.S. Geological Survey; mL, milliliters; °C, degrees Celsius; H_2SO_4, sulfuric acid; HNO_3, nitric acid; <, less than; $K_2Cr_2O_7$, potassium dichromate; NaOH, sodium hydroxide; >, greater than]

Inorganic constituent[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation
Nutrients: Nitrogen and phosphorus (raw)	125-mL translucent polyethylene bottle. **Field rinse**.	WCA	Raw sample, treated: Add 1 mL of H_2SO_4. Chill/maintain at 4°C.
Nitrogen and phosphorus (filtered)	125-mL brown polyethylene bottle. **Field rinse.**	FCC FCA	Filtered sample, untreated. Chill/maintain at 4°C. Filtered sample: Add 1 mL of H_2SO_4. Chill/maintain at 4°C.
Anions	250-mL polyethylene bottle. **Field rinse.**	RU FU	Raw sample, untreated. Filtered sample, untreated.
Cations (major cations, trace elements)	250-mL polyethylene bottle, acid rinsed. **Field rinse.**	RA FA	Raw sample. Acidify with HNO_3 to pH<2. Filtered sample. Acidify with HNO_3 to pH<2
Mercury	250-mL glass bottle, (clear), ~~acid rinsed~~. **Field rinse. Del. 2/11**	RAM FAM	Raw sample. Acidify with HCl, 6N, 2 mL, ultrapure Filtered sample. Acidify with HCl, 6N, 2 mL, ultrapure
Antimony Arsenic Selenium	250-mL polyethylene bottle, acid rinsed. **Field rinse.**	RAH	Raw sample. Acidify with HNO_3 to pH<2.
Cyanide	250-mL polyethylene bottle. **Field rinse.**	LC0023 LC0880	Raw sample. Add NaOH to pH >12. Chill/maintain at 4°C. Filtered sample. Add NaOH to pH >12. Chill/maintain at 4°C.

[1]List of constituents and sample-designation codes is not complete or comprehensive. Some notable omissions include chemical oxygen demand and sulfide. Check with NWQL for a comprehensive list of analyses and sample designations and instructions. Check National Water Quality Technical Memorandum 97.05 for requirements of the USEPA Drinking Water Program.

[2]Container size is subject to sample-volume and analytical-method requirements. Acid-rinsed bottles must be received from the laboratory capped. Do not use acid-rinsed bottles that arrive uncapped.

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water

[NWQL, National Water Quality Laboratory of the U.S. Geological Survey; L, liter; LC, laboratory code; DIC, dissolved inorganic carbon; mL, milliliters; $HgCl_2$, mercuric chloride; °C, degrees Celsius; HNO_3, nitric acid; <, less than; TDS, total dissolved solids]

Stable isotopes and radiochemicals[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
$^{13}C/^{12}C$	1-L glass bottle, narrow neck, with Teflon™/silicon septum. **Field rinse**.	RUS LC440	Raw sample, untreated. Contact laboratory for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ combined sample (LC1243). Fill bottle to overflowing.
^{14}C	Safety-coated or glass bottles with Teflon™/silicon septum. **Field rinse**. Secure cap with electrical tape. Bottle size depends on sample pH and concentration of DIC per volume of sample.	RUS/RUR	Raw or filtered sample—Filter samples with visible particulates; untreated. Fill bottle to overflowing. Exclude air and (or) flush headspace with nitrogen gas. Store chilled and in the dark. Contact NWQL.
$^{2}H/^{1}H$	60 mL clear glass bottle. Leave small headspace. Option: 250 mL polyethylene, no headspace. Use caps with polyseal conical inserts. Do not use plastic bottles if sample will be held or archived. **No field rinse.**	RUS, LC1574 or SH1142 if analyzing together with $^{18}O/^{16}O$.	Raw or filtered sample, untreated. Fill bottle to overflowing; then decant to leave a slight headspace. (Can be collected with $^{18}O/^{16}O$.)
$^{18}O/^{16}O$	Same as $^{2}H/^{1}H$ (LC1574) No field rinse.	RUS, LC0489 or SH1142 if analyzing together with $^{2}H/^{1}H$.	Filtered or unfiltered sample, untreated. Fill bottle to overflowing.

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water —*Continued*

Stable isotopes and radio-chemicals[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
$^{15}N/^{14}N$	1-L amber glass bottle or high-density polyethylene (HDP) bottle. Use caps with polyseal conical inserts. **No field rinse.**	RUS, LC1717 (ammonia), LC1718 (as nitrate), or LC1921 (as nitrate plus ammonia)	Filtered sample, untreated. Fill bottle to shoulder. Wrap HDP bottle in aluminum foil. (Do not add $HgCl_2$.) Chill/maintain at 4 °C. **Send overnight to NWQL.**
$^{34}S/^{32}S$	[Refer to Carmody and others (1998) or E-mail **isotopes@usgs.gov**.]	RUS, Add appropriate laboratory code.	[Refer to Carmody and others (1998) or E-mail isotopes@usgs.gov.]
Radium 226	2-L polyethylene bottle, acid rinsed. (Check with laboratory.) **No field rinse.**	FAR, LC794	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.
Radium 228	2-L or 7-L polyethylene bottle (check laboratory requirements), acid rinsed. **No field rinse.**	FAR, LC1364	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.
Uranium U-234 U-235 U-238	Two 1-L polyethylene bottles, acid rinsed. **No field rinse.**	FAR, SH1130	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.
Gross radio-activity (Gross alpha and gross beta)	1-L polyethylene bottle(s), acid rinsed. **No field rinse.**	FAR, SH456 or SH458, depending on TDS	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water —*Continued*

Stable isotopes and radio-chemicals[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
Tritium[1]	High-density, nonbreakable, poly-ethylene (HDPE) or 1-L glass GCC bottle. **No field rinse.**	RUR	Raw sample, untreated. Leave slight headspace. Do not store sample near radium (for example, glowing clocks, watches, signs)
Radon-222	Glass vial containing liquid-scintillation solution. **No field rinse.**	RURCV	Raw sample. Inject 10 mL of sample below liquid-scintillation solution.

[1]This table is not complete or comprehensive. Check with NWQL for the most current information on analytical schedules, laboratory codes, parameter codes, sample requirements, prices, and associated information. "G" indicates glass container; "CC" indicates chilled sample; "LC", laboratory code; "SH," laboratory schedule; "R" designates a raw or wholewater sample. For tritium/helium-3 and chlorofluorocarbon sampling requirements, see sections 5.6.3.J and 5.6.3.K, respectively.

[2]If glass bottles are used, leave enough air space in bottles to accommodate expansion of chilled samples unless instructed otherwise. Seal cap with wax or plastic tape, or as directed by laboratory. Send electronic mail requests to isotopes@usgs.gov. Container size is subject to sample-volume and analytical-method requirements. Acid-rinsed bottles must be received from the laboratory capped. Do not use acid-rinsed bottles that arrive uncapped.

[3]Procedures for collection and processing of isotope and radiochemical samples are also described in Shelton and others (1994), Koterba and others (1995), and Timme (l995).

Appendix A5-D. Procedures for Processing Samples for Analysis of Dissolved and Suspended Organic Carbon Using a Silver Filter and Gas-Pressurized Filtration Apparatus.

This appendix describes the original procedure ("Gas-Pressurized Filter Procedures for Processing Samples for Analysis of Dissolved and Suspended Organic Carbon," NFM 5.2.2.C, Version 5/99) for processing samples for analysis of dissolved organic carbon (DOC) and suspended organic carbon (SOC).[1] This procedure may be used as an alternative to those described in section 5.2.2.C. The laboratory analysis of SOC samples requires a different method from that of POC or TPC samples. The field team needs to ensure that the correct method code has been entered onto the laboratory analytical request form.

SOC and DOC can be processed through a 47-mm-diameter, 0.45-µm pore-size, silver-metal filter medium. A gas-pressurized filter assembly (SOC/DOC filter apparatus) constructed of either stainless steel or fluorocarbon polymer is required for this procedure (fig. A5-D.1). In addition, either a peristaltic pump, a manual air pump, or compressed gas (usually organic-free nitrogen gas) is used to pressurize the filtration apparatus and force the sample through the silver filter. Filtration procedures are identical for ground-water and surface-water samples.

A. Stainless steel filter assembly

B. Fluorocarbon polymer filter assembly

Figure A5-D.1 . Apparatus for filtering samples for analysis of dissolved/ suspended organic carbon: (A) stainless steel pressure-filter assembly and (B) fluorocarbon polymer pressure-filter assembly. (Published with permission: A, Gelman Sciences; B, Savillex Corporation.)

[1]Refer to Office of Water Quality Technical Memorandums 2000.05, 2000.07, and 2000.08 for an explanation of changes to the field procedures for collecting and processing samples for organic carbon analysis.

A different set of procedures and separate silver filters are used to process the SOC and the DOC samples, unless suspended-material concentrations are low (up to about 30 mg/L). This section describes methods for (1) filtration of SOC samples only, (2) combined SOC and DOC sample filtration, and (3) filtration of DOC samples only.

- **If sample contains a large amount of suspended materials, at least two filtrations must be performed: one for SOC and one for DOC.**
- If sample contains low concentrations of suspended materials, filtration procedures can be combined using the same silver filter.
- Unless the study plan dictates an additional sample for quality control, only one silver filter should be needed for the SOC filtration.
  - The SOC filtration requires a minimum of 0.5 mg of suspended material in the 125-mL sample.
  - If filter clogging is a problem, or if it is difficult to obtain the 125-mL volume of sample needed for the SOC analysis, 64 mL of sample or multiple 64-mL samples can be substituted.
- Immediately after each use, rinse the filter apparatus several times with organic-grade DIW.
  - Field clean the filter apparatus while still wet if it is to be used at the next site. Otherwise, rinse, bag, and return the apparatus to the office laboratory for cleaning.
  - Thoroughly rinse the white (fluorocarbon polymer) O-ring and any other fluorocarbon polymer parts.
  - After cleaning, double-wrap all apertures and the filter apparatus with aluminum foil and place filter apparatus inside a sealable plastic bag.
- Blank water (VBW or PBW) from a freshly opened bottle should be used for quality-control samples for the DOC analysis. This blank water can also be used for prerinsing the filter media, if necessary. Once the bottle has been opened, the VBW or PBW must not be used for collection of future quality-control samples.
- Document on field forms and in field notes the filtration procedures used.

Do not use methanol or any other solvent to clean SOC, DOC, or TOC equipment (NFM 3).

TECHNICAL NOTE: Use of 64 mL or 125 mL baked glass bottles (available from OWQRL) is recommended instead of a graduated cylinder to measure sample volume for the DOC or combined SOC/DOC analysis. The advantage of using the baked glass bottles to measure volume is that they are certified as clean, whereas graduated cylinders can be difficult to clean adequately, especially under field conditions (Burkhardt and others, 1997), and cannot be baked because calibration will be lost.

- Bottles for DOC samples must have been baked at 400°C and meet a detection limit criterion for organic carbon of <0.1 mg/L.
- Volumetric accuracy of the 125-mL and 64-mL baked glass bottles is about ±1 mL.

SOC sample processing:

SOC analysis of the suspended material left on the silver filter requires that the volume of sample passed through the silver filter be measured and recorded. Determination of the volume of sample to be filtered for SOC analysis can depend on the concentrations of suspended materials; however, the concentration of humic and other substances that cause colored water, such as organic and inorganic colloids, will affect the volume that can pass through the silver filter. The sample volume that can pass through the silver filter decreases as the concentration of suspended materials increases. A graph of the historical stream stage compared to a graph of the suspended-material concentration will aid in estimating suspended-material concentrations at a given surface-water site. Guidelines for selecting the volume of sample to be filtered for SOC analysis, based on suspended-material concentrations, are shown in table 5-6d.

1. Collect the SOC sample(s) in a baked glass bottle, either at the centroid of the streamflow (NFM 4) or as a subsample from the churn or cone splitter. The data-quality requirements of the study and site characteristics determine where to withdraw the sample. If collecting sample at the centroid of flow with a weighted-bottle sampler, fill the bottle to the top; this is not necessary if subsampling from the churn or cone splitter. Cap the bottle securely.

    - Use a 125-mL baked glass bottle for water with relatively small concentrations of suspended materials (concentrations approximately less than 250 to 300 mg/L) (table 5-6d).
    - 64-mL baked glass bottles are recommended for samples that are colored or particulate laden.
    - A clean, graduated cylinder may be used when the volume of sample to be filtered is less than 64 mL.

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Table 5-6d. Guidelines for selecting the volume needed for filtration of samples for analysis of suspended and particulate organic carbon
[Guidelines are based on sand-sized materials; other physical property factors and chemical composition were not taken into account; mg/L, milligrams per liter; mL, milliliters; >, greater than]

Approximate concentration of suspended materials (mg/L)	Volume of sample to be filtered (mL)
1 - 30	250
> 30 - 300	100
> 300 - 1,000	30
> 1,000	10

2. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves. Assemble necessary equipment on the clean work surface.

   a. To remove airborne particulates, attach an in-line, 0.2-µm pore-size filter (Acrodisc 50™) to the inlet side of a dry pump hose that goes to the filter apparatus when using peristaltic or hand pumps to pressurize the apparatus.

   b. Change gloves.

   c. Remove the aluminum foil wrapping from equipment.

3. Disassemble the clean filter apparatus.

4. Using metal forceps, place a silver filter on the base of the filter apparatus between the support screen and the fluorocarbon polymer gasket, and screw the barrel onto the filter base. (There is no gasket in the fluorocarbon polymer apparatus.)

5. Pour a minimum of 100 mL of ASTM Type II reagent water (Burkhardt and others, 1997) or VBW or PBW into the barrel. Analysis of the water used must indicate less than 0.1 mg/L of organic carbon.

6. Screw the top part of the filter apparatus onto the barrel and attach a clean, dry hose, either from a peristaltic pump, hand pump, or compressed gas cylinder (use a clean metal hose clamp to secure the discharge hose to the inlet connector). Set the filter apparatus into a stand.

7. Apply pressure to start the flow of rinse water through the filter apparatus, using either a peristaltic pump or hand pump, or by regulating the flow of compressed gas (usually nitrogen).

   a. The pump pressure must be regulated to less than 15 lb/in^2.

   b. If compressed gas (for example, organic-free nitrogen) is used, ensure that the gas is clean by way of gas-purveyor certification or by attaching an in-line 0.2-mm Gelman Acro™ 50 hydrophobic membrane filter disk. **Do not use any other type of filter**. Proceed as follows:

      i. **Make sure that the pressure regulator valve is closed.** Turn the handle on the pressure regulator counterclockwise for several turns until the pressure-regulator valve is closed.

      ii. Open the valve to the nitrogen cylinder.

      iii. Open the pressure-regulator valve by turning the handle clockwise until up to 15 lb/in^2 registers on the pressure gage. Do not exceed 15 lb/in^2 of pressure.

   c. Discard rinse water.

8. Depressurize the filter apparatus. **Always point the apparatus away from your body, face, and other people.** When using compressed gas,

   a. Close the valve to the pressure regulator after the pressure gage shows no pressure.

   b. Close the valve to the gas cylinder.

   c. Change gloves.

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

9. Remove the top of the filter apparatus carefully.

10. Shake the sample vigorously (swirl if using a graduated cylinder) to suspend all particulate matter. (This is possible even if the bottle is filled to the top.)

11. Pour an aliquot of the sample immediately into the barrel of the filter apparatus, keeping particulates suspended.

12. Screw the top part of the filter apparatus onto the barrel and pressurize to filter the sample. Follow the instructions in step 7 (above) for pressurizing the filter apparatus.

13. After an aliquot of sample has been filtered or filtrate is being collected at less than one drop per minute:

    a. Depressurize apparatus (step 8).

    b. Remove the top of the filter apparatus.

    c. Check if there is water on the silver filter and if it is covered with particulates.

    - If the silver filter is dry but not covered with particulates, add another aliquot of sample by repeating steps 10–12.
    - After the silver filter is dry and covered with particulates, continue to step 14.

TECHNICAL NOTES:

It is important that all the water in the barrel be passed through the silver filter, leaving the filter "dry." To accomplish this, it might be necessary to filter the sample as separate aliquots, repeating steps 10–13 until the filter is loaded to capacity.

Shake the sample to resuspend particulates before pouring each aliquot into the barrel.

If using a 125-mL or 64-mL bottle, it is not necessary to empty the entire sample volume. Use of a clean, graduated cylinder also is acceptable.

It is recommended (but not required) that the sides of the barrel of the filter apparatus be rinsed with organic-grade DIW.

14. Collect the filtrate in a 50-mL or other appropriately sized graduated cylinder.

    - If additional aliquots will be filtered through the same silver filter, collect all the filtrate in the graduated cylinder.
    - When the entire filtration is complete, record the total volume of filtrate on field forms and on the Analytical Services Request (ASR) form.
    - Discard filtrate in the graduated cylinder—**Do not send to laboratory for analysis.**

15. Depressurize (step 8) and disassemble the bottom of the filter apparatus.

    a. Use a pair of metal forceps to remove the silver filter.

    b. Fold the silver filter in half with suspended material on the inside, taking care not to lose any suspended material. **Do not wrap the silver filter in aluminum foil.**

    c. Place the folded silver filter into a petri dish for SOC analysis.

    d. Close the petri dish and label it with site identification, date and time, total filtered volume of sample, and laboratory sample designation code. (The total volume of filtered sample includes the volume used to precondition the silver filter(s).)

    e. Maintain SOC sample at or below 4°C during storage and shipment to the laboratory.

Combined SOC/DOC sample processing:

Procedures for a combined filtering of samples for SOC and DOC analysis are listed below. Additional information can be found in Burkhardt and others (1997).

1. Collect the sample for SOC/DOC analysis as instructed in NFM 4.

2. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves. Assemble necessary equipment on the clean work surface.

    a. To remove airborne particulates, attach an in-line, 0.2-µm pore-size filter (Acrodisc 50™) to the inlet side of a dry pump hose that goes to the filter apparatus when using peristaltic or hand pumps to pressurize the apparatus.

    b. Change gloves.

    c. Remove the aluminum foil wrapping from equipment.

3. Disassemble the clean filter apparatus.

4. Using metal forceps, place a silver filter on the base of the filter apparatus between the support screen and the fluorocarbon polymer gasket, and screw the barrel onto the filter base. (There is no gasket in the fluorocarbon polymer pressure-filter apparatus.)

5. Pour a minimum of 100 mL of ASTM Type II reagent water (Burkhardt and others, 1997) or VBW or PBW into the barrel. Analysis of the water used must indicate less than 0.1 mg/L of organic carbon.

6. Screw the top part of the filter apparatus onto the barrel and attach a clean, dry hose, either from a peristaltic pump, hand pump, or compressed gas cylinder (use a clean metal hose clamp to secure the discharge hose to the inlet connector). Set the filter apparatus into a stand.

7. Apply pressure to start the flow of rinse water through the filter apparatus, using either a peristaltic pump or hand pump, or by regulating the flow of compressed gas (usually nitrogen).

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

   a. The pump pressure must be regulated to less than 15 lb/in^2.
   b. If compressed gas (for example, organic-free nitrogen) is used, proceed as follows:
      i. **Make sure that the pressure regulator valve is closed.** Turn the handle on the pressure regulator counterclockwise for several turns until the pressure-regulator valve is closed.
      ii. Open the valve to the nitrogen cylinder.
      iii. To pressurize the filter apparatus, open the pressure-regulator valve by turning the handle clockwise until up to 15 lb/in^2 registers on the pressure gage.
   c. Discard rinse water.

Do not exceed 15 lb/in^2 of pressure.

8. Depressurize the filter apparatus. **Always point the apparatus away from your body, face, and other people.** When using compressed gas,
   a. Close the valve to the pressure regulator after the pressure gage shows no pressure.
   b. Close the valve to the gas cylinder.
   c. Change gloves.
9. Remove the top of the filter apparatus carefully.
10. Condition the silver filter for the SOC/DOC sample:
   a. Select the volume of wholewater (either 64 mL or 125 mL) to be filtered based on the estimated suspended-materials concentration of the sample, and record the volume on the ASR and the field forms. The volume to be filtered can be based on the table 5-6 guidelines and on previous experience of filtering samples from the site.

b. Shake the sample vigorously to resuspend settled particles and measure the sample volume using a clean, baked 64-mL or 125-mL bottle filled to the very top. **Do not field rinse baked glass bottles.** Immediately transfer the entire volume of the sample container to the barrel of the filter apparatus.

c. Screw the top part of the filter apparatus onto the barrel and pressurize to filter the sample. Follow the instructions in step 7 (above) for pressurizing the filter apparatus.

d. Condition the silver filter by passing 15 to 25 mL of sample water through the filter to waste. (Pass 15 mL of sample water through the silver filter if using a 64-mL volume of sample; 15 mL is the minimum volume of sample that should be used.) Record the total volume of water that was passed through the silver filter.

Do not field rinse DOC bottle.

11. Place a 125-mL baked glass bottle under the discharge tube of the filter apparatus and collect the sample filtrate for the DOC analysis (100 mL is recommended; a minimum of 50 mL is required). If the silver filter clogs before sufficient volume for the SOC analysis can be filtered, start the process over and filter a smaller volume of water; the 64-mL bottles are useful for such conditions. **If the silver filter clogs before the entire volume of the 64-mL bottle can be filtered, this combined SOC/DOC method cannot be used. Start over and filter SOC and DOC samples separately.**

    - If the volume needed for the SOC analysis is insufficient for a DOC analysis (less than 50 mL), two or more filtrations through separate silver filters can be combined into one DOC bottle. (Retain two of the filters if a duplicate SOC analysis is planned and record the total volume of sample that passed through each of the retained filters.)
    - Each time a new silver filter is used, repeat steps 3–10, rinsing and conditioning the silver filter as described. Discard the first 15 or 25 mL of sample filtrate to waste. Reposition the DOC bottle under the discharge tube and collect the sample filtrate. Record the total volume of sample that was passed through each silver filter.
    - If the volume needed for SOC analysis is greater than the 100 mL of sample to be used for DOC analysis, remove DOC bottle after filling with 100 mL of filtrate, but continue filtering until the entire volume needed for SOC analysis has been filtered. (Record total volume filtered and discard extra filtrate.)

12. After the DOC sample has been collected and the volume for SOC analysis has been filtered, cap the DOC bottle securely and check that the bottle is labeled correctly and completely. Place the bottle in a foam sleeve before placing in an ice-filled shipping container.

13. Depressurize the filter apparatus (step 8), then disconnect the hose from the filter apparatus cylinder and remove the top. When depressurizing the compressed-gas-operated apparatus:

    a. Close the valve to the pressure regulator only after the gage indicates no pressure.

    b. Close the valve to the nitrogen cylinder.

14. Using no more than a total of 20 mL of organic grade DIW:

    - Rinse residual suspended matter from the bottle that was used to measure sample volume and pour into the filter barrel.
    - Rinse any residual suspended matter from the sides of the filter barrel.

15. Reconnect the top of the filter apparatus. Attach the pressure hose and pressurize (step 7), passing the organic-grade DIW rinse water through the silver filter. Discard rinse water to waste. Depressurize the filter apparatus (step 8).

16. Disassemble the bottom of the filter apparatus and remove the silver filter.

    a. Use a pair of metal forceps when removing the silver filter.

    b. Fold the filter in half with suspended material on the inside, taking care not to lose any suspended material. **Do not wrap the silver filter in aluminum foil.**

    c. Place the folded filter in a petri dish for SOC analysis.

    d. Close the petri dish and label dish with site identification, date and time, total filtered volume of sample, and the laboratory sample designation code. (Include the volume used to precondition the silver filter(s) in the total volume of filtrate.)

    e. Place the labeled petri dish in a sealable plastic bag.

    f. Chill DOC and SOC samples and maintain at or below 4°C without freezing (section 5.5). For SOC samples submitted to NWQL, record the total volume of filtrate on the comment line of the ASR form.

g. If more than one silver filter was needed for the SOC sample, place each silver filter into a separate petri dish that is labeled as described in step 16d. Place all the petri dishes for a single sample into one sealable plastic bag labeled with the site identification and the date and time of sample collection. This is submitted as a single sample.

- Package the silver filter(s) for duplicate SOC analysis separately.
- Ship samples for SOC analysis to the laboratory with a note on the ASR form stating the number of silver filters used.

For SOC analysis, record TOTAL VOLUME of sample that passed through each silver filter.

DOC sample processing:

Procedures for filtering a DOC-only sample are listed below. Additional information can be found in Burkhardt and others (1997).

1. Collect the sample for DOC analysis (NFM 4).
2. Cover a bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves. Assemble necessary equipment on the clean work surface.
   a. To remove airborne particles, attach an in-line filter, 0.2-µm pore size, (Acrodisc 50™) to a dry pump hose in front of the filter apparatus when using peristaltic or hand pumps to pressurize the apparatus.
   b. Change gloves.
   c. Remove the aluminum foil wrapping from equipment.
3. Disassemble the clean filter apparatus.
4. Using metal forceps, place a silver filter on the base of the filter apparatus between the support screen and the fluorocarbon polymer gasket, and screw the barrel onto the filter base. (There is no gasket in the fluorocarbon polymer pressure-filter apparatus.)
5. Pour a minimum of 100 mL of ASTM Type II reagent water (Burkhardt and others, 1997) or VBW or PBW into the barrel. Analysis of the water used must indicate less than 0.1 mg/L of organic carbon.
6. Screw the top part of the filter apparatus onto the barrel and attach a clean, dry hose, either from a peristaltic pump, hand pump, or compressed gas cylinder (use a clean metal hose clamp to secure the discharge hose to the inlet connector). Set the filter apparatus into a stand.

7. Apply pressure to start the flow of rinse water through the filter apparatus, using either a peristaltic pump or hand pump, or by + regulating the flow of compressed gas (usually nitrogen).

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

   a. The pump pressure must be regulated to less than 15 lb/in^2.
   b. If compressed gas (for example, organic-free nitrogen) is used, proceed as follows:
      i. **Make sure that the pressure regulator valve is closed.** Turn the handle on the pressure regulator counterclockwise for several turns until the pressure-regulator valve is closed.
      ii. Open the valve to the nitrogen cylinder.
      iii. Open the pressure-regulator valve by turning the handle clockwise until up to 15 lb/in^2 registers on the pressure gage. Do not exceed 15 lb/in^2 of pressure.
   c. Discard rinse water.

8. + Depressurize the filter apparatus. **Always point the apparatus away from your body, face, and other people.** When using compressed gas,
   a. Close the valve to the pressure regulator after the pressure gage shows no pressure.
   b. Close the valve to the gas cylinder.
   c. Change gloves.
9. Remove the top of the filter apparatus carefully.
10. Condition the prerinsed silver filter:
   a. Open the barrel of the filter apparatus and pour about 125 mL of wholewater sample into the barrel (or about 64 mL if silver filter media is expected to clog). For water with large concentrations of suspended materials, collect the sample first into a baked glass bottle, allow suspended materials to settle, and pour 125 mL of the clear supernatant into the filter barrel.
   b. Screw the top part of the filter apparatus onto the barrel.
11. Apply pressure to start the flow of sample through the filter apparatus (step 7).
   + • **Do not exceed 15 lbs/in^2.**
   • If using compressed gas, open the pressure-regulator valve first, then the valve to release gas from the cylinder (tank).

12. Condition the silver filter media by passing about 25 mL of sample through the silver filter to waste.

13. Filter the sample:

    a. Place a 125-mL organic-free amber glass bottle under the discharge tube of the filter apparatus. **Do not prerinse the DOC bottle.**

    b. If the silver filter media clogs, depressurize the filter apparatus and replace the silver filter.

        i. Rinse the new filter with blank water as described in steps 5–9.

        ii. Fill a clean DOC bottle with the water to be sampled and let the suspended materials settle before decanting the sample into the barrel of the filter apparatus.

        iii. Condition the new silver filter by passing about 25 mL of sample through the filter to waste.

        iv. Reposition the DOC bottle under the discharge tube and continue to collect the filtrate.

    c. Fill the bottle until sufficient volume for DOC analysis has been collected (50 mL is the minimum requirement; 100 mL is recommended). Cap the bottle securely and check that the bottle is labeled correctly. Place the bottle in a foam sleeve before placing in an ice-filled shipping container.

14. Depressurize the filter apparatus (step 8).

15. Chill and maintain the DOC sample at or below 4°C without freezing (section 5.5).

16. Disassemble the bottom of the filter apparatus. Remove the silver filter with metal forceps and place the filter in a plastic bag for disposal or recycling. **Do not reuse silver filters.**

Never increase the pressure in a filter apparatus to greater than 15 lb/in^2 in order to increase the rate of filtration.

5.2.2.B. Syringe-Filter Procedure for Processing Samples for Analysis of Organic Compounds by DAI LC-MS/MS[1]

By Mark W. Sandstrom and Franceska D. Wilde

This section of chapter 5 of the *National Field Manual for the Collection of Water-Quality Data* (NFM) describes the field procedures for collecting small-volume samples using a syringe-tip filtration method. The samples are sent to the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) for analysis of organic compounds by direct aqueous injection high-performance liquid chromatography/tandem mass spectrometry (DAI LC-MS/MS).[2]

The DAI LC-MS/MS method was developed specifically for NWQL analytical schedules 2437 (pesticides) and 2440 (pharmaceuticals) and should not be considered transferrable or applicable to other types of samples to be analyzed using methods other than those that use DAI LC-MS/MS or other tandem mass spectrometry methods.

The filter medium required for the filtration procedure must be rinsed and conditioned as described in table 5.2.2.B–1. While some of the filtration equipment can be reused after it is cleaned and otherwise decontaminated, all filter media are non-reusable and are to be discarded after one use (table 5.2.2.B–1).

- Clean hands/dirty hands (CH/DH) techniques and the associated quality-assurance procedures that are required for inorganic analytes with a concentration at parts per billion or less are recommended for organic analytes as a general good field practice to maintain the integrity of the sample chemistry.
- Field personnel must wear disposable, powderless gloves (gloves) while processing samples. The gloves must be able to withstand solvents or other chemicals that will be used during sample processing and equipment cleaning; generally, nitrile gloves (elbow length, if available) are recommended. Requirements regarding the selection, preparation, and use of the disposable gloves for USGS water-quality sample collection and handling are described in NFM 2.02 and NFM 4.02.

Compared with the plate-filter procedures described in NFM section 5.2.2.A, use of the syringe-filter technique requires a relatively small volume of sample (10 mL) for analysis. Tandem mass spectrometry, as is used in schedules 2437 and 2440, is more selective than other instruments that typically are used and is less prone to interferences from plastics and other materials, allowing for use of this disposable equipment.

[1] Section 5.2.2.B, in previous versions of this National Field Manual (NFM) chapter, addressed the sample processing procedure for analysis of organonitrogen herbicides (versions 2 through 2.2, dated 4/2002). The method rarely was used and has been deleted from this version of NFM chapter 5.

[2] Depending on individual project requirements for the collection of multiple samples, the plate-filter and filter-holder assemblies also can be used to collect samples for DAI LC-MS/MS (DAI) analysis. Equipment and supplies used to filter samples for DAI analysis are described in NFM 2, section 2.2.3.B; see figure 2–17. The term DAI LC-MS/MS, as used in this National Field Manual, is synonymous with DAI-HPLC/MS/MS and other variations of acronyms that are used in the literature to refer to the direct aqueous injection high-performance liquid chromatograph/tandem mass spectrometry analytical method.

Table 5.2.2.B–1. Field-conditioning requirements for media used to filter samples for organic-compound analysis.

[mm, millimeter; GF/F, glass-fiber filter; µm, micrometer; PBW, pesticide-grade blank water; mL, milliliter; PFA, perfluoroalkoxy alkane (a fluoropolymer); DAI LC-MS/MS, direct aqueous injection high-performance liquid chromatography/tandem mass spectrometry (synonymous with DAI-HPLC/MS/MS and other variations of those acronyms); LS, laboratory schedule of the USGS National Water Quality Laboratory (NWQL); GMF, graded multi-filter; DOC, dissolved organic carbon; FEP, fluorinated ethylenepropylene; IBW, inorganic blank water; VPBW, nitrogen-purged blank water for volatile organic compounds; DIW, distilled deionized water; WSC, a water science center of the U.S. Geological Survey; L, liter]

Filtration equipment ***Application***	**Housing material**	**Filter media**	**Filter cleaning and conditioning[1]**
Plate-filter assemblies: 142 or 293 mm *General trace organic compounds*	Stainless steel or aluminum	GF/F (glass-fiber filter)[2]: 0.7-µm pore	• Wet with PBW: - 10–20 mL (for 142 mm), or - 50–75 mL (for 293 mm). • Rinse and condition filter with 100–125 mL of sample.
Inline PFA filter-holder assembly: 47 mm *General trace organic compounds*	Teflon® PFA	GF/F[2]: 0.7-µm pore	• Wet with 5–10 mL of PBW. • Rinse and condition filter with 50 mL of sample.
Disposable syringe-tip filter: 25 mm (DAI LC-MS/MS) • *LS 2437 Pesticides* • *LS 2440 Pharmaceuticals*	High-purity polypropylene	GF/F with GMF[3]: 0.7-µm pore	Rinse with 15 mL of sample water or 15 mL of PBW[4] to clean and condition the filter.
Pressure filter-holder assembly—DOC 25[5]: 25 mm *Dissolved and particulate organic carbon*[6]	FEP	GF/F[2]: 0.7-µm pore	• Rinse with 50 mL of IBW, PBW, VPBW, or other certified DOC-free DIW (WSC-produced). • Condition filter with 10 mL of sample.
Disposable capsule or disk filter[5] *Dissolved organic carbon (DOC)*	Polypropylene	Thermapor®: 0.45-µm pore	• Using IBW, PBW, VPBW, or other certified DOC-free DIW: - Rinse with 2 L for large-capacity capsule, or - Rinse with 50 mL for small-capacity disk. • Condition capsule filter with 25 mL and disk filter with 10 mL of sample water.

[1] Filter media (filters) must be prepared as described and discarded after one use.

[2] Use only glass-fiber filters that have been baked and quality-assured at the USGS National Water Quality Laboratory.

[3] Graded multi-filter (GMF): prefilter having a coarse top layer of borosilicate glass microfibers meshed with a fine bottom layer.

[4] PBW is used only in cases when the quantity of suspended sediment is enough to cause the filter to clog.

[5] Produced for the USGS by Savillex Corporation, Part 401-61-25-53-60-2. A polysulfone funnel is required when sample will be analyzed for particulate nitrogen and carbon concentrations.

[6] Disposable capsule and disk filter are illustrated in NFM 2, version 3.1, figure 2–11.

The equipment and procedure used when processing samples for syringe-tip filtration can differ, depending on the manner in which a surface-water or groundwater sample will be collected. Syringe-tip filtration equipment should be obtained from the NWQL-supported national field supply service (NFSS), either as a complete kit (Q765FLD) or as individual components: Q762FLD, syringe-tip filter; Q763FLD, 20-mL syringe; Q764FLD, wide-bore needle; and 20-mL PEST or PHARM borosilicate glass amber vial with septum (refer to NFM 2, ver. 3.1, p. 48–49).

- For samples collected in a Teflon churn or other noncontaminating wide-mouth compositing container (generally for surface-water applications), the sample is withdrawn using a graduated 20-mL high-purity disposable syringe with a Luer-Lock outlet, a large-bore 1-in. stainless-steel needle with Luer fitting and blunt tip. (Note that if the sample is composited in a precleaned narrow-mouth glass carboy, it needs to be pumped to a precleaned container with an opening wide enough (for example, a 50-mL beaker or 2-oz glass jar) in which the needle attached to the syringe can be submerged).
- When using a submersible pump to collect a groundwater sample, two sampling options (described below) are provided. For both options the groundwater rate of flow being pumped to land-surface must be reduced to about 50 to 100 mL/min.
  - In Option A, the syringe and bore needle are not needed. The 25-mm syringe-tip filter is connected directly to the outlet of the pump tubing using reducer fittings (table 5.2.2.B–2).
  - In Option B, there is a choice to collect sample water using either the syringe with a bore needle or the syringe without the needle.

Table 5.2.2.B–2. Reducer fittings used for connecting a syringe-tip filter to an inline groundwater sampling pump (used when filtering groundwater samples for DAI LC-MS/MS methods pertaining to pesticides [NWQL schedule 2437] and pharmaceuticals [NWQL schedule 2440]).

[in., inch; PTFE, polytetrafluoroethylene; PFA, perfluoroalkoxy alkane; OD, outer diameter; ETFE, ethylene tetrafluoroethylene]

Vendor	Part number	Description	Number required for assembly
Swagelok[1]	T-400-6-2	Reducer union, 1/4 to 1/8 in., PTFE	1
		— OR —	
Swagelok[1]	T-810-6-2	Reducer union, 1/2 to 1/8 in., PTFE	1
Upchurch Scientific	1641	PFA high purity tubing, 1/8-in. OD	[2]1
Upchurch Scientific	XP-315	Flangeless nut, ETFE for 1/8-in. OD tubing (includes ETFE ferrule; or order P-315 flangeless nut and P-300N ferrule separately)	1
Upchurch Scientific	P-623	Union, ETFE, for 1/8-in. OD tubing[3]	1
Upchurch Scientific	P-625	Male Luer to 1/4-28 male fitting, ETFE	1

[1]The reducer union selected depends on the size of the tubing of the inline groundwater pump system. Examples listed in the table include the reducer fitting for a ½-in. tube (figure 5.2.2.B–1) or a ¼-in. tube (figure 5.2.2.B–2).

[2]Tubing about 2 to 3 inches in length is needed for each fitting assembly.

[3]Alternatively, the P-631 union assembly includes two P-300N ferrules and a P-345 nut that connect the 1/8-in. tubing to the union.

When collecting surface-water samples for DAI LC-MS/MS analysis, use the following syringe-filter procedure:

1. Prepare a clean work surface by covering the field bench or table with a fresh sheet of aluminum foil. Wearing nitrile gloves:

    a. Place the composite sample, waste container, and the plastic bag containing the syringe, large-bore blunt needle, and disposable filter near the clean work surface. Change gloves.

    b. Open the plastic bag. Remove the syringe, needle, and syringe disk filter from the bag and their wrappings and place them and a sample container (amber glass vial) on clean foil.

2. Homogenize the composited sample following standard USGS water-quality protocols (NFM 5, section 5.1.1.A). Collect samples for inorganic analysis first.

    Use the Teflon churn to collect and homogenize a composite sample for DAI LC-MS/MS analysis. This facilitates direct withdrawal of the sample when using the required syringe and bore needle. If samples for inorganic analyses will be taken from the same churn, complete that sampling step first to avoid potential metal contamination of sample water from the bore needle. Alternatively, use separate churns.

3. Clean and condition filtration equipment by rinsing the equipment with sample:

    a. Attach needle to Luer-Lock fitting on the syringe by twisting the female end of the syringe onto the male Luer-Lock fitting of the needle.

        • Avoid touching the blunt needle that will be inserted into the sample.

        • **Hold only the plastic Luer-Lock fitting of the needle.**

    b. Submerge the needle in the sample (subsample or Teflon churn) and pull the plunger on the syringe to draw about 15 mL of sample water to rinse the syringe.

    c. Invert the syringe while carefully removing the needle and placing it on a clean piece of aluminum foil.

    d. Attach a filter to the syringe by pushing straight down and twisting the open female end of the syringe filter onto the male Luer-Lock fitting on the syringe to provide a secure fit.

    e. Slowly depress the plunger to force a sample-water rinse through the syringe and filter and into a waste container.

    f. Remove the filter and place it on the clean foil.

4. Carefully reattach the needle to the syringe and draw 20 mL of sample water into the syringe. Invert the syringe.

    a. Push the plunger to about the 15 mL (or other whole-number) mark.

    b. Remove the needle and reattach the rinsed filter, as described in steps 3c and 3d.

5. Invert the syringe-tip filter downward, press the plunger, and half-fill the 20-mL sample container (amber glass vial) with 10 mL of sample filtrate.

a. These samples are stored in a freezer at the NWQL, requiring that there be sufficient headspace to prevent the glass container from breaking.

b. If the samples have high suspended sediment, 15 mL of pesticide-grade blank water (PBW) can be used to clean and rinse the syringe and filter instead of sample (steps 1–3). Then, about 5 mL of sample should be used to condition the syringe and filter after the PBW rinse. Document in field notes any use of PBW (for example, to rinse and condition equipment).

c. If the syringe filter medium becomes clogged before a sufficient amount of sample has been filtered, replace it with a new syringe filter and repeat steps 1–5a until the designated volume of filtrate has been collected to half-fill the 20-mL container.

6. After the filtered sample has been collected, cap the container firmly.

   a. Dry the outside of the container and label it with the appropriate site ID number, date, time, and schedule number.

   b. Seal the sample in doubled zip-lock bags to prevent contact of the container with melting or melted ice.

7. Package samples with care in an ice-filled cooler (section 5.5) and ship overnight to the NWQL. Samples must remain chilled at 4±2 °C and unfrozen until received by the NWQL. Refer to NWQL Technical Memorandum 2011.01 (Zogorski, 2011) for shipping procedures for samples containing potential biohazards.

8. Discard (**do not reuse**) the filter, syringe, and blunt needle (the syringe, however, can be recycled with plastic recyclables). Other reusable items, such as a compositing device or beaker, need to be cleaned in preparation for use at the next site (refer to NFM 3 for cleaning procedures).

9. Document on field forms and in field notes the filtration procedures used.

When using a submersible pump to collect a groundwater sample for DAI LC-MS/MS analysis, select either Option A or Option B, below:

Samples must be collected and processed in a sample-processing chamber using USGS “clean hands/dirty hands” (CH/DH) techniques. When working in the chamber, use of elbow-length powderless nitrile gloves (instead of wrist-length gloves) is recommended to avoid contamination of samples for pharmaceutical analysis.

Option A: Direct connection between sample line and filter. Neither the disposable syringe nor the bore needle (needle) is used for this procedure.

1. Assemble the processing chamber, installing a clean chamber cover. Prepare a clean work surface and waste container within the chamber. Wearing elbow-length nitrile gloves:

   a. Place the sample container(s) (amber glass vial), precleaned reducer fittings (table 5.2.2.B–2), and bag containing the filter in the processing chamber.

   b. Remove the filter from the protective packaging and place on a clean work surface. Change gloves.

2. Using the manifold flow-valve system, follow USGS groundwater sampling protocols as directed in NFM 4, sections 4.2.3 and 4.2.4. Direct the flow of sample to and from the processing chamber and the syringe filter as needed to complete the following steps:

    a. Connect the precleaned reducer fittings inline to the discharge end of the pump tubing using reducer fittings consisting of a male Luer-Lock connector, a 1/8-in. union, a short length (2 to 3 in.) of 1/8-in. PFA (perfluoroalkoxy alkane) tubing, and a reducer union (table 5.2.2.B–2). The reducer union selected depends on the size of the tubing of the inline groundwater pump system. Examples shown in table 5.2.2.B–2 include reducer fittings for either a 1/2-in. tube (fig. 5.2.2.B–1) or a 1/4-in. tube (fig. 5.2.2.B–2).

    b. Purge air from the sample tubing, directing sample from the waste (discharge) line to the waste container.

    c. Reduce the rate of sample flow to about 50 to 100 mL/min.

    d. Without interrupting sample flow, connect the discharge end of the sample tubing to the syringe filter.

    e. Allow about 5 mL of sample to rinse and condition the syringe filter, discharging the rinsate to waste.

3. Maintaining a low and uniform rate of flow, collect about 10 mL of sample filtrate in a 20-mL sample vial (container).

    a. Samples are stored in a freezer at the NWQL and require sufficient headspace to prevent the glass container from breaking.

    b. If the syringe-filter medium becomes clogged before a sufficient amount of sample has been filtered, replace it with a new syringe filter and repeat steps 2 and 3.

4. After the filtered sample has been collected, cap the vial firmly.

    a. Dry the outside of the vial.

    b. Place a label on the vial with the appropriate site ID number, date, time, and schedule number.

    c. Place the sample vial in a foam sleeve and seal it inside doubled zip-lock bags to prevent contact of the vial with melting or melted ice.

5. Package samples with care in an ice-filled cooler (section 5.5) and ship overnight to the NWQL. Samples must remain chilled at 4±2 °C until they are received by the laboratory. (Samples should not be frozen.) Refer to NWQL Technical Memorandum 2011.01 (Zogorski, 2011) for shipping procedures for samples containing potential biohazards.

6. Discard the syringe filter appropriately (do not reuse). Reusable equipment, such as the sample tubing and reducer fittings used on the filter and the submersible pump must be cleaned in preparation for use at the next site.

7. Document on field forms and in field notes the filtration procedures used.

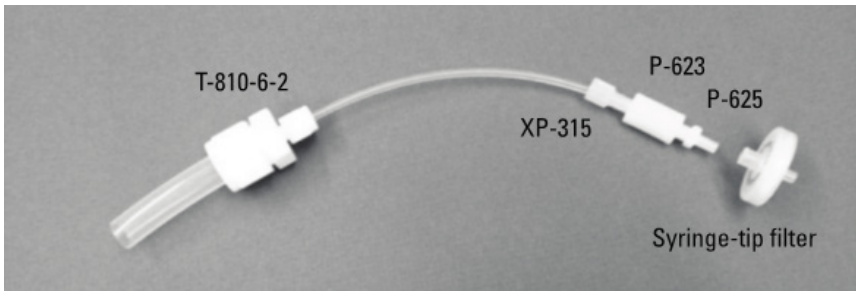

Figure 5.2.2.B–1. Reducer fittings to connect a syringe-tip filter to a 1/2-inch outer diameter tube (see table 5.2.2.B–2).

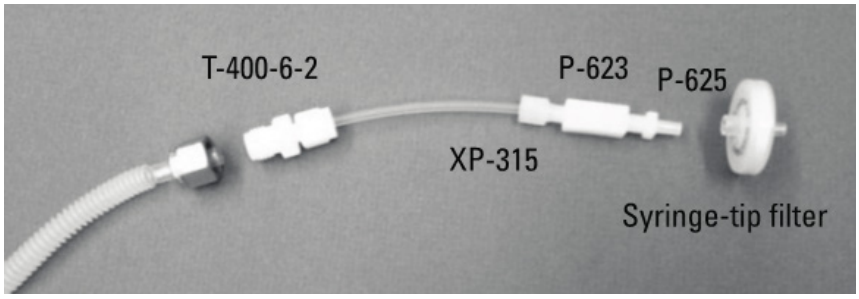

Figure 5.2.2.B–2. Reducer fittings to connect a syringe-tip filter to a 1/4-inch Swagelok nut and 1/2-inch tube (see table 5.2.2.B–2).

Option B: Using the syringe to collect the sample, either with or without the needle (figs. 5.2.2.B–3, 5.2.2.B–4, 5.2.2.B–5).

1. Assemble the processing chamber, installing a clean chamber cover. Prepare a clean work surface and waste container within the chamber. Ensure that the groundwater rate of flow to the processing chamber has been reduced to about 50 to 100 mL/min (refer to step 2 of the Option A groundwater sampling procedure). Select either procedure 2A or 2B below.

2. Syringe procedures:

   A. ***Using the syringe with a needle*** (figs. 5.2.2.B–3 and 5.2.2.B–4):

      a. Wearing nitrile gloves, place the sample container(s) (amber glass vial) in the processing chamber. Remove the syringe, needle, and filter from the protective packaging and place on a clean work surface. Change gloves.

      b. Attach the bore needle to the syringe and start the flow of groundwater into the chamber. Rinse the exterior of the syringe (or syringe and needle) (fig. 5.2.2.B–3).

      c. Taking care that the needle does not contact the sample tubing, insert the tip of the needle into the stream of water flowing into the chamber (fig. 5.2.2.B–4). To rinse and condition the syringe filter, syringe and needle, gently pull back on the syringe plunger and collect about 15 to 20 mL of water. (Skip to step 3.)

B. ***Using the syringe without a needle*** (figs. 5.2.2.B–3 and 5.2.2.B–5):

a. Place the sample container(s) in the processing chamber. Remove the syringe and filter from the protective packaging and place on a clean work surface. Change gloves.

b. Rinse the syringe casing with flowing groundwater. Insert the tip of the syringe into water flowing from the end of the sample tubing.

c. To rinse and condition the syringe filter and syringe, gently pull back on the syringe plunger and collect about 15 to 20 mL of water.

Note: If the sample in the syringe contains a sizable air bubble, repeat the collection process to reduce the amount of air introduced to the sample.

3. Attach the filter to the syringe, invert, and slowly expel 5 mL of sample to rinse and condition the filter.

4. Holding the syringe-with-filter over a sample container, depress the plunger slowly to half-fill the vial with 10 mL of sample.

5. Cap the container securely and wipe dry. Fill out the sample label, check it for accuracy, and attach the label.

6. Prepare the sample for shipping—Wrap in a protective sleeve and ship on ice overnight to the NWQL.

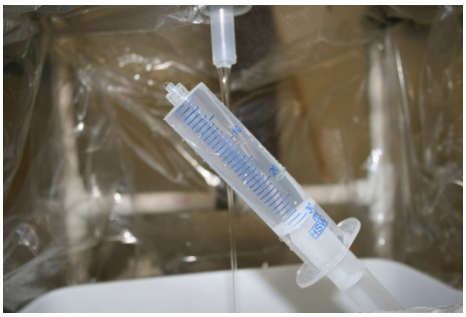

Figure 5.2.2.B–3. Groundwater flowing into a processing chamber is used to rinse the syringe casing. (Photograph by Michael Manning, U.S. Geological Survey.)

Figure 5.2.2.B–4. Use the bore needle to obtain groundwater for rinsing and conditioning the bore needle and syringe. (Photograph taken inside a sample-processing chamber by Michael Manning, U.S. Geological Survey.)

Figure 5.2.2.B–5. Groundwater flowing directly into a syringe. (Photograph taken inside a sample-processing chamber by Michael Manning, U.S. Geological Survey.)

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INSTRUCTIONS FOR FIELD USE OF SPIKE SOLUTIONS FOR ORGANIC-ANALYTE SAMPLES 5.3.2

By **Mark W. Sandstrom and James A. Lewis**

A matrix spike is a type of quality-control sample used to evaluate the effects of sample matrices on the performance of an analytical method. Matrix spikes are used most often for quality control of organic-analyte samples because the analytical methods for organic-analyte samples involve extraction and analysis steps that can be affected by other chemicals in the sample (referred to as the sample matrix). For example, naturally occurring organic matter can be co-extracted with the organic analytes in the sample and interfere with the gas chromatographic analysis. For some methods, extreme levels of pH, ionic strength, or the concentration of naturally occurring organic matter in the sample enhance the detector response, resulting in biased results for the analyte concentration.

Matrix spikes can be prepared at the sampling site or in the laboratory. If spiked at the sampling site, matrix spikes are called **field matrix spikes**. If spiked at the USGS National Water-Quality Laboratory (NWQL), matrix spikes are called **laboratory matrix spikes**. Field matrix spikes are used to monitor the stability of the organic analytes in the sample bottles, from the time of collection at the site to the time of extraction and analysis at the laboratory, in addition to determining potential bias from the sample matrix. Organic analytes can be degraded by microorganisms in the sample, or undergo chemical reactions such as oxidation or hydrolysis. Many organic-analyte sampling methods do not use a preservative to prevent sample degradation and loss because the preservatives can negatively affect some (although not all) of the analytes. Instead, samples are shipped to the laboratory and extracted within a short time period. This time period is called the sample holding time, and is determined by the laboratory to represent a reasonable time for samples to be shipped and stored until analysis, with minimal change in analyte concentration. **Field matrix spikes can be used to verify that the sample holding times were sufficient for the sites sampled during the course of a project.**

This section of NFM5 provides detailed instructions for using organic-analyte spike solutions that meet the criteria for NWQL methods as part of the USGS quality-assurance and quality-control (QA/QC) protocol for incorporating field spikes into water-quality investigations. Information obtained from the analysis of matrix-spike samples can be used to determine the recovery, bias, and variability of analytes based on sampling conditions encountered at specific sites. Field spiking is not designed to replace routine laboratory QC programs or the Organic Blind Sample Project that currently is administered by the USGS Branch of Quality Systems (http://bqs.usgs.gov/obsp/). Although field spiking is a useful component of quality assurance for all laboratories used by the USGS, the instructions in this document were developed specifically for the analytical methods used at the NWQL and for the spike solutions provided by the NWQL through One-Stop Shopping (the NWQL-supported national field supply service (NFSS) for USGS employees). The number and type of matrix spike samples collected depend on the data-quality objectives and the requirements of individual projects. National programs, such as the National Water-Quality Assessment (NAWQA) Program, might have additional requirements.

- Laboratory matrix spikes provide information about bias from sample matrices.
- Field matrix spikes (samples that are spiked at the field site) provide information about bias from degradation during shipping and storage, in addition to bias from the sample matrices.

Field staff might collect a combination of a laboratory spike (for water samples only; not for solid phase extraction cartridges shipped to the laboratory), a field spike, and a field-spike replicate to provide the most information relating to the performance of the overall method. The relative percent difference between the duplicate spiked-sample results is calculated and used to assess variability at the spike concentration. Some projects may determine that only laboratory spikes, or only one field spike, will provide sufficient data for the analytes of interest. **In all cases, field staff must collect a regular (unspiked) sample along with the spiked sample(s) to determine the ambient levels of any organic analytes in the samples.**

5.3.2.A Supplies and Materials

Be sure to procure the equipment and supplies required for sample matrix spiking before the sampling trip.

Spike kits can be assembled from components listed in table 5.3.2-1 and can be obtained from One-Stop Shopping or from commercial laboratory-supply vendors. The micropipette and Teflon® squeeze bottle can be re-used. **Matrix spike solutions and glass capillaries are used only once.** About 30 glass capillaries are contained in a N1300 kit, enough to perform 30 spikes. The composition of each spike solution is described in separate Certificates of Analysis, available to USGS employees by laboratory schedule from the NWQL Intranet Web site (*click on "Technical Information" and scroll to the link "Organic Spiking Solutions"*).

Spike solutions are prepared and distributed by the NWQL (either through USGS One-Stop Shopping or by special request to NWQL LabHelp for those schedules not listed in One-Stop Shopping). Solutions in a 500-microliter (µL) methanol or ethyl acetate solution are usually supplied in flame-sealed, 2-milliliter (mL) amber glass ampoules, although in some cases screw-cap 2-mL vials are used. For most analytical schedules, concentrations of the spike solutions are designed to provide 0.1 microgram per liter (µg/L) of each analyte in a water sample by injecting 100 µL of the spike solution into a 1-L filtered water sample.

- **Use the spike solutions as soon as possible after opening to prevent changes in concentration caused by evaporation of the solvent.**
- **Do not save an unused portion of the spike solution for re-use** (*see section 5.3.2.F on disposal of used spiking materials).*
- **Keep matrix-spike ampoules chilled at less than (<) 6°C at all times—even in the field.** Many of the compounds included in the spike solutions are unstable and can degrade rapidly at room temperature. **Store the ampoules in a freezer (preferred) or refrigerator, and on ice in a cooler during the site visit.**

CAUTION: Perform spiking in a well-ventilated area to avoid inhaling vapors from the spike solution, and wear gloves and other protective gear to avoid contact with skin and eyes. Organic-analyte spike solutions contain toxic compounds that are either known to cause or are suspected of causing cancer and other diseases.

Table 5.3.2–1. Equipment and Supplies for Preparing Matrix Spikes for Organic-Analyte Samples.

[µL, microliter; mL, milliliter; oz, ounce; na, not available from One-Stop Shopping—purchase on the open market]

One-Stop Item Number	Description
N1370	Pipette, fixed volume, 100 µL (also called Microdispenser)
N1300	Kit, glass capillaries, baked/replacement, 100 µL (kit contains 30 capillaries)
N1124	Bottle, polyethylene, natural, 500 mL/16 oz, wide-mouth, with cap, sold individually (used for waste)
Disposable Gloves	
Q520FLD	Glove, Softwear®, white, nitrile, small
Q522FLD	Glove, Softwear, white, nitrile, medium
Q524FLD	Glove, Softwear, white, nitrile, large
Q526FLD	Glove, Softwear, white, nitrile, extra large
Organic-Analyte Spike Solutions for National Water Quality Laboratory (NWQL) Analytical Schedules	
N1420	Field spike solution, schedules 2003, 2032, 2033
N1430	Field spike solution, schedules 1433 and 4433
N1470	Field spike solution, schedules 2001 and 2010
N1490	Field spike solution, schedule 2060
N1510	Surrogate solution, schedule 2010
Miscellaneous Equipment/Supplies	
na	Teflon® squeeze bottle, 250-mL (for dispensing methanol rinse solvent)
na	American Chemical Society (ACS) pesticide-grade (high purity) methanol
na	Department of Transportation (DOT) Exemption packaging for hazardous waste shipping to contain waste material generated at a field site; for example, see http://hazplus.com/.
na	Breakers for removing ampoule tips

5.3.2.B Unpacking Equipment and Spike Preparations

Spike solutions should be placed into chilled storage promptly after arrival from the NWQL (for example, in a refrigerator or on ice in a cooler). Glass ampoules containing spike solutions can be chilled, stored, and transported to the field in their original containers; however, if the original containers are too bulky, glass ampoules can be placed inside of a zip-top plastic storage bag cushioned by foam or bubble wrap. When unpacking glass ampoules, work over a tray, shallow box, or similar surface to minimize the risk of ampoules breaking or rolling off of a countertop.

The spike solutions are assigned a 5-digit National Water Information System (NWIS) lot number for tracing the contents and concentrations of the spike solutions. The lot number, analytical schedule, and expiration date are listed on the ampoule label. Verify that the correct product was shipped, and check the expiration date before use. One current (2009) analytical schedule (Schedule 2060) has a spike solution that is shipped in two glass ampoules (an acid and a base fraction); both ampoules are used to prepare a spike for Schedule 2060.

The glass capillaries used to transfer the spike solution should be stored inside their sealed container (40-mL glass vial with screw cap), and the micropipette should be stored in its padded box inside doubled zip-top plastic storage bags or a dedicated storage container. The Teflon tip of the micropipette should be protected from contamination with aluminum foil or a glass vial. Spiking equipment should be stored away from extreme temperatures or acid vapors, which can lead to degradation of the rubber O-ring in the pipette.

A freezer is recommended for long-term storage of spike solutions.

5.3.2.C Sample Coding and Bottle Labeling

Field staff may wish to collect additional (replicate) spikes or laboratory spikes. If so, replicates must be clearly labeled to minimize confusion during login, and to prevent respiking of the samples in the laboratory. Identify on the bottle labels the field-spike samples and field-spike replicate samples as "FS" and "FSR," and the sample to be spiked in the laboratory as "LS."

Place the laboratory-spike ampoule into the sturdy plastic vial that is supplied from the laboratory and secure it with a rubber band (do not use tape) either to the container of the corresponding sample or in the protective foam sleeve with the sample bottle.

Laboratory Login and Analytical Services Request Form 5.3.2.D

Review of data entered into the Laboratory Information Management System (LIMS) enables the NWQL to monitor results of the spiking program.

Use the following procedures to fill out the laboratory analytical services request form:

1. For both field and laboratory spikes, enter "1" for "Sample Type" and either "WSQ" (surface water) or "WGQ" (ground water) for "Sample Medium."
2. In the fields for "Parameter Code (P Code)" and "Value" enter parameter code "99106" and a value of either "10.00" for field spikes or "20.00" for laboratory spikes.
3. In the fields for "Parameter Code (P Code)" and "Value" enter parameter "99104" (Reference Material or Spike Source, Code Number) and the 5-digit NWIS-I lot number—located on the vial label—in order to track lot numbers in the NWIS-I database. The value for NWQL for parameter "99103" is "10."
4. Under "Comments" indicate whether the sample was spiked in the field or is to be spiked at the laboratory.

The additional NWIS/QWDATA coding required to completely identify spiked samples for the NAWQA Program is provided in the NAWQA water-quality sample-coding outline, found on the NAWQA Intranet Web page under "Field Technical Support" (*click on "SWQA Site and Sample Coding"*).

Laboratory spikes and field spikes require additional, separate Analytical Services Request (login) forms. Because the database currently in use at the NWQL does not allow for more than one sample with the same combination of schedule, station ID, date, and time, it is necessary to vary at least one of these fields (for example, the time) within a set of samples. This usually is done by adding one minute to the time of collection designated for each of the spikes.

Whenever samples are collected to be field and (or) laboratory spiked it is important to collect an unspiked environmental sample for analysis to determine the ambient concentrations of any organic analytes that might be present. This sample should be coded as a regular sample, and the parameter code "99111" can be used to indicate "QC sample associated with this environmental sample."

5.3.2.E Field Spiking Instructions

Use the following procedure when preparing a field-matrix spike sample:

1. Put on disposable gloves. Wearing gloves is a reminder to not handle the glass capillary tip, and will protect hands from accidental spills of methanol or spiking solutions.
2. Wear protective eyewear to protect eyes from accidental splashes of methanol, spike solutions, or shards of broken glass.
3. Loosen (but do not remove) the black knurled nut (the collet) on the micropipette (fig. 5.3.2–1). The nut compresses a rubber O-ring that grips the glass capillary.
4. Position the orange Teflon tip of the micropipette plunger over the wide-mouth polyethylene jar that is being used as a waste container and rinse the tip with a few drops of methanol from the squeeze bottle. This will lubricate the tip so it will slide through the glass capillary more easily. Gently shake off any residual methanol left on the tip. Be careful not to drip methanol on the O-ring, as the methanol could cause corroding.
   - Remove the cap from the vial containing the precleaned glass capillaries. The glass capillaries have colored bands inscribed on the outside of the glass—thin alignment bands and a wider insertion band.
   - The alignment bands are used to check the position of the Teflon tip inside the glass capillary, while the wider insertion band is used to indicate that the end of the capillary has been fire polished to prevent damage to the Teflon tips when inserted into the glass capillary. The capillaries are shipped as a kit in a 40-mL glass vial with their wide band near the top (open) end of vial.

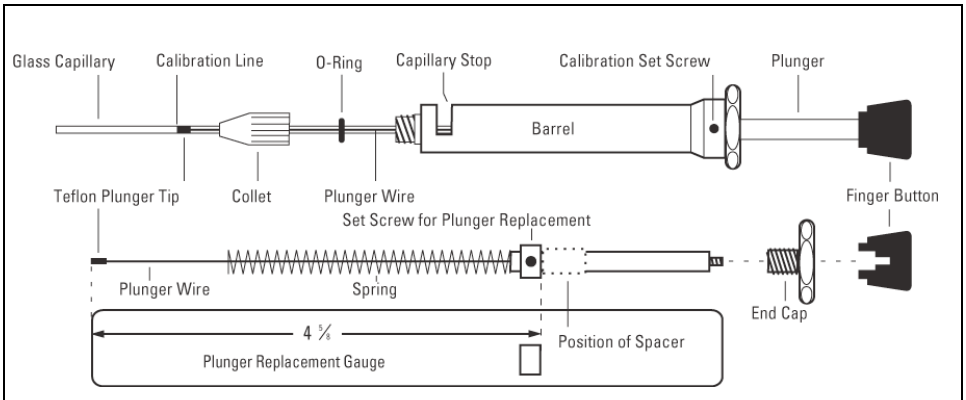

Figure 5.3.2–1. Diagram of a Drummond fixed-volume micropipette and available replacement parts. (Diagram provided by Drummond Scientific Company and published with permission.)

CAUTION: Organic-analyte spike solutions contain toxic compounds. Perform spiking in a well-ventilated area; avoid inhaling the fumes, and wear gloves at all times. Take adequate precautions to prevent contact with eyes and skin.

5. Insert the orange Teflon tip of the plunger into a glass capillary, wide alignment band first. The Teflon tip of the plunger wire can be partially inserted into a capillary while the tip is in the vial. This ensures that the Teflon tip always is inserted into the polished end of the glass capillary and minimizes handling of the glass capillary, which might contaminate the capillary (and the sample).
6. Remove the attached glass capillary from the vial and continue to slip the capillary through the O-ring and black nut until it rests against the stop on the barrel of the micropipette. When the capillary is properly seated, the lower alignment band will be adjacent to the end of the Teflon tip. The volume inside the capillary is 100 µL.
7. Tighten the nut firmly. Press the button of the micropipette and verify that the orange Teflon tip of the plunger slides through the glass capillary and exits out the end. If the glass capillary is not seated properly, the plunger tip will not exit the end of the glass capillary.
8. Place the micropipette on a clean aluminum foil-covered surface while the spike solution ampoule/vial is opened. Be careful to prevent contamination of the glass capillary.
9. Loosen the cap on the sample bottle.
10. Break open the ampoule containing the spike solution (or remove the screw-cap from the vial). As the ampoule is snapped open, aim the break away from the face to avoid breathing any vapors expelled. **RECOMMENDED: As a safety measure, use ampoule-tip "breakers"; these inexpensive tools are readily available and can be purchased from laboratory and medical supply vendors.**
11. Depress fully the finger button on the end of the micropipette and then immerse the capillary tip into the spike solution.
12. Release the finger button slowly as the micropipette is filled.
13. Withdraw the capillary from the spike solution. Make sure the capillary is full and that no droplets are retained on the outside of the capillary. **If the capillary is not full, return the capillary tip to the spike solution and repeat the capillary filling (steps 11 and 12 above).**
14. Remove the sample bottle cap and immerse the capillary tip into the sample, with the tip about 1 to 2 centimeters (cm) below the surface of the sample.
15. Expel the spike solution by rapidly depressing the finger button.
16. After dispensing the spike solution, with the button still depressed, withdraw the tip from the sample and touch the tip to the side of the bottle to allow any water drops to drain into the sample.
17. Replace and securely tighten the cap on the sample bottle; swirl the sample bottle to thoroughly mix.
18. Loosen the black nut one-half turn and remove the capillary from the micropipette.
19. Place the used capillary in a wide-mouth polyethylene bottle labeled for waste disposal.
20. Rinse the Teflon tip of the plunger with methanol to prepare for the next spike. Position the orange Teflon tip of the micropipette plunger over the wide-mouth polyethylene jar (the waste container) and rinse with a stream of methanol from the Teflon squeeze bottle. Be careful to prevent methanol from contacting the rubber O-ring on the micropipette plunger.

21. Use a new glass capillary for each spike. If spiking more than one matrix sample, start again with Step 3 and repeat the same process using 100 µL of the spike solution for the second water sample bottle. If a spike solution is contained in two glass ampoules (for example, schedule 2060), start again with Step 3, using the second ampoule for the same water sample bottle.
22. Place used ampoules/vials and any unused spike solution into a wide-mouth polyethylene waste bottle that is labeled for disposal. Ampoules contain toxic solutions that must be disposed of properly. Recommended: Place the polyethylene waste bottle inside a Hazardous Waste shipping container for safe transport of the waste material from the field site to the Science Center.
23. The spike solutions must be used at one site only. The solutions are not meant to be re-used after the ampoule has been opened.

5.3.2.F Disposal of Used Spiking Materials

When the project or field work has been completed, the field staff must carefully dispose of all waste materials in accordance with current local area or USGS Science Center guidelines for disposal of hazardous materials. Used spiking materials cannot be returned to the NWQL for disposal. For USGS employees, the NWQL Rapi-Note 03-043 provides additional information.

5.3.2.G Shipping Reminders

Field personnel are reminded to:

- Ship spiked samples to the laboratory so they arrive within the recommended holding time. USGS personnel can access holding-time information through the Intranet page of the NWQL by clicking on “Technical Information” and the “Holding time Table.”
- Ship samples on ice to maintain the sample temperature at < 6°C.

WASTEWATER, PHARMACEUTICAL, AND ANTIBIOTIC COMPOUNDS 5.6.1.F

M.E. Lewis and S.D. Zaugg

The USGS differentiates between samples collected for analysis of wastewater compounds and those collected for analysis of pharmaceutical and antibiotic compounds, based on the analytical schedule for the laboratory method.[1] Currently, only the wastewater laboratory method for field-filtered samples (SH1433) is an approved, routine (production) method. (The unfiltered wastewater method LC 8033 also is available but requires a proposal for custom analysis.) At this time, analysis of samples for pharmaceutical and antibiotic compounds is confined to research studies and is available only on a custom basis.

To collect and process surface-water and ground-water samples that will be analyzed for concentrations of wastewater, pharmaceutical, and antibiotic compounds, the standard USGS procedures for collecting and filtering organic compounds are used (see NFM 4, 5.1, 5.2.2). However, special considerations related to personal safety and to sample contamination are required.

Samples collected for analysis of these compounds may be collected directly from sources of raw or treated wastewater. Sources of wastewater include treated and untreated domestic sewage, leaking septic systems or sewer lines, sanitary sewer overflows, and runoff from animal feeding operations. **Handling of such samples can expose personnel to pathogenic microorganisms, and therefore requires strict adherence to safety protocols.**

[1]The compounds included in a given laboratory schedule are subject to change and should be checked when planning a sampling activity that involves collecting data on wastewater, pharmaceutical, or antibiotic compounds.

Samples collected for analysis of wastewater, pharmaceutical, and antibiotic compounds are susceptible to contamination because they are ubiquitous in daily use. **To ensure sample integrity, field personnel should avoid contact with or consumption of products that contain the compounds targeted for analysis, and must adhere scrupulously to equipment-cleaning, equipment-handling, sample-processing, and sample-handling protocols**.

CAUTION: Raw or treated wastewater samples can contain microorganisms harmful to human health—use safe handling protocols.

- **Adhere to safety protocols.** The following precautions must be followed by field personnel when collecting, processing, or handling raw or treated wastewater samples for analysis of wastewater, pharmaceutical, or antibiotic compounds:
  - Be familiar with the basic procedures to minimize exposure to and effects from contaminated water, as described in NFM 9.7.
  - Receive proper immunizations before engaging in field activities and consult with your safety officer on this issue.
  - Avoid direct contact with sewage and other types of wastewater and with equipment still contaminated through contact with the sample or source water.
  - Avoid breathing in sewage and wastewater fumes or mist.
  - Do not use workspace surfaces or equipment that have come into contact with polluted water until they have been decontaminated. Use only those decontamination procedures that are described below under "Prevent sample contamination."

► **Prevent sample contamination:**

— On the day of sampling activities, avoid contact with or consumption of the products listed below. Where contact with or consumption of these products is unavoidable, the collection of field blanks is strongly recommended.

Wastewater compounds

- Soaps and detergents, including antibacterial cleansers
- DEET (active ingredient in most insect repellents)
- Fragrances (cologne, aftershave, perfume)
- Sunscreen
- Animal or human urine or excrement
- Caffeine (coffee, tea, colas)
- Tobacco

Pharmaceutical compounds

- Prescription drugs, medications, and hormonal substances
- Over-the-counter medications
- Selected human antibiotics

Antibiotics

- Human antibiotics
- Veterinary antibiotics

— Wear powderless nitrile laboratory gloves during sampling and processing. Change to clean gloves with each change in activity or potential glove contamination.

— Avoid breathing directly over open samples/equipment.

— Avoid direct contact between yourself (including clothing) and the sample, sampling device, and processing equipment. Clothing is a source of detergents, fragrances, and fire retardants.

- Thoroughly field rinse and seal in a plastic bag all reusable equipment that comes in contact with sewage until the equipment can be properly decontaminated and disinfected (NFM 3.2.2).
- Clean scrupulously all workspace surfaces that come into contact with sewage—use a non-antibacterial soap[2] and water, followed by wiping all potentially contaminated sufaces with a clean, disposable isopropyl alcohol (70-90 percent) pad.
- Avoid any actions at the field site that result in the disposal or release of wastewater and pharmaceutical substances.

► **Implement quality control.** Quality-control samples are a required, integral part of water-quality investigations. As previously noted, samples for analysis of wastewater, pharmaceutical, and antibiotic compounds are vulnerable to contamination.

- Check your quality-control plan for instructions on the collection of field blanks and replicates for these sample types. Although the specific type, number, and distribution of quality-control samples are determined by the design and data-quality requirements of the study (NFM 4.3), field blanks are processed more frequently for these samples than for most other sample types.
- When using a a custom analysis, consult with the laboratory analysts for quality-control recommendations.
- Process an initial field blank to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment. Distribute subsequent field blanks areally and temporally to meet data-quality requirements of the project.
- Use either pesticide- or VOC-grade blank water as the source solution for the field blanks.

[2]The laboratory analysis of wastewater includes triclosan, an active ingredient in most antibacterial soaps. Triclosan is also commonly found in some deodorants, toothpastes, mouthwashes, skin creams, lotions, laundry detergents, and dish soaps.

— The analytical methods used for pharmaceuticals and antibiotics are currently unapproved and are available only on a cutsom basis for research projects. It is reasonable to assume that blank water tested and certified contaminant free for approved organic constituent methods is an appropirate source solution for field blanks for these unapproved methods; however, a more rigorous approach would be to include a source solution blank as an integral part of the project quality-control plan.

— Process the field blanks in the same manner and under the same environmental conditions as the environmental sample (NFM 4.3.1.B).

Wastewater, pharmaceutical, and antibiotic samples are vulnerable to contamination and thus require rigorous quality control, usually by processing field and source-solution blanks.

► **When planning sampling activities that will result in a request for a custom analysis:**

— Contact the NWQL in Lakewood, Colorado, (http://nwql.usgs.gov/) before collecting any samples for unfiltered wastewater-compound analysis or pharmaceutical-compound analysis.

— Check One-Stop Shopping for supplies for USGS projects.

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— Contact the Organic Geochemistry Laboratory in Lawrence, Kansas, (http://ks.water.usgs.gov/Kansas/reslab/) before collecting any samples for antibiotics that will be analyzed using this laboratory's methods.

Replacement page, 11/19/2004

To collect and process samples:

1. Order and assemble all equipment. Select sampling and processing equipment made of fluorocarbon polymers, glass, aluminum, or stainless steel. Avoid equipment made of Tygon®, polyethylene, or other plastics.

2. Clean equipment thoroughly before use, following the general protocols for organic-compound samples described in NFM 3.2.2, but with the following caveats:

   - Use non-antibacterial detergents.
   - Take extra care to ensure that equipment is copiously rinsed with deionized water (DIW) after the detergent wash—detergents are a source of interference in the analysis of pharmaceutical compounds and may include a target analyte (triclosan) of the wastewater analytical method.
   - Follow the DIW rinse with a methanol rinse. Collect the used methanol solution into an appropriate container for disposal.
   - Do not clean or field-rinse the baked-glass sample bottles obtained from OWQRL or another laboratory.

3. Collect and process the samples using methods appropriate for organic compounds, as described in NFM 4 and 5.2.2. Use laboratory-baked, brown (amber) glass sample bottles.

   - For wastewater and pharmaceuticals being shipped to the NWQL for analysis, use 1-L GCC bottles.
   - For antibiotic samples being shipped to the OWQRL for analysis, use 1-L GCC bottles.
   - For antibiotic samples being shipped to the Lawrence Organic Geochemistry Laboratory for analysis, use two 125-mL baked-glass bottles with Teflon® caps per sample.

4. Label bottles with site ID (identifier), date, time, sample type ("filtered" or "unfiltered"), and laboratory code or schedule number.

   a. For samples being shipped to the NWQL:

      - Wastewater, field-filtered – Label sample bottle "GCC–-SH 1433"
      - Wastewater, raw – Label sample bottle "GCC–LC 8033" (add this laboratory code to the Analytical Services Request (ASR) form: **currently this is a custom analysis**)
      - Pharmaceuticals – Label sample bottle "LC9003"

   b. For antibiotic-analysis samples being shipped to the OWQRL – Label sample bottle "Antibiotics"

   c. For antibiotic-analysis samples being shipped to Lawrence, Kansas – Label sample bottles "LC-AN"

5. If collecting wholewater samples for custom wastewater analysis – Fill the 1-L GCC bottle to the shoulder.

6. When collecting filtered samples for wastewater, pharmaceutical, or antibiotic analyses – Filter the samples at the field site.

   - Pass samples through a 0.7-µm nominal pore-size glass microfiber plate filter (GF/F grade), following the procedures for organic compounds described in NFM 5.2.2.A.
   - Fill the 1-L GCC or two 125-mL baked-glass bottles to the shoulder.

7. For samples collected from polluted water, decontaminate the exterior of bottles:

   a. Rinse bottles with copious amounts of water.

   b. Wipe each bottle with a clean, disposable isopropyl alcohol (70-90 percent) pad.

   c. Rinse off each bottle with water.

8. Keep the samples chilled to 4°C or less until they are prepared for shipping.

9. After sample collection and processing, use a non-antibacterial soap and water to thoroughly clean any workspace surfaces that have come into contact with polluted water. Follow the cleaning by decontaminating the workspace with isopropyl alcohol. **Do not use a bleach solution for decontamination of surfaces that come in contact with samples, since any bleach residue will degrade target analytes**.

To ship the sample(s):

1. For raw or treated wastewater, use the following precautions when packing and shipping, as these samples can pose a health hazard to field and laboratory personnel.

   a. Decontaminate any sample bottles containing raw or treated wastewater as described in step 7 above.

   b. Check bottle cap to ensure a tight closure.

   c. Place each bottle inside a foam sleeve and then place bottles into a ziplock bag along with four 3M high-capacity chemical sorbent pads (pads are available from Lab Safety and Supply at www.labsafety.com). Seal the bag.

   d. Place the sealed bag inside two additional ziplock bags (a total of three bags) and seal each bag.

   e. Clearly note in the "Login Comments" section of the ASR form "SAMPLE CONTAINS RAW OR TREATED SEWAGE. HANDLE WITH CARE." Sampling staff or shipping staff should notify the laboratory login staff by telephone or e-mail of the expected delivery of these samples, in advance of their arrival at the lab.

2. For all other samples,

   a. Check that sample bottles are securely capped.

   b. Check that sample bottles are correctly labeled and match the information shown on the ASR form.

   c. Pack all samples in ice to maintain a temperature of or below 4°C without freezing, using standard procedures (NFM 5.5.3 - 5.5.4). Check that the ASR form has been properly sealed in doubled plastic bags and included with the samples.

3. Ship all samples to the laboratory via overnight delivery.

CONSTITUENT SPECIES 5.6.4

ARSENIC SPECIATION 5.6.4.A

By **J.R. Garbarino, M.J. Lewis, and A.J. Bednar**

The speciation method used at the USGS National Water Quality Laboratory (NWQL), Lab Code LC 3142[1], uses liquid chromatography to separate inorganic and organic arsenic species and inductively coupled plasma-mass spectrometry (ICP-MS) to measure the associated arsenic concentration . When using this speciation method, prior knowledge is needed of the major-cation concentrations present in the filtered sample. The major-cation data are necessary to determine (1) the volume of ethylenediaminetetraacetic acid (EDTA) that will be required for sample preservation, and (2) if sample dilution is required. The necessity for major-ion data is related to the amount of sample preservative (EDTA) that is required.

TECHNICAL NOTE:
This speciation method (LC 3142) uses a strong anion exchange column and high-performance liquid chromatography to separate inorganic (arsenite and arsenate) and organic arsenic species (monomethylarsonate, dimethylarsinate) in a filtered water sample. As the species elute from the column, the corresponding arsenic concentration is determined using ICP–MS.

All samples must be collected and filtered using standard USGS procedures, as described in NFM 4 and NFM 5, respectively.

- **Laboratory-speciation method** (NWQL Lab Code 3142)

  - Select Lab Code 3142 to determine concentrations of arsenite (As (III)), arsenate (As (V)), monomethylarsonate (MMA), dimethylarsinate (DMA).[2]
  - Samples must be collected in an opaque sample bottle (One-Stop #N1615).
  - Sample matrix information (major-cation concentrations) is needed to determine the volume of EDTA to be added to preserve the sample.

The laboratory arsenic speciation method can be affected by the precipitation of metal oxides. Many suboxic or anoxic ground-water samples having arsenic concentrations greater than the USEPA 10-µg/L drinking-water standard also can contain substantial concentrations of reduced aluminum, iron, or manganese. Oxidation of these metal species during sample collection and processing produces metal-oxide precipitates that can sorb arsenic, resulting in negatively biased data. Furthermore, arsenite can be oxidized to arsenate by photolytically produced free radicals; therefore, the exposure of the sample to light also should be minimized.

- Exposure of the sample to air and sunlight should be minimized to prevent metal-oxide precipitation.

- **EDTA must be added immediately after sample filtration**.

[1] The following NWQL laboratory schedules (LS) were replaced by LC 3142 as of April 1, 2010: LS1729, LS1730, LS1731, and LS1732.
[2] For a discussion of other methods for As(III)/As(V) species analysis, see McCleskey and others, 2004.

Quality Control

Collection and analysis of quality-control samples are required as an integral part of all USGS water-quality investigations. The final types, number, and distribution of quality-control samples generally are determined according to the design and data-quality requirements of the study (NFM 4.3).

The general recommendation for studies collecting arsenic speciation data is to collect, at a minimum, a set of blank, replicate, and spike QC samples with every 20 environmental samples, as follows:

1. Process an initial field blank to evaluate the potential for contamination associated with the field methods and materials used, and the sampling environment. Distribute subsequent field blanks to address field-site concerns, the sampling timeframe, and data-quality requirements.
   - Use inorganic (IBW) blank water as the source solution for field blanks (table 5.6.4.A—1).
   - Process field blanks in the same manner and under the same environmental conditions as environmental samples (NFM 4.3.1.B). Take precautions to limit exposure of samples to air (NFM 4.0.3).

2. Collect and process replicate environmental samples to evaluate variability of the sampling, sample processing, and analytical measurement.
   - Duplicate or triplicate samples are collected and processed one after the other and in the same manner as the other environmental samples.
   - An additional replicate sample is collected and processed for use as a field spike.

3. Process an initial field-spike sample for an evaluation of matrix effects. Distribute subsequent field-spike samples to address field-site concerns, the sampling timeframe, and data-quality requirements.
   - Use one of the replicate samples that was processed as the spike sample.
   - Always submit the spike sample for analysis along with an unspiked (duplicate) sample.

   a. Using a 100-µL micropipet and a clean micropipet glass bore or disposable plastic tip, dispense the spike solution into the replicate sample (table 5.6.4.A—1).
   b. Record spiking information on the laboratory-speciation method worksheet (fig. 5.6.4.A—1) so that the percentage recovery can be calculated.

Calculation of diluent and EDTA volumes

The volume of EDTA preservative added to the sample depends on the estimated cation concentration of the sample filtrate.

To determine the volume of EDTA needed to preserve samples (NWQL LC 3142), estimate the cumulative concentration of major cations in the sample, as follows:

1. Estimate the concentration of cations in the sample using historical data for the same site or a representative site, if available.

2. To calculate the volume of 250 mM (millimolar) EDTA required for a 10-mL sample:

$$V_{EDTA} = 4.0(10^{6}) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8\ (10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$$

where:

V_{EDTA} = microliters of 250-mM EDTA required for a 10-mL sample
Al = dissolved aluminum concentration, in µg/L as Al
Fe = dissolved iron concentration, in µg/L as Fe
Mn = dissolved manganese concentration, in µg/L as Mn
Ca = dissolved calcium concentration, in mg/L as Ca
Mg = dissolved magnesium concentration, in mg/L as Mg
Sr = dissolved strontium concentration, in µg/L as Sr

3. If V_{EDTA} is less than 100 µL, add 100 µL of EDTA to the sample.

4. Record the volume of EDTA added to the sample on the worksheet (fig. 5.6.4.A—1). If the EDTA volume is not provided, it will be assumed that 100 µL was added.

Sample Processing for Laboratory Arsenic-Speciation Method

Equipment for sample collection and processing should be cleaned according to USGS protocols for inorganic-constituent sampling (NFM 3.2.1). If an acid rinse is used, be sure to follow it with a thorough deionized-water rinse. **Do not acid rinse a filter membrane** through which samples for arsenic analysis will be passed.

To process samples for arsenic speciation analysis by NWQL LC3142:

1. Before processing samples, begin to fill out the sample worksheet (fig. 5.6.4.A—1), specifying NWQL LC 3142.

2. Assemble and organize on a clean work surface the necessary processing equipment and supplies (table 5.6.4.A—1).

3. Wear appropriate disposable, powder-free gloves. Before proceeding, prepare the 0.45-µm capsule filter (NFM 5.2.1.A), making sure that the capsule filter has been precleaned with DIW and is ready to be used. Study objectives may dictate use of a filter membrane with a smaller pore size (McCleskey and others, 2004); these also should be precleaned (NFM 5, table 5-3). **Do not rinse the filter with acid.**

4. Collect environmental surface-water or groundwater samples and quality-control samples, using the prescribed procedures for samples with trace-element concentrations at the part-per-billion level (NFM 4). **Prevent exposure of samples to the atmosphere and light** to prevent oxidation.

    - **Surface-water samples should be collected from single vertical or a point and should not be composited.** If stream-mixing conditions are a concern, multiple samples from different points in the cross section should be individually collected and processed or a sample should be collected from a different cross section where mixing is not a concern. Collection of a multiple vertical, EWI, or EDI composite surface-water sample can result in substantial aeration of the sample, causing the distribution of arsenic species to change.
    - Groundwater samples are particularly susceptible to changes in arsenic species distribution when sampling waters with low dissolved-oxygen concentration and redox potential (Eh). Appropriate precautions should be taken to avoid the aeration or light exposure of groundwater samples (NFM table 4-4).

5. Rinse an opaque polyethylene sample bottle twice with IBW.

6. Using the micropipet and disposable glass bores or plastic tips or an adjustable micropipet and a clean tip, add at least 100 µL of EDTA solution to the sample bottle (see "*Calculation of diluent and EDTA volumes*"). If more than 100 µL of EDTA is needed, use either an adjustable volume micropipet that is capable of delivering the calculated volume of EDTA, or use a 100-µL micropipet and round the calculated volume of EDTA up to the nearest 100-µL increment.

7. If processing a spike sample, add the field spike solution (One-Stop # N1613) using a 100-µL micropipet and clean, disposable glass bore or plastic tip.

8. Record the volumes of EDTA solution and spike solution used on the laboratory-speciation methods worksheet (fig. 5.6.4.A—1). If the EDTA volume is not provided, it will be assumed that 100 µL was added.

9. Filter the sample, filling the opaque sample bottle to the top. Do not fill to overflowing. The opaque sample bottle holds about 11.5 plus 0.1 mL when completely full. **The bottle must be filled completely to the brim** so that the dilution factor and spike recovery can be accurately calculated. Cap bottle tightly.

    - Filter the environmental samples using in-line procedures as described in NFM 5.2.
    - Take precautions to prevent oxidation of chemical species when filtering groundwater; the risk of oxidation is of lesser concern for aerated surface water.

10. Label bottle with station ID, date, and time.

11. Complete the worksheet (fig. 5.6.4.A—1). Retain the original copy of the worksheet in the station folder and place a copy in a sealed bag with the sample bottle.

12. Chill and maintain the sample at 4°C. Although the sample is stable for up to 3 months, the **sample should be shipped to the NWQL to arrive within 14 days of sample collection**.

Selected References

Bednar, A.J., Garbarino, J.R., Ranville, J.F., Wildeman, T.R., 2002, Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples: Environmental Science and Technology, v. 36, p. 2213-2218.

Garbarino, J.R., Bednar, A.J., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic speciation in natural-water samples using laboratory and field methods: U.S. Geological Survey Water-Resources Investigations Report 02-4144, 40 p.

McCleskey, R.B., Nordstrom, D.K., and Maest, A.S., 2004, Preservation of water samples for arsenic (III/V) determinations: an evaluation of the literature and new analytical results: Applied Geochemistry, v. 19.p. 995-1009.

Nordstrom, D.K., 2002, Worldwide occurrence of arsenic in ground water: Science, v. 296, no. 5576, p. 2143-2145.

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Table 5.6.4.A—1. Checklist of supplies and equipment required for arsenic speciation using the laboratory-speciation methods (NWQL Lab Code 3142)

[mL, milliliter; µg-As/L, micrograms-arsenic per liter; mM, millimoles per liter; EDTA, ethylenediaminetetraacetic acid; µL, microliter; As(III), arsenite; As(V), arsenate; DMA, dimethylarsinate; MMA, monomethylarsonate]

✓	**Supplies**	**Description**	**Number required**	**Supplier and One Stop Shopping Item number for USGS studies**
	Blank water	Inorganic-grade (IBW)	As needed	Q378FLD
	Lab Code 3142 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III), As(V), DMA, and MMA. Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Lab Code 3142	N1613
	EDTA solution (store at room temperature)	25 mL of 250 mM EDTA for sample preservation. EDTA shelf life is one year from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed	N1611
	Micropipet	100-µL fixed volume or adjustable-volume, for EDTA and spikes	1	N1370 (fixed volume) or Open market
	Glass bores or plastic micropipet tips	Disposable glass bores, for 100-µL fixed-volume micropipet or disposable 100-µL fixed-volume or larger volume plastic tips for adjustable-volume micropipets	Ample supply	N1300 (glass bores) Or Open market (plastic tips)
	Sample bottles	Opaque (brown) "8-mL" polyethylene (holds 11.5 mL of sample when full)	1 per sample	N1615

TECHNICAL NOTE: Material Safety Data Sheets are supplied with the EDTA and arsenic field spike solutions. Persons using these materials should become familiar with the associated warnings and safety guidelines prior to using the materials in the field. Expired EDTA and spike solutions must be disposed of according to Federal, State, and local regulations. USGS NWQL or local or regional safety officers can be consulted for proper disposal methods.

Arsenic Laboratory-Speciation Methods Checklist and Worksheet
(Lab Code 3142)

Site ID: _____ *Date/Time:* _____
Site Name: _____ *Collector:* _____
Lab schedule requested: LC 3142

- ❑ Filter sample using 0.45-µm disposable capsule filter; do not clean media with acid

- ❑ EDTA preservative added to opaque bottle: _____µL
  (100 µL or the volume calculated below, whichever is greater)

  $V_{EDTA} = 4.0(10^{-6}) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8\ (10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$

  where:
  V_{EDTA} = microliters of 250-mM EDTA required per sample
  Al = dissolved aluminum concentration, in ☐I = disso
  Fe = dissolved iron concentration, in ☐Fe = diss
  Mn = dissolved manganese concentration, in ☐= dissoMn
  Ca = dissolved Ca concentration, in mg/L as Ca
  Mg = dissolved magnesium concentration, in mg/L as Mg
  Sr = dissolved strontium concentration, in ☐= dissoSr

- ❑ Spike Solution lot number: _____**L or F** *(circle one)*
  Solution concentration: _____ µg/L
  Volume added: _____ µL

- ❑ Spiked or unspiked sample volume: 11.5 mL
  Note: When completely full, the "8-mL" opaque bottle contains 11.5 ± 0.1 mL.

- ❑ Write Station ID, date, and time on bottle
- ❑ Maintain at 4 °C. Ship chilled sample and a copy of the worksheet to the NWQL within 14 days of collection.

Comments:

Figure 5.6.4.A—1. Worksheet for laboratory-speciation methods to determine arsenic species in water samples

LOW-LEVEL MERCURY 5.6.4.B

By M.E. Lewis and M.E. Brigham

Collecting and processing water samples for analysis of mercury at a low (subnanogram per liter) level requires use of ultratrace-level techniques for equipment cleaning, sample collection, and sample processing. **Established techniques and associated quality-assurance (QA) procedures for the collection and processing of water samples for trace-element analysis at the part-per-billion level (NFM 3–5) are not adequate for low-level mercury samples.** Modifications to the part-per-billion procedures are necessary to minimize contamination of samples at a typical ambient mercury concentration, which commonly is at the subnanogram-per-liter level.

Few laboratories provide low-level mercury analyses for filtered, unfiltered, and particulate total mercury and methylmercury samples. USGS samples are analyzed at the USGS Wisconsin District Mercury Laboratory (WDML)[1], which developed the sample-collection, processing, and handling procedures described in this section. The procedures described herein ensure that the requirements and recommendations of the WDML are fulfilled. Note that the general guidelines and precautions specified in this section are applicable to all mercury sampling at nanogram-per-liter or lower levels, regardless of the laboratory to be used.

Low-level mercury samples are susceptible to contamination from many sources, including improperly cleaned equipment; improper sample-collection techniques that allow dust, dirt, or metallic surfaces to contact samples; contaminated preservatives; atmospheric inputs from dust, dirt and rain; and the breath of field personnel having dental amalgam fillings, if the breath contacts the sample. To prevent equipment contamination, the protocol for cleaning low-level mercury equipment is exacting (see “Equipment, Supplies, and Equipment-Cleaning Procedures” below) and utilizes equipment not normally found in office laboratories. Therefore, the WDML provides the precleaned sampling and processing equipment and associated supplies needed for low-level mercury sampling. **USGS field personnel are advised to contact the WDML when planning their low-level mercury sampling and when ordering supplies.**

[1]The WDML’s Web address is http://infotrek.er.usgs.gov/mercury/ (accessed June 3, 2004). USGS personnel can e-mail the WDML at mercury@usgs.gov

It is strongly recommended that USGS project personnel maintain close communication with the WDML throughout the planning, sampling, and analysis phases of a low-level mercury-sampling project.

To prevent contamination of the sample being collected for low-level mercury analysis:

- Use appropriate equipment and reagents.
  - With few exceptions (discussed below), all sampling and sample-processing equipment must be composed of relatively inert materials, such as fluoropolymer or fluorocarbon polymer[2] (hereafter abbreviated as FP, unless the trade name is used). FP materials are used to minimize mercury adsorption to equipment or container walls and to eliminate mercury exchange into or out of the equipment or containers (Horvat and others, 1993).
  - Trace-pure 6 *N* hydrochloric acid is required for preserving unfiltered and filtered total mercury and methylmercury samples.
  - Project personnel are advised to obtain the precleaned and quality-assured containers, preservatives, and other supplies from the WDML.
- Use appropriate equipment-cleaning procedures. Contaminated equipment, including sampling containers, is the principle source of bias associated with low-level mercury analyses.

[2]**Fluorocarbon polymers and fluoropolymers (FP):** Fluorocarbon polymers (polyfluorocarbons) or fluoropolymers are composed of monomers (the smallest repeating compound segment of a polymer) consisting of carbon, fluorine, hydrogen, and, for one polymer, oxygen. The fluoropolymers have trade names that include, for example, Teflon® and Tefzel® (ethylene tetrafluoroethylene, products of the DuPont Company) and Kynar® (a polyvinylidene fluoride, a product of the Atofina Chemicals Company). Common types of fluoropolymers include FEP (fluorinated ethylene polypropylene), PFA (perfluoroalkoxy), PTFE (polytetrafluoroethylene), and PVDF (polyvinylidene fluoride). Each fluorocarbon polymer has different chemical and physical properties; however, at ambient temperatures all are relatively nonreactive chemically and do not leach monomers.

- Use Clean Hands/Dirty Hands (CH/DH) techniques when collecting and processing mercury samples (NFM 4.0.1). In addition:
  - Wear lint-free, non-particle-shedding clothing; avoid clothing that is an obvious source of particles (for example, natural wool, synthetic fleece, or dusty or dirty clothing). If particle-shedding clothing cannot be avoided, wear a disposable Tyvek suit or clean, nylon wind suit over the clothing.
  - Wear shoulder-length polyethylene gloves under wrist-length disposable powder-free gloves (nitrile, latex, or vinyl).
  - Double-bag all precleaned sample containers in zip-sealed plastic bags. Rebag all samples until processing and preservation.
  - Store and transport all clean sampling and processing equipment and supplies in a clean plastic container lined with a clean, clear plastic bag.
  - Avoid breathing directly over the samples.
  - Triple rinse the sampling equipment and sample bottles with the water to be sampled before beginning sample collection.

- **Implement quality control.** The collection and analysis of quality-control samples are required as an integral part of water-quality investigations. The quality-control plan should include collection of equipment-blank, field-blank, and replicate samples. Guidance on quality-control sample collection and processing can be found in NFM 4.3. The specific types, number, and distribution of quality-control samples should be determined according to the study design and data-quality requirements of the project.

  — Use reagent-grade water of the quality supplied by the WDML (WDML blank water) as the source solution for equipment blanks and field blanks. (The WDML assures the quality of the blank water as well as the other field equipment and supplies they provide).

  — Process and analyze equipment blanks before collecting any environmental samples. Identify the source of any contamination detected in the blanks, and correct the problem before using the equipment for sampling or processing.

  — Process an initial field blank to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment. Subsequent field blanks should be collected to address field-site concerns, the sampling timeframe, and data-quality requirements. Field blanks are processed in the same manner and under the same environmental conditions as environmental samples (NFM 4.3.1.B).

  — Test at least 10 percent of the precleaned equipment used for sample collection and processing to assure cleanliness as follows: pass WDML blank water through the cleaned equipment and analyze this sample for total mercury. Note that the WDML only supplies equipment that has been appropriately precleaned and quality assured.

Equipment, Supplies, and Equipment-Cleaning Procedures

Refer to table 5–9 for a list of the equipment and supplies needed for low-level mercury sample collection and processing. Note that either FP (Teflon®) or polyethylene terephthalate copolyester, glycol-modified (PETG) bottles may be used, as described below.

- **Total mercury analysis**: Use 500-mL bottles for unfiltered (UTHg) and filtered (FTHg) samples.
- **Methylmercury analysis**: Use 250-mL bottles for unfiltered (UMHg) and filtered (FMHg) samples.

Contamination of sample containers and other sampling equipment is the most common source of bias associated with low-level mercury analysis. Equipment contamination can be prevented or at least minimized by (1) using equipment constructed of appropriate materials and (2) rigorously employing appropriate equipment-cleaning protocols, as described below. Most commercial plastics contaminate water samples with mercury at concentrations greater than the nanogram-per-liter level. Therefore, it is important to use only the plastics specified below.

- **Fluorocarbon polymer or fluoropolymer (FP) materials.** With a few notable exceptions, most equipment, including tubing and all sample-contacting equipment components, are to be composed of FP materials. FP equipment is reusable, but must be cleaned and stored properly.
- **Polyethylene terephthalate copolyester, glycol-modified (PETG)**. When collecting surface-water dip samples, **use only new PETG bottles–never previously used bottles.** (The samples subsequently are field filtered into FP sample bottles.)
  - — PETG bottles do not fit into any of the isokinetic samplers.
  - — PETG bottles do not require cleaning before use.
  - — PETG bottles are to be disposed of after each use. **Do not clean or reuse these bottles.**
- **C-flex tubing**. A small section of C-flex tubing may be used in the pump head of a peristaltic pump. FP connectors are used to connect the C-flex section with the FP tubing.

The rigorous nature of the cleaning protocol for equipment that directly contacts the water sample cannot be performed readily at most office laboratory facilities. Therefore, the WDML supplies and quality controls selected equipment that has been cleaned using the required, rigorous procedures listed later in this section. It is recommended that USGS project personnel contact WDML, either to obtain precleaned FP bottles and other FP equipment or to ship their equipment to the WDML for cleaning.

TECHNICAL NOTE: WDML precleaned Teflon® or other FP sample containers (bottles for unfiltered and filtered samples and petri dishes for particulate mercury filters) have two bar-code labels that contain: (1) the unique identification number of the container, and (2) a code representing the date that the container was removed from the acid bath. One bar code is placed in the sealed inner plastic bag with the sample container and the second bar code is placed in the outer plastic bag (see "Sample Preservation, Storage, and Shipment" below). The outer plastic bag is labeled by the WDML with the unique identification number using a permanent marker. Samples are tracked using the bar code to identify shipping and receiving dates and laboratory sample preparation and analysis steps.

- Sampling and processing equipment that directly contacts the water sample must be cleaned before use, using the procedures described below, unless the equipment has been obtained from or cleaned by the WDML.
- Sampling and processing equipment that does not directly contact the water sample should be cleaned using the standard cleaning protocols for inorganic constituents described in NFM 3.2.1.

Contact the WDML at least 2 to 4 weeks in advance of sampling for low-level mercury to arrange for the use of appropriately cleaned equipment.

Table 5–9. Checklist of equipment and supplies used for processing samples for low-level mercury analysis

[FISP, Federal Interagency Sedimentation Project; NFM, *National Field Manual for the Collection of Water-Quality Data*; FP, fluoropolymer or fluorocarbon polymer; PETG, polyethylene terephthalate copolyester, glycol modified; UTHg, unfiltered total mercury; FTHg, filtered total mercury; UMHg, unfiltered methylmercury; FMHg, filtered methylmercury; *N*, normal; PTHg, particulate total mercury; PMHg, particulate methylmercury; mL, milliliter; mm, millimeter; HIF, Hydrologic Instrumentation Facility of the USGS]

Item	Description	Applicable constituent(s)	Quantity required
Churn, US SS-1[1]	Fluoropolymer "churn" sample splitter, FISP part no. 011000. For compositing and splitting samples.	All, if splitting samples	1 per composited sample
Sample processing chamber[2]	For filtration and preservation of samples. NFM 2.2.2.	All	1
1,000 mL PETG bottle[2]	1,000-mL, square, wide-mouth sample bottle for collecting dip samples.	All, if collecting dip samples	1 per sample
UTHg bottle[3]	500-mL FP sample bottle for unfiltered total mercury samples.	UTHg	1 per sample
FTHg bottle[3]	500-mL FP sample bottle for filtered total mercury samples.	FTHg	1 per sample
UMHg bottle[3]	250-mL FP sample bottle for unfiltered methylmercury samples.	UMHg	1 per sample
FMHg bottle[3]	250-mL FP sample bottle for filtered methylmercury samples.	FMHg	1 per sample
6 *N* trace-pure hydrochloric acid[3]	Preservative for unfiltered and filtered mercury samples.	UTHg, FTHg, UMHg, and FMHg	10 mL for total mercury and 5 mL for methylmercury
Dry ice	For field preservation and shipment of particulate mercury samples.	PTHg and PMHg	As needed
Blank water[3]	Quality-assured, ultrapure deionized water for equipment and field blanks.	UTHg, FTHg, UMHg, and FMHg	1 bottle per blank sample
Vacuum desiccator fitted with modified filtration assembly, Tygon tubing, and 12-volt vacuum pump[3]	Equipment for vacuum filtration of samples for particulate and filtered mercury samples. See figs. 1 and 2, Savillex® filtration assembly, used with quartz fiber filters described below	FTHg[4], FMHg[4], PTHg, and PMHg	1 complete unit (must be precleaned for each sample)
Portable electronic bench scale, 1,200 grams minimum capacity[2]	For calculation of volume filtered for particulate mercury samples.	PTHg and PMHg	1

Table 5–9. Checklist of equipment and supplies used for processing samples for low-level mercury analysis–Continued

[FISP, Federal Interagency Sedimentation Project; NFM, *National Field Manual for the Collection of Water-Quality Data*; FP, fluoropolymer or fluorocarbon polymer; PETG, polyethylene terephthalate copolyester, glycol modified; UTHg, unfiltered total mercury; FTHg, filtered total mercury; UMHg, unfiltered methylmercury; FMHg, filtered methylmercury; *N*, normal; PTHg, particulate total mercury; PMHg, particulate methylmercury; mL, milliliter; mm, millimeter; HIF, Hydrologic Instrumentation Facility of the USGS]

Item	Description	Applicable constituent(s)	Quantity required
12-volt battery[2]	To power the vacuum pump for vacuum filtration of samples for particulate and filtered mercury samples.	FTHg[4], FMHg[4], PTHg, and PMHg	1
Quartz fiber filters (QFF)[3]	47-mm 0.7-micron nominal pore size, precombusted quartz fiber filters for particulate mercury samples; one precleaned filter per sample.	FTHg[4], FMHg[4], PTHg, and PMHg	1 per sample
FP petri dish[3]	50-mm stackable FP petri dish for storing particulate mercury filters.	PTHg and PMHg	1 per sample
FP forceps[3]	For handling quartz fiber filters for particulate mercury processing.	PTHg and PMHg	1 per sample
Peristaltic pump[2]	For processing filtered mercury samples when using capsule filters. Also used for sampling.	FTHg[5] and FMHg[5]	1
Capsule filters[3]	0.45-micron disposable capsule filter, polypropylene microfiber media, precleaned.	FTHg[5] and FMHg[5]	1 per filtered sample
C-Flex tubing[3]	Pump-head tubing for use with the peristaltic pump.	FTHg[5] and FMHg[5]	1 length per sample
Gloves[2]	Shoulder-length polyethylene gloves for sample collection and processing.	All	1 pair per person per site
Gloves[2]	Powderless nitrile, latex, or vinyl gloves to be worn over shoulder-length gloves.	All	As many as necessary
Tyvek coveralls[2]	Optional disposable clothing for personnel.	All	1 pair per person per site

[1]Contact Federal Interagency Sedimentation Project at http://fisp.wes.army.mil/ for vendors. For USGS use, obtain through One-Stop Shopping (supplied through HIF).
[2]Available on open market.
[3]Available from the USGS Wisconsin District Mercury Laboratory.
[4]Not required if using a capsule filter to process FTHg and FMHg samples.
[5]Not required if using vacuum filtration to process FTHg and FMHg samples.

To clean fluorocarbon polymer (FP) containers and equipment:

Note that new as well as previously used FP containers and equipment must be cleaned in advance of the current sampling effort (see step 2).

1. Wearing disposable powderless gloves, rinse bottles and other equipment with tap water.
2. Prepare a 4 *N* hydrochloric acid bath and heat to 65-75^{o} C.
   - **New FP containers and equipment:** Immerse rinsed equipment in the heated bath for at least 48 hours.
   - **Previously used FP containers and equipment:** Immerse rinsed equipment in the heated bath for at least 24 hours.
3. Remove the equipment from the bath and immediately immerse it in fresh reagent-grade water.
4. Repeat step 3 at least three times with fresh reagent-grade water.
5. Partially fill the FP bottles with a 1.0-percent (v/v) hydrochloric acid solution.
6. Cap the bottles and place them in a mercury-free Class 100 clean bench or laminar-flow hood until the outside surfaces are dry.
7. Double bag the dry equipment in new plastic zip-seal bags.

To clean FP and C-flex sample tubing:

1. Wearing disposable powderless gloves, fill tubing with a 50-percent (v/v) trace element-grade nitric acid solution.
2. Immerse tubing in a 10-percent (v/v) hydrochloric acid bath for a minimum of 7 days.
3. Dry tubing by purging with mercury-free air or nitrogen at the clean bench.
4. Double bag the tubing in new plastic zip-seal bags.

To prepare the capsule filter:

Many capsule filters are not chemically resistant to acids, and therefore, cannot undergo the preparation needed for low-level mercury sample processing (the standard capsule filter used to process samples for inorganic analysis should not be subjected to the acid-cleaning steps described below). It is recommended that precleaned filtration equipment, including acid-washed capsule filters, be obtained from the WDML, if possible. If WDML filtration equipment is not available for the study, obtain and prepare WDML-recommended filters as described below. Be sure to dispose appropriately the acid solutions used.

1. Wearing disposable powderless gloves, fill the capsule filter with a 50-percent (v/v) trace element-grade nitric acid solution and allow to stand for 4 days.
2. After 4 days, rinse the filter using 20 filter volumes of reagent-grade water.
3. Refill the filter with hydrochloric acid and immerse it in a 10-percent (v/v) solution of hydrochloric acid at room temperature. Soak for 3 days.
4. Empty the hydrochloric acid from the filter. Rinse the filter by sequentially filling it with 20 filter volumes of fresh reagent-grade water.
5. Fill the filter with reagent-grade water, cap it securely to prevent leakage, and double bag the filter until filtration.

USGS projects are advised to use the capsule filters that are precleaned and supplied by the WDML, if possible.

Sample Collection

To minimize the potential for sample contamination, collect samples using the least complex sampling method possible that results in a representative sample and meets study objectives. The potential for sample contamination increases with the increasing complexity of sampling methods. Follow the sampling procedures described below. If specific study objectives or site conditions necessitate procedure modifications, ensure that the modifications are well documented in field notes.

- **For surface-water sites with flowing water,** the selection of a sampling method depends on stream-mixing conditions and stream access.
  - **Well-mixed stream site**
    - Collect a dip sample (NFM 4.1.1.B) at the centroid of flow using an FP or PETG bottle of appropriate size (table 5-9).
    - Specific bottle requirements for surface-water dip samples are discussed below under "Sample Processing" and in table 5-9.
  - **Poorly mixed stream site**
    - Collect an isokinetic sample (NFM 4.1.1) using an appropriate isokinetic sampler.
    - Use a sampling device with an FP bottle, cap, and nozzle.
  - **Sites with boat access only**
    - Collect a dip sample or isokinetic sample, as appropriate for site conditions and study objectives.
    - Approach the sampling location from downstream; avoid collecting samples in water that has been disturbed by boat traffic.
    - In streams with slow velocities, sample from the bow of the boat while heading slowly upstream.

- **For surface-water sites with still water,** collect samples using either the dip-sampling, point-sampling, or pump-sampling method, depending on the site conditions and study objectives.

  If sampling an area with floating vegetation or detritus, pass the sampler beneath these materials before collecting a sample. In the case of a dip sample, open the bottle once it is submerged beneath these materials, and cap the bottle securely before removing it from the water.

  — **Dip-sampling method** (NFM 4.1.1.B): collect samples using either FP or PETG bottles. Specific bottle requirements for surface-water dip samples are discussed below under "Sample Processing" and in table 5-9.

    - Head upwind while sampling, if possible.
    - If samples are collected while wading, then collect the sample while slowly moving away from the area of disturbed bottom sediment.
    - If samples are collected from a boat, then sample from the bow of the boat, moving slowly away from the water disturbed by the boat.

  — **Pump- and point-sampling methods**: To collect samples at depth, use either a peristaltic pump with FP tubing, an FP weight, and C-Flex® pump-head tubing, or use an FP thief-type sampling device (NFM 4.1.2).

    - When using the pump-sampling method, run the pump for 5 to10 minutes to purge the tubing before collecting the sample.
    - Use clean (NFM 3.2.1) Kevlar rope to avoid sample contamination.

- **For ground-water sites,** the type of sampling system and method selected depends on the type of well and depth to water from land surface.
  - Follow standard guidelines for well purging and sample collection (NFM 4.2).
  - Peristaltic pumps with FP tubing and an FP weight are recommended for sampling shallow wells (for example, depth to water is less than about 25 feet or 9 meters). Use clean (NFM 3.2.1) Kevlar rope to attach the weight to the tubing.
  - Wells with a depth to water exceeding 25 feet can be sampled using an FP bladder pump and FP tubing. Use clean (NFM 3.2.1) Kevlar rope.
  - Avoid using a submersible, metallic pump wherever possible. If using a submersible, metallic pump, clean the pump following prescribed guidelines (NFM 3.3.9.A) and collect a pump-blank sample (NFM 4.3) well in advance of collecting environmental samples to assess the potential for contamination.

Sample Processing

Samples can be processed on-site, in a District laboratory, or at the WDML, but processing must be done within 24 hours of collection and under appropriately clean conditions. By prior agreement, the WDML can filter and acidify samples upon request, if samples are received via overnight courier.

- When processing samples on-site, minimize the potential for contamination.
  - The processing chamber should be fitted with a clean, clear plastic bag in which to work (NFM 2.2.2).
  - Work away from traffic, dusty roadways, or any other source of dust or other potential airborne contaminants.
  - Never work in vehicles in which mercury has been transported.
  - Avoid contact with metal work surfaces.
  - Wear lint-free, non-shedding clothing, a disposable Tyvek suit or a clean nylon wind suit.
  - Wear shoulder-length polyethylene gloves under disposable, wrist-length powderless (nitrile or latex) gloves.

- Use a 500-mL FP sample bottle for unfiltered total mercury (UTHg) and filtered total mercury (FTHg) samples. Use a 250-mL FP sample bottle for unfiltered methylmercury (UMHg) and filtered methylmercury (FMHg) samples.
- Use CH/DH techniques (NFM 4.0.1) when filling the FP sample bottles.
  - Discard the 1-percent hydrochloric acid contained in the FP sample bottles, before rinsing the sample bottles.
  - Triple rinse the bottles with small amounts (10 to 20 mL) of the water to be sampled.
  - Fill bottle to shoulder, leaving approximately 20 mL of headspace for later addition of preservative and laboratory reagents.
  - Cap bottle securely, dry off the bottle, and rebag until sample preservation.
- **If the sample will be processed off-site**, label outer sample bag with (a) site name and site number, (b) date and time of sample collection, and (c) type of analysis being requested.

To process samples for unfiltered total mercury and methylmercury analysis *(the processing method to be used depends on how samples are collected)**:***

Surface-water dip samples

1. Collect samples directly into the appropriate FP sample bottle.

Surface-water point samples

1. Dispense sample directly from an FP thief-type sampler into the appropriate FP sample bottle or FP churn.
2. If compositing the sample in a churn:
   a. Following sample collection, rebag the churn and place it in the churn carrier until sample splitting.
   b. Split the sample into FP sample bottles following guidelines for the churn splitter (NFM 5.1.1.A).

Surface-water pumped samples

1. Using a peristaltic pump and FP tubing, direct the sample flow into the appropriate FP sample bottle.

Isokinetic samples

1. Composite isokinetic samples in an FP churn. Rebag churn and place it into the churn carrier until sample splitting.
2. Split the sample into FP sample bottles following guidelines for the churn splitter (NFM 5.1.1.A).

Ground-water samples

1. Direct the sample flow into the appropriate FP sample bottle.

To process aqueous samples for filtered total mercury and methylmercury analyses *(the sample-processing method used depends on the choice of filter type and filtration equipment, as well as on the sample-collection method)**:***

- **Capsule-Filter Method**. Use an acid-resistant 0.45-µm polypropylene capsule filter, precleaned as previously described. When filtering the sample using the capsule filter and a peristaltic pump, follow the guidelines in NFM 5.2.1.A ("To filter a composite sample"), but implement the following modifications to that standard procedure:

  1. Using CH/DH techniques and a sample-processing chamber, remove capsule filter from plastic bag; uncap and discard reagent-grade water from capsule filter, shaking the filter to expel entrained water.
  2. Load the peristaltic pump head with precleaned C-Flex® pump-head tubing obtained from the WDML.
  3. Discard appropriately the 1-percent hydrochloric acid solution contained in the clean sample bottles. Triple rinse the sample bottles with small amounts (10 to 20 mL) of sample filtrate before collecting the sample.
  4. Fill bottles to shoulder with the sample filtrate, leaving approximately 20 mL of headspace for later addition of preservative and laboratory reagents.
  5. Cap each bottle securely, then dry off and rebag it until ready for sample preservation.

- **Vacuum-Filtration Method**. An alternative filtration method uses a vacuum filtration chamber, FP filtration assembly (for example, a Savillex® PFA/PFTE filtration assembly to hold a quartz fiber filter), and a 47-mm 0.7-µm precombusted quartz fiber filter (QFF) (described below in "*To filter samples for particulate mercury analysis*"). **The vacuum filtration method is recommended if collecting samples for both filtered and particulate mercury analysis.**

Surface-water dip samples

1. Collect samples directly in 1-L FP bottles or 1-L PETG bottles, after triple rinsing bottles with water to be sampled.
2. Fill bottles to the top. Cap bottles securely and rebag until ready for filtration.
3. Filter samples using either a capsule filter or vacuum filtration.

Surface-water point samples

1. Dispense samples directly from a thief-type sampler into 1-L FP or 1-L PETG bottles.
2. Fill bottles to the top. Cap bottles securely and rebag until filtration.
3. Filter samples using either a capsule filter or vacuum filtration.

Surface-water pumped samples

- **For on-site sample filtration**, connect a 0.45-µm WDML capsule filter in-line and follow filtration guidelines described above under "Capsule-Filter Method."
- **For off-site filtration**:
  1. Direct sample flow into either 1-L FP or 1-L PETG bottles and fill bottles to the top.
  2. Cap bottles securely and rebag until filtration.
  3. Use either the capsule-filter or vacuum-filtration method to filter samples off-site.

Surface-water isokinetic samples

1. Composite subsamples in an FP churn (NFM 4.1.1.A). Rebag churn and place into churn carrier until sample filtration.
2. Filter the sample using either the capsule-filter or the vacuum-filtration method.
   a. If using a capsule filter, then filter directly from the churn.
   b. If using vacuum filtration, then follow guidelines for the churn splitter (NFM 5.1.1.A), splitting the sample into either 1-L FP or 1-L PETG bottles before filtration and then capping the bottles securely and rebagging until the samples can be filtered.

Ground-water samples

1. Connect a 0.45-µm WDML capsule filter in-line with the pump and follow filtration guidelines described above under "Capsule-Filter Method."

To process aqueous samples for particulate total mercury and methylmercury analyses:

- Collect samples or split samples into 1-L FP or PETG bottles, as previously described in "Sample Collection."
- A 1-L sample is required for each particulate total mercury (PTHg) or particulate methylmercury (PMHg) analysis.
- Particulate total mercury and particulate methylmercury are processed using a vacuum-desiccator filtration chamber, an FP filtration assembly, and a 47-mm 0.7-µm pre-combusted QFF (figs. 1 and 2).
- Depending on study requirements for filter pore size, the filtrate for particulate mercury can be collected for filtered total mercury (FTHg) and filtered methylmercury (FMHg) samples.
- USGS projects are advised to obtain all filtration supplies from the WDML, if possible.

Figure 1. Vacuum-desiccator filtration chamber with a modified Savillex® PFA/PFTE filtration assembly attached.
(Photograph by Michael E. Lewis)

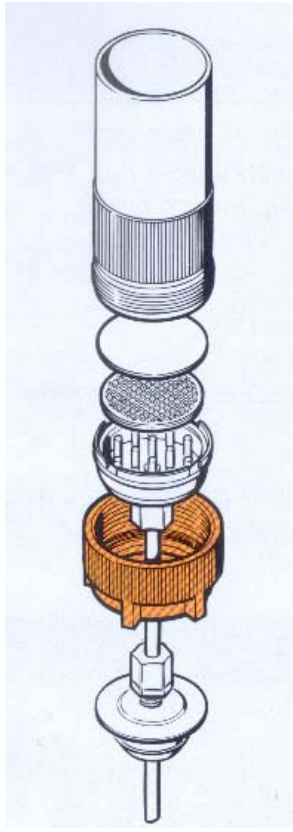


Figure 2. Savillex® PFA/PTFE filtration assembly. (From Savillex Corporation. Published with permission.)

To filter samples for particulate mercury analysis:

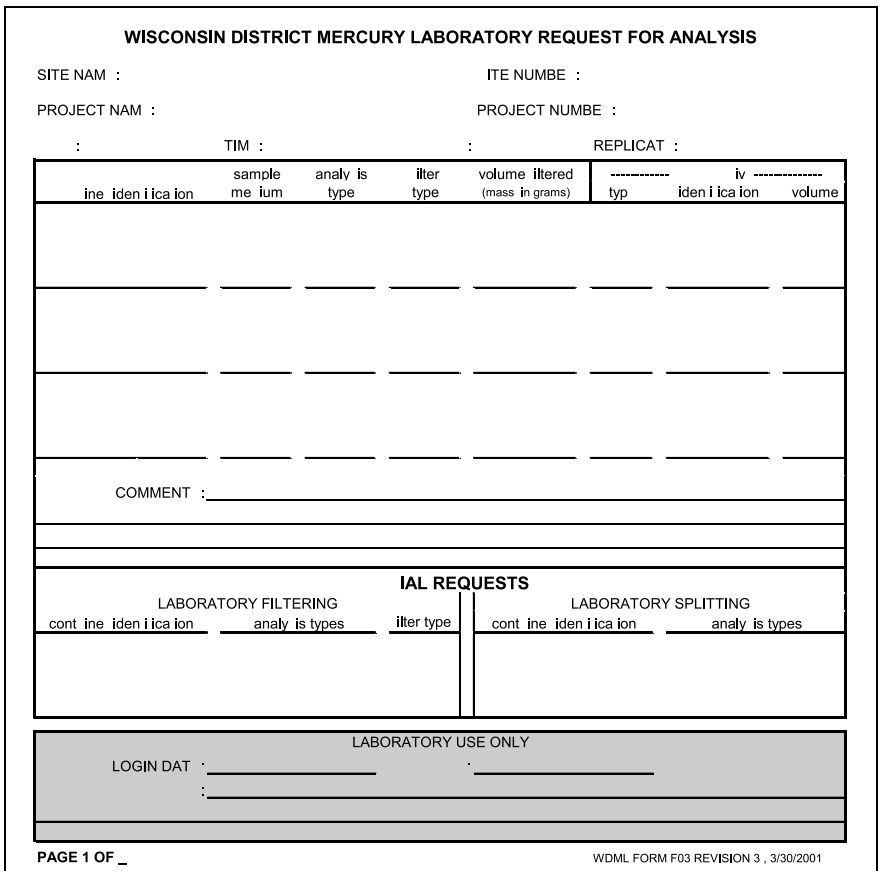
- If the particulate concentration is very low, evidenced by little or no slowing of the filtration rate, then filter an entire 1-L sample for total mercury (PTHg) and an entire 1-L sample for methylmercury (PMHg).
- At modest particle concentrations, evidenced by a slowing filtration rate, filtering approximately 500 mL of sample is sufficient.
- High particle-concentration water may require several filter changes to collect sufficient volumes for filtered-water sample analysis (for example, 500 mL for FTHg and 250 mL for FMHg). In such cases, retain only one filter for PTHg and one filter for PMHg, recording the volume of water filtered through each filter. **Do not calculate sample volumes that pass through the subsequent filters after the PTHg and PMHg filters have been collected.**

1. Weigh the bottled 1-L samples, recording mass in grams.
2. Filter each sample in a sample-processing chamber that is fitted with a clean plastic covering (NFM 2.2.2). Use CH/DH techniques. The chamber must be large enough to contain the vacuum filtration unit (approximately 16 inches in height) and allow enough room to pour water into the top of the filter reservoir. A chamber height of 24 inches is suggested; however, existing chambers of 21 to 23 inches should suffice.
3. Using CH/DH techniques, prepare the vacuum filtration chamber (fig. 1). Using a clean FP filtration assembly (fig. 2), insert a ¼-inch FP tube into the vacuum-desiccator filtration chamber (see fig. 1). Place the inverted orange nut on top of the chamber. Attach the filter support. Using FP forceps, place a quartz fiber filter (random pattern facing up) onto the filter support. Place the filtration-assembly reservoir on the filter and secure it with the orange nut, holding the reservoir firmly to avoid tearing the filter.
4. If processing samples for filtered total mercury, discard the 1-percent HCl solution from the 500-mL FP bottle for FTHg analysis. Place the open 500-mL FTHg bottle inside the vacuum desiccator, positioned directly beneath the FP tube. Close the filtration chamber. Attach the vacuum pump line and turn on the vacuum pump.

5. Agitate each 1-L sample bottle to keep the sample well mixed (do this frequently during the filtration process), and begin pouring small volumes of water into the top of the filter chamber.
6. Filter the sample into the 500-mL FTHg bottle, triple rinsing the bottle with small amounts (10 to 20 mL) of filtrate before filling the bottle to the shoulder. Leave about 20 mL of headspace for the addition of preservative and laboratory reagents; decant excess water if necessary.
7. If a noticeable particle load has collected on the filter, evidenced by a slowing filtration rate, remove the PTHg filter and place it into an FP petri dish. For low particle loads, filter the remaining water in the first 1-L sample. It is acceptable to overflow the filtered-water bottle that is inside the vacuum chamber in order to filter sufficient water volume for the particulate sample.
8. Label the outer bag with all sample information.
9. When filtration is complete, re-weigh the 1-L sample bottle; calculate and record the mass of water (in grams) that passed through the filter. Place the filter in its FP petri dish and cover with a stackable petri dish. Record on the laboratory request form (fig. 3) all the necessary sample information, including the calculated mass (in grams) of water that passed through the filter (volume filtered).
10. Remove the FTHg bottle from the chamber, securely capping, drying off, and bagging the bottle until sample preservation.
11. **PMHg and FMHg samples:** Repeat steps 1-10 above. Save the filter for PMHg, recording the sample mass (in grams—see step 9 above) that passed through the filter.
12. **Particulate mercury samples:** When filtration is complete and the quartz fiber filters are stacked in their petri dishes, tape the petri dishes together to prevent separation during sample storage and shipping. Place petri dishes in zip-seal bag(s). Ensure that all sample information is recorded on the bags. Place bagged filters into a cooler stocked with dry ice or frozen, bagged blue-ice packs. **Do not use wet ice.** Keep particulate-mercury filters frozen or chilled in the field. Upon return to the office, store the bagged filters in a freezer until all mercury sampling is complete. Every petri dish has two corresponding bar codes with the petri dish identification. Place one bar code on the Request for Analysis form; retain the other bar code with the petri dish in the inner bag.

13. When filtration is complete, empty any water that has spilled in the filtration chamber. The FP filtration-assembly reservoir and filter support (fig. 2) must be cleaned rigorously before use, as previously described in "Equipment, Supplies, and Equipment-Cleaning Procedures". All other components of the vacuum filtration apparatus, including the vacuum chamber, can be cleaned utilizing standard procedures for inorganic constituents (NFM 3.2.1).

14. Place used FP filtration parts into a bag to be returned to the WDML for cleaning and reuse.



WISCONSIN DISTRICT MERCURY LABORATORY REQUEST FOR ANALYSIS

SITE NAM : ITE NUMBE :

PROJECT NAM : PROJECT NUMBE :

: TIM : : REPLICAT :

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COMMENT :

IAL REQUESTS

LABORATORY FILTERING			LABORATORY SPLITTING	
cont ine iden i ica ion	analy is types	ilter type	cont ine iden i ica ion	analy is types

LABORATORY USE ONLY

LOGIN DAT : :

:

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Figure 3. Wisconsin District Mercury Laboratory (USGS) request-for-analysis form (available on the Internet at http://infotrek.er.usgs.gov/doc/mercry/doc/Analysis_Request_Form.pdf).

Sample Preservation, Storage, and Shipment

Preserve unfiltered and filtered total and methylmercury samples with trace-pure 6 *N* hydrochloric acid preservative as soon after collection as practical, **but ensure that the acid treatment is added to the samples within 24 hours of filtration.**

Sample preservation is the most susceptible step in sample processing, with respect to the potential for sample contamination.

- The WDML provides the ultra-trace hydrochloric acid and the measurement vial. Wear appropriate protective eyewear, gloves, and clothing when handling the 6 *N* hydrochloric acid.
- If multiple sites are to be sampled per day, all samples should be preserved at the same time to minimize the number of times the hydrochloric acid preservative is opened.

To preserve samples for mercury analyses:

1. Prepare a clean workspace. Using CH/DH procedures, prepare a sample-processing chamber with a new plastic cover.
2. Rinse the measurement vial three times with small volumes of 6 *N* hydrochloric acid. Collect the waste in a clean, sturdy, sealable plastic container. Neutralize and dispose of the used hydrochloric acid solution appropriately and in accordance with local regulations.
3. Fill the vial to the 10-mL mark with hydrochloric acid. Pour 10 mL of the hydrochloric acid into each of the 500-mL FTHg and UTHg bottles.
4. Fill each vial to the 5-mL mark. Pour 5 mL into each of the 250-mL FMHg and UMHg bottles.
5. Reseal all bottles as tightly as possible by hand. Rebag bottles in their zip-seal bags, leaving one sample bar code label in the bottom of the inner bag with the sample bottle.
6. Save at least 30 mL of the hydrochloric acid because the WDML must analyze the remaining solution to assess potential preservative contamination. Return the hydrochloric acid and the measurement vial to the WDML along with the samples.
7. Record on the WDML laboratory request form (fig. 3) the identification number of the hydrochloric acid preservative that was used with each sample.

To store and (or) ship samples:

Do not store or ship samples on ice. Ice meltwater invariably invades the sealed bags, potentially compromising a bottle's clean environment. **Do not expose samples to light or heat.**

1. Enter all sample-header data (site name, date, time, sample depth, medium code, sample type) on the WDML laboratory request-for-analysis form (fig. 3).
2. Place bar codes from the outer bag of the double-bagged sample bottles on the WDML request-for-analysis form under "container identification" (fig. 3).
3. Transport and store preserved water samples in a cool, dark environment, such as in a clean cooler. Line the cooler with a clean plastic bag. **Do not store samples on ice.** If field conditions are particularly warm, use bagged and sealed frozen blue-ice packs to keep samples cool.
4. Fill out the cooler inventory form for all samples to be shipped to WDML (fig. 4). Consolidate and ship samples to WDML when sampling is completed; **samples must be shipped within 14 days of collection.**
5. Enclose the WDML laboratory request-for-analysis form (fig. 3) and cooler inventory form (fig. 4) in a sealed plastic bag in the cooler with the samples.
6. Notify WDML of sample shipment via e-mail mercury@usgs.gov.

Samples for low-level mercury analysis must be shipped to the laboratory within 14 days of collection.

COOLER INVENTORY FORM

page _____ of _____

USGS -- WISCONSIN DISTRICT
MERCURY LABORATORY
8505 RESEARCH WAY
MIDDLETON, WI 53562

PROJECT:

SAMPLERS:

SITE NAME	DATE	TIME	DEPTH	SAMPLE MEDIA	TOTAL NUMBER OF CONTAINERS	125 ML TEFLON	250 ML TEFLON	500 ML TEFLON	1 L TEFLON	2 L TEFLON	5 L TEFLON	PETRI DISHES	40 ML GLASS	SEDIMENT VIAL			LABORATORY CHECK-IN COMMENTS

Relinquished by:	date/time:	Received by:	date/time:	COMMENTS:
Relinquished by:	date/time:	Received by:	date/time:	
Relinquished by:	date/time:	Received by:	date/time:	

WDML F02 REVISION 3 SEPTEMBER 15,1998

Figure 4. Wisconsin District Mercury Laboratory (USGS) cooler inventory form (available on the Internet at http://infotrek.er.usgs.gov/doc/mercury/doc/Cooler_Inventory_Form.pdf)

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U.S. Geological Survey
Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A6.

FIELD MEASUREMENTS

F.D. Wilde
Managing Editor

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
KEN SALAZAR, *Secretary*

U.S. GEOLOGICAL SURVEY
Suzette M. Kimball, *Acting Director*

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192
This report is accessible online at http://pubs.water.usgs.gov/twri9A/

FIELD MEASUREMENTS

National Field Manual for the Collection of Water-Quality Data

Chapter A6.

Notes:
Table of contents current as of October 2008.

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Chapter A6. FIELD MEASUREMENTS

Edited by **F.D. Wilde**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* is comprised of nine chapters that provide guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter presents procedures and guidelines for the collection of water data on temperature, dissolved-oxygen concentration, specific electrical conductance, pH, reduction-oxidation potential, alkalinity, and turbidity, and for the use of multiparameter instruments for taking such measurements.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters are posted on the Web on the USGS page "National Field Manual for the Collection of Water-Quality Data" (http://pubs.water.usgs.gov/twri9A).

INTRODUCTION

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the impartial collection of quality-assured data that accurately describe the physical, chemical, and biological attributes of environmental water systems. The quality assurance of data is essential to the credibility of the water-resources appraisals

carried out by the USGS. These data are available to, and used by, environmental agencies, scientific organizations, and the general public.

Documentation of the methods used by USGS personnel serves to maintain consistency and technical quality in our data-collection activities. The *National Field* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters that are designed to be used in conjunction with each other. Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6.4 refers to the section in NFM 6 that pertains to pH data collection.

PURPOSE AND SCOPE

The *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to water-quality data collection and analysis. This manual is targeted specifically toward data collectors in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, and (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this report. The *National Field Manual* is meant to guide and complement such training. Chapter A6 provides procedures, protocols, and guidelines for the collection of those standard physical and chemical properties of water that are, in general, routinely collected for USGS water-quality investigations. These include measurement of water temperature, pH, specific electrical conductance, dissolved oxygen, Eh, alkalinity, and turbidity.

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. It is the fundamental responsibility of data collectors to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. Whenever a standard procedure is modified or is not used, a description of the procedure that is used and the supporting quality-assurance information are to be reported with the data.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual,* the terms **required** and **recommended** have the following USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected Water Science Center[1] or other professional personnel, as appropriate. Technical memorandums or other documents that define the policy pertinent to such requirements are referenced in this manual. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented in permanent and readily accessible records.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this chapter to the extent that such documents are available. Specific data-quality requirements, study objectives, or other

[1]"Water Science Center" refers to an organizational unit of the USGS in any of the States or Territories of the United States.

constraints can affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment. Departure from or modifications to recommended procedures must be quality assured and documented in permanent and readily accessible records.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* are reviewed, revised, and reissued periodically to correct any errors, update information, incorporate technical advances, and address additional water-quality topics. Dates of revisions appear in the footer of each chapter section. Each chapter's revision history can be found under "Comments and Errata" on the *National Field Manual's* Home Page (http://pubs.water.usgs.gov/twri9A/). Comments on the *National Field Manual*, and suggestions for updates or revisions, should be sent to nfm-owq@usgs.gov.

ACKNOWLEDGMENTS

This *National Field Manual* responds to advances in technology and science and to the developing needs for water-quality monitoring through an ongoing process of review and revision. In the course of time, the expertise of numerous scientists has been tapped to provide scientifically sound guidance to personnel who collect and report field-measurement and field-analytical water-quality data. Our greatest debt of gratitude goes to the following early authors, editors, and reviewers of this field manual, without whom this project could not have succeeded: D.B. Radtke, J.V. Davis, J.B. Kurklin, R.T. Iwatsubo, K.A. Pearsall, W.E. Webb, I.M. Collies, and the analysts of the USGS National Water Quality Laboratory.

Special appreciation is due our colleagues and collaborators from the Hach and Hydrolab Companies, In-Situ Incorporated, and YSI Incorporated, who have given of their time and expertise.

It also is imperative to acknowledge the rich resources that formed the foundation of this "Field Measurements" chapter, as well as other *National Field Manual* chapters. The authors and editors have relied

on the broad spectrum of colleague expertise found in unpublished USGS and U.S. Environmental Protection Agency training and field manuals and technical memorandums, in addition to the references cited at the end of each section of Chapter A6.

Many thanks go to T.L. Miller and former Chiefs of the Office of Water Quality whose encouragement, faith, and practical support have been the force behind our ability to produce and maintain a national field manual for water-quality studies.

GUIDELINES FOR FIELD-MEASURED WATER-QUALITY PROPERTIES 6.0

By Franceska D. Wilde

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GUIDELINES FOR FIELD-MEASURED WATER-QUALITY PROPERTIES 6.0

By **Franceska D. Wilde**

This section summarizes general information, guidelines, and standard procedures that apply to the direct determination of water properties that are measured onsite. Procedures at sites where water-quality data are being transmitted continuously are beyond the scope of this chapter.[1]

FIELD MEASUREMENTS[2] **:** Determinations of physical or chemical properties that must be measured onsite, as close as possible in time and space to the medium being sampled.

Onsite measurement is necessary to preserve sample integrity and ensure data accuracy for the following field measurements: water temperature, dissolved-oxygen (DO) concentration, specific electrical conductance (SC), pH, reduction-oxidation potential (redox/ORP), alkalinity and acid-neutralizing capacity (ANC)[3], and turbidity.[4] In addition, guidance is provided in section 6.8 for the use of multiparameter instruments—instruments for which the individual field-measurement sensors are bundled in a sonde and deployed to the water body for in situ measurements.

QUALITY ASSURANCE 6.0.1

Adherence to standard U.S. Geological Survey (USGS) quality-assurance protocols is mandatory, and quality-control procedures are to be incorporated into every USGS water-quality data-collection effort. Quality assurance of the data collected includes the timely and accurate documentation of field information in electronic and paper records, second- or third-party auditing of such records, consistent and conscientious use of procedures and protocols to ensure sample integrity and data quality, and training in measurement techniques and the collection of quality-control data. Quality-control data for field measurements includes records of replicate measurements.

[1] USGS guidelines for continuous monitoring of selected field measurements are described in Wagner and others (2006).
[2] The term *field measurements*, as used in this National Field Manual, is synonymous with *field properties* and *field parameters*, terms that are used commonly in environmental water-quality literature.
[3] Alkalinity/ANC is a field analysis, not a direct field measurement; however, the analysis is performed routinely during the same field trip in which the other field-measurement data are collected. In this section, the term alkalinity is used when referring either to alkalinity or acid-neutralizing capacity.
[4] Each of these field measurements is discussed in detail in the following sections of this chapter of the National Field Manual: temperature (section 6.1), dissolved oxygen (section 6.2), specific electrical conductance (section 6.3), pH (section 6.4), reduction-oxidation potential (section 6.5), alkalinity and acid neutralizing capacity (section 6.6), and turbidity (section 6.7).

6.0.1.A Records

Record keeping is the responsibility of all field personnel. Electronic and paper records must be established and maintained for each uniquely identified sampling location to permanently document field activities, measurement readings, instrument calibration, and any other information needed to meet programmatic or regulatory requirements (see NFM 4.1.1 and 4.2.1 for detailed information that relates to records for surface water and ground water, respectively).

- For every field visit, instrument performance and the field-measurement data are transcribed onto paper and (or) electronic field and laboratory-request forms by the data collector. Much of the documentation process should be completed at the field site. Records should be checked independently by a field partner and (or) data administrator. Additional field forms—such as chain-of-custody or land-use forms—may be required, depending on project needs.
  - **USGS personnel are encouraged to use the Personal Computer Field Form (PCFF) instead of the paper field-notes form to increase efficiency and decrease transcription errors.**
  - A separate log book must be maintained for each field instrument and into which are recorded instrument repair, maintenance, and calibration history. The log book travels with the instrument. The pages of the instrument log books should be pre-numbered consecutively. Do not skip or tear out pages. Water-resistant paper is recommended. Log books are available to USGS personnel through the One-Stop Shop (item Q609FLD).
  - Use a blue or black indelible ballpoint pen to write on paper forms and in log books. If recording in a Rite in the Rain® log book or on other water-resistant surface, an all-weather or bullet pen is recommended. Use of a pencil is not acceptable; felt-tipped pens (for example, Sharpie®) should not be used, and could compromise the quality of data for samples for analysis of volatile organic compounds.
  - Fill out the forms as completely as possible. Erroneous or mistaken entries should be crossed out with one line and initialed.
- Final or "reported" field-measurement values for USGS studies are to be entered into the following parts of the National Water Information System (NWIS) (see NFM 4 for more detailed information).
  - **QWDATA**: Contains discrete (noncontinuous) field-measurement data in addition to laboratory analyses.
  - **GWSI**: Contains all final noncontinuous, nonautomated ground-water water-level measurements.
  - **ADAPS**: Contains automated, continuous water data.
- The conventions used for reporting field-measurement data are described at the end of each field-measurement section of chapter 6. Stabilization criteria for recording direct field measurements are given in table 6.0–1.

Table 6.0–1. Stabilization criteria for recording direct field measurements

[±, plus or minus value shown; °C, degrees Celsius; ≤, less than or equal to value shown; µS/cm, microsiemens per centimeter at 25°C; >, greater than value shown; unit, standard pH unit; ~, about; DO, dissolved-oxygen concentration; mg/L, milligram per liter; FNU, formazin nephelometric unit]

Standard direct field measurement[1]	**Stablization criteria**[2] (variability should be within the value shown for about five or more measurements)
Temperature:	
Thermistor thermometer	± 0.2°C
Liquid-in-glass thermometer	± 0.5°C
Conductivity (SC):	
≤100 µS/cm	± 5 percent
> 100 µS/cm	± 3 percent
pH:	
(meter displays to 0.01)	± 0.1 to 0.2 pH unit[3] Allow ± 0.3 pH units if drifting persists, or measurement is in low-conductivity (~75 µS/cm) water, or for continous monitor.
DO[4]	
Amperometric sensors	± 0.2 mg/L (± 0.3 mg/L for continous monitor)
Optical/luminescent-method sensors	± 0.2 mg/L (± 0.3 mg/L for continous monitor)
Turbidity[5, 6]	
≤ 100 FNU (or other turbidity unit)	± 0.5 turbidity unit or ± 5% of the measured value, whichever is greater.
> 100 FNU (or other turbidity unit)	± 10 percent[6]

[1] Eh is not considered to be a routine or direct field measurement (see NFM 6.5). Alkalinity and acid neutralizing capacity determinations require a titration procedure and are not considered direct measurements.
[2] Refer to NFM 6.8 for similar criteria when using multiparameter instruments. For continuous monitors, consult Wagner and others, 2006.
[3] Select pH sensor criteria based on precision and accuracy listed for the sensor being used.
[4] **Amperometric sensors**: Note that the calibration criterion when DO is measured by a continuous monitor can be extended to ± 0.3 mg/L. **Optical/Luminescent sensors**: The criterion for luminescent-method sensors is biased conservatively, owing to the differing technologies that are employed among the various manufacturers of these sensors and current paucity of field data. **Spectrophotometric method**: Stabilization is not applicable to the spectrophotometric method.
[5] Multiparameter instruments used for most USGS turbidity applications contain single-beam infrared wavelength turbidity sensors and are reported in FNU. Check the Excel spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls to determine the appropriate turbidity unit of measure; consult NFM 6.7 for detailed guidance on turbidity measurement and instrumentation.
[6] In high-turbidity conditions, especially when collecting data during storms, lengthening the averaging period to help smooth out the signal (assuming this is an option for the instrument in use) or increasing the time period between measurements, is recommended.

6.0.1.B Criteria for Performing Field Measurements

Field measurements should represent, as closely as possible, the ambient physical and chemical properties of the surface-water or ground-water system at the time of sampling. **Properties such as temperature, DO concentration, and Eh must be measured directly (in situ) in the water body.** Other properties such as pH, conductivity, and turbidity may be measured either in situ or from a sample withdrawn from the source, depending on the type of equipment selected for field measurements. Alkalinity determination requires titration on a measured volume of subsample. These properties are to be measured at the field site.

Expertise. Collecting data for USGS studies requires training, practice, and a knowledge of required and recommended protocols.

- **Training:** Field personnel are to enroll in USGS water-quality classes. Fundamental training for performing water-quality field activities in accordance with USGS protocols and standard procedures includes a 2-week Field Water-Quality Methods class (QW1028). Other foundational training includes Water-Quality Principles (QW1022), Statistical Methods for Environmental Data Analysis (QW1075), Quality-Control Sample Design and Interpretation (QW2034), and Water-Quality Toolbox for NWIS Users (QW1297). These classes provide a practicum for the knowledgeable execution of field and office project activities and help to ensure proper management and valid interpretation of the data being collected.
- **National Field Quality Assurance Program (NFQA):** All field personnel, including non-USGS employees, who collect field-measurement data that are entered into NWIS are to participate annually in the NFQA Program (http://nfqa.cr.usgs.gov/NFQA-overview.html, accessed 8/22/08), which evaluates the proficiency of personnel in measuring pH, SC, and alkalinity (or ANC).

Equipment. A variety of single-parameter and multiparameter field-measurement instruments are available that use various technologies to measure the same water property and that require differing calibration, maintenance, and measurement methods.

- Single-parameter instruments include, for example, stand-alone temperature sensors; DO, SC, and pH meters (with or without temperature sensors); and turbidimeters (for example, nephelometers). The protocols and procedures that pertain to these instruments are a primary focus of NFM 6.1 through NFM 6.5. Single-parameter instruments are selected according to project needs and convenience, or when required because site conditions do not allow use of a multiparameter instrument, or for the purpose of instrumenting a flowthrough cell or chamber.
- Multiparameter instruments have measurement sensors that fit into the body of a sonde. Measurements using the sonde can be made either by submersing the sensor sonde in surface water or ground water, or by pumping a sample inline from its source to an airtight cell/chamber into which the sonde fits.

- Field teams must determine if the instruments and methods to be used will produce data of the type and quality required to fulfill study needs as well as USGS requirements.
  - Check the appropriate section in this chapter for the required and recommended methods and equipment, instructions for measurement and quality-control procedures, and guidelines for troubleshooting and data reporting.
  - Become familiar with the instructions and precautions provided by the manufacturers of the instruments to be used. Field personnel are encouraged to contact instrument manufacturers for answers to technical questions about the operation of their instrument. Apparent conflicts between USGS protocols and a manufacturer's instructions should be identified and resolved by consulting the local or regional water-quality specialist or the USGS Office of Water Quality. Field instruments constantly are being improved or replaced using newer technology that often is unique in some aspect to the manufacture of the instrument. Personnel should be knowledgeable about emerging technologies that can improve the quality and efficiency of their field activities.
  - **Make field measurements only with properly calibrated instruments.** Calibration is required at the field site for many, but not all, instruments. This requirement depends on the technology employed by the instrument; consult the manufacturer's instructions.
  - Review the instrument log book(s) before leaving for the field site to ensure that problems previously encountered have been resolved and that the appropriate instrument and site maintenance were performed.
  - Backup instruments and batteries should be readily available and in good working condition.

Test meters and sensors before leaving for the field. If the instrument or measurement is new to you, practice your measurement technique with a mentor who has current experience and is up-to-date with USGS field-method protocol and procedures.

Performance. Be aware of sampling and field or other conditions that could introduce bias to the determination of field-measurement values. Execute field measurements in a manner that avoids or minimizes bias from data-collection activities.

- Check instrument precision and accuracy (variability and bias) periodically while at a field site; precision and accuracy may vary, depending on the instrument used, sampling conditions, and the expertise of personnel.
- The USGS standard procedure is to allow sensors that are calibrated in the field to equilibrate to the temperature of the water being monitored to the extent possible before making field measurements, as is appropriate for the instrument in use. Calibration buffers and standards also should be brought to ambient sample temperature before the instrument sensor(s) are field-calibrated.

- Sensors have equilibrated adequately when instrument readings have stabilized; that is, when the variability among measurements does not exceed an established criterion. **The USGS criteria for stabilized field readings are defined operationally in table 6.0–1 for a set of about five (or more) sequential measurements.**
- The natural variability inherent in surface water or ground water at the time of sampling generally falls within the stability criteria given in table 6.0–1 and reflects the accuracy that should be attainable with a properly calibrated instrument.
  - **Surface water:** Allow at least 60 seconds (or follow the manufacturer's guidelines) for sensors to equilibrate with sample water. Take instrument readings until the stabilization criteria in table 6.0–1 are met. Record the median of the final three or more readings as the value to be reported for that measurement point (section 6.0.2).
  - **Ground water:** Start recording measurements after sensors have equilibrated with purge water. Take instrument readings until the stabilization criteria in table 6.0–1 are met and the required number of well volumes of ground water have been purged. Record the median of the final five or more readings as the value to be reported for that site (section 6.0.3).
- **For sites at which variability exceeds the criteria shown in table 6.0–1:** Allow the instrument a longer equilibration time and record more measurements. To determine the value to be reported for that measurement point, either use the median of the final five or more measurements recorded, or apply knowledge of the site and professional judgment to select the most representative of the final readings.

RULE OF THUMB:

For field analyses that are made on subsamples, such as alkalinity, check your precision in the field at least every tenth sample by making the measurement three times using separate sample aliquots from the same sample volume.

SURFACE WATER 6.0.2

Field measurements must accurately represent the physical or chemical properties of the surface water being studied. In order to collect data that represent water conditions at the time of sampling, it is necessary to correctly locate the point(s) of measurement, select equipment appropriate to site conditions and study needs, and use appropriate methods to make accurate field measurements.

Properties of water temperature, DO concentration, and Eh must be measured directly within the water body (in situ). Other properties, such as pH, conductivity, and turbidity, often are measured in situ but may be measured in a subsample of a composite or grab sample, as appropriate for the study.

Summary of Surface-Water Sampling Methods 6.0.2.A

Standard USGS procedures for locating points of sample collection and sample-collection methods for surface-water sampling are detailed in NFM 4.1. **This section (6.0.2.A) provides an abbreviated description of surface-water isokinetic sampling methods, and should not be used without a detailed understanding of the method as given in NFM 4.1.3.** The quality and interpretation of the field-measurement data collected depend also on the equipment with which samples are withdrawn, composited, and subsampled. Guidance for equipment selection is detailed in NFM 2.1.1. **Familiarity with the USGS protocols and standard procedures prescribed in these chapters of the National Field Manual is the responsibility of all USGS water-quality field personnel.**

Normally, the point or points at which field measurements are made correspond to the location(s) at which samples are collected for laboratory analysis (NFM 4.1.3). The decision for whether grab-sampling methods or isokinetic sampling methods will be used is based on the characteristics of the water body to be sampled or monitored and on study objectives.

- **Still-water conditions** are found in storage pools, lakes, and reservoirs. Field measurements often are made in situ at multiple locations and depths. The location, number, and distribution of measurement points are selected according to study objectives.
  - — Measurements made at discrete depths through the vertical water column must not be averaged or reported as a median value that represents the entire vertical.
  - — Report the value selected to represent each point measured in the vertical as individual stations, or distinguish measurements in that vertical by assigning a unique time to each measurement.
- **Flowing-water conditions** are found in perennial and ephemeral streams. The location and the number of field measurements depend on stream conditions and study objectives (NFM 4.1). Generally, a single set of field-measurement data is used to represent an entire stream cross section at a sampling site and can be useful when calculating chemical loads.
  - — To obtain data representative of the section, the variability of discharge and field measurements across the stream must be known.
    - An exploratory field-measurement profile across a section of a stream can be used to estimate the magnitude of variation along the cross section.
    - A field-measurement profile can be useful also—especially at new or poorly documented sites—to determine which isokinetic method (equal-discharge increment (EDI) or equal-width increment (EWI)) should be used for sampling.

— The final points of measurement are determined according to whether the EDI or EWI method will be used. Make individual measurements at a number of equally spaced verticals along the cross section and at multiple depths within each vertical. Alternatively, consult previous records for the site.

To locate measurement points:

1. Check the cross-sectional profile data of the stream site to determine the variability of discharge per unit width of the stream and of field-measurement values across the section.
   - Make individual measurements at a number of equally spaced verticals along the cross section and at multiple depths within each vertical—or consult previous records for the site.
   - Make in situ (6.0.2.B) field measurements for the profile.
   - Field-measurement profiles of stream variability are needed for low- and high-flow conditions and should be verified at least every 2 years or as study objectives dictate.
2. Select the EDI or EWI method to locate points of measurement (refer to NFM 4.1.3 to select and execute the appropriate method).
   - If stream depth and velocities along the cross section are relatively uniform, use EWI.
   - If stream depth and velocities along the cross section are highly variable, use EDI.
   - In a small (usually less than 5 feet (ft) in width) and well-mixed stream, a single point at the centroid of flow may be used to represent the cross section. (The stream is considered well mixed if the variability of field-measurement values noted in the cross-sectional profile is considered negligible; for example, within the stabilization criteria given on table 6.0–1 plus best professional judgment of what is reasonable for the field site.) The centroid of flow is defined as the point in the increment at which discharge in that increment is equal on both sides of the point.

Equal-Discharge Increments (EDI)

The stream cross section is divided into increments of equal discharge. Field measurements can be made in situ at the centroid of each increment or by collecting an isokinetic depth-integrated sample at the centroid of each increment and determining the value either of each sample or of a composite of the samples. These methods result in data that are discharge weighted (Edwards and Glysson, 1999).

- ▶ Knowledge of streamflow distribution in the cross section is required to select verticals at which measurements will be made or subsamples collected.
- ▶ Streamflow distribution can be based on the long-term discharge record for the site or on a discharge measurement made just prior to sample collection.

RULE OF THUMB:

Divide the stream into a minimum of four increments. More increments could be needed for a stream site that is poorly mixed.

To divide the cross section into increments of equal discharge:

The following comprises a summary of some steps needed in applying the equal-discharge-increment method, and should not be used without an understanding of the method and the detailed instructions as given in NFM 4.1.3.

1. Visually inspect the stream from bank to bank, observing velocity, width, depth distribution, and the apparent distribution of sediment and aquatic biota in the cross section. Note the location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other obstructions.
2. If the channel and the control governing the stage are stable, historical streamflow data can be used to determine the measurement locations. If the channel is unstable or if no historical data are available, make a discharge measurement and preliminary field measurements across the selected section of channel.
   a. From the available discharge data, either:
      - Construct a graph using cumulative discharge or cumulative percent of total discharge plotted against the cross-sectional width, or
      - Determine EDI sections directly from the discharge-measurements note sheet.
   b. If profile values of pH, conductivity, temperature, and DO differ by less than 5 percent and show that the stream is well mixed both across the section and from top to bottom, a single measurement point at the centroid of flow can be used to represent field-measurement values of the cross section.
3. From the graph or measurement notes, determine the number and locations of EDIs and the centroids (the far midpoints) of those increments.

EXAMPLE: If five increments will be used, select points of measurement by dividing the total stream discharge by 5 to determine increment discharge: in this case, each EDI equals 20 percent of discharge. The first vertical is located at the centroid of the initial EDI, the point where cumulative discharge equals 10 percent of the total discharge. The remaining 4 centroids are found by adding increment discharge to the discharge at the initial EDI centroid. The far midpoints also need to be calculated. The EDI centroids will correspond to points along the stream cross section where 10, 30, 50, 70, and 90 percent of the total discharge occur.

When making field measurements:

1. Select either the in situ or subsample method and follow the instructions in 6.0.2.B or 6.0.2.C.
   - **In situ method**—Go to the centroid of the first equal-discharge increment. Using submersible sensors, measure at mid-depth (or multiple depths) within the vertical. Repeat at each vertical. The value recorded at each vertical represents the median of values observed within approximately 60 seconds after sensor(s) have equilibrated with stream water.
   - **Subsample method**—Collect an isokinetic depth-integrated sample at the centroid of each equal-discharge increment, emptying the increment sample into a compositing device. Measure field parameters either in the sample collected at each increment or in a subsample taken from the composite of all the increment samples.
2. The final field-measurement value is the mean of the in situ or individual increment-sample value for all the EDI verticals in the section (the composite subsample yields a single value). (Note: for pH, use the median value or compute a mean pH using the method described in section 6.4.3.A). Enter data on field forms.

EXAMPLE: Table 6.0–2 provides an example of how mean conductivity measured in situ is calculated using the EDI method.

- In the example, the correct value for the discharge-weighted mean conductivity is 163 µS/cm, calculated from 815 divided by 5 (the sum of the recorded median values divided by the number of median measurements). This mean value should be entered into the QWDATA database as a calculated value.
- Note that at the midpoint of the center centroid of flow (increment 3) the median conductivity would have been reported as 155 µS/cm; if conductivity had been measured near the left edge of the water (increment 1), the conductivity would have been reported as 185 µS/cm.

Table 6.0–2. Example of field notes for a discharge-weighted conductivity measurement

[ft/sec, feet per second; ft, feet; ft^2 square feet; ft^3/sec, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; LEW, left edge of water; —, not available; REW, right edge of water]

Equal discharge increment	Percent of flow in increment	Mean velocity, in ft/sec	Width of increment, in ft	Depth of increment, in ft	Area of increment, in ft 2	Increment discharge, in ft3/sec	Median conductivity, in µS/cm
LEW	0	—	—	—	—	—	—
1	20	2.0	22	5.7	125	250	185
2	20	2.2	11	10.4	114	250	170
3	20	2.3	9	12.0	109	250	155
4	20	3.9	5	12.8	64	250	155
5	20	3.4	10	7.4	74	250	150
REW	0	—	—	—	—	—	—

Calculation of conductivity: mean of median conductivity measurements $\left(\frac{815}{5} = 163\,\mu S/cm\right)$

Equal-Width Increments (EWI)

The stream cross section is divided into increments of equal width. Knowledge of the streamflow distribution in the cross section is not required.

- In situ field measurements are made at the midpoints of each increment. Area-weighted concentrations can be computed from these measurements (table 6.0–3).
- Subsample field measurements are made in discrete samples that usually are withdrawn from a composite sample collected using an isokinetic sample and isokinetic depth-integrating method. The volume of the isokinetic sample must be proportional to the amount of discharge in each increment and measurements in subsamples taken from the compositing device result in discharge-weighted values.

To divide the cross section into increments of equal width:

The following comprises a summary of some steps needed in applying the EWI method, and should not be used without an understanding of the method and the detailed instructions given in NFM 4.1.3.

1. Visually inspect the stream from bank to bank, observing velocity, width, depth distribution, and the apparent distribution of sedment and aquatic biota in the cross section. Note the location of stagnant water, eddies, backwater, areas of faster than normal flow, and piers or other obstructions.
2. Determine stream width using a tagline or from station markings on bridge railings or cableways.
3. Divide the section into increments of equal width based on flow and stream-channel characteristics along the cross section, field-measurement variability from the cross-section profile, and data objectives for the study. This interval width will govern the number of verticals used, and applies also to streams in which flow is divided (for instance, in a braided channel).
4. Locate the midpoint of the first vertical at a distance of one-half of the selected increment width from the edge of the water. Locate other measurement verticals at the centers of the remaining increments.

EXAMPLE: In a stream 60 ft wide that has been divided into 15 increments of 4 ft each, the first measurement vertical would be 2 ft from the water's edge, and subsequent verticals would be at 6, 10, 14 ft, and so forth, from the starting point at water's edge.

RULE OF THUMB:

- **In streams 5 ft wide or greater, a minimum of 10 equal-width increments generally is recommended.**
- **In streams less than 5 ft wide, use as many increments as practical, but they must be equally spaced and a minimum of 3 inches (in.) apart.**

When making field measurements:

1. Select either the in situ or the subsample method and follow the instructions in 6.0.2.B or 6.0.2.C, respectively.
   - **In situ method**—Measure at the midpoint of each equal-width increment. Using submersible sensors, measure at mid-depth within the vertical.
   - **Subsample method**—Collect an isokinetic depth-integrated sample at the midpoint of each equal-width increment, emptying each sample into a compositing device. **Use of the correct sampling equipment is critical to execute this method successfully; standard samplers cannot meet isokinetic requirements when stream velocity is less than 1.5 feet/second (NFM 2.1.1.A).**
2. Record a value for each field measurement at each vertical. The value recorded represents the stabilized values observed within approximately 60 seconds after the sensor(s) have equilibrated with the stream or subsample water.

EXAMPLE: Table 6.0–3 provides an example of an area-weighted median measurement for conductivity measured in situ.

- In the example, the area-weighted median conductivity equals 130 µS/cm.
- To calculate an area-weighted median, multiply the area of each increment by its corresponding field measurement, sum the products of all the increments, and divide by total cross-sectional area.
- Note that if the conductivity reported were selected at mid-depth of the vertical of centroid of flow (section 10), it would have been reported as 125 µS/cm; if the conductivity reported were near the left edge of the water, it would have been reported as 150 µS/cm.

▶ The final field-measurement value normally is calculated as the mean of the values recorded at all EWI increments, resulting in an area-weighted mean. (Note: for pH, take the median value or, to calculate a mean pH, be sure to use only the method described in section 6.4.3.A).

▶ Alternatively for EWI, if the area-weighted median best represents integrated stream chemistry, then the median can be reported instead of the mean, but be sure to document this on the field form and in the final data report if a parameter code is not available in NWIS for median values.

Table 6.0–3. Example of field notes for an area-weighted conductivity measurement

[ft, feet; LEW, left edge of water; ft^2, square feet; SC, conductivity (specific electrical conductance); µS/cm, microsiemens per centimeter at 25 degrees Celsius;—, not available; REW, right edge of water]

Section number	Cumulative percent of flow in section	Vertical location, in ft from LEW	Width of section, in ft	Depth of vertical, in ft	Area of section, in ft^2	Median SC, µS/cm	Product of median SC and area
LEW	0	0	—	—	—	—	—
1	2	2	4	1.0	4.0	150	600
2	4	6	4	2.0	8.0	145	1,160
3	6	10	4	2.6	10.4	145	1,508
4	10	14	4	3.2	12.8	140	1,792
5	16	18	4	3.5	14.0	135	1,890
6	22	22	4	4.0	16.0	130	2,080
7	28	26	4	4.5	18.0	130	2,340
8	34	30	4	5.4	21.6	125	2,700
9	42	34	4	6.0	24.0	125	3,000
10	50	38	4	5.7	22.8	125	2,850
11	62	42	4	5.1	20.4	125	2,550
12	76	46	4	4.6	18.4	125	2,300
13	88	50	4	3.5	14.0	125	1,750
14	96	54	4	1.4	5.6	135	756
15	99	58	4	1.0	4.0	140	560
REW	100	60	—	—	—	—	—

Calculation of SC: sum of values in last column divided by the total cross-sectional area $\left(\frac{27,836}{214} = 130\,\mu S/cm\right)$

In situ field-measurement procedures 6.0.2.B

An in situ measurement (fig. 6.0–1), made by immersing a mutiparameter sonde or one or more single-parameter field-measurement sensors directly into the water body, is used to determine a profile of variability across a stream section. In situ measurement can be repeated if stream discharge is highly variable and if measurement points need to be located at increments of equal discharge. **Note that in situ measurements are point samples and thus are not depth integrated.**

- **In situ measurement is mandatory for determining temperature, DO concentration, and Eh.**
- In situ measurement also can be used for pH, conductivity, and turbidity. The alkalinity determination can only be performed on a stirred subsample contained in a vessel.
- If field measurements for pH, DO, and Eh are to be determined in anoxic water, the measurements must be made in situ.

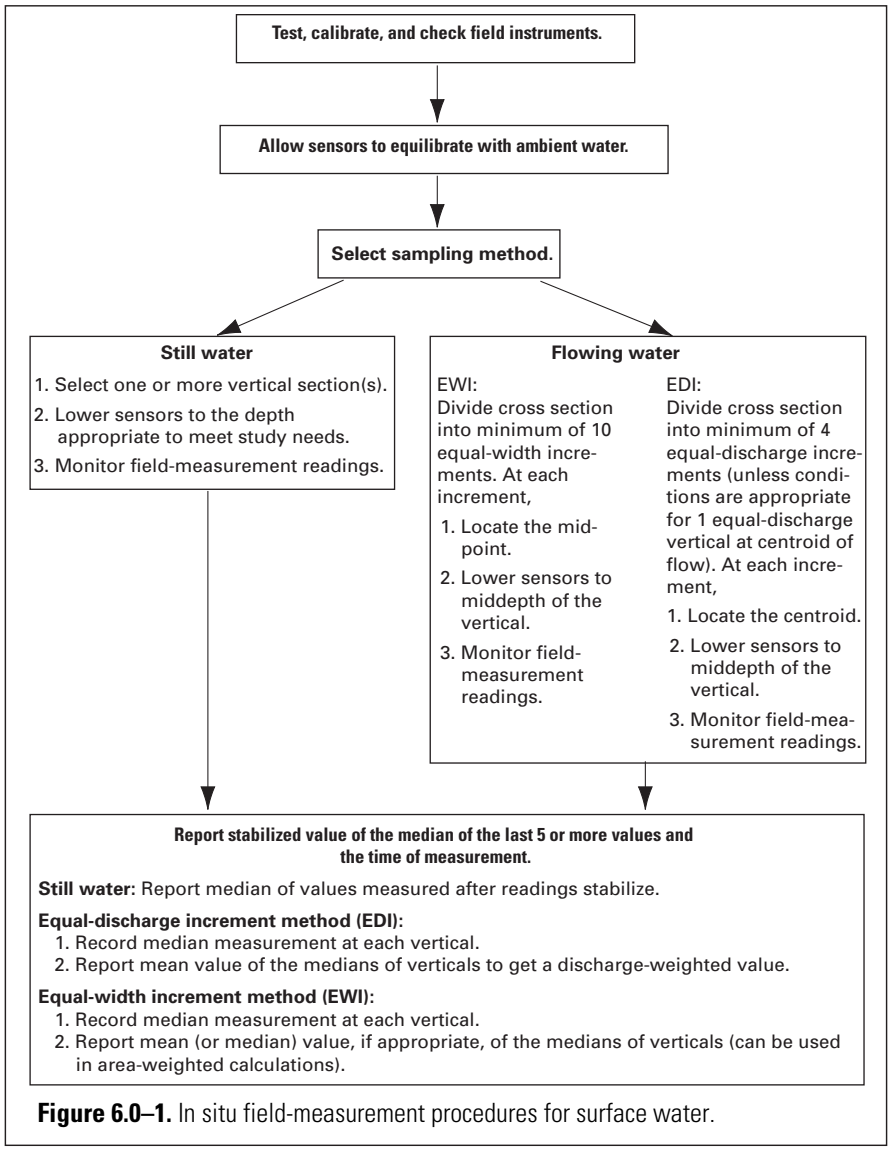

Figure 6.0–1. In situ field-measurement procedures for surface water.

6.0.2.C Subsample field-measurement procedures

Subsamples (discrete samples that have been withdrawn from a sample-compositing device or point sampler) contained in a measurement vessel open to the atmosphere can yield good data for conductivity, pH, turbidity, and alkalinity, as long as correct procedures are followed. (The results for pH and alkalinity cannot be considered valid if the water is anoxic.) Subsample field measurements should be completed as soon as possible after collection, minimizing temperature changes and exposure to the atmosphere (fig. 6.0–2). Remember that measurements of water temperature, DO concentration, and Eh cannot be taken from a subsample and must be made in situ.

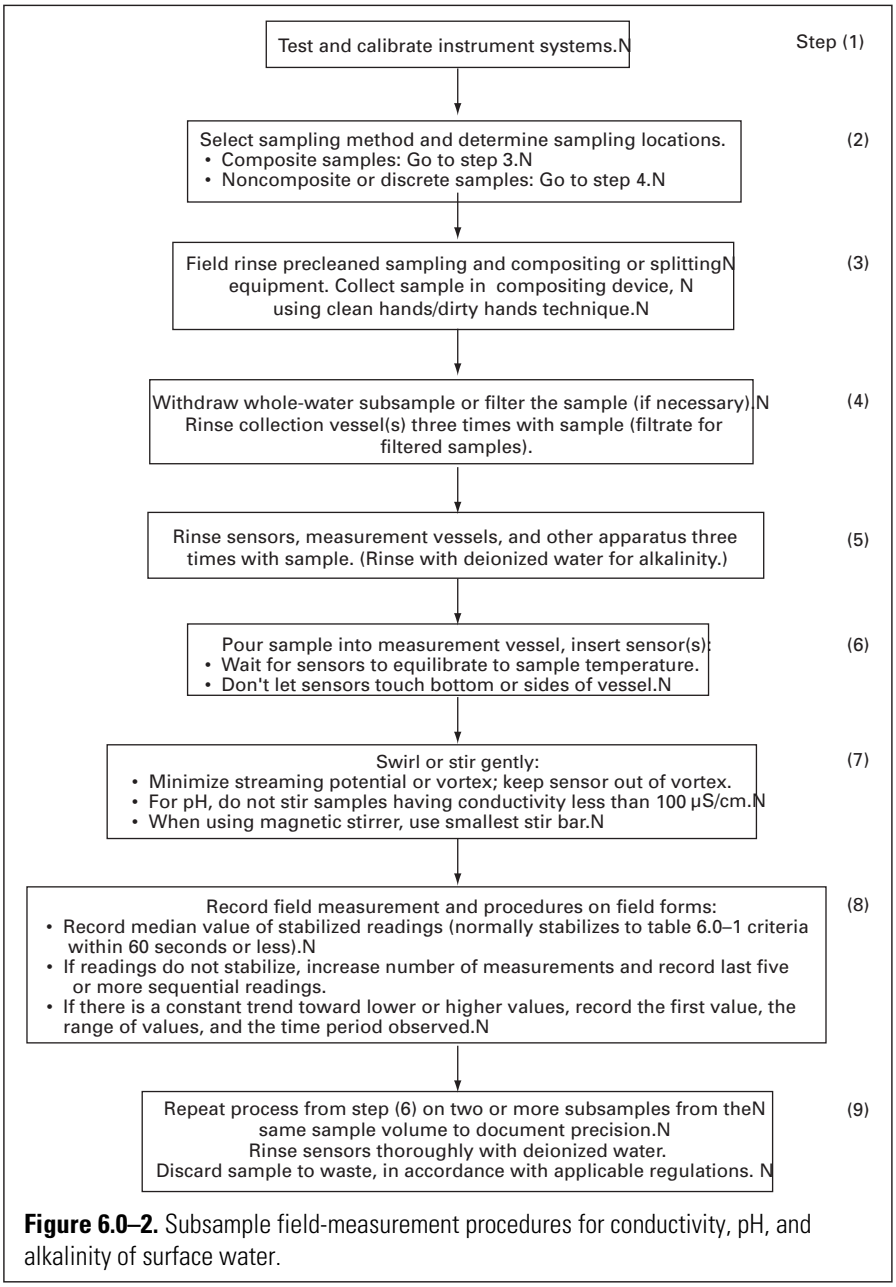

Figure 6.0–2. Subsample field-measurement procedures for conductivity, pH, and alkalinity of surface water.

GROUND WATER 6.0.3

Field measurements in ground water must accurately represent the physical and chemical properties of water in the formation (aquifer) at the time of data collection. This normally requires purging the well of standing water while monitoring field measurements. The purge procedures applied can, however, depend on the type of well from which sample water will be withdrawn (for example, a public-supply, domestic, or monitor well), well-construction and aquifer characteristics, and study objectives. The final field-measurement values to be recorded for the ground-water site for that date are determined toward the end of the purging process. Consult NFM 4.2 for additional guidance on well purging and USGS protocols and standard procedures for ground-water withdrawal at wells.

> **TECHNICAL NOTE:** Well purging removes standing water from a well. Purging reduces chemical and biochemical artifacts caused by well installation, inadequate well development, well-construction materials, or infrequent pumping (ASTM International, 2005). Purging also serves to rinse and condition sampling equipment with the ambient ground water to be sampled.

Ground water can be withdrawn from wells using submersible or above-ground pumps, or bailers or similar discrete-volume samplers (for example, syringe or Kemmerer samplers). Well type and construction, sampling objectives and target analytes, and site conditions can constrain the equipment selected; which method of ground-water withdrawal will be used; and how it will be employed. NFM 2.1.2 provides detailed information on equipment for ground-water withdrawal at wells and sample collection.

- **Pumps.** The pumping mechanism can affect the degree to which certain measurements represent true ground-water properties. For example, pumps that introduce turbulence or heat to the water column can result in nonrepresentative DO and temperature values. The pump should produce a smooth, solid stream of water with no air or gas bubbles and without pump cavitation during field measurements and sample withdrawal.
  - A positive-displacement submersible pump is recommended for environmental sampling at depths greater than 28 ft and generally is recommended for use at wells (unless the well has a permanently installed pump).
  - A peristaltic pump often is a good choice for obtaining samples collected from wells at a depth of 28 ft or less, but the stream of water from this or other suction-lift pump should not be used when measuring DO, Eh, or other properties sensitive to oxygen contamination or volatilization.
  - When the depth to water is greater than 250 ft and (or) a large volume of water must be purged, a dual-pump system can be used: position a submersible pump downhole and a centrifugal pump at the surface (see NFM 4.2 for additional information). An inflatable packer system set above the pump can be used to reduce the volume and time required for purging; this can be especially useful in deep wells or if regulations require that purge water be contained.
- **Bailers. Bailers are not recommended for purging** because they have limited use for routine field-measurement determinations and also are inefficient for well purging. The bailed sample must be decanted to obtain subsamples for field measurements, exposing the sample to atmospheric conditions. Thus, **water subsampled from a bailer sample may not be used for measurements of DO concentration, Eh, and water temperature.** The action of the bailer being deployed downhole can introduce atmospheric gases and particulates into the water column, also resulting in biased turbidity and other field measurements.

Ground water is sampled for field measurements in one of three ways: (1) by pumping formation water inline to a flowthrough cell or chamber[5] containing measurement sensors (inline-flow procedure); (2) by deploying measurement sensors downhole (downhole or in situ procedure); or (3) by subsampling water collected from a discrete-volume sampler (for example, bailer), and making measurements using individual instruments (subsample procedure). Inline-flow and in situ procedures comprise direct-measurement methods (section 6.0.3.B), in contrast to the subsample method (section 6.0.3.C). **For most field applications, using inline-flow procedures (the flowthrough cell/chamber system) is recommended and most efficient.**

RECOMMENDED:

- **Use a positive-displacement submersible pump for ground-water withdrawal.**
- **Use inline-flow (flowthrough cell/chamber) procedures for field measurements.**

The measurement system selected can be constrained by the type of well being sampled and its accessibility.

- **Supply wells[6]**—Downhole access for a pump or sensors might be limited or not possible at public or domestic supply wells, and water withdrawal may be located at or near the well head or from a tap (for drinking-water studies). The flowthrough cell/chamber field-measurement system (inline-flow procedure) should be used in this case.
  - The standard purging protocol may not be appropriate. (Consult "Exceptions to the standard purging procedure" in NFM 4.2.)
  - Identify equipment permanently installed in or at the well (such as a pump) that can affect the logistics and quality of the field measurement.
  - The field-measurement system should be connected to the wellhead so as to bypass holding tanks, backflow pressure tanks, flow meters, or chemical treatment systems.
- **Monitor wells**—At wells that allow downhole access, it is necessary for the study to determine the specific depth interval at which measurements will be made or from which water will be withdrawn for field-measurement determinations. Again, selection of the sampling-depth interval depends on how the well was constructed, in addition to the sampling design of the study. Record the depth at which the pump intake is set within a given screened or open interval.
  - The standard purging protocol usually is appropriate. (Consult NFM 4.2 before field work begins; the summary given in section 6.0.3.A does not provide all the information needed to ensure adequate performance.)
  - Either direct-measurement or subsample procedures can be used at monitor wells, depending on study needs and sampling objectives. If samples for laboratory analysis will be collected, however, use of the flowthrough cell/chamber system (inline-flow procedure) is recommended in order to avoid sample contamination from use of a downhole sensor system or bailer.

[5] The terms flowthrough cell and flowthough chamber are synonymous, although "cell" is more commonly used by manufacturers of such equipment.

[6] Supply wells designed for public-supply systems, domestic supply, or commercial or agricultural use.

Summary of Well-Purging Protocols 6.0.3.A

As a rule of thumb, the standard USGS purge protocol is to remove three or more well volumes of standing water while monitoring water level and the stabilization of routine field measurements as a function of time, pumping rate, and the volume of water being removed (see NFM 4.2.3). Routine field measurements include pH, temperature, SC, DO, and turbidity. Inherent in the purge procedure is an assumption that stabilization of field properties indicates that the water being discharged from the well represents ambient formation water. Field personnel should examine this assumption for each well, using their knowledge of the well and aquifer hydraulics. Field experience, understanding of the effects of hydrologic and geochemical conditions, and knowledge of data-collection and data-quality requirements are necessary to determine the most accurate field value.

Before purging begins:

1. Select and set up the field-measurement system that best fits the requirements for the data-collection effort. Options include:

   a. A clear, air-tight flowthrough chamber, holding the sensors of single-parameter instruments (generally temperature, pH, DO, SC; often turbidity; and sometimes Eh (ORP)). The flowthrough chamber is connected to tubing through which the sample is pumped directly from the well to the measurement chamber.

   b. A clear, air-tight flowthrough cell/chamber fitted to the sensors-containing sonde of a multiparameter instrument, to which the sample is pumped directly from the well to the measurement chamber.

   c. A multiparameter instrument without the flowthough cell on the sonde, deployed downhole in the well.

   d. Selected single-parameter meters with sensors allowing for downhole submergence.

   e. Single-parameter meters; the measurement is made with each sensor immersed in separate subsamples collected from a discrete-volume sampler.

Options (a) and (b) generally are preferred and constitute what is termed in this report as the **"Inline-flow Procedure**." Options (c) and (d) constitute what is termed in this report as the "**Downhole (in situ) Procedure.**" Option (e) is termed in this report as the "**Subsample Procedure**."

2. Check the identification number on the well and well depth to verify that this is the well intended for data collection or sampling. Review the well's record of water levels, drawdown, and field-measurement variability (if available), and prepare the necessary field forms (for example, the well-purge record, national or study field form, and chain-of-custody record). Record the type of equipment being used.

3. Lay plastic sheeting around the well to prevent contaminating the equipment. Unlock the well housing or top of the protective casing and remove the well cap. Set up the field-measurement system, paying attention to the sequence in which sensors are inserted into the flowthrough chamber with respect to water flow (if a flowthrough chamber is used). Figure 6.0–3 illustrates a typical sample-collection manifold, through which water is directed either to waste, to the flowthrough (field-measurements) cell/chamber, or to the sample-collection chamber. To adjust the direction of flow, a flow-regulating needle valve or ball valve should be kept either full on or full off and should not be used to adjust either the proportion or rate of flow.

4. Review the purging history of the well, particularly the field-measurement data previously recorded. This can save time and help determine the procedures and length of time over which the well should be purged.

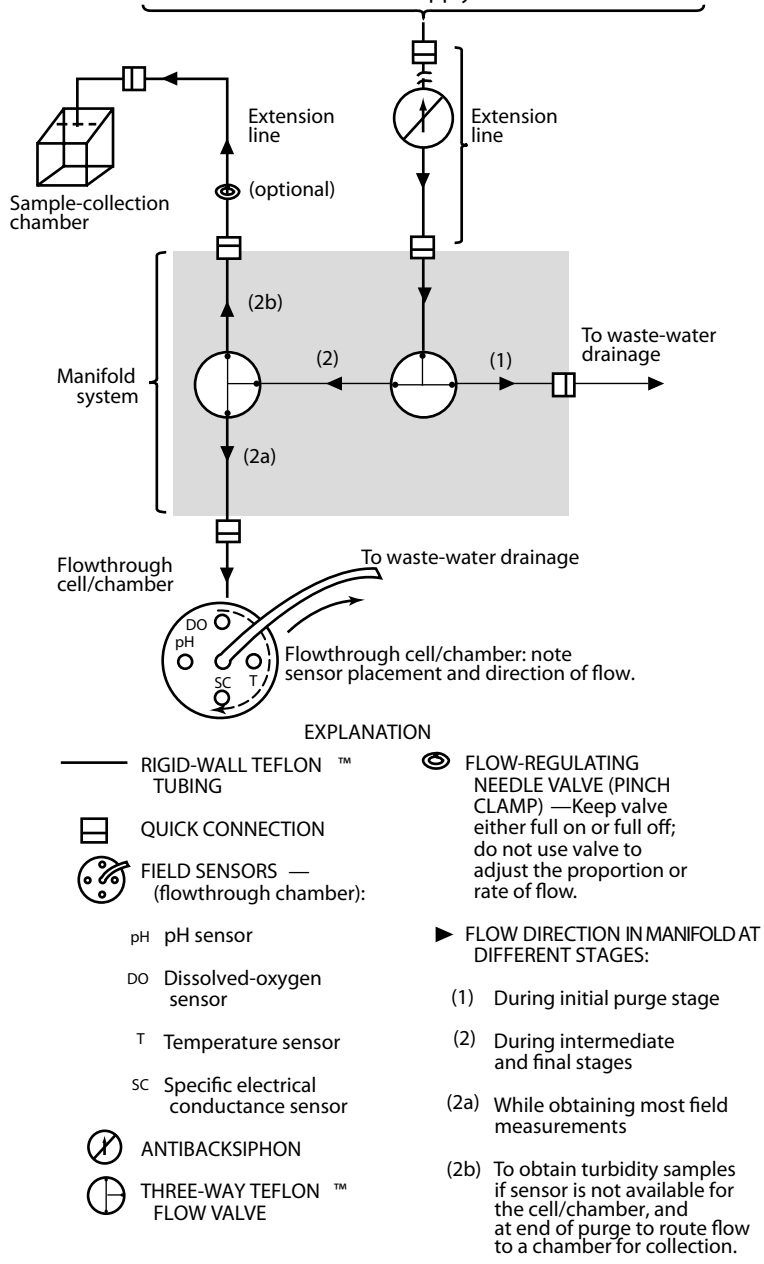

Figure 6.0–3. Sketch of a manifold and flowthrough cell/chamber used during well purging and sample collection (top view) (modified from NFM 4, Figure. 4–10).

To purge a monitor well (assuming that the well will be pumped and that a flowthrough cell/chamber system and water-level sensor will be used):

1. Measure and record the depth to static water level (fig. 6.0–4). Instructions for water-level measurement are given in NFM 4, appendix A4–B.
2. Calculate and record the well volume using the information on fig. 6.0–4. Note that the depth to the screened or open interval and the inside casing diameter must be known to calculate well volume.
   - Calculate the casing volume using the height of the water column to the bottom of the well (instead of the water column height to the top of the screen).
   - Include an estimate for the volume of water stored in the annular space between the casing and the borehole wall, using knowledge of the borehole diameter.
3. **In monitor and other wells with downhole access,** lower a submersible pump followed by a water-level sensor to the desired location of the pump intake. The final pump intake position always is located at the point of sample collection. Lower the equipment slowly and smoothly to avoid stirring up particulate matter.
   - Position the pump intake between 3 ft (~0.9 meter (m)) below the static water surface and a minimum distance above the top of the open/screened interval of 10 times the well diameter (for example, 20 in. for a 2-in. well diameter), if the sample is to be integrated over the entire screened or open area of the aquifer. The location of the intake depends on the study objective, well construction, and the type of equipment used. Unless the intended sampling interval can be isolated adequately, locating the intake at a point within a well screen or open borehole will result in extracting a sample that includes water from the entire screened or open interval (Varljen and others, 2006; Reilly and Gibs, 1993).
   - The water-level sensor should be a maximum of 1 ft (~0.3 m) below the static water surface.
4. Start the pump. Gradually increase and (or) adjust the pumping rate to limit drawdown to between 0.5 and 1.0 ft (~0.15 to ~0.3 m, or as determined by field practice).
   - If the final intake position is above the screened or open interval, the final pumping rate should be about 500 to 1,000 milliliters (mL) per minute. Do not exceed 1 ft of drawdown.
   - If the pump and intake position are fixed, as in a supply well, control the rate of flow for field measurements through flow-splitting valve(s).
   - Monitor the water level as purging progresses. Ideally, drawdown will be at a steady state, with the water level remaining above the top of the open or screened interval.
5. Purge a minimum of three well volumes or the purge volume dictated by study objectives (consult NFM 4.2.3 for detailed guidance on exceptions to the standard three-well-volume purging procedure).
   - Monitor values for field properties sequentially and at regular time intervals throughout purging (fig. 6.0–4). The frequency of these measurements depends on the purging rate, which in turn is a function of well depth and diameter, and aquifer transmissivity.
   - If required by Federal, State, or local regulations, contain purge water as directed.

6. **As the third or last well volume is purged, slowly adjust the purge rate to the pumping rate to be used during sampling, if necessary; do not halt or suddenly change the pumping or flow rate during the final phase of purging or while sampling.**

   - Record field measurements at regular time intervals, about 3 to 5 minutes apart.
   - Check the last three to five or more measurement values for each field property against the criteria for field-measurement stabilization (table 6.0–1).
   - Determine final field-measurement values.
     - — **If the criteria are being met**—report the median value.
     - — **If criteria are not being met**—consult the study requirements and objectives. Extend the purge time if readings still do not stabilize; report the median value of the last five or more sequential measurements and document problems encountered and how they were resolved.

To purge a supply well (assuming that a flowthrough cell/chamber will be used):

A supply well that is in regular service and that is pumping continuously or that has been operating long enough to have removed three casing volumes of water within several hours of sample collection does not require removal of three well volumes. Before withdrawing a sample in this case, flush one tubing volume of sample water through the tubing and monitor measurement values.

1. Determine or estimate and record the depth to static water level (fig. 6.0–4). Instructions for water-level measurement are given in NFM 4, appendix A4–B.

2. Calculate and record the well volume (fig. 6.0–4).

3. Select the location and method of tubing hookup to the well and connect sample tubing as close as possible to the wellhead.

   - There must be no water-storage tanks, holding or pressurization tanks, or chemical disinfection or water-softening systems connected inline between the pump and the tap/faucet to which sample tubing will be connected.
   - Select a faucet without an aerator or obtain written permission to remove the aerator (replace the aerator after sampling).

4. Regulate the flow using a manifold with a needle valve, if possible.

   a. Open any additional valves or taps/faucets to ensure that the pump will operate continuously and reduce the possibility of backflow stored in ancillary plumbing lines; keep these open throughout purging and sample withdrawal.

   b. The pump should produce a smooth, solid stream of water with no air or gas bubbles and without pump cavitation during field measurements and sample withdrawal.

5. Purge three well volumes or the purge volume dictated by the pumping status of the well or sampling objectives.

   - Throughout purging, monitor and record field-measurement readings (fig. 6.0–4).
   - If required by Federal, State, or local regulations, contain purge water as directed.

6. **As the third or last well volume is purged, when the final field measurements are recorded, adjust the purge rate to the pumping rate to be used during sampling, if necessary.**

   - Record field measurements at regular time intervals, about 3 to 5 minutes apart.
   - Check the last three to five or more measurement values for each field property against the criteria for field-measurement stabilization (table 6.0–1).
   - Determine final field-measurement values.
     - — **If the criteria are being met**—report the median value.
     - — **If criteria are not being met**—consult the study requirements and objectives. Extend the purge time if readings still do not stabilize; report the median value of the last five or more sequential measurements and document problems encountered and how they were resolved.

RECORD OF WELL PURGING

Date: _____ By: _____
SITE ID _____ STATION NAME _____

HEIGHT OF WATER COLUMN_____ DEPTH OF WELL _____
PUMP INTAKE (ft or m below MP): Start_____ End _____
WELL-PURGING METHOD AND PUMP TYPE (describe):_____
_____

TIME	WATER LEVEL below *MP LS	DRAW-DOWN	TEMPER-ATURE	CONDUC-TIVITY	pH	DISSOLVED OXYGEN	TURBID-ITY	APPROX. PUMPING RATE
HR:MIN	*ft or m	*ft or m	°Celsius	µS/cm	standard units	mg/L	**	*gpm or L/min

*Circle the unit used; MP, measuring point; LS, land surface; HR:MIN, hour and minutes; ft, feet; m, meter; µS/cm, microsiemens per centimeter at 25° C; mg/L, miligrams per liter; gpm, gallons per minute; L/min, liters per minute.
**Select the appropriate turbidity unit from http://water.usgs.gov/owq/turbidity_codes.xls.

Well volume = V= 0.0408 HD^2 = ____ gallons. **Purge volume =** $(n)(V)$ **=** ____ gallons.
V = volume of water in well, in gallons; D = inside well diameter, in inches; H = height of water column, in feet; n = number of well volumes to purge.
Well volume is 0.16 gallons per foot for a 2-in. diameter casing.

Figure 6.0–4. Example of a field form for recording measurements during well purging (modified from NFM 4, Figure 4-12).

6.0.3.B Direct Field-Measurement Procedures

Direct field measurements are those that are performed either (a) above ground by pumping water from the well, inline, directly to a sensor-instrumented flowthrough cell or chamber (inline-flow measurement procedure performed using either single-parameter instruments within a flowthrough chamber or a multiparameter instrument), or (b) downhole, using individual submersible sensors or a multiparameter sonde (in situ measurement procedure). Ambient ground-water temperature, SC, DO, pH, Eh, and turbidity can be determined using either procedure (fig. 6.0-5), but use of the in situ procedure can have more limitations and, to avoid sample contamination, should not be used if samples for laboratory or other offsite analyses will be collected.

Inline-flow (Flowthrough Cell/Chamber) Procedure

A flowthrough cell/chamber is an airtight, transparent vessel with a pressure-relief valve and with either (1) leak-proof ports (compression fittings) to accommodate individual sensors, or (2) a multiparameter instrument. Several types of flowthrough cell/chamber systems are available and can be designed for a specific measurement or simultaneous measurements (for example, see NFM 6.2.2 for the description of a flowthrough cell for the spectrophotometric determination of DO concentration). Figure 6.0–3 is a diagram of a flowthrough cell system and figure 6.0–5 shows the steps for inline-flow measurement of field parameters using a flowthrough cell/chamber system.

All sensors must be calibrated before use, as described in the relevant sections of this chapter (sections 6.1 through 6.8) and according to the manufacturer's guidelines for the instrument in use.

When using a flowthrough cell/chamber system, install the cell/chamber inline from the pump and as close to the wellhead as possible.

- Keep the cell/chamber, field-measurement instruments, and tubing off the ground, shaded from direct sunlight, and shielded from wind. Keep the tubing as short as possible.
- For a system for which sensors are to be installed in the chamber, insert the DO sensor directly downstream from the chamber inflow, and install the pH sensor downstream from the conductivity sensor. Turn on the pump; direct initial flow to waste to avoid introducing sediment into the chamber.
- For a multiparameter instrument system, place the sonde into the cell provided by the manufacturer, according to the manufacturer's instructions.
- Adjust the flow into the chamber so that a constant stream of water is maintained at the rate required for DO measurements (see NFM 6.2). Correct any backpressure conditions; tilt the chamber to expel trapped air.

Downhole (In Situ) Procedure

When deploying sensors or a multiparameter sonde downhole, ground water should be pumped to flow upward past downhole sensors in order to obtain values representative of the depth interval being sampled; therefore, a submersible pump follows the downhole instrument. Because of this constraint, the downhole method may not be practical at wells with dedicated pumps or when using multiple equipment in small-diameter wells. Figure 6.0–5 shows the steps for downhole measurement of field parameters.

- The depth at which sensors are located depends on study objectives. If a sample is to represent ground water that is integrated over the screened interval, locate sensors approximately 1 ft above the screened interval in a 2-in.-diameter well and just below the pump intake.
- Remove downhole sensors from the well before collecting samples for chemical analysis in order to prevent these instruments from affecting sample chemistry. Note that the process of removing these instruments and putting the pump back in the well causes disturbances that can affect the quality of samples subsequently collected for chemical analyses (Puls and others, 1991; Kearl and others, 1992; Puls and Powell, 1992).

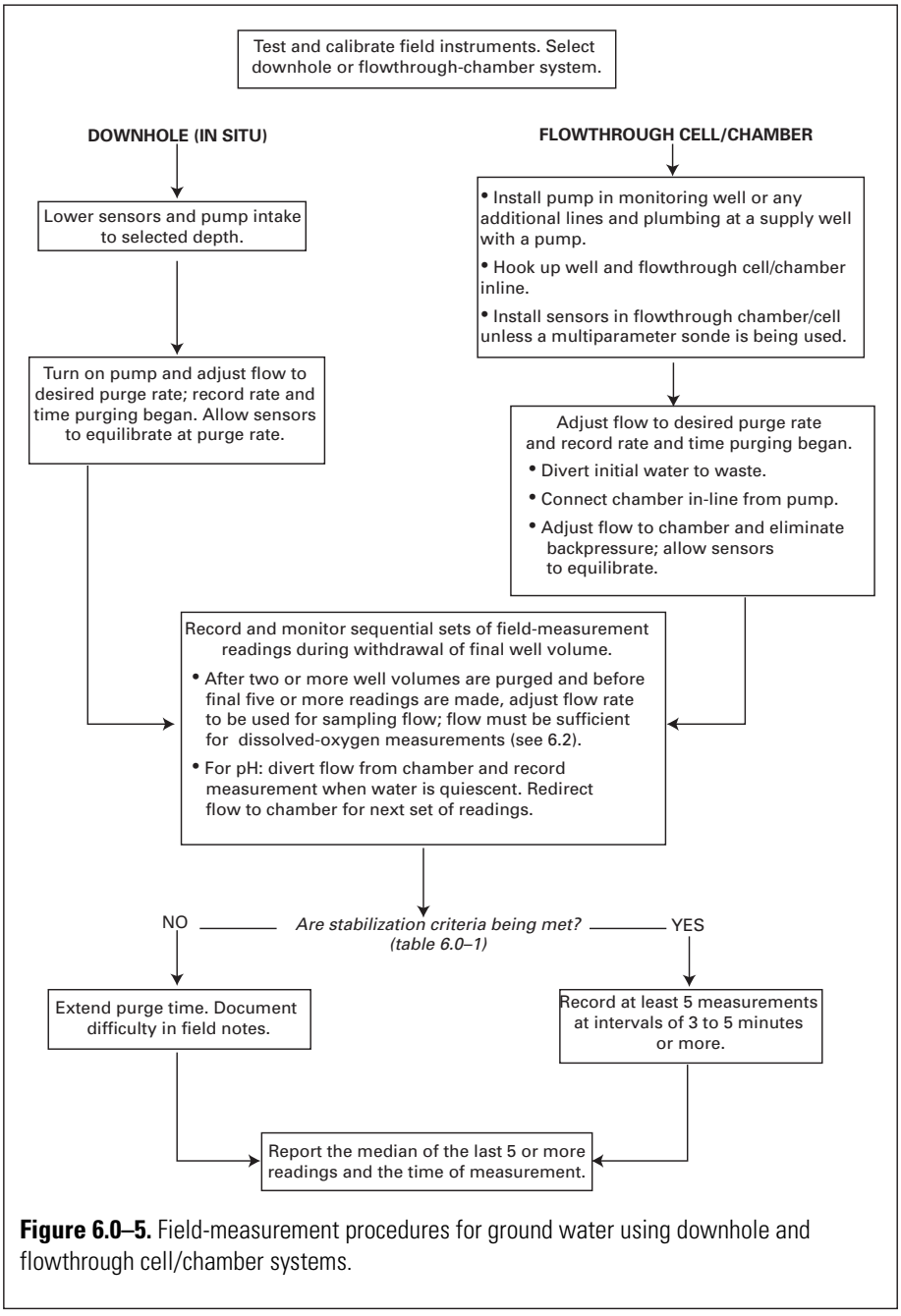

Figure 6.0–5. Field-measurement procedures for ground water using downhole and flowthrough cell/chamber systems.

6.0.3.C Subsample Field-Measurement Procedures

Subsamples or discrete samples are aliquots of sample collected from a nonpumping sampling device such as a bailer, a thief sampler, or a syringe sampler. Measurements of field parameters made in discrete or nonpumped samples are more vulnerable to bias from changes in temperature, pressure, turbidity, and concentrations of dissolved gases than measurements using inline-flow or in situ measurement procedures.

- **Subsamples must not be used for reported measurements of temperature, DO, Eh, or turbidity.**
- Subsamples can be used to determine ambient ground-water conductivity, pH, and alkalinity and other carbonate species.
- Subsample procedures must not be used for any field-measurement determination if the ground-water conditions are in reducing (anoxic) waters, unless the sample is decanted and measurements are made within a chamber or glove box filled with an inert gas (for example, ultrapure nitrogen or argon gas).

Figure 6.0–6 shows the steps for measurement of field parameters on a bailed sample. Use bailers having a double (top and bottom) check valve and a bottom-emptying device. Field rinse the bailer or other discrete-volume sampler with sample water before using. To shield the sample from atmospheric contamination, make measurements within a collection chamber or a glove box.

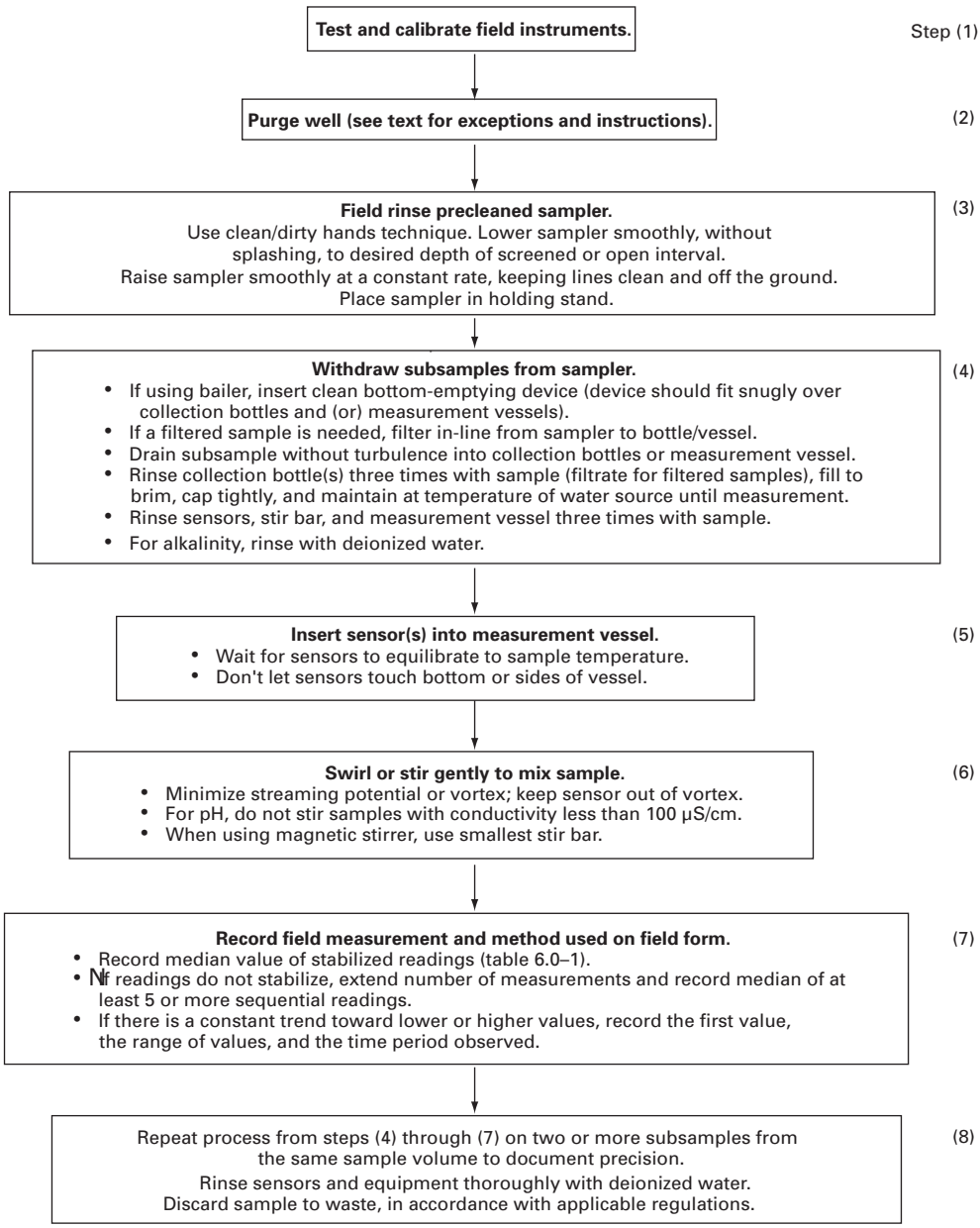

Figure 6.0–6. Subsample field-measurement procedures for conductivity, pH, and alkalinity of ground water.

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TEMPERATURE 6.1

Revised by **Franceska D. Wilde**

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TEMPERATURE 6.1

Measurements of air and water temperature at a field site are essential for water-quality data collection. Determination of dissolved-oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties relies on accurate temperature measurements.

Accurate air- and water-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by human activities. Water temperature can be subject to environmental regulation and monitoring by State and local agencies.

TEMPERATURE: a measure of warmth or coldness of a substance with reference to a standard value.

This section describes methods for measuring temperature in air, surface water, and ground water. The methods are appropriate for fresh to saline waters.

- A thermometer is any device used to measure temperature, consisting of a temperature sensor and some type of calibrated scale or readout device. Liquid-in-glass thermometers and thermistor thermometers are commonly used to measure air and water temperature.[1]
- The U.S. Geological Survey (USGS) uses the Centigrade or Celsius (C) scale for measuring temperature.

[1]Some of the equipment and procedures recommended herein may not reflect the most recent technological advances; in this case, follow the manufacturer's instructions but comply with standard USGS quality-control practices.

6.1.1 EQUIPMENT AND SUPPLIES

Thermometers and other temperature-measurement equipment and supplies must be tested before each field trip and cleaned soon after use (table 6.1–1). Each temperature instrument must have a log book in which all calibrations and repairs are recorded, along with the manufacturer make and model and serial or property number.

Table 6.1–1. Equipment and supplies used for measuring temperature[1]
[–, minus; +, plus; °C, degrees Celsius; L, liter; µS/cm, microsiemens per centimeter at 25°C]

- ✓ Calibration thermometer, liquid-in-glass or electronic-thermistor thermometer, either National Institute of Standards and Technology (NIST) certified or manufacturer-certified as NIST traceable. Must carry certificate of NIST traceability; its use not allowed after expiration of certification.
  - Temperature range, at least –5 to +45°C
  - 0.1°C graduations (liquid-in-glass) or less
- ✓ Thermometer, liquid-in-glass sensor, nonmercury-filled for field use
  - Temperature range, at least –5 to +45°C
  - Minimum 0.5°C graduated
  - Calibrated accuracy within 1 percent of full scale or 0.5°C, whichever is less
  - Calibrated and office-laboratory certified against a properly certified calibration thermometer (see above)
- ✓ Thermistor Thermometer
  - Calibrated accuracy within 0.1°C to 0.2°C
  - Digital readout to at least 0.1°C
  - Office-laboratory certified against a calibration thermometer (see above)
- ✓ Dewar flask and (or) plastic beakers (assorted sizes)
- ✓ Water bath, refrigerated (if available—see section 6.1.2)
- ✓ Soap solution (1 L), nonphosphate laboratory detergent
- ✓ Deionized water (1 L), maximum conductivity of 1 µS/cm
- ✓ Flowthrough chamber (for ground-water applications as an alternative to instruments with downhole capabilities)
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Log book, for recording all calibrations, maintenance, and repairs

[1]Modify this list to meet specific needs of the field effort.

Temperature-measuring instruments for field and laboratory (calibration) use can be either a liquid-in-glass or thermistor thermometer. Field personnel should be familiar with the instructions for use of the thermometer that are provided by the manufacturer.

- **Liquid-in-glass field thermometer**—Total immersion thermometers that are filled with a stable liquid, such as alcohol, are recommended for water measurements in the field. (Partial immersion thermometers are not recommended: these have a ring or other mark to indicate the required immersion depth.) Thermometers for field use must not be mercury filled. Before making temperature measurements, check the type of liquid-filled thermometer being used.
- **Thermistor thermometer**—A thermistor thermometer is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity. An electrical signal processor (meter) converts changes in resistance to a readout calibrated in temperature units. Thermistors are incorporated into digital thermometers, individual-parameter instruments (such as conductivity and pH meters), and multiparameter instruments used for surface-water and ground-water measurements.

CAUTION:
Do not use mercury-filled thermometers in the field.

MAINTENANCE, CLEANING, AND STORAGE

Liquid-in-glass and thermistor thermometers can become damaged or out of calibration, especially as a consequence of thermal shock or extended exposure to direct sunlight. It is important to be familiar with and to follow the manufacturer's instructions for use and care.

- Keep a log book for each thermometer in which the date, time, and location of every calibration are recorded.
  - — Avoid direct exposure of the thermometer to sunlight.
  - — Avoid submerging the thermometer sensor in corrosive solutions.
  - — Follow the calibration guidelines and protocols described in section 6.1.2.

- — Digital thermometer casings should not be submerged in water unless the manufacturer affirms that they are waterproof. Do not allow any liquid to enter open jacks that are part of some digital thermometers.

- Keep thermometers clean.
  - — Clean thermometer sensors with a soft cloth dipped in a mild solution of lukewarm water and nonphosphate detergent.
  - — If the digital thermometer case needs to be disinfected, use a weak (0.005 percent) bleach solution.
  - — **Do not autoclave the thermometer** (unless autoclaving is sanctioned by the manufacturer).
  - — If your digital thermometer has a detachable sensor with a plug termination, periodically wipe off or clean the sensor contacts. **Dirty contacts can affect temperature readings.**
  - — Blot the thermometer sensor dry after use.
  - — To clean an LCD lens, use only plastic-approved lens cleaners; do not use alcohol, acetone, or other harsh chemicals, as these will fog the lens.

- Store thermometers securely when not in use.
  - — Keep thermometers in a clean protective case when not in use. Each thermometer sensor and the case must be free of sand and debris.
  - — Keep thermometers dry and in a protective case during transit.
  - — Store liquid-filled thermometers with the bulb down.
  - — Store thermometers in a cool place and inside a building when not in use; do not leave a thermometer in a vehicle that could change in temperature to very hot or very cold, resulting in thermal shock to the thermometer.
  - — Check the batteries of thermistor-type thermometers for proper voltage before using.
  - — Record the calibration data in the log book for each thermometer—liquid-in-glass, thermistor thermometer, or thermistor-containing field-measurement instrument. Note if a thermometer has been serviced or replaced.

CALIBRATION 6.1.2

Thermometer calibration differs from the process by which a pH or conductivity sensor is adjusted until the accuracy of its performance conforms to that of an accepted calibration standard. For temperature measurements, calibration[2] refers to a comparison or accuracy check at specified temperatures against a thermometer that is certified by the National Institute of Standards and Technology (NIST), or is manufacturer-certified as NIST traceable. Calibration should be performed in a laboratory environment every 6 to 12 months, depending on the manufacturer's recommendation.

- **Field thermometers:** Only calibration thermometers having current NIST certification or traceability can be used for checking the accuracy of (calibrating) field thermometers.
  - — **In the case of continuous monitors,** a nonmercury calibration thermometer can be used in the field to check or monitor temperature readings whenever other field-measurement sensors are calibrated. See Wagner and others (2006) for specific guidelines for continuous monitors.
- **Calibration thermometers** are calibrated during their manufacture and certified as NIST-certified or NIST-traceable at the manufacturing laboratory. The USGS requires that calibration thermometers be recertified by a professional calibration service at least every 2 years, or be replaced with a calibration thermometer having current certification.
  - — Calibration thermometers should be reserved for calibration and should not be used routinely as field thermometers (see **TECHNICAL NOTE**). **Mercury-filled thermometers must never be used outside of the laboratory.**
  - — The thermistors included in other field-measurement instruments must be calibrated (checked) routinely, as specified below for thermistor thermometers, since accurate determination of other field measurements depends on the accuracy of temperature measurements. Thermistors that are incorporated into instruments designed to measure, for example, specific electrical conductance, dissolved oxygen, and pH commonly provide automatic temperature compensation.

[2]Calibrate: "To check, adjust, or systematically standardize the graduations of a quantitative measuring instrument" (American Heritage Dictionary, 1976).

— **All thermometers must be tagged with their most recent date and source of certification** (NIST-certified or -traceable source for calibration thermometers and office-laboratory source for field thermometers).

- **A log book is required** in which the calibration and certification history of each calibration and field thermometer is recorded.

TECHNICAL NOTE: The accuracy of a thermometer may vary over time, depending on factors such as the quality of its manufacture, the frequency of its use, and the conditions to which it is exposed. Shock, contamination, rapid heating and cooling, and mechanical stress are some factors that can affect the stability of a liquid-in-glass or thermistor thermometer (ICL Calibration Laboratories, 2003, 2005; ASTM International, 2005).

6.1.2.A CALIBRATION THERMOMETERS

Calibration thermometers (table 6.1-1) can be either a liquid-in-glass (mercury or spirit) or thermistor (digital) type thermometer, but must carry a current NIST certification or NIST-traceable certification that is no more than 2 years old. The actual duration of the calibration depends on the date of thermometer certification (not the date of purchase), how frequently the thermometer is used, and the conditions (thermal, chemical, and physical) to which it has been subjected during field operations and storage (see "Maintenance, cleaning, and storage" in section 6.1.1).

- **Check that the calibration thermometer has an NIST certification or traceable certificate that is within a 2-year period of original certification or recertification.**
- **Liquid-in-glass calibration thermometer:**
  - — Before each use, inspect the thermometer for cracks, internal condensation, and liquid separation; if any of these conditions are observed, the thermometer must be replaced.
  - — If the thermometer has been stored or used improperly, exposed at some length to sunlight or heat, or if its accuracy is otherwise in question, **check its readings at temperatures of approximately 0°, 25°, and 40°C, against those of another calibration thermometer that has been certified within the past 2 years.** If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.

- **Thermistor calibration thermometer:**
  - — Before each use, inspect the instrument (temperature sensor, digital display, wires or leads, and plugs) for signs of wear or damage; check that batteries are at full voltage.
  - — If the thermometer has been improperly stored or used, exposed at some length to sunlight or heat or extreme cold, or if its accuracy is otherwise in question, check its readings at five temperatures within the range of 0° to 40°C, against those of another currently certified calibration thermometer. If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.
- **Once NIST certification has expired** (exceeded the 2-year USGS limit):
  - — The thermometer either must be replaced with a currently certified thermometer or be recertified through a professional calibration service.[3] An office-laboratory calibration check does not constitute recertification of NIST traceability of a calibration thermometer.
  - — It is advisable to replace all mercury thermometers with a spirit or thermistor thermometer in order to avoid potential mercury contamination. The mercury thermometer must be disposed of in strict accordance with safety regulations.

Do not use calibration thermometers as routine field thermometers. Reserve their use for calibrating field thermometers.

FIELD THERMOMETERS 6.1.2.B

Field thermometers, whether of the liquid-in-glass or thermistor (digital) type, and whether or not they are themselves NIST-traceable,

[3]The cost of commercial calibration services can vary widely. Examples of laboratories that are accredited to perform thermometer calibrations and certification include: National Institute of Standards and Technology (http://ts.nist.gov/ts/htdocs/230/233/calibrations/); ICL Calibration Laboratories (www.icllabs.com); Lab Safety Supply, Inc. (https://www.labsafety.com/calibration). (URLs cited were accessed 11/28/2005).

require regular accuracy checks against a calibration thermometer. Carry an extra thermometer in the event that the accuracy of a field thermometer is in question. **Note, however, that field checking of a thermometer's accuracy does not substitute for the required annual laboratory calibration.**

- At a minimum, calibrate each field thermometer every 12 months—the time interval depends on the amount of use and abuse to which the thermometer has been subjected and on its manufacture. According to thermometer manufacturers, some models of thermistor thermometers require calibration every 6 months (YSI, 2005). Quarterly or possibly monthly calibration can be required if the thermometer is in heavy use; was exposed to thermal shock, an extended period of direct sunlight, or extreme shifts in temperature; or was exposed to aggressive chemical solutions. The calibration history from the log book can indicate the expected life of the thermometer.
- **Each thermometer that passes the accuracy check must be tagged with the date of calibration.** Thermometers that do not pass the accuracy check must be repaired, if possible, or else discarded or otherwise retired from use.
- The annual calibration of field thermometers can be performed in the office laboratory or by an NIST-accredited commercial laboratory. To calibrate a thermometer, check its readings across a range of temperatures as described below in the instructions for water-bath calibration procedures. Temperature checks must bracket and include points that represent the temperature range expected to be encountered in the field. **EXCEPTION:** Thermistors in continuous water-quality monitors can be field-checked annually (or more frequently, if necessary) with a nonmercury NIST-certified or NIST-traceable thermometer.
  - — Fully submerge the bulb and liquid column if using a total-immersion liquid-in-glass thermometer.
  - — Keep calibration and field temperature sensors (thermistor or liquid-in-glass type) submerged throughout the calibration process.
  - — Record thermometer readings throughout the bath warming and cooling periods and while keeping the water stirred or otherwise circulated (thermistor readings will be recorded with greater frequency).
  - — Check meter batteries periodically for proper voltage when using a thermistor-type thermometer.

— Record the calibration data in the instrument log book for each thermistor thermometer (including thermistor-containing field meters), noting if a temperature sensor has been replaced.

Calibrate field thermometers every 12 months.

To calibrate field thermometers when a commercial refrigerated water bath is available:

1. Precool the sensor of the thermometer(s) being tested (field thermometer) to 0°C by immersing it in a separate ice/water bath.
2. Immerse the field and calibration temperature sensors in the refrigerated bath with a water temperature of approximately 0°C.
3. Position the temperature sensor(s) so that they are properly immersed and so that the scales can be read. Stir the water bath and allow at least 2 minutes for the thermometer readings to stabilize.
4. Without removing the temperature sensor(s) from the refrigerated water bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
   a. Take three readings within a 5-minute span for each field thermometer.
   b. Calculate the mean of the three temperature readings for each field thermometer and compare its mean value with the calibration thermometer.
   c. If a liquid-filled field thermometer is found to be within ±1 percent of full scale or ±0.5°C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
   d. If a field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.
5. Repeat steps 1–4 in 25°C and 40°C water. Keep the bath temperature constant. Check the thermistors at two or more additional intermediate temperatures (for example, 15°C and 30°C).
6. Tag acceptable thermometers as “office-laboratory certified” with calibration date and certifier’s initials.

To calibrate field thermometers when a commercial refrigerated water bath is not available:

A. For the 0°C calibration

1. Freeze several ice cube trays filled with deionized water.
2. Fill a 1,000-milliliter (mL) plastic beaker or Dewar flask three-fourths full of crushed, deionized ice. Add chilled, deionized water to the beaker. Place the beaker of ice/water mixture in a larger, insulated container or Dewar flask. Place the calibration thermometer into the ice/water mixture and make sure that the temperature is uniform at 0°C by stirring and checking at several locations within the bath.
3. Precool the sensor of the field thermometer(s) to 0°C by immersing in a separate ice/water bath.
4. Insert the field thermometer(s) into the ice/water mixture. Position the calibration and field thermometers so that they are properly immersed and so that the scales can be read. Periodically stir the ice/water mixture and allow at least 2 minutes for the thermometer readings to stabilize.
5. After the readings stabilize, compare the temperature of one field thermometer at a time with that of the calibration thermometer. Without removing the temperature sensor(s) from the test bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
   a. Take three readings for each thermometer within a 5-minute span.
   b. Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the calibration thermometer.
   c. If the field liquid-filled thermometer is found to be within ±1 percent of full scale or ±0.5°C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
   d. If the field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.

B. For the "room temperature" calibration (25°C)

1. Place a Dewar flask or container filled with about 1 gallon of water in a box filled with packing insulation. (A partially filled insulated ice chest can be used for multiparameter instruments.) Place the calibration container in an area of the room where the temperature is fairly constant (away from drafts, vents, windows, and harsh lights).
2. Properly immerse the calibration and field thermometer(s) in the water. Cover the container and allow the water bath and thermometers to equilibrate.
3. Stir the water and, using the calibration thermometer, check the bath for temperature uniformity. Repeat this every 2 hours. It may be necessary to let the bath equilibrate overnight.
4. Compare one field thermometer at a time against the calibration thermometer, following the procedures described above in step A5 for the 0°C calibration.

C. For each temperature that is greater than 25°C

1. Warm a beaker of 1,000 mL or more of water to the desired temperature (for example, 40°C) and place it on a magnetic stirrer plate.
2. Follow the procedures described above in step A5 for the 0°C calibration.

Tag acceptable field thermometers as "office-laboratory certified" with the calibration date and certifier's initials.

Corrections can be applied to measurements made with a thermometer that is within ±1 percent of full scale or ±0.5°C of the calibration thermometer. Corrections should be applied by using a calibration curve or table, which is plotted in the log book for the instrument. **Thermistors found to be out of calibration by more than 0.2°C must be returned to the manufacturer for repair or replacement.**

Remember to tag and date acceptable field thermometers after calibration.

6.1.3 MEASUREMENT

Air temperature, in addition to water temperature, should be measured and recorded whenever water-quality samples are collected. Water temperature must always be measured in situ and in a manner that ensures that the measurement accurately represents the intended sample conditions. Before measuring air or water temperature:

- Inspect the liquid-in-glass thermometer to be certain that the liquid column has not separated.
  - — Inspect the glass bulb to be sure it is clean.
  - — Inspect the protective case to be sure it is free of sand and debris.
- Check that batteries are fully charged for thermister thermometers or temperature sensors incorporated into other field meters.

6.1.3.A AIR

Measure air temperature using a dry, calibrated thermometer.

- Place or hang the thermometer about 5 feet above the ground in a shaded area that is protected from strong winds but open to air circulation. Avoid areas of possible radiant heat effects, such as metal walls, rock exposures, or sides of vehicles.
- Allow 3 to 5 minutes for the thermometer to equilibrate, then record the temperature and time of day.
- Measure the air temperature as close as possible to the time when the temperature of the water sample is measured.
- Report routine air temperature measurements to the nearest 0.5°C. If greater accuracy is required, use a thermistor thermometer that has been calibrated to the accuracy needed.

6.1.3.B SURFACE WATER

The reported surface-water temperature must be measured in situ—**do not measure temperature on subsamples** from a sample compositing device. Measure temperature in such a manner that the mean or median temperature at the time of observation is represented (consult NFM 6.0 and fig. 6.0–1). Record any deviation from this convention in the data base and report it with the published data.

To measure the temperature of surface water:

- Making a cross-sectional temperature profile first, to determine the temperature variability of the stream section, is recommended—a hand-held digital thermometer works best for this purpose.
- To determine which sampling method to use (NFM 6.0), examine the cross-sectional profile and consider study objectives.
- Measure temperature in those sections of the stream that represent most of the water flowing in a reach. Do not make temperature measurements in or directly below stream sections with turbulent flow or from the stream bank (unless this specifically represents the intended condition to be monitored).

1. Use either a liquid-in-glass thermometer or a thermistor thermometer tagged as "office-laboratory certified" and dated within the past 12 months.
2. Record on field forms the temperature variation from the cross-sectional profile, and the sampling method selected.
    - **Flowing, shallow stream—**wade to the location(s) where temperature is to be measured. To prevent erroneous readings caused by direct solar radiation, stand so that a shadow is cast on the site for temperature measurement.
    - **Stream too deep or swift to wade—**measure temperature by lowering from a bridge, cableway, or boat a thermistor thermometer attached to a weighted cable. Do not attach a weight directly onto the sensor or sensor cable.
    - **Still-water conditions—**measure temperature at multiple depths at several points in the cross section.

3. Immerse the sensor in the water to the correct depth and hold it there for no less than 60 seconds or according to the manufacturer's guidelines until the sensor equilibrates thermally. The sensor must be immersed properly while reading the temperature; this might require attaching the thermistor to a weighted cable.

> **TECHNICAL NOTE:** For in-situ measurement with liquid-filled, full-immersion thermometers—the water depth to which the thermometer is immersed must be no greater than twice the length of the liquid column of the thermometer in order to make an accurate measurement.

4. Read the temperature to the nearest 0.5°C for liquid-in-glass and 0.2°C for thermistor readings—**do not remove the sensor from the water.**
   - When using a liquid-in-glass thermometer, check the reading three times and record on field forms the median of these values.
   - When using a thermistor thermometer, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last five values.
5. Remove the temperature sensor from the water, rinse it thoroughly with deionized water, blot it dry, and store it.
6. Record the stream temperature on field forms. Determine the values as follows:
   - **In still water—median** of three or more sequential values.
   - **For equal discharge increments (EDI)—mean** value of subsections measured (use median value if measuring one vertical at the centroid of flow).
   - **For equal width increments (EWI)—mean or median** value of subsections measured.

6.1.3.C GROUND WATER

Measurements of ground-water temperature must be made downhole or with a flowthrough system at the end of purging to ensure that the temperature measured accurately represents ambient aquifer water conditions (consult NFM 6.0 for guidance). **Do not report a temperature value measured from a bailed ground-water sample.**

To measure the temperature of ground water:

- ▶ Select either the downhole or flowthrough-chamber sampling system (see NFM 6.0, fig. 6.0–4) and record the method used.
- ▶ Measure temperature with a thermometer that has been office-laboratory certified within the past 12 months and within the temperature range to be encountered.

1. Prepare the instruments for either the downhole or the flowthrough-chamber system.
   - **Downhole system—**lower the sensor in the well to just below the pump intake (the intake location depends on the sampling objectives).
   - **Flowthrough-chamber system—**properly immerse the thermistor or liquid-in-glass thermometer in the chamber. Keep the pump tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground. Keep the chamber out of direct sunlight and wind.
2. Begin water withdrawal from the well. Allow the thermometer to equilibrate with ground-water temperature for no less than 60 seconds or in accordance with the manufacturer's guidelines; record the readings and time intervals throughout the period of purging.
3. Toward the end of purging, record five or more sequential measurements, spaced at increments of 3 to 5 minutes or more.
   - If the thermistor temperature is stable within the 0.2°C criterion, report the median of the final five measurements (table 6.0–1). (For a liquid-in-glass thermometer, there should be only slight fluctuation around 0.5°C.)
   - If the stability criterion has not been met, extend the purge time and consult the well-purging objectives of the study. Report the median of the last five (or more) sequential measurements and record any instability on field forms.
4. Remove the thermometer from the water, rinse it thoroughly with deionized water, blot it dry, and store it as described in 6.1.1.

6.1.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions on table 6.1-2 fail to resolve the problem, or if additional information is needed.

When using thermistor thermometers:

- Check the voltage of the batteries.
- Start with good batteries in instruments and carry spares.

Table 6.1–2. Troubleshooting guide for temperature measurement

Symptom	Possible cause and corrective action
Liquid-in-glass thermometer does not read accurately	• Check thermometer to see that the liquid is not separated—if separated, take back to the office laboratory to reunite column or for disposal.
Thermistor thermometer does not read accurately	• Dirty sensor—remove dirt and oil film. • Weak batteries—replace with new batteries.
Erratic thermistor thermometer readings	• Bad or dirty connection at meter or sensor—tighten or clean connections. • Break in the cables—replace cables. • Weak batteries—replace with new batteries.
Thermistor thermometer slow to stabilize	• Dirty sensor—clean sensor to remove dirt and oily film.

6.1.5 REPORTING

USGS temperature measurements should be stored in the National Water Information System (NWIS) data base. These data may be published electronically and (or) on paper as the verified negative or positive value measured, as described below.

- **Thermistor thermometer measurements:** Store manually recorded temperature measurements in the data base to the user-verified precision of the instrument (generally, 0.1 or 0.2°C, provided that the thermometer calibration verifies this accuracy). Electronically recorded temperature data may be stored unrounded. Unrounded temperature data in the database must be rounded when retrieved for publication.
- **Liquid-in-glass thermometer measurements:** Record temperature measurements in the data base to the nearest 0.5°C.
- Any values less than 0.1°C are highly questionable and should be published only after a complete calibration check of the equipment used.
- USGS field measurements of air and water temperature must be entered on the paper or electronic field form and stored in the NWIS data base.
  - — Be sure to store all data under the correct parameter and method (if available) codes.
  - — Store air and water temperature measurement data with replicate samples **only if replicate measurements were made.** Enter replicate measurements under the correct medium code for quality-control (QC) samples; alternatively, distinguish the replicate from the regular sample by using the unique time-of-sampling that was assigned to QC samples for that site and date.
  - — Do not store the regular-sample measurement data with the replicate-sample data. **Enter regular-sample data only once in the NWIS data base.**
- Record the accuracy range of the instrument in the data base, if possible. Report the accuracy range with the published values.

Report only those water temperature values that were measured in situ.

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National Field Manual for the Collection of Water-Quality Data

Chapter A6 Field Measurements

Section 6.2 DISSOLVED OXYGEN

Revised by Stewart A. Rounds, Franceska D. Wilde, and George F. Ritz

Techniques of Water-Resources Investigations Book 9–A6

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U.S. Geological Survey

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SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

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This National Field Manual for the Collection of Water-Quality Data (National Field Manual) responds to advances in technology and science and to the ever-developing needs for water-quality monitoring. Its aim is to provide scientifically sound guidance to U.S. Geological Survey (USGS) personnel and to document USGS requirements for collecting water-quality data. As a result, the expertise of numerous scientists has been tapped in developing the various chapters of this manual and keeping them current.

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6.2 Dissolved Oxygen

Revised by Stewart A. Rounds, Franceska D. Wilde, and George F. Ritz

The concentration of dissolved oxygen in water is affected by many factors, including ambient temperature, atmospheric pressure, and ion activity (ionic strength of the water body). Accurate dissolved-oxygen (DO) data are essential for understanding and documenting effects on environmental water resources that result from natural phenomena and human activities. Sources of DO in water include atmospheric aeration and photosynthetic activities of aquatic plants. Sinks of DO in water include respiration, aerobic decomposition processes, ammonia nitrification, and other chemical/biological reactions. Many chemical and biological reactions in groundwater and surface water depend directly or indirectly on the amount of available oxygen. The presence of DO in aquatic systems is necessary for the survival and growth of many aquatic organisms and is used as an indicator of the health and geochemical quality of surface-water and groundwater systems.

DISSOLVED OXYGEN: Molecular oxygen (oxygen gas) dissolved in water.

Standard procedures used by the U.S. Geological Survey (USGS) for determining concentrations of DO in surface water and groundwater involve the use of luminescence-based (optical sensor), amperometric (Clark cell[1]), or spectrophotometric methods of analysis. The iodometric (Winkler) method (section 6.2.3) no longer is used by the USGS for routine measurement of DO at field sites, but remains a standard method for verifying the results of DO measurements made using other methods.

The selection of field equipment and measurement methods takes into consideration (a) whether equipment will be used at varying and discrete locations and times or be deployed at a single location over a period during which it will be unattended, (b) anticipated environmental conditions, (c) the specific data-quality objectives of the data-collection program, and (d) the inherent benefits of a given technology as applied to given site characteristics and project or program objectives. The measurement methods described are employed by the USGS onsite for routine determination of DO concentrations in fresh to saline surface water and groundwater.

The primary USGS field procedure employed for DO determinations during the past two decades required the use of amperometric sensors until luminescence-based (optical) sensors became more common (around 2005). Although both optical and amperometric methods yield accurate results, optical DO sensors are considered a major technological advance over amperometric sensors because optical DO sensors are more robust in the field environment.

- Optical and amperometric sensor methods (section 6.2.1) are applicable to the same aqueous environmental conditions. Both sensor technologies are available in single-parameter DO meters or in multi-parameter sondes and can be either handheld for discrete measurements or deployed for longer term, unattended continuous and real-time measurements.

[1] This document refers to the "amperometric" method or sensor interchangeably with the "Clark cell" sensor. Other terms applied to amperometric methods include polarographic and galvanic technology.

- Spectrophotometric (colorimetric) methods (section 6.2.2) yield consistent results when applied to the determination of DO concentrations in oxygen-depleted waters (for example, in certain aquifers and deep-lake horizons). Noninstrumental colorimetric methods that are available for visually determining DO concentrations to zero milligram per liter (mg/L) can be useful for a quick reconnaissance of DO conditions and an accuracy check of DO sensor performance.
- The iodometric (Winkler) method (section 6.2.3) is regarded as an accurate and precise method for the calibration of DO sensors and the determination of DO concentration in water, when performed under controlled laboratory conditions. Before sensors that could be immersed directly in the water column became commonly available, USGS personnel were trained to perform Winkler titrations onsite. Standard USGS practice no longer sanctions the transport of field samples offsite for DO determination.

- **Some procedures for equipment operation as recommended in this guidance document may not apply to your equipment because of technological advances or other changes.**
- **Be sure to record any modifications made to the standard USGS procedures given in this field manual.**

6.2.1 Optical (Luminescence) and Amperometric Sensor Methods

Either the optical or amperometric sensor methods can yield accurate results for measurement of DO concentrations under most of the field conditions encountered for routine USGS data-collection activities. Both methods are relatively simple to use, whether deployed for single (discrete) or continuous (unattended) DO measurements in surface water or groundwater. Because of the advantages introduced by advances in applying luminescence technology to DO measurement, optical sensors are generally favored for most standard USGS field operations.

- **Optical sensors.** The technology used in optical DO sensors involves the measurement of light-emission characteristics of a luminescence-based reaction at the sensor-water interface (see TECHNICAL NOTE 1). In contrast to amperometric sensors:
  - Oxygen is not consumed at the sensor-water interface.
  - The optical sensor is not dependent on water flow; consequently, no stirring mechanism is required at sites with slow or stagnant waters.
  - Optical sensors are stable. They are considerably more robust than amperometric sensors in maintaining calibration over long-term deployment and over a wide range of environmental conditions, and sensor drift over time is minimal when the sensor is kept clean.
  - There are no known sources of interference to the luminescence method in natural aquatic systems. Optical sensors will measure accurately in the presence of hydrogen sulfide (H_2S) and also when deployed in fresh, brackish, and mildly polluted waters. Contact, however, with organic solvents can compromise sensor integrity or performance.
  - Cleaning and maintenance are simplified. The optical sensor contains no anode or cathode to service, and uses no electrolyte solution, amperometric-type membranes, O-rings, or stirrer.

— The maintenance routine and schedule for optical sensors is less frequent than for amperometric sensors. Optical-sensor maintenance is dictated by manufacturer guidelines that are specific to the type of sensor in use and the conditions to which the sensor has been subjected.

- Optical-sensor luminophore-containing modules[2] (referred to as sensor caps, probe tips, or luminophore-coated membranes or foil, depending on the manufacturer) are rugged and resistant to punctures or other damage in storm or high-flow conditions, while amperometric (Teflon-membrane) sensors are considerably more vulnerable and require frequent replacement.
- Compared with the amperometric sensor, the frequency of a calibration check for an unattended (for example, continuously deployed) optical sensor should occur at least every 4 to 8 weeks, which depends primarily on environmental conditions and the age and condition of the luminophore, while the amperometric sensor typically requires recalibration every week or two, depending on environmental conditions.
- The manufacturers generally recommend annual to biannual replacement of the luminophore-containing module. The modules are easily replaced and should be calibrated or undergo a calibration check after being replaced.

TECHNICAL NOTE 1. The luminescence sensor employs a light-emitting diode (LED) to provide incident light of a specific wavelength, which excites a luminescent-dye molecule substrate (luminophore) of the sensor. After some dissipation of the excitation energy, longer wavelength light is emitted. The intensity of the fluorescence is proportional to the DO concentration because the presence of oxygen can quench, or suppress, the fluorescence response of the dye. Higher DO concentrations result in greater quenching and a decreased fluorescence response. More importantly, the timescale, or lifetime, of the fluorescence reaction is dependent also on the DO concentration and is not dependent on the light intensity of excitation or fluorescence, therefore allowing reliable determination of the DO concentration. Temperature stability during calibration and measurement is extremely important for optical and amperometric sensors alike.

► **Amperometric sensors** (Clark cell). The amperometric measurement method was the most commonly used field method for DO determination for USGS water data-collection efforts before introduction of the luminescence method. In this method, the DO concentration is determined using a temperature-compensating meter connected to an amperometric-membrane type of sensor or an amperometric sensor bundled with other sensors in a multiparameter sonde.

— Amperometric sensors require use of membranes and electrolyte solutions (*see* TECHNICAL NOTE 2 below).

— The method is flow-dependent, requiring that an adequate flow of water (approximately 1 foot per second (ft/s)) passes across the membrane.[3] Manual stirring is required when making handheld measurements. Use of an additional stirring mechanism fitted to the sensor or sonde is needed for discrete or continuous measurements at sites with slow or stagnant waters.

— Contact of the amperometric sensor with hydrogen sulfide (H_2S) interferes with the DO determination by degrading the electrode surfaces under the membrane.

[2] See TECHNICAL NOTE 1 for definitions of luminescence and luminophore.

[3] The "Rapid Pulse" (YSI) sensor, however, does not require a stirrer and was designed to be virtually flow-independent for DO measurement in environmental waters. As of this writing, it is the only amperometric technology designed for this purpose and that allows a two-point calibration.

— Amperometric sensors are vulnerable to changes in temperature and the instrument must be temperature compensating. Be cognizant of the relation between sensor membranes and temperature. The permeability of the membrane changes as a function of temperature, as does the solubility of oxygen in water.

— Method performance can be negatively affected by:

- calibration drift
- a loose, wrinkled, or damaged membrane
- air bubbles in the electrolyte
- use of expired or contaminated electrolyte solution
- loose-fitting O-rings and membranes
- damaged, dirty, or otherwise contaminated electrodes under the membrane

— Extreme temperature change and (or) shock/vibration may cause a shift in the calibration, resulting in biased data.

TECHNICAL NOTE 2. Some manufacturers provide amperometric-sensor membranes of various thicknesses, the selection of which depends on the intended use of the instrument. Select the sensor membrane based on manufacturer's recommendations. Two basic types of membrane design are available: (a) individual membranes and (b) membrane-cap assemblies. Individual membranes are considerably less expensive but require more care and skill to install properly. Sensor performance can be affected by the manner in which individual membranes are installed and conditioned after installation.

6.2.1.A Equipment and Field Preparations

DO instruments (meters and sensors) are available from a number of commercial vendors. Because of differences among manufacturers in the instrument design and instructions for use, calibration, and maintenance, it is important that the user be thoroughly familiar with the instructional manual for the specific instrument system to be used in addition to the guidance given here.

Equipment Description and Maintenance

Meters, sondes, and the DO sensors used in these instruments are sophisticated electronic equipment that require care in handling and operation. Information about the equipment and supplies required for the optical and amperometric methods of determining aqueous DO concentrations is summarized in table 6.2–1.

► **Amperometric sensor.** The amperometric "instrument system" refers to the entire sensor assembly, including electrolyte solutions, membranes, and thermistors. Protect all sensors and supplies from being jostled during transportation, from sudden impacts, sudden temperature changes, and from extremes of heat and cold below 0 °C.

- **Optical sensor.** Guidance for when to replace the luminophore-containing cap or membrane varies among manufacturers and can be based on the specific design and materials used, the environmental conditions to which the sensor is exposed, the age of the sensor, and (or) the amount of time it is deployed. For example:
  - Hach Company states that the need for replacement of the luminophore module depends on environmental factors to which their LDO (Luminescent Dissolved Oxygen) probe is exposed, rather than be scheduled solely on the basis of frequency or length of use. Environmental factors such as photobleaching of the luminophore surface from irradiation (for example, overexposure to sunlight), and substantial changes in water properties such as salinity or atmospheric conditions (air pressure), can affect the need for luminophore-module replacement.
  - YSI Environmental advises annual replacement of the luminophore membrane assembly for their ROX (Reliable Oxygen) optical sensor.
  - In-Situ, Inc. advises that the RDO (Rugged Dissolved Oxygen) sensor cap has a 2-year shelf life from the time of manufacture when not in service, but the cap must be replaced after one year of field deployment.
- **Storage of optical and amperometric sensors.** Become familiar with the specific manufacturer's recommendations for short-term (field) and long-term (office) storage.
  - Amperometric sensors should not be allowed to dry out and should be kept moist during storage.
  - Storage of optical sensors in a humid environment differs among manufacturers; consult the manual provided for the sensor.

Table 6.2–1. Equipment and supplies for the optical and amperometric sensor methods of dissolved oxygen determination.[1]

[DO, dissolved oxygen; mg/L, milligram per liter; NFM, *National Field Manual for the Collection of Water-Quality Data*; –, minus; +, plus; °C, degrees Celsius; ±, plus or minus]

For amperometric method only
Amperometric instruments must be pressure-compensated (as well as temperature-compensated).
DO sensor membrane replacement kit includes membranes, O-rings, electrolyte (filling) solution; electrode reconditioning supplies; stirring attachment for low- or no-flow waters.
For optical and amperometric measurement methods
Instrument must be equipped with temperature compensation • DO instrument and DO sensor or multiparameter instrument with DO capability and digital temperature readout display • Operating range in water, from at least –5 °C to +45 °C • Measure concentrations from 0.05 to 20 mg/L (instrument capability can range to 50 mg/L) • Minimum scale readability (display resolution), preferably 0.01 mg/L DO • Calibrated accuracy within ±0.1 mg/L DO[2]
Calibration equipment, per manufacturer's recommendation.[3]
Pocket altimeter-barometer or DO instrument with built-in barometer; barometer measures to nearest 1 millimeter of mercury and its calibration has been checked before use.
Thermometer (see NFM 6.1 and 6.8 for calibration-check criteria) (for verification of air and water temperature and accuracy of instrument built-in thermistor).
Zero DO solution.[4] Dissolve 1 gram sodium sulfite in 1 liter of deionized water (0.008M solution, prepared fresh just before the field trip or during week of use).[5]
Flowthrough chamber for determining groundwater DO, if downhole sensor deployment is impractical.
Oxygen-solubility table (table 6.2–6), or access *http://water.usgs.gov/software/DOTABLES/*.
Waste-disposal containers.
Spare batteries. • Calibration and maintenance log books for DO instrument and barometer. • Calibrated specific conductance sensor, if working in saline or brackish systems.

[1] Modify this list to meet specific needs of the field effort.

[2] Refer to Wagner and others (2006) for long-term sensor deployment.

[3] Equipment needs and additional information specific to each calibration procedure are provided in section 6.2.1.B.

[4] Optionally, a few crystals of cobalt chloride ($CoCl_2$) can be added to the solution as a catalyst in order to speed up the reaction; however, routine USGS field operations omit the addition of $CoCl_2$, as it is a toxic substance, is regulated for proper disposal, and is not a necessary component to achieve a solution of the zero DO. If $CoCl_2$ will be used, personnel are advised to check the Material Safety Data Sheet for proper handling and disposal of the solution.

[5]Take special note of the manufacturer's guidance as applicable to your sensor. Some manufacturers supply the zero-DO solution required or document the specific instructions for preparing the zero-DO solution recommended for their sensors, including an alternative by which nitrogen gas is forced into tap or deionized water to produce a zero-DO solution (consult with the manufacturer's division of technical support).

Field trip preparations

The service performed on all equipment, whether a full calibration, calibration check, or replacement or repair of parts for the instrument, and whether performed in the office, laboratory, or field, must be accurately recorded and dated in the log book using black or blue non-erasable ink.

Field-measurement instruments are to be maintained on a regular schedule and performance-tested before field deployment, as described below:

1. Check all electrical connections and the charge on the batteries, as applicable for the instrument in use.
2. Thermistors/thermometers must be calibrated and field checked before use, as described in NFM 6.1 ("Temperature").

3. Perform a 100-percent saturation calibration check (see section 6.2.1.B). This performance check does not negate the need for onsite sensor calibration at oxygen saturation.

4. Perform a zero-DO sensor-performance check.

   a. Prepare the zero-DO sodium sulfite solution (see table 6.2–1).

   b. Before immersing sensor in the zero-DO solution, it is imperative to **remove the wiper** (or sponge) from the unit to avoid saturating it with the sodium sulfite solution. (Not all instruments have a DO sensor wiper.)

   c. Rinse sensor and wiper thoroughly and then reinstall wiper elements. Multiple and thorough rinses with deionized water are necessary to restore the sensor to proper operating condition and prevent bias to subsequent measurements.

5. Review the care and maintenance guidance provided by the manufacturer for the specific sensor being used; instructions can differ appreciably depending on the instrument type, make, and model.

   a. **Optical DO-sensor instrument:** Check the condition and (or) deployment history of the luminophore-containing sensor module, referring to the manufacturer's guidance for replacement of the luminophore module.

      - Depending on the instrument, sensor modules are replaced annually or at least every 2 years, even if the probe is idle.

      - If the instrument reading exceeds 0.2 mg/L in the zero-DO solution, check DO again with a freshly prepared zero-DO solution; if a greater than 0.2 mg/L reading persists, contact the instrument manufacturer and inquire if the luminophore module should be replaced.

   b. **Amperometric instrument:**

      - Inspect the instrument closely, checking for loose, wrinkled, or torn membrane; air bubbles beneath the membrane; a loose O-ring, and a tarnished or discolored cathode or anode. If any of these problems are detected, do not use the sensor until it has been serviced according to the manufacturer's guidance.

      - If the instrument reading exceeds 0.2 mg/L in the zero-DO solution, check DO again with a freshly prepared zero-DO solution; if a greater than 0.2 mg/L reading persists, replace the sensor membrane and electrolyte (if present) or repair.

      - **Membrane type** – Consult manufacturer recommendations to select a sensor membrane of the thickness required for the field operation. (Only one membrane thickness is available for some amperometric sensor makes or models.)

      - **Membrane replacement** – After replacing, the new membrane should be allowed to condition over a given period of time before sensor calibration and deployment.

        – Depending on the manufacturer and whether replacement involves using the O-ring or membrane-cap method, conditioning time depends on the type of membrane. Conditioning of membranes with O-rings, for example, generally ranges from a minimum of 2 hours up to 6 hours. For greater stability during calibration, allow the new membrane to condition overnight before calibration and use.

        – Membranes in caps are prestretched and require less conditioning.

  - For continuous monitoring applications with field-replaceable sensors, either condition the replacement sensor before the site visit, or replace the sonde with a second, clean and calibrated sonde and perform maintenance of the replaced sonde at the office.
  - When the sonde is deployed for discrete measurement, and conditions necessitate use of a new membrane before the recommended overnight conditioning time, more frequent calibration checks and possibly recalibration may be needed to ensure accurate DO measurements.[4] This is not recommended for continuous monitoring applications.

6. Remember to document field preparations and all instrument tests and adjustments in the meter log book. **Do not use an instrument that fails calibration.**

CAUTION:
Before handling sodium sulfite, cobalt chloride, or any other chemicals, refer to safety precautions on the Material Safety Data Sheet (MSDS) for that chemical.

6.2.1.B Calibration of Optical and Amperometric Sensors

Sensor-based instrument systems used to determine DO in water must be calibrated properly before being deployed. Proper calibration procedures are necessary to ensure the overall accuracy and precision of DO measurements. Amperometric sensors are more likely to require frequent calibration than optical sensors. While equipment manufacturers advise performing the calibration in the office laboratory before going onsite, USGS protocols call for onsite calibration checks and possible recalibration at the field site, as necessary to meet the specific data-quality requirements of the project.

The accuracy required by the project for sites at which DO will be determined and the capabilities of the selected instrument will govern whether a one-point calibration will be sufficient or a two-point calibration should be used. In addition, some manufacturers of the DO equipment commonly used for USGS data-collection efforts recommend testing of the equipment in a laboratory setting to determine the accuracy of room-temperature calibrations compared with measurements made under the anticipated warmer or colder field conditions. Project personnel are advised to be familiar with recommendations from the manufacturer of their equipment.

- **One-point calibration.** The main goal of the one-point calibration procedure is to create a 100-percent saturated oxygen environment where the DO sensor (optical or amperometric) and its regulating thermistor are at the same temperature. Amperometric sensors used in multiparameter instruments, for the most part, are capable of only a one-point calibration).[5]
  - **Procedure 1** (Air calibration chamber in air)
  - **Procedure 2** (Calibration with air-saturated water)
  - **Procedure 3** (Air calibration with a wet towel)

[4] One sensor manufacturer recommends running the DO sensor for at least 15 minutes after a membrane change or if the electrodes were reconditioned. Check the manual or handbook of your instrument for corroboration.

[5] The "Professional Plus" multiparameter instrument (YSI Incorporated) with amperometric sensor can be calibrated at zero DO and 100 percent saturation. Other such instruments also may be in production.

- — **Procedure 4** (Air calibration chamber in water). Unlike Procedures 1, 2, and 3, this procedure currently is applied to amperomeric instrument systems only. The potential applicability of this procedure to calibration of optical sensors is a topic of discussion and review that can be followed in the chapter 6 section of the NFM Comments and Errata page (*http://water.usgs.gov/owq/FieldManual/mastererrata.html*).

► **Two-point calibration (for optical sensors).** The two-point calibration typically involves calibration of the sensor at 100 percent saturation, followed by calibration at zero DO. Only specific makes and models of optical DO sensors have the capacity to be calibrated to two points. The two-point calibration adds complexity to the calibration process and is not recommended by all manufacturers of optical sensors. Be sure first to understand the instrument capabilities and then determine the best course of action for your field work.

- — For routine applications, it is advisable to rely on a zero-DO performance check rather than a zero-DO recalibration, which would risk corrupting the manufacturer's zero-DO calibration.
- — Use of a two-point calibration should be considered if (a) the calibration is needed to satisfy the data-quality objectives of the project,[6] (b) oxygen concentrations of less than 1 mg/L are likely to be encountered and zero-DO performance tests fail at this concentration level, or (c) the calibration is deemed necessary by experienced field personnel knowledgeable of site conditions.
- — Before starting or planning for a two-point calibration, it is advisable to consult the manufacturer's instructions or technical support for the specific optical DO sensor being used.
- — If using a two-point DO calibration, calibrate the DO sensor only after calibrating other field-measurement sensors to prevent possible interference of the sodium sulfite (zero-DO) solution with the calibration of the other sensors. Complete the DO calibration at 100 percent saturation before the zero calibration.

► **Sensor-performance checks.** Verifying sensor performance (calibration checks) is a required standard procedure in USGS field operations (*see* section 6.2.1.A)

- — All DO sensors have the capability to undergo a performance check at zero DO as well as at saturation.[7]
- — Verifying instrument performance at zero DO and using the two-point calibration can be particularly important for data accuracy when the instrument will be used to measure low DO concentrations (for example, DO less than 5 mg/L).

Do not use an instrument that fails to calibrate properly.

[6] Although optical instruments undergo zero-calibration procedures by the manufacturer, the accuracy of factory calibrations may not satisfy the data-quality objectives of some USGS field studies.

[7] It should be underscored that manufacturers uniformly caution against zero recalibration of sensors but allow for zero DO checks, stipulating the need to thoroughly rinse the zero-solution from the sensor.

Correction for Atmospheric Pressure and Salinity

Calibration procedures include corrections for atmospheric pressure and ionic strength (ionic strength is estimated from the conductivity or salinity measurement for routine field applications). Atmospheric pressure, the temperature of the water or water vapor, and the ionic strength (estimated by conductivity or salinity) of the water must be known to determine the theoretical amount of oxygen that can be dissolved in water. **Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.**

TECHNICAL NOTE 3. DO sensors do not actually measure oxygen in milligrams per liter or parts per million. Both of these expressed concentrations are based on calculations that relate instrument reading with the temperature and salinity of the sample water. The actual sensor measurement is proportional to the ambient partial pressure of oxygen, which can be displayed either as percent saturation or in milligrams per liter, depending on user input.

Ambient atmospheric pressure is true atmospheric pressure at the measurement site, not that which has been adjusted to sea level. Atmospheric pressure reported by the National Weather Service generally is not the true (ambient) value. National Weather Service atmospheric readings usually are adjusted to sea level and must be adjusted back to the elevation of the weather station. Upon request, a weather station may provide ambient atmospheric pressure.

- Determine the ambient atmospheric pressure to the nearest 1 millimeter (mm) of mercury. A calibrated pocket altimeter-barometer typically has been used to determine atmospheric pressure; however, many instruments that now are in common use include an internal barometer.
- Check the accuracy of all field barometers before each field trip (including barometers built into instrument systems) and record readings and adjustments in the instrument log book. If possible, check barometer accuracy while at an official weather station. If this is not an option, adjust the official weather station barometric pressure to the elevation at the field site at which the barometer reading is being recorded.
- To correct weather-station readings adjusted to sea level to ambient atmospheric pressure: subtract appropriate values shown (table 6.2–2, fig. 6.2–1) from atmospheric readings adjusted to sea level (shown in millimeters of mercury).

Although atmospheric pressure does not decrease linearly with increases in elevation, linear interpolation is acceptable within the elevation ranges given in table 6.2–2. Alternatively, plot the values from table 6.2–2 and extrapolate subtraction factors directly from the graph (fig. 6.2–1). Section 6.2.5 contains the table of oxygen solubility at various temperatures and pressures.

Most modern multiparameter instruments (see NFM 6.8) incorporate a pressure-temperature and salinity compensation algorithm in their firmware for DO measurements; the instruments have a built-in conductivity sensor that corrects the DO-concentration (in milligrams per liter) data for salinity automatically. For instruments that are not equipped with a conductivity/specific conductance (SC) sensor, a manual salinity correction of the DO data would be required.

- If a user-specified salinity correction is needed, **the preferred USGS method is to apply salinity correction factors after calibrating and** measuring DO concentration of the environmental water body (see section 6.2.5). Interactive tables are available for user-specified temperature, pressure, and salinity at *http://water.usgs.gov/software/DOTABLES/*.

► **When a manual salinity** correction is made by the user during calibration, the instrument requires recalibration for each field variation in salinity (*see* section 6.2.5).

TAKE NOTE: If using a multiparameter sonde that includes a calibrated conductivity sensor, salinity corrections to the DO concentration reading (in mg/L) are performed automatically in the sonde; that is, the DO sensor communicates with the SC sensor.

Table 6.2–2. Factors used to correct reported atmospheric pressures that have been adjusted to sea level.

[NGVD, National Geodetic Vertical Datum of 1929]

Elevation of weather station (in feet, NGVD)	Value to subtract (millimeters of mercury)
0	0
1,000	27
2,000	53
3,000	79
4,000	104
5,000	128
6,000	151

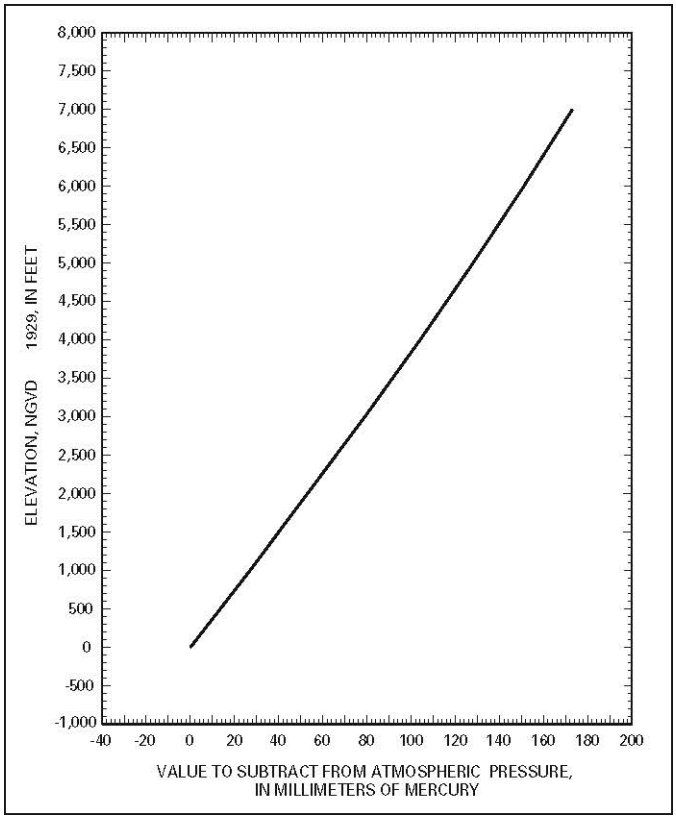

Figure 6.2–1. Factors used to correct reported atmospheric pressures that have been adjusted to sea level. NGVD 1929, National Geodetic Vertical Datum 1929.

Selection of Calibration Method

A saturated-oxygen calibration of DO sensors is recommended uniformly by manufacturers, regardless of which of the following methods is used: Air Calibration Chamber in Air (Procedure 1), Calibration in Air-Saturated Water (Procedure 2), or Air Calibration with a Wet Towel (Procedure 3). With minor modifications, these procedures can be applied to a one-point calibration of either luminescent-sensor (optical) or amperometric instruments (not all instruments allow or can accommodate a two-point calibration). A fourth method, Air Calibration Chamber in Water (Procedure 4), is described in the section on calibration for amperometric sensors. Although Procedure 4 has, in some cases, been applied when calibrating optical sensors, the pressure differentials and aqueous vapor properties at various temperatures experienced at the field site increases the potential for undetected water droplets on the thermistor and luminophore membrane and the risk for larger measurement error compared with the other calibration methods described below. It is important to refer to the manufacturer-provided guidance, as each of the procedures has inherent advantages and disadvantages and may include instrument-specific sources of error.

- The saturated-water method (Procedure 2) tends to be favored by manufacturers for calibrations in an office laboratory because it ensures equilibration of the temperature sensor with the DO amperometric membrane or the optical luminescence-coated sensor. Procedure 2 is considered to provide the best accuracy for calibration of optical sensors.
- The air calibration with a wet towel method (Procedure 3) is performed at the field site and is the method recommended most commonly by manufacturers for calibrating the amperometric (Clark cell) sensor, given advances in instrument technology. While the Wet Towel method can be used in the calibration of optical as well as amperometric sensors, the Air Calibration Chamber in Water method is applicable to amperometric sensors only. In previous versions of this field manual, the Air Calibration Chamber in Water (Procedure 4) method was published as "Procedure 3."

- **Check DO meter calibration at each field site.**
- **Calibration of amperometric sensors should be checked each time after an instrument has been powered off and recalibrated, as necessary.**

Optical (Luminescence) DO Sensors: Calibration Procedures

The introduction of luminescence technology to DO field instruments has improved and simplified the data-collection process for field determination of DO. In addition to being more rugged, having fewer interferences, and undergoing decreased calibration drift relative to amperometric sensors, optical DO sensors tend to be more accurate, with accuracy specifications of ±0.1 mg/L or 1 percent after calibration.[8] This level of accuracy is best achieved by calibrating under controlled conditions in a laboratory or simulated laboratory environment.

[8] USGS field scientists have corroborated the accuracy of the optical sensor to 0.05 mg/L DO by using repeated comparisons of results with the Rhodazine-D spectrophotometric method described in section 6.2.2 of this field manual (Gerolamo Casile, U.S. Geological Survey, written commun., 2012). These results can be entered into the USGS NWIS database.

TECHNICAL NOTE 4. Optical DO sensors often contain internal calibration information from the manufacturer. Although some manufacturers advise that no further calibration is warranted, the accuracy of factory calibrations do not necessarily satisfy the data-quality objectives required for USGS applications. **Because the validity of a calibration can substantially affect the overall accuracy and precision of DO measurements, users are advised to check the calibration frequently in order to meet specific data-quality objectives.**

- Because the optical DO sensors are not subject to drift, shock, or temperature extremes, the office-performed calibration is likely to remain stable after transport to the field; nevertheless, calibrations must be verified at the field site.[9]
- The Rhodazine-D spectrophotometric and iodometric methods for DO measurement described in sections 6.2.2 and 6.2.3, respectively, have been used to check the calibration of these instruments (see footnote 8).
- All calibration information is to be recorded in instrument-specific log books and the calibration data copied onto field forms at the time of calibration. Some instruments produce calibration reports generated by manufacturer-specific firmware; such reports that can be downloaded should be reviewed and incorporated in the instrument log book.
- Procedure 1 (air calibration chamber in air), Procedure 2 (calibration with air-saturated water) and Procedure 3 (air calibration with a wet towel) are described below for calibration of optical sensors at 100 percent saturation.
  - Refer to the NFM Comments and Errata, chapter 6, for the potential applicability of the "air calibration chamber in water" method to calibration of optical sensors (*http://water.usgs.gov/owq/FieldManual/mastererrata.html)*.
  - A description of the "air calibration chamber in water" method is given below as Procedure 4 in the section titled "Amperometric (Clark cell) DO Sensors: Calibration procedures".

Procedure 1: Air calibration chamber in air

This procedure (which is similar to Procedure 3) is commonly used for calibrating **handheld** optical DO instruments. Calibration chambers either are built into the instrument case or are provided as separate components by the manufacturer. **Use the calibration chamber that is provided or recommended by the manufacturer.**

1. Wet the inside of the calibration chamber with water and then pour out the water, leaving a few drops.
   a. Remove any water droplets on the temperature and optical sensors.
   b. Insert the sensor into the chamber (this ensures 100 percent humidity).
      - If using a screw-on calibration cup, make sure it is loose and not making an airtight seal in order to maintain ambient pressure.
      - Keep the calibration assembly in a stable temperature environment and out of direct sunlight.

[9] Laboratory calibration is favored by manufacturers in general, who advise that DO instruments rarely should require recalibration in the field.

2. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the calibration chamber to equilibrate. If appropriate for the instrument being used, run the instrument during the equilibration period.
3. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
4. Monitor the temperature and DO outputs in the calibration chamber, observing readings until the instrument readings stabilize. Read the temperature to the nearest 0.1 °C.

> **TECHNICAL NOTE 5.** To maximize accuracy, a recommended practice is to maintain or approximate air temperatures during calibration that are within 10 °C of the ambient temperature of the water to be measured (see Procedure 3 – Wet Towel Method).

5. If calibrating to a given DO concentration rather than calibrating to a condition of 100 percent saturation, use table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine DO saturation at the calibration temperature and atmospheric pressure.
6. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration simply to a 100-percent saturation condition, all that may be needed is to provide the ambient atmospheric pressure for the instrument to determine (with internal software) the resulting DO concentration.
7. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study.
8. Remove the sensor from the calibration chamber to check if water droplets were on the optical tip or membrane during calibration; water droplets on the sensor tip or membrane and on the temperature sensor can cause improper calibration.
    - **Recalibrate the instrument if water droplets were present.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

During saturated-air calibration, it is necessary to keep water droplets off of the optical sensor module (luminescence tip or membrane) and temperature probe.

Procedure 2: Calibration with air-saturated water

This procedure, in which the DO sensor or instrument system is calibrated in water that is saturated with oxygen at a known temperature and ambient atmospheric pressure, generally is preferred by manufacturers for optical-sensor calibration.[10] Procedure 2 is considered the most accurate for optical measurements of DO because the saturated water ensures that all equipment parts equilibrate with water temperature simultaneously, and the method eliminates the need to check for water droplets on the optical tip/membrane or temperature sensor. Great care is required, however, to ensure that the water is indeed saturated with oxygen.

Equipment: Calibration with Air-Saturated Water	
1	5-gallon bucket or manufacturer-provided aeration chamber
1	10-gallon-aquarium air pump with two outlets
1	10-foot-length of aquarium pump tubing
2	Gas-diffusion (air) stones

For this procedure, producing aerated water under controlled laboratory conditions is preferred; calibrate the DO sensor in the office laboratory before departing for the field site (step 4a below).

1. In the laboratory, fill a 5-gallon bucket to three-quarters full with tap water.
2. Attach the pump tubing to the pump and then the two air stones to the ends of the tubing. Place the tubing with air stones at the bottom of the filled bucket.
3. Turn on the pump and aerate the water for a minimum of 30 minutes.[11]
   Tip: The pump could be left to operate continuously (24/7) in order to have a ready supply of air-saturated water on hand for calibration in the laboratory or for transport and calibration in the field.
4. **Calibration**—Take care to keep air bubbles off of the optical sensor (the luminescence tip or membrane).
   a. For laboratory calibration, place the DO sensor (or multiparameter sonde) in the bucket and allow 5 to 10 minutes for the sensor to come to thermal equilibrium with the aerated water. Take care not to place the sensor over or in the bubbles from the air stone!
   b. For field calibration of a handheld DO sensor:
      - Fill a 1-gallon (approximately 4-liter) container to three-quarters full with the laboratory-aerated water for transport to the field. In the field vehicle, shake the container vigorously for 2 minutes to fully aerate the water and immerse the DO sensor. Allow about 5 minutes for the sensor to come to thermal equilibrium with the aerated water.
      - Alternatively, use the Wet Towel Method (Procedure 3).
5. Read and record the temperature of the calibration water to the nearest 0.1 °C.

[10] Some manufacturers provide the necessary aeration equipment with the instrument.

[11] Previous versions of this procedure described in this field manual specified that a sensor or sonde be immersed in the water while the water is being aerated with a battery-operated aquarium pump. Owing to uncertainties in pump quality, battery power, and possible supersaturation, this technique is not universally recommended by the manufacturers who reviewed this protocol and has been modified accordingly. If the former procedure is used, it is imperative to avoid placing the sensor in the stream of air bubbles.

6. Using a calibration-checked altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
7. Using oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*), determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)
8. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value. Alternatively, use more stringent accuracy criteria that reflect the data-quality requirements of the study. If the field calibration or calibration check fails to meet the established criterion, (a) use a different instrument (if available), and (b) do not collect or report data using an instrument that has failed calibration.
9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

For accurate calibration, ensure that the water is 100 percent saturated with oxygen (see step 4b above).

Procedure 3: Air calibration with a wet towel

For many multiparameter instruments a 100-percent humidity environment can be created by wrapping a moist towel around the sensor guard and inserting into a plastic bag. The Wet Towel Method is almost identical to Procedure 1, the main difference being that the sensor (or sonde) guard will be wrapped in a wet towel instead of being inserted into a calibration cup or chamber.

Equipment: Calibration with a Wet Towel	
1	Towel, sized so that it will wrap around the sensor at least two full wraps
1	Trash bag, clear or white plastic

1. Bring sensor to thermal equilibrium.
    a. If attempting to match the temperature of the water being monitored (for example, stream, lake, or groundwater), place the sensor directly in the water body (alternatively, for groundwater, into a flowthrough cell through which well water is being pumped continually).
    b. Allow 5 to10 minutes for thermal equilibration of the sensor with ambient water temperature until temperature readings have stabilized.
2. Once temperature readings are stable, soak the towel either (a) in the water for DO measurement, or (b) with tap or deionized water.

3. Remove the towel, wring it out, and then wrap the wet towel completely around the sensor guard, cup, or chamber, two full wraps or more.
    - As you wrap the sensor, ensure that no water droplets are either on the temperature sensor or on the luminescent sensor (sensor tip or membrane).
    - Place the wrapped sensor into the plastic bag and keep it out of direct sunlight in order to keep the temperature from changing.
4. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the towel (calibration chamber) to equilibrate. Run the instrument during the equilibration period, if so directed by manufacturer instructions.
5. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
6. Monitor the temperature and DO outputs and observe readings until the instrument stabilizes. Read the temperature to the nearest 0.1 °C.
7. If calibrating to a DO concentration rather than to 100 percent saturation, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine the DO saturation concentration at the measured temperature and atmospheric pressure.
8. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration only to 100 percent saturation, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
    - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study.
9. Remove the sensor from the towel and check if any water droplets were on the membrane. Water droplets on the membrane and temperature probe can cause improper calibration.
    - **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
10. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Amperometric (Clark cell) Do Sensors: Calibration Procedures

The calibration and operation of amperometric instruments differ among instrument types, makes, and models—refer to the instrument manual provided by the manufacturer. Calibration for amperometric sensors typically is performed using one of the following procedures for a one-point calibration at 100 percent saturation:

- Procedure 1 (Air Calibration Chamber in Air)
- Procedure 2 (Calibration with Air-Saturated Water)
- Procedure 3 (Air Calibration with Wet Towel)
- Procedure 4 (Air Calibration Chamber in Water)

Manufacturers recommend different calibration frequencies for membrane-electrode (amperometric) DO meters. Depending on equipment capabilities, instrument performance and data quality can be enhanced by checking sensor performance; that is, making calibration checks as frequently as needed or as directed by project protocols. Sensor manufacturers generally agree that optimum performance and data quality will be obtained by frequent calibration and performance checks. Sensor performance checks at zero DO are implemented routinely by trained USGS field personnel (see section 6.2.1.B).

Tip: Many amperometric DO sensors require the meter to be powered on for 10 to 15 minutes before calibration (and use) to stabilize the probe. Refer to the manufacturer's instrument-specific guidelines for the requirements of your instrument.

Procedure 1: Air calibration chamber in air

This procedure, similar to Procedure 3, is the most commonly used method for amperometric instruments. Calibration chambers are either built into the instrument case or are provided as separate components by the manufacturer. **Use the calibration chamber provided or recommended by the manufacturer.**

1. Wet the inside of the calibration chamber with water, then pour out the water (but leave a few drops).
2. Remove any water droplets on the sensor membrane and temperature sensor, then insert the sensor into the chamber (this ensures 100 percent humidity).
    - If using a screw-on calibration cup, ensure it is loose (not making an airtight seal) to avoid causing a change in the pressure around the sensor compared to the onsite barometric pressure. Alternatively, consider using the Wet Towel Method (Procedure 3).
    - Be sure to keep the DO assembly in a stable temperature environment and out of direct sunlight, as applicable for the instrument in use.
3. Allow 10 to 15 minutes for the air to saturate and for the DO sensor and the air inside the calibration chamber to equilibrate. Apply power to the instrument during the equilibration period, as applicable for the instrument in use.
4. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.

5. Monitor the temperature and DO outputs in the calibration chamber and observe readings until the instrument stabilizes. Read the air temperature in the chamber to the nearest 0.1 °C. To the degree possible, the temperature in the chamber should approximate the temperature of the water body in which DO will be determined within about 10 °C.

> **TECHNICAL NOTE 6.** Most instrument manufacturers recommend calibrating at temperatures that are at least within 10 °C of the ambient water temperature. The most accurate calibration will be achieved if the temperature difference between the environmental water and the calibration chamber is minimized as much as possible (see Procedure 3, the Wet Towel Method, for additional information). In addition, the manufacturers of DO equipment that currently (2013) is in common use for USGS data-collection efforts advise testing the equipment in a laboratory setting to determine the accuracy of room-temperature calibrations compared with measurements made under the anticipated warmer or colder field conditions.

6. If calibrating to a DO concentration rather than to a 100-percent saturation condition, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine the DO saturation value at the measured temperature and atmospheric pressure.
7. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration simply to a 100-percent saturation condition, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
    - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study. If the criteria are not met, repeat the calibration procedure after checking for water droplets in step 2 above.
8. Remove the sensor from the calibration chamber and again check for water droplets on the membrane. Water droplets on the membrane and temperature sensor can cause improper calibration.
    - **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Procedure 2: Calibration with air-saturated water

In this procedure, the DO sensor or instrument system is calibrated in water that is saturated with oxygen at a known temperature and ambient atmospheric pressure. **Manufacturers advise that the calibration with air-saturated water is best done in the laboratory under controlled conditions.**[12]

Equipment: Calibration with Air-Saturated Water	
1	5-gallon bucket or manufacturer-provided aeration chamber
1	10-gallon-aquarium air pump with two outlets
1	10-foot-length of aquarium pump tubing
2	Gas-diffusion (air) stones

1. In the laboratory, fill the 5-gallon bucket about three-quarters full with tap water.
2. Using two air stones, saturate the water for at least 30 minutes before use. However, some manufacturers recommend that the pump be left on continuously (24/7) so that the water is always saturated and ready to use.
3. Place the DO sensor in the water, avoiding contact with the bubble stream, and allow the sensor to come to thermal equilibrium.
4. Read the temperature of the calibration water to the nearest 0.1 °C.
5. Using a calibration-checked altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
6. **Move the sensor so as to ensure a 1 foot per second (ft/s) flow across the membrane;** alternatively, use a sensor that is equipped with a stirrer. Ensure that sufficient flow passes over the DO sensor during the saturated-water calibration method as well as when making a field measurement.
    - Move the sensor to stir the water, using either a horizontal stirring motion or a "teabag" dipping motion. Take care not to remove the sensor from the water.
    - The DO reading may rise as the water is stirred.
    - **After the DO reading has peaked and is stable, start to calibrate the DO sensor.**
    - Maintain this flow rate while monitoring measurements and adjusting the instrument calibration.

> **TECHNICAL NOTE 7.** The various types of amperometric sensors can have different levels of flow dependency; however, the 1 ft/s flow is not detrimental to sensors with little or no flow dependence.

7. Using the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*), determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)

[12] Field calibrations with battery-powered pumps are not recommended by manufacturers who reviewed this report (see footnote 11). Trained USGS field personnel have, however, demonstrated success using Procedure 2 in the field.

8. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality objectives of the study.
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
9. Record calibration information in instrument log books and transfer the calibration data into electronic records or onto paper field forms at the time of calibration.

For accurate calibration, ensure that the water is 100 percent saturated with oxygen.

Procedure 3: Calibration with a Wet Towel

This method is almost identical to Procedure 1, the main difference being that the sensor (or sonde) guard will be wrapped in a wet towel instead of being inserted into a calibration cup or chamber.

Equipment: Wet-Towel Calibration	
1	Towel, sized so that it will wrap around the sensor at least two full wraps
1	Trash bag, clear or white plastic

1. Bring the sensor to thermal equilibrium.
    - If attempting to match the temperature of the water being monitored (for example, stream, lake, or groundwater), place the sensor directly in the water body (alternatively, for groundwater, into a flowthrough cell through which well water is being pumped continually).
    - Allow 5 to10 minutes for thermal equilibration of the sensor with the ambient water temperature until temperature readings have stabilized.
2. Once temperature readings are stable, soak the towel either (a) in the environmental water for DO measurement, or (b) with tap or deionized water.
3. Remove the towel, wring it out, and wrap the wet towel completely around the sensor guard, cup, or chamber, two full wraps or more.
    - As you wrap the sensor, **ensure that no water droplets are either on the temperature sensor or on the sensor tip or membrane.**
    - Place the wrapped sensor into the plastic bag and **keep it out of direct sunlight** to keep the temperature from changing.
4. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the towel (calibration chamber) to equilibrate. Run the instrument during the equilibration period, if so directed by manufacturer instructions.
5. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure to the nearest 1 mm of mercury.
6. Monitor the temperature and DO outputs and observe readings until the instrument stabilizes. Read the temperature to the nearest 0.1 °C.

7. If calibrating to a specific DO concentration rather than to 100 percent saturation, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine the DO saturation value at the measured temperature and atmospheric pressure.
8. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration to 100 percent saturation, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
    - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study or program.
9. Remove the sensor from the towel and check if any water droplets are on the membrane. Water droplets on the membrane or temperature sensor can cause improper calibration.
    - **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
10. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Water droplets on the DO membrane and thermistor will result in improper calibration. Recalibration is required if water droplets are observed.

Procedure 4: Air calibration chamber in water

A specialized air-calibration chamber permits calibration of the DO sensor at the temperature of the water in which DO concentration is to be measured. This calibration procedure minimizes errors caused by temperature differences; for example, at sites having field conditions with a wide disparity between ambient air and water temperature. For many multiparameter water-quality instruments, the manufacturer-provided groundwater flow cell may be modified and used as an air calibration chamber in water.[13] The modification requires the cell to be mounted on the sonde with one port of the cell tightly plugged and the other port vented to the atmosphere with tubing. The method is subject to large errors, especially in cold temperatures, if the port is not adequately vented to the environment. **Before using this method, check with the manufacturer for its applicability to the instrument to be used**.

1. Insert the sensor probe and calibration chamber into the surface water or groundwater to be measured. Once the temperature readings stabilize (allow 10 to 15 minutes), remove the sensors and calibration chamber from the water to be measured. Empty the calibration chamber, leaving a few drops of water.
    - Check for and remove any water droplets on the sensor membrane and the thermistor.
    - Insert the DO sensor into the wet chamber (this ensures 100 percent humidity).

[13] Air calibration chambers for in-water calibrations no longer are available on the open market (for example, the YSI 5075A calibration chamber is no longer manufactured).

- Check that the port is adequately vented, that no water can leak into the calibration chamber, and that droplets of water are not adhering to the membrane and thermistor. The water droplets reduce the rate of oxygen diffusion through a membrane, producing erroneous results.

2. Immerse the calibration chamber into the water to be measured. Allow 10 to 15 minutes for the air temperature inside the chamber to equilibrate with the water (see TECHNICAL NOTE 6 in Procedure 1).
    - For streams, choose an area of the stream that closely approximates mean stream temperature. In shallow streams, try to place the chamber in an area that represents the stream but that is shaded from direct sunlight.
    - For groundwater, use temperature-stabilized purge water or other clean water having a temperature that closely approximates that of the groundwater.
3. Using a calibration-checked pocket altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
4. Read the temperature within the chamber to the nearest 0.1 °C, using a calibrated thermometer (NFM 6.1).
    - The temperature inside the chamber should approximate the water temperature.
    - If the two temperatures do not match, allow additional time for equilibration of the chamber with the water temperature.
    - If the temperature of the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Compare water temperature measured by the DO meter and a calibrated field thermometer. If the two measurements vary by more than ±0.5 °C, the calibration should be discontinued and the DO meter thermistor should be repaired following the manufacturer's recommendations.
5. Use table 6.2–6 (section 6.2.5) to determine the DO saturation value at the measured water temperature and atmospheric pressure. If a salinity correction will be applied during calibration, consult the instructions in section 6.2.5 and table 6.2–7.
6. Following the manufacturer's instructions, set or adjust the calibration control until the instrument reads a DO saturation value determined from oxygen solubility (table 6.2–6).
    - Verify that the instrument reading is within ±0.2 mg/L of the computed saturation value, or use more stringent accuracy criteria per the data-quality objectives of the study.
    - Verify that no water droplets are on the membrane or thermistor. **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
    - Remove the sensor from the calibration chamber for cleaning and storage.
7. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Water droplets on the DO membrane and thermistor will result in improper calibration. Recalibration is required if water droplets are observed.

6.2.1.C Measurement

The solubility of oxygen in water depends on the partial pressure of oxygen in air, the temperature of the water, and the content of dissolved solids in the water.

- The higher the atmospheric pressure and the lower the temperature and conductivity, the more oxygen can be dissolved in the water.
- Degassing, mineral precipitation, and other chemical, physical, and biological reactions can cause the DO concentration of a water sample to change substantially within minutes after sample collection. These sample reactions are especially important when sampling groundwater that is not in equilibrium with the atmosphere.

The solubility of oxygen in water decreases as salinity increases. Correction factors for salinity normally are applied after measuring DO for single-point samples; however, for continuously deployed DO probes on multiparameter instruments that include calibrated specific-conductance sensors, it is wise to activate the instrument's internal salinity correction algorithms to account for a dynamically changing environment. Information that pertains to oxygen solubility and salinity is given in section 6.2.5, including the link to an on-line program that generates tables of DO solubility values and (or) salinity correction factors over a range of user-specified temperature, pressure, and salinity or specific conductance (*http://water.usgs.gov/software/DOTABLES/* accessed March 11, 2013).

Surface water

Standard determinations of DO in riverine surface water represent the cross-sectional median or mean concentration of dissolved oxygen at the time of observation.

- Multiparameter instruments (sondes) are in common use for USGS measurement of DO and other field properties, both for in situ discrete measurements in surface water and for short- or long-term deployment in streams, lakes and reservoirs, and other bodies of surface water. Refer to NFM 6.8, Wagner and others (2006), and manufacturer guidance for additional information regarding the siting and use of multiparameter instruments.
- Measuring the DO concentration at one distinct point in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L. Discerning such variation requires a reconnaissance cross-section measurement. **Measurements made at multiple locations in the cross section are recommended as a routine practice, when possible.**
- Determining DO concentration for a single channel at the centroid of flow at the midpoint of the vertical only represents the cross section under ideal mixing conditions.
- Do not measure DO in or directly below sections with turbulent flow, in still water, or from the bank, unless these conditions represent most of the reach or are required to fulfill study objectives.
- Verify whether or not the instrument in use applies salinity corrections automatically. If not, apply a salinity correction to the saturation values after the DO measurement, referring to section 6.2.5 and table 6.2–7.

Dissolved oxygen must be measured in situ.
Never measure DO in subsamples from a sample splitter or other vessel.

Follow the steps below to measure DO in surface water:

1. Calibration checks:
    - Check that the thermistor is accurate and that its calibration has been certified by the USGS Water Science Center within the past 12 months; more frequent calibration checks are performed in the field, depending on the field conditions encountered (see NFM 6.1.2.B for specifics).
    - Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
    - If a calibration adjustment is necessary or if it is required to address program protocols, data-quality requirements, or site-specific conditions, calibrate the DO sensor onsite, in accordance with the procedures described in section 6.2.1.B.
2. Examine the variation in DO measured at multiple locations along the cross section (if this reconnaissance step was performed) to help select the sampling method (NFM 6.0):
    - **Flowing, shallow stream**—Wade to the location(s) where DO is to be measured.
    - **Stream too deep or swift to wade**—Lower a weighted DO sensor with a calibrated temperature sensor from a bridge, cableway, or boat.
        – Do not attach the weight directly to the sensors or sensor cables, because this could damage the sensors or sensor cables.
        – To avoid damaging sensors or cables, contact the instrument manufacturer or vendor for information regarding the weights approved for use with the instrument and how to attach them.
    - **Still-water conditions**—Measure DO at multiple depths at several points in the cross section (see TECHNICAL NOTE 8).
    - **Lakes and reservoirs**—Measure DO at a series of specific depths to determine a vertical profile at each location of interest (see TECHNICAL NOTE 8).

> **TECHNICAL NOTE 8.** For amperometric sensors: If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device to increase the flow velocity.[14]
>
> - To hand stir, raise and lower the sensor at a rate of about 1 ft/s, but do not break the surface of the water. The stir-by-hand method may not be appropriate in lakes, reservoirs, or slow-moving waters (for example, bayous); these water bodies may be stratified at the point of measurement, making accurate DO measurements impossible with a non-stirred amperometric DO probe. This could be especially problematic in areas where DO concentrations change substantially over short distances, such as near the thermocline or bottom sediments.
> - High stream velocity also can cause erroneous DO measurements.

3. Immerse the DO and temperature sensors directly into the water body and allow the sensors to equilibrate to the water temperature (no less than 60 seconds).
4. Record the temperature without removing the sensor from the water.

[14] Refer to footnote 3 if using a YSI "Rapid Pulse" sensor, for which a stirrer is not needed.

5. After the instrument reading has stabilized, record the median DO concentration (see NFM 6.0). The reading should stabilize to within ±0.2 mg/L.
6. For EWI, EDI, or multiple-vertical measurements, proceed to the next station in the cross section and repeat steps 3 through 5. When measurements for the stream have been completed, remove the sensor from the water, rinse it with deionized water, and store it according to the manufacturer's instructions.
7. Record DO concentrations on the field forms:
    - **In still water**—Median of three or more sequential values.
    - **EDI**—Mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
    - **EWI—Mean (or median)** of all subsections measured.

Groundwater

Before the concentration of DO in groundwater can be determined, standing water must be evacuated from the well to ensure that measurements of DO concentration in the well will be representative of formation-water concentration. An adequate well purge ensures the flow of freshwater from the formation into the well (refer to NFM 4.2 and NFM 6.0.3.A for detailed information). Measurement of ambient DO concentrations in groundwater additionally requires use of equipment and procedures that avoid aeration and mitigate losses or gains of dissolved gases in the water being sampled. A bailed sample, for example, is inadmissible for DO measurement because the field sample-decanting process exposes the sample to the atmosphere (NFM 6.0.3); this provision likewise applies to any type of sampling device from which the sample is brought in contact with air when transferred to a measurement or analysis vessel.

Project or program data-quality requirements and objectives, site characteristics, and equipment availability will dictate whether (a) measurements will be made *in situ* (DO measured downhole) or *ex situ* (DO measured above land surface, the inline-flow procedure), and if (b) optical, amperometric, or spectrophotometric methods will be used for DO measurement. This section addresses the use of optical and amperometric sensors, for which the lower threshold for measurement of aqueous DO concentrations is from 1 to 2 mg/L, depending on the instrument being used and the accuracy required.[15] **If the anticipated DO concentration is less than 1.0 mg/L, consider use of spectrophotometric methods (section 6.2.2).**[16]

- ► If using an optical-sensor instrument at DO less than 1.0 mg/L, first perform a zero-DO calibration check or calibration (instrument permitting), and document the results.
- ► When anticipating DO concentrations in the hypoxic or suboxic range on a routine or regular basis,
    - — Optical sensor: Readings to 0.05 mg/L should be verified using the methods described in sections 6.2.2 or 6.2.3. The presence of hydrogen sulfide, however, will not affect the accuracy of the measurement.
    - — Amperometric sensor: The sensor can be adversely affected by hydrogen sulfide and misread the true DO value.

[15] The accuracy of DO measurements to 0.05 mg/L with an optical sensor has been field verified against Rhodazine-D spectrophotometric measurement on numerous occasions by USGS field-methods instructors (Gerolamo Casile, U.S. Geological Survey, oral commun., 2012).

[16] Note that spectrophotometric methods for determining DO concentration generally are not approved by the U.S. Environmental Protection Agency for regulatory assessments.

Refer to NFM sections 6.0.1 and 6.0.3 for guidance related to the selection, preparation, and procedures for in situ and ex situ measurement of field-determined properties. Study objectives and site characteristics will dictate the specific method selected. Select the field-measurement system that best fits the requirements for the data-collection effort.

- **Downhole (in situ) measurement** (see NFM 6.0.3.B)**.** Submersible multiparameter sondes and single-parameter sensors are deployed downhole to the targeted depth interval. Deployment typically involves data collection for a single field trip. The sonde or sensor sometimes is deployed for unattended monitoring, but the appropriate conditions and protocols must be followed (see NFM 6.8). Use of the optical DO sensor makes longer-term deployment more practical, compared to that of the amperometric sensor.
- **Inline flowthrough cell/chamber (ex situ) measurement.** Sample is pumped directly (inline) to an airtight, transparent chamber or manufacturer-provided cell having either (1) leak-proof ports (compression fittings) that accommodate either the optical or amperometric DO single-parameter sensor (and other single-parameter sensors), or (2) a multiparameter sonde instrumented with either an optical or amperometric DO sensor. NFM 6.0, figure 6.0–3, diagrams a flowthrough cell system; figure 6.0–5 charts downhole and inline sampling processes.[17]
  - Sample is transferred using a positive-displacement submersible pump fitted with high-density plastic or fluorocarbon-polymer tubing that is relatively gas impermeable.
  - Use of transparent materials for the tubing and chamber is needed to allow checking for air bubbles in the water stream or adhering to the sides of the tubing and flowthrough cell or chamber (that have been introduced as an artifact of the sampling procedure, as distinguished from gas bubbles that are native to the formation water). Such air bubbles add significant error to low-level DO measurements and should be excluded (A.F. White, U.S. Geological Survey, written commun., 1993).
  - Protect exposed sample tubing and the flow-through cell or chamber from direct sunlight.

Do not measure groundwater DO concentration in a sample extracted from a bailer or other sampling device that results in sample exposure to the atmosphere.

Follow the steps below to measure DO in groundwater:

1. Calibration checks: Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
   - Check that the thermistor gives an accurate reading and that its calibration has been verified by the USGS Water Science Center within the past 12 months (see NFM 6.1).
   - Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
   - If field calibration is necessary or if it is required to address program protocols, data-quality requirements, or site-specific conditions, calibrate the DO sensor in accordance with the procedures and restrictions described in section 6.2.1.B.

[17] See section 6.0, "General Information and Guidelines," in chapter 6 of this field manual (*http://water.usgs.gov/owq/FieldManual/Chapter6/6.0_contents.html*).

2. Install the DO equipment (see NFM 6.0 for more detailed instructions):
    - **Downhole system**—Lower the DO and temperature sensors to the measuring point, followed by the pump, to monitor DO variation during purging. When an amperometric sensor is used, water needs to flow past the sensor at a velocity of no less than 1 ft/s; attach a mechanical stirrer, if necessary, to maintain this velocity. The optical sensor is not flow dependent.
    - **Inline flowthrough system**—Refer to NFM 6.0 for installation guidelines. If sensors are to be installed in a flowthrough cell or chamber, install the DO sensor immediately downstream of the point of sample inflow. For a system using a multiparameter instrument sonde, install the sonde in the flowthrough cell provided by the manufacturer and in accordance with manufacturer instructions. Be sure to:
        - Install the DO sensor through an airtight grommet, if using a chamber instrumented with single-parameter sensors. Check that the seal around the DO sensor is intact and that the sensors are properly immersed.
        - Shield the sample tubing and flowthrough cell/chamber from direct sunlight to minimize changes to sample temperature (this step is most critical for users of amperometric sensors).
        - Dislodge and flush entrained air bubbles from the tubing walls and flowthrough chamber by tapping the tubing with a blunt tool (see TECHNICAL NOTE 9 below). Note that air bubbles are an indication of air leakage into the sampling system and should be distinguished from gas bubbles that could be native to formation water chemistry.
        - Check for and eliminate backpressure in the flowthrough chamber.
3. **If using an amperometric instrument,** be sure to maintain constant, laminar flow past the DO sensor (refer to footnote 3). Measure and record DO at regular intervals throughout purging. Allow the sensors to equilibrate with groundwater for 5 minutes or more at the flow rate to be used for sampling.
4. Check the stability (measurement variability) of DO toward the end of purging.
   The stability criterion is met when five consecutive readings made at regularly spaced intervals of 3 to 5 minutes or more are within ±0.2 mg/L. (For each reading, monitor fluctuations for 30 to 60 seconds and record the median value, if necessary.) If the ±0.2 mg/L criterion is not met, increase the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals.
5. Report sample DO as the median of the final five DO readings recorded. Record on field forms any difficulty with stabilization.
6. Remove the sensor from the water and rinse it with deionized water.

Air bubbles in the lines and flowthrough chamber can add substantial error to DO readings in low DO or oxygen depleted groundwater.

TECHNICAL NOTE 9. Anomalously high DO measurements commonly are caused by aeration of groundwater during pumping. This can result from air leakage through loose fittings on production-well pumps (for example, turbine pumps) and also if drawdown in the aquifer introduces air into the cone of depression or through well-screen perforations. To avoid these problems, review information about the pump, well-construction and drawdown data, and previous data records (A.F. White, U.S. Geological Survey, written commun., 1993).

6.2.1.D Troubleshooting for Amperometric Instruments

The troubleshooting suggestions given in table 6.2–3 are for amperometric instruments and are not exhaustive; consult the manufacturer of your amperometric instrument for additional guidance. For problems with calibration or measurement using optical sensors, periodically wipe the sensor with a wet cloth. Do not wipe the Teflon membrane; rather, remove water droplets by shaking or other means. Wiping the Teflon membrane may scratch the membrane, resulting in erroneous readings. If problems with the amperometric sensor persist, consult the manufacturer. Faulty batteries can cause erratic readings.

- ► Check the voltage of the batteries.
- ► Start with good batteries in the instrument and carry spares.

Table 6.2–3. Troubleshooting guide for amperometric instruments.

Symptom	Possible cause and corrective action
Instrument drifts or takes excessive time to stabilize	• Thermal equilibrium of water and sensor has not been reached—wait longer. • Weak batteries—replace. • DO sensor needs maintenance—recondition.
Erratic instrument readings	• Break in cable—replace cable. • Faulty connection at instrument or sensor—clean contact and tighten. • Hole in membrane—replace membrane, recondition. • Air bubble in sensor—recondition sensor. • Weak batteries—replace.
Instrument too slow to react	• Gold or silver cathode tarnished—buff with pencil eraser, manufacturer-provided polishing paper, and recondition sensor. • Fouled membrane—replace membrane and recondition sensor.
Instrument will not read zero in sodium sulfite solution	• Solution contains oxygen—make fresh solution. • Instrument still does not read zero— replace membrane and recondition sensor.
Instrument cannot be calibrated to read standards	• Unable to adjust upward—check to see if more than one membrane is on the sensor. • Unable to adjust downward (membrane is probably too tight or too thin)—replace membrane.
Instrument reads inaccurate temperature	• Faulty thermistor or cable—repair or replace.

6.2.2 Spectrophotometric (Rhodazine-D and Indigo-Carmine) Methods

Various spectrophotometric methods (*see* TECHNICAL NOTE 10) are available for determining DO over a broad range of concentrations. The information given in this section, however, is limited to the application of spectrophotometric analysis of Rhodazine-D[18] and Indigo-Carmine reagents for determining DO concentrations in relatively oxygen-deficient (hypoxic) and anoxic[19] waters; that is, DO concentration from about 2 to zero mg/L.[20] The option to measure DO by spectrophotometry in the higher concentration ranges generally is selected when field conditions limit use of optical or amperometric sensor methods. (Non-instrumental analyses of Rhodazine-D and Indigo-Carmine reagent indicators also are available for measuring aqueous DO concentrations, but the analysis can be subject to considerable operator variability, is not applicable to standard USGS field protocols, and is thus beyond the scope of this guidance.)

TECHNICAL NOTE 10. The purpose of photometry is to measure light in a way that takes the sensitivity of human visual system into account. Photometry only measures in the visible spectral region from 360 nm to 830 nm, where human eyes are sensitive. Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. The National Institute of Standards and Technology (NIST) maintains the national scales for reflectance and transmittance in the ultraviolet, visible, and near-infrared spectral regions; that is, 250 nm to 2,500 nm (*see http://www.nist.gov/pml/div685/grp03/photometry.cfm,* and *http://www.nist.gov/pml/div685/grp03/spectrophotometry.cfm*).

Spectrophotometric methods for DO measurement have been used in USGS field work for measuring DO in oxygen-depleted groundwater and can be adapted for work in oxygen-depleted zones of lakes and reservoirs, but are not approved by the U.S. Environmental Protection Agency for application to regulatory assessments. The Rhodazine-D spectrophotometric method for determining DO in groundwater was introduced by White and others (1990) as a means for obtaining accurate DO data for groundwater at a time when sensor methods lacked the capability of in situ measurement.

- The Rhodazine-D spectrophotometric method is applicable to a range from 0.1 to 1.0 mg/L dissolved oxygen in aqueous environments. The Rhodazine-D (phenzone dye) compound, in reduced form, reacts with dissolved oxygen to form a deep rose to red-purple reaction product.
- Low-level Indigo-Carmine spectrophotometric methods are applicable to DO concentration ranges from either 0.006 to 0.8 or 0.2 to 2.0 mg/L, depending on the specific manufacturer kit ("ampul" or "ampoule" kit) being used for the range of interest. Indigo Carmine reacts with the dissolved oxygen present in the sample to form a highly colored blue reaction product.
- As mentioned previously, USGS technical staff have documented optical sensor measurements[21] at DO concentrations of 0.05 mg/L and Rhodazine-D spectrophotometric readings to be of comparable accuracy. To date, these findings have not been published or verified using different types of optical sensors. Before measuring and reporting hypoxic to anoxic DO concentration data from optical

[18] Rhodazine-D™ is a proprietary product of CHEMetrics, Inc. (White and others, 1990).

[19] Hypoxic: *Hypoxia* – "A condition in which natural waters have a low concentration of dissolved oxygen (about 2 milligrams per liter compared with a normal level of 8 to 10 milligrams per liter). Stevenson and Wyman (1991); *http://toxics.usgs.gov/definitions/hypoxia.html*. ***Anoxic***, in this document, refers to water that has a very low concentration of dissolved oxygen (that is, less than 0.5 milligrams per liter) (U.S. Geological Survey, 2010; *http://toxics.usgs.gov/definitions/anoxic.html*), or total deprivation of oxygen (U.S. Environmental Protection Agency, 2009).

[20] The information for the concentration range of the spectrophotometric methods discussed was provided from and reviewed by technical specialists representing CHEMetrics, Inc. and the Hach Company. See *http://www.chemetrics.com and www.hach.com*.

[21] Unpublished data. Comparisons were made using an In-Situ Inc. TROLL 9500 Profiler equipped with a rugged dissolved oxygen (RDO) optical sensor (Gerolamo Casile, U.S. Geological Survey, oral commun., 2012).

sensors, the capability and accuracy of the optical sensor in this low DO-concentration range needs to be documented by making side-by-side measurements onsite to compare results with values obtained using a spectrophotometric method.

6.2.2.A Equipment and Supplies

The Rhodazine-D and Indigo-Carmine spectrophotometric methods were designed to minimize atmospheric interaction with the water sampled. Two sampling systems commonly are used: (1) an in situ (submersible or downhole) sampler, such as the assemblies discussed in White and others (1990), and (2) a plastic overflow cell through which sample water is pumped (see equipment and supplies in table 6.2–4).

The sampling system is configured to utilize a self-filling ampoule system with the Rhodazine-D or Indigo Carmine reagent vacuum-sealed inside. DO concentration is determined instrumentally on the resultant solution using a spectrophotometer or photometer. The ampoule kits and spectrophotometer (or photometer) are available commercially. The spectrophotometer (or photometer) selected must be able to be adjusted, either manually or automatically, to the appropriate wavelength of incident light needed for the determination of DO in the resultant colored sample, based on the reagent used. Applicable spectrophotometers, photometers, and ampoule kits are available commercially from various companies and for a variety of concentration ranges.

- The accuracy of commercially available reagent kits may not be included with the equipment or supplies purchased. Always check with the manufacturer regarding the accuracy of the specific test kit(s) of interest.
- The accuracy of the test kits will typically be a function of the concentration range of DO in the sample.
- A spectrophotometer is used to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light received by a detector (*http://www.chm.davidson.edu/vce/spectrophotometry/Spectrophotometry.html*).
- Some spectrophotometers are precalibrated specifically for the products or kits developed by the kit manufacturer. If using a spectrophotometer that is not precalibrated for the products being used, calculate the DO concentration using the regression equations provided by the manufacturer of the reagent kit.

Table 6.2–4. Equipment and supplies for the spectrophotometric method of dissolved-oxygen determination using Rhodazine-D™ and Indigo Carmine reagents.

[mm, millimeter; DO, dissolved-oxygen concentration; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Portable spectrophotometer (or photometer)
Appropriate reagent kits for the expected DO range of the environmental condition
Blank ampoule (zero DO), included in each kit
Submersible sampling tool, used in situ, to meet criteria described in White and others (1990). For example, • Manganous sulfate reagent • Plastic sampler device (overflow cell), length of C-flex tubing, and sample pump
Safety gloves, glasses, and apron
Waste disposal container
White background sheet
Deionized water (maximum conductivity of 1 µS/cm)
Bottle, squeeze dispenser, for deionized water
Lint-free wipes to remove moisture from surface of the ampoule

6.2.2.B Calibration and Interferences

DO is measured as percent absorbance by the spectrophotometer. A calibration chart typically is provided with each chemical reagent kit, along with a regression formula to convert absorbance to micrograms per liter (µg/L) of DO for use with a spectrophotometer that does not perform the conversion in its firmware. Most current spectrophotometers and photometers available for measurement of dissolved oxygen are precalibrated for direct readout of DO concentration in milligrams per liter.

- Ensure that an appropriate blank ampoule is used to zero the spectrophotometer (or photometer).
- Additional calibration is needed if the method will be used to determine DO in heavily contaminated or acidic waters. This can be done by equilibrating a water sample with known partial pressures of atmospheric oxygen (White and others, 1990). Atmospheric oxygen standards are available from suppliers of gas chromatography equipment.

These chemical reagent-based methods are not subject to salinity or dissolved-gas interferences (ASTM D5543-09, ASTM D 888-12, White and others, 1990; Gilbert and others, 1982). Interferences from total salinity, major dissolved inorganic species, dissolved gases, or temperature are typically negligible with this method. However, color and turbidity in the environmental sample may interfere with both the Rhodazine-D and Indigo-Carmine methods, causing positively biased results. If using these methods in colored or turbid water, first conduct an assessment of the amount of bias attributable to such effects.

- Rhodazine-D. The spectrophotometric method using Rhodazine-D reagent is affected by the presence of oxidizing agents, including chlorine, ferric and cupric ions, and hexavalent chromium, resulting in high-biased DO readings (White and others, 1990).[22]
  - The presence of cupric copper and ferric iron at a concentration less than 50 µg/L may cause a bias of less than 1 µg/L; at 100 µg/L concentration, cupric copper may cause a bias of 5 µg/L, and ferric iron may cause a bias of 7 µg/L.
  - Sample pH at or below a pH of 2 may cause erroneous results.

[22] See also *http://www.chemetrics.com*/products/pdf/oxygen_rhodazined.pdf, accessed September 20, 2012.

- — A hydroquinone concentration greater than 200 µg/L is a positive interferent and its oxidation byproduct, benzoquinone, causes a false positive result. The effect from oxidizing agents can be corrected if the concentrations of the interfering species are known (White and others, 1990).

- ► Indigo Carmine. The spectrophotometric method using Indigo Carmine reagent[23] is affected by ferric iron, hypochlorite (chlorine), and chromate, which can cause a false positive at concentrations equal to or greater than 10 mg/L.
  - — Cupric copper interferes positively at or above 100 mg/L.
  - — Seawater may cause the reagent to precipitate.

6.2.2.C Measurement

USGS spectrophotometric measurement procedures have been tested and quality assured for the determination of DO concentration using the Rhodazine-D and Indigo-Carmine reagents provided in commercially available kits supplied by the CHEMetrics and Hach companies, respectively.[24] While the instructions provided by the manufacturers generally should be followed, augmented instructions and information are provided below to ensure that DO measurement meets USGS standards for accuracy and reproducibility. USGS personnel are advised to make the adjustments described here to the manufacturer-provided instructions.

Rhodazine-D and Indigo-Carmine reagents react with DO to produce an oxidized complex characterized by deep-rose or brightly blue-colored reaction products, respectively. The color intensity is proportional to the concentration of the initial DO present. **Timing is very important for colorimetric analyses made with a spectrophotometer.** Follow the explicit instructions for the waiting time after the sample mixes with the reagent. The reaction with the reagents occurs almost instantaneously for both the Rhodazine-D and Indigo-Carmine methods. Color development continues after the time interval specified for these methods because oxygen from the atmosphere continuously diffuses into the sample through the broken ampule tip.

- ► Do not extend the waiting times specified in the Rhodazine-D and Indigo-Carmine methods, but adhere to them strictly.
- ► Excessive mixing of the ampule before reading the spectrophotometer also may introduce atmospheric oxygen, which can bias the results, resulting in erroneous readings.

Follow the steps below to measure DO using the spectrophotometric method:

1. Familiarize yourself with instructions from the manufacturer for the kit to be used and adjust the instructions to incorporate the procedures that follow, as applicable.
2. Accounting for site characteristics and study objectives, purge the well following guidelines in NFM 4.2.
3. Set the spectrophotometer to an appropriate wavelength for the kit being used. When using a manufacturer-designated DO photometer (or spectrophotometer), verify whether or not introduction of the ampoule provided in the kit will trigger the correct wavelength setting automatically.

[23] ASTM D 888-12; ASTM D 5543-09; Gilbert and others (1982).

[24] Instructions from the Hach Company and CHEMetrics Inc. for selected colorimetry-based methods at DO concentration ranges relevant to routine USGS sampling were selected for testing because USGS field personnel currently use the equipment and reagent kits from these companies.

4. Zero the spectrophotometer using the blank provided in the kit (follow the manufacturer's instructions).[25]

5. When collecting the sample:

    - Prevent sample aeration. Use a positive-displacement submersible pump and high-density plastic or fluorocarbon polymer sample tubing that is relatively gas impermeable, if possible, throughout measurement.
    - Operate equipment to mitigate losses or gains of dissolved gases. (Consult NFM 6.0 for proper downhole and inline flowthrough-chamber sampling procedures.)

6. Select your sample-collection method: Use either a downhole or overflow-sampler device.
    - *Go to Step 7* for the downhole sampling tool method,[26] *or*
    - *Go to Step 8* for the plastic overflow-sampler device with a suitable pump method.

7. **Downhole system**: After purging the well (NFM 4.2), follow steps 7a through d.

    a. Carefully immerse a reagent-containing ampoule on the sampling tool that is attached to a wire line.

    b. At the desired depth of sample collection (in a well or in surface water), break the scored tip of the ampoule by using a sharp upward tug on the sampling tool.
        - This permits sample water to be drawn into the ampoule.
        - During transit to the surface, progressively decreasing pressure in the ampoule prevents cross contamination from overlying water through the ampoule tip.

    c. Withdraw the ampoule from the sampling device and invert once to mix the contents of the ampoule, allowing the bubble to travel from end to end; follow the kit-specific instructions regarding the number of ampoule inversions.[27]
        - Take care that this process does not introduce atmospheric oxygen into the ampoule.
        - Make sure the time required to bring the ampoule to the surface does not exceed the waiting times specified by the method. (This method may work best for shallow wells).

    d. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue. Skip to step 9.

8. **Overflow device**: After purging the well (NFM 4.2), follow steps 8a through f.

    a. Connect the plastic overflow-sampling device (table 6.2–4) to the outlet of the pump tubing with C-flex tubing 3 feet (ft) or less in length. The overflow device is used to break the ampoule in the flowing stream of water.
        - If using the **Rhodazine-D** method, the kit is equipped with the appropriate overflow sampling device needed to crack the ampoule.

[25] Native water may be used if this option is provided by the kit manufacturer.

[26] A downhole sampling tool is described by White and others (1990).

[27] Instructions provided by kit manufacturers specify inverting the ampoule several times with the bubble traveling from end to end to facilitate mixing of reagent and sample. USGS field observations, however, indicate that vigorous or repeated mixing can introduce atmospheric oxygen and bias the measurement (Gerolamo Casile, U.S. Geological Survey, written commun., 2013).

- If using the **Indigo-Carmine** method, adapt the Rhodazine-D instructions as follows, instead of using the directions provided[28]:
  - Obtain a plastic funnel with a funnel size of approximately 1 cup.
  - Adapt the funnel to the end of a length of C-flex tubing. This funnel, while overflowing, will allow the tip of the Indigo-Carmine ampoule to be broken very close to where the sample water flows in.

TECHNICAL NOTE 11. Use optically clear materials to enable seeing whether bubbles are entrained in the tubing or flow cell (chamber). Air bubbles that adhere to the sides of the tubing and chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

b. Reduce the pumping rate to achieve an even, nonturbulent, laminar rate of flow (for groundwater, about 500 milliliters per minute) that is used for sample collection. While pumping, allow the sampling device to overflow during sample collection.
   - Check for air bubbles in or adhering to the tubing and flowthrough cell (chamber).
   - Tap the tubing with a blunt tool to dislodge entrained air bubbles.

c. Insert the glass ampoule, tip first, into the overflowing sampling device so that the tapered tip is at the bottom of the device, close to the point of water inflow.

d. Snap the tip by gently pressing the upper end of the ampoule toward the wall of the sampling device.
   - The vacuum ampoule will draw in the sample water, leaving a small bubble at one end.
   - Ensure that the ampoule is full before proceeding to step e; this will prevent entraining excess atmospheric oxygen and thereby producing erroneous readings.

e. Withdraw the ampoule from the sampling device and invert to mix the contents of the ampoule, allowing the bubble to travel from end to end; follow the kit-specific instructions regarding the number of ampoule inversions (see footnote 27).

f. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue.

9. Insert the ampoule directly into the spectrophotometer cell holder, either immediately after retrieval or as specified in the kit-specific instructions.

10. Read concentration or absorbance:

a. Make spectrophotometer readings, adhering as strictly as possible to the manufacturer-specified time interval.
   - **Rhodizine-D**—Record the reading within the time interval directed by the kit manufacturer (for example, within 30 seconds when using the CHEMetrics ampoule kit).

[28] The Hach Company Indigo Carmine kit instructs placing the sample tube at the bottom of an overflowing beaker, then breaking the ampoule near the sample tubing at the bottom of the beaker. Tests conducted by USGS personnel indicated that substituting the directions in step 8a substantially improve measurement accuracy and reproducibility. (Gerolamo Casile, U.S. Geological Survey, written communication, 2013).

- **Indigo-Carmine**—Record the reading within the time interval directed by the kit manufacturer.

b. If using a spectrophotometer that does not convert absorbance values of DO measurements to milligrams per liter for the kit being used, use regression equations to make the conversion (see White and others, 1990).

11. **Quality control**: Consider utilizing multiple determinations to document the precision and (or) accuracy of the DO concentration to be reported.
    - Repeat steps 9 and 10 twice in rapid succession to document measurement precision.
    - To document the variability of DO concentrations within the water system being measured, repeat steps 4 through 10 on three sequentially collected samples.

Do not exceed the time interval specified for completion of color development.

6.2.3 Iodometric (Winkler) Method

The USGS currently uses the Alsterberg-Azide modification to the Winkler titration procedure for iodometric determination of DO. The precision of measurements using the iodometric method should be within at least ±0.05 mg/L[29] when performed by experienced analysts (American Public Health Association, 2005).

► The iodometric (Winkler) method no longer is being used routinely as a standard field method for measurement of DO in USGS investigations because (1) the accuracy and reproducibility achievable are dependent on the experience and expertise of the data collector, (2) potential environmental interferences (for example, the presence of nitrite, ferrous and ferric iron, and organic matter) require advanced knowledge of the chemistry of the sample, and (3) field conditions can make preventing exposure of the sample to atmospheric oxygen difficult. Nevertheless, the iodometric method is recognized as a reliable standard for producing accurate results when correctly implemented.

► The iodometric (Winkler) method is widely accepted in the scientific community and is used to check the calibration of, and the measurements made with, electrometric DO instrument systems.

— The Winkler method was used to verify the accuracy of optically and amperometrically determined DO concentrations reported by the USGS in an oil spill investigation, in accordance with a request by the U.S. Environmental Protection Agency (Wilde and Skrobialowski, 2011).

— Checking the calibration of electrometric instruments using the Winkler procedure is performed in a controlled (that is, laboratory) environment. The DO instrument is calibrated with air-saturated deionized water in which the DO concentration has been determined by the Winkler method; the DO instrument is then adjusted to the concentration determined from the titration.

— If a saline solution is used to approximate the environmental water, do not apply a salinity correction factor.

[29] Based on a standard deviation (SD) of ±0.02 mg/L for a three SD accuracy of ±0.06 mg/L.

6.2.3.A Equipment and Supplies

Equipment and supplies needed for the iodometric method are listed in table 6.2–5. The procedure involves the use of reagents available in premeasured pillow packets from commercial suppliers. Alternatively, reagents may be prepared by a chemist or titration technician, as described in American Public Health Association (2005).

- The accuracy of commercially obtained reagent packets may differ among manufacturers and other preparers of the reagents and should be recorded in field notes.
- Clean all equipment before use.

Table 6.2–5. Equipment and supplies for the iodometric (Winkler) method of dissolved-oxygen determination.

[mL, milliliter; *N*, normal; µS/cm, microsiemens per centimeter at 25 degrees Celsius; NFM, *National Field Manual for the Collection of Water-Quality Data*]

Beaker, 2,000 mL, glass or Teflon
Bottles for biochemical oxygen demand (BOD) analysis, glass stoppered, 300 mL
Stirrer, magnetic
Stirring bars, Teflon coated
Cylinder, graduated, 250 mL
Flask, Erlenmeyer, 250 mL
Buret, 25-mL capacity with 0.05-mL graduations and Teflon stopcock
Buret, support stand
Buret, clamp, double
Chemical reagents:[1] • Alkaline iodide-azide reagent • Manganous sulfate reagent • Sulfamic acid granules • Sodium thiosulfate, 0.025 *N* titrant • Starch indicator solution
Clippers, for opening reagent pillows
Appropriate safety gloves, glasses, and apron
Waste disposal container
White background sheet
Deionized water (maximum conductivity of 1 µS/cm)
Bottle, squeeze dispenser, for deionized water
Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
Pocket altimeter-barometer, calibrated, or DO-measurement equipment that includes barometer

[1] Use either commercially prepared reagent pillow packets or analyst-prepared reagents, depending on the data-quality requirements of the study.

6.2.3.B Measurement

This section describes how to make an iodometric determination of DO concentration.

- When the purpose of using the Winkler method is to check calibration of an amperometric or luminescent-sensor instrument, start at step 1 below and continue to the end. For quality control, steps 5 and 6 are written so as to verify the Winkler determination in duplicate. This is standard practice and should be followed.
- If making a Winkler determination for the DO concentration of an environmental sample, start at step 5, substituting the sample water for deionized water (DIW). Collect the sample and perform the titration as described below on at least two subsamples to provide the appropriate quality control. When filling the BOD bottles, a minimum of three bottle volumes of sample should pass through the bottle to collect the final volume.
  - **In surface water:** To fill the bottles, use of a sewage sampler is recommended. If a hand-held method is needed, fill the bottles in the water body by tilting them slightly to allow the bottle to slowly fill in a manner so as to avoid turbulence, bubbling, or otherwise entraining air. Keep the filled bottles submerged (in the surface-water body) for about 30 seconds. Next, while the bottle is submerged, insert the stopper firmly in the bottle, taking care not to trap air bubbles.
  - **In groundwater:** A laminar-flow sample is pumped inline from the well into the bottle, from the bottom to overflowing the top of the bottle and in a manner so as to avoid any turbulence and bubbles. Allow the sample to overflow for at least 30 seconds. Next, while still overflowing, insert the stopper firmly into the bottle, taking care not to trap air bubbles.
  - Pour off excess water that is trapped on the lip of the stoppered bottle.
  - Follow step 6 procedures as described below, substituting the sample-filled biochemical oxygen demand (BOD) bottles.
- Results of two iodometric titrations should agree within 0.1 mg/L. If they do not agree, repeat the titration on one or more additional subsamples until this quality-assurance criterion is met.

Follow the steps below to check calibration of an optical or amperometric DO instrument using the Winkler Alsterberg-Azide titration:

1. Fill a clean 2,000-mL beaker with deionized water that is near DO saturation. The water temperature should be close to the ambient (field or laboratory) temperature.
2. Prepare the DO-sensing instrument for operation, in accordance with the manufacturer's instructions.
3. Place the DO sensor in a beaker of DIW. If using an amperometric sensor, maintain a water velocity of at least 1 ft/s flowing passed the sensor. If the sensor is not equipped with a stirring mechanism, use a magnetic stirrer.
4. Monitor the DO concentrations of the DIW with the DO instrument and record the value after the readings have stabilized.
5. Carefully fill two clean BOD bottles with three or more bottle volumes of DIW from the beaker, taking care not to introduce any air bubbles by slowly overflowing the bottles adequately to remove any trapped air bubbles.
6. Determine the DO concentration of the DIW in each BOD bottle, as follows:

a. Add one each of the following dry reagent pillow packets[30]
   - Alkaline iodide-azide (white powder).
   - Manganous sulfate (pinkish-colored powder).

b. Recap the bottle **to prevent air bubbles from being trapped in the bottle.**

c. Invert the bottle 25 times or more to completely dissolve the reagents.
   - An orange-brown flocculent indicates the presence of DO.
   - Allow the flocculent to settle halfway down the bottle (approximately 5 minutes).
   - Invert the bottle 25 times again; let the flocculent settle again until the upper half of the solution is clear.

d. Add one reagent pillow of sulfamic acid (see footnote 30).

e. Recap the bottle without introducing air or air bubbles. Invert the bottle 25 times until all of the flocculent and granules are dissolved, leaving a yellow color.

f. Fill a clean 25-mL buret with 0.025 *N (Normal)* sodium thiosulfate titrant. Remove any air bubbles from the delivery tube beneath the stopcock and zero the meniscus.

g. Using either a clean 200-mL pipet or a 200-mL volumetric flask, measure 200 mL of the sample and dispense the sample into a clean, wide-mouth Erlenmeyer flask.

h. Place the flask on a magnetic stirrer. Carefully insert a clean Teflon stirring bar and stir the sample at a moderate rate without aerating the sample.

i. Add increments of sodium thiosulfate titrant until the color turns pale straw-yellow.

j. Add 1 to 2 mL of starch indicator solution. (This causes the sample to turn dark blue.)

k. Very slowly add more sodium thiosulfate titrant until the sample just turns clear. (A white background behind or below the flask will help to see the color change.)

l. Record the volume of sodium thiosulfate titrant used, in milliliters.
   - For a 200-mL sample, the volume of titrant added is directly proportional to the amount of DO in milligrams per liter.
   - To calculate DO for a sample volume greater or less than 200 mL,

$$DO\ (mg/L) = \left(\frac{200}{sample\ volume}\right) \times titrant\ added,\ in\ mL \qquad (1)$$

m. Record the DO value. Rinse the equipment thoroughly with deionized water.

7. **Quality control**. Titration values for the duplicate samples should agree within 0.1 mg/L.
   - If they do not agree, repeat the titration process (steps 5 and 6a through 6m, above) on one or more additional subsamples until this quality-assurance criterion is met.
   - Record the final, quality-assured value for DO concentration.

[30] Laboratory-prepared reagents might be prepared instead, depending on data-quality requirements, if titration will be performed by an analyst.

8. Recheck the field instrument for proper functioning, following the manufacturer's recommendations and instructions.
    - Consult the manufacturer if the field instrument does not calibrate properly.
    - Do not use an instrument that fails calibration.

6.2.4 Reporting

USGS personnel are instructed to enter the DO value on the field form indicating method (optical, amperometric, spectrophotometric, or iodometric) used for DO determination.

- DO concentrations for the amperometric and optical-sensor methods are measured to the nearest 0.01 mg/L, but currently are reported to the nearest 0.1 mg/L.
- DO concentrations for the spectrophotometric/Rhodazine-D and Indigo-Carmine methods are reported to the nearest 0.01 mg/L.
- **Note that the percentage of DO saturation in water can be greater than 100.** When the concentration exceeds 20 mg/L, check manufacturer's specifications and:
    - Report ">20 mg/L" if the manufacturer's instrument range specifications do not exceed 20 mg/L.
    - Report concentration values up to the maximum specified limit if the manufacturer's instrument range specifications exceed 20 mg/L.
    - Report "> the listed numerical limit" if the concentration exceeds the manufacturer's specified instrument range.

6.2.5 Correction Factors for Oxygen Solubility Concentrations and Salinity

Solubility concentrations of oxygen in freshwater at various temperatures and pressures (table 6.2–6) and correction factors for salinity based on specific conductance (table 6.2–7) were generated from the equations of Benson and Krause (1980, 1984) and can be customized to cover the range and decimal places needed; see U.S. Geological Survey Office of Water Quality Technical Memorandum 2011.03 (Myers, 2011). **By accessing "DOTABLES," the interactive software that generated tables 6.2–6 and 6.2–7, the user can self-generate individual values or tables of a specific range of oxygen-solubility and salinity correction factors: http://water.usgs.gov/software/DOTABLES/.**[31]

- To adjust freshwater oxygen-saturation values for the effects of salinity, use correction factors based on chloride concentration or specific conductance. Refer to the manufacturer's instructions for the DO instrument before applying a salinity correction.
- Correcting DO solubility for saline waters (greater than 2,000 microsiemens per centimeter or 1,000 mg/L chloride) varies with instrument type, calibration method, and the salts in solution.

[31] DOTABLES is an online program that generates tables of dissolved oxygen (DO) solubility values and (or) salinity correction factors over a range of user-specified values for water temperature, barometric pressure, and salinity or specific conductance. In addition to generating tables, DOTABLES can compute a single-value of oxygen solubility and percent saturation for a specific instance of temperature, pressure, and salinity.

— The correction based on specific conductance (table 6.2–7) is more useful because accurate conductivity can be determined easily from a field measurement.

— Salinity correction factors based on chloride can be calculated using information provided in U.S. Geological Survey Quality of Water Branch Technical Memorandum 79.10 (Pickering, 1979).

► DO instruments either use an automatic internal salinity correction, a manual salinity control knob for internal correction, or the calibration control knob for manual correction of salinity. Check that instruments with automatic internal salinity correction use approved salinity correction factors.

Example of salinity correction

Suppose a DO measurement is made in water with a temperature of 20.0 degrees Celsius, an atmospheric pressure of 750 millimeters of mercury, and a specific conductance of 8,000 microsiemens per centimeter (µS/cm). The freshwater oxygen solubility from table 6.2–6 is 8.97 mg/L for that temperature and pressure; the salinity correction factor from table 6.2–7 is 0.9733 for that temperature and specific conductance. The solubility of oxygen under these conditions then is:

$$8.97\ mg/L \times 0.97331 = 8.73\ mg/L \qquad (2)$$

The presence of more dissolved ions in the saline water decreases the oxygen solubility.

► If calibrating an instrument that does not have an internal salinity compensation algorithm, you could adjust the DO instrument to read 8.73 mg/L for a 100 percent saturation condition.

► If the DO measurement made with an amperometric or optical sensor under the above conditions were 7.50 mg/L and the DO probe did not have an internal salinity compensation algorithm, then the actual DO concentration should be reported as 7.50 mg/L multiplied by 0.9733, which equals 7.30 mg/L.

► **Do not use a salinity correction factor for measurements made with the iodometric (Winkler) or spectrophotometric methods.**

Example of percent saturation calculation

To express results as percent saturation, use the following equation:

$$DO\ (percent\ saturation) = \frac{measured\ DO\ (mg/L)}{DO\ (mg/L\ at\ 100\ percent\ saturation)} \times 100 \qquad (3)$$

For a salinity-corrected DO measurement of 7.30 mg/L for a sample in which the oxygen solubility (salinity corrected) is 8.73 mg/L as in the above example, the percent DO saturation would be the dividend of 7.30 divided by 8.73, multiplied by 100, which equals 83.6 percent. Note that for measurements with the iodometric (Winkler) or spectrophotometric methods, salinity correction factors are not applied to the measurement concentration.

Table 6.2–6. Solubility of oxygen infreshwater at various temperatures and pressures.

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795
0.0	13.46	13.56	13.65	13.75	13.85	13.94	14.04	14.14	14.23	14.33	14.43	14.52	14.62	14.72	14.81	14.91	15.01	15.10	15.20	15.30
0.5	13.27	13.37	13.46	13.56	13.65	13.75	13.84	13.94	14.03	14.13	14.23	14.32	14.42	14.51	14.61	14.70	14.80	14.89	14.99	15.08
1.0	13.09	13.18	13.28	13.37	13.46	13.56	13.65	13.75	13.84	13.93	14.03	14.12	14.22	14.31	14.40	14.50	14.59	14.69	14.78	14.87
1.5	12.91	13.00	13.09	13.19	13.28	13.37	13.46	13.56	13.65	13.74	13.84	13.93	14.02	14.11	14.21	14.30	14.39	14.48	14.58	14.67
2.0	12.73	12.82	12.91	13.01	13.10	13.19	13.28	13.37	13.46	13.56	13.65	13.74	13.83	13.92	14.01	14.10	14.20	14.29	14.38	14.47
2.5	12.56	12.65	12.74	12.83	12.92	13.01	13.10	13.19	13.28	13.37	13.46	13.55	13.64	13.73	13.82	13.91	14.00	14.10	14.19	14.28
3.0	12.39	12.48	12.57	12.66	12.75	12.84	12.93	13.02	13.10	13.19	13.28	13.37	13.46	13.55	13.64	13.73	13.82	13.91	14.00	14.09
3.5	12.23	12.31	12.40	12.49	12.58	12.67	12.75	12.84	12.93	13.02	13.11	13.19	13.28	13.37	13.46	13.55	13.63	13.72	13.81	13.90
4.0	12.07	12.15	12.24	12.33	12.41	12.50	12.59	12.67	12.76	12.85	12.93	13.02	13.11	13.20	13.28	13.37	13.46	13.54	13.63	13.72
4.5	11.91	11.99	12.08	12.17	12.25	12.34	12.42	12.51	12.59	12.68	12.77	12.85	12.94	13.02	13.11	13.20	13.28	13.37	13.45	13.54
5.0	11.75	11.84	11.92	12.01	12.09	12.18	12.26	12.35	12.43	12.52	12.60	12.69	12.77	12.86	12.94	13.03	13.11	13.19	13.28	13.36
5.5	11.60	11.69	11.77	11.86	11.94	12.02	12.11	12.19	12.27	12.36	12.44	12.52	12.61	12.69	12.78	12.86	12.94	13.03	13.11	13.19
6.0	11.46	11.54	11.62	11.70	11.79	11.87	11.95	12.04	12.12	12.20	12.28	12.37	12.45	12.53	12.61	12.70	12.78	12.86	12.94	13.03
6.5	11.31	11.39	11.48	11.56	11.64	11.72	11.80	11.88	11.97	12.05	12.13	12.21	12.29	12.37	12.46	12.54	12.62	12.70	12.78	12.86
7.0	11.17	11.25	11.33	11.41	11.49	11.58	11.66	11.74	11.82	11.90	11.98	12.06	12.14	12.22	12.30	12.38	12.46	12.54	12.62	12.70
7.5	11.03	11.11	11.19	11.27	11.35	11.43	11.51	11.59	11.67	11.75	11.83	11.91	11.99	12.07	12.15	12.23	12.31	12.39	12.47	12.55
8.0	10.90	10.98	11.06	11.14	11.21	11.29	11.37	11.45	11.53	11.61	11.69	11.76	11.84	11.92	12.00	12.08	12.16	12.24	12.32	12.39
8.5	10.77	10.84	10.92	11.00	11.08	11.16	11.23	11.31	11.39	11.47	11.54	11.62	11.70	11.78	11.86	11.93	12.01	12.09	12.17	12.24
9.0	10.64	10.71	10.79	10.87	10.94	11.02	11.10	11.18	11.25	11.33	11.41	11.48	11.56	11.64	11.71	11.79	11.87	11.94	12.02	12.10
9.5	10.51	10.59	10.66	10.74	10.81	10.89	10.97	11.04	11.12	11.19	11.27	11.35	11.42	11.50	11.57	11.65	11.73	11.80	11.88	11.95
10.0	10.39	10.46	10.54	10.61	10.69	10.76	10.84	10.91	10.99	11.06	11.14	11.21	11.29	11.36	11.44	11.51	11.59	11.66	11.74	11.81
10.5	10.26	10.34	10.41	10.49	10.56	10.64	10.71	10.78	10.86	10.93	11.01	11.08	11.16	11.23	11.30	11.38	11.45	11.53	11.60	11.68
11.0	10.15	10.22	10.29	10.37	10.44	10.51	10.59	10.66	10.73	10.81	10.88	10.95	11.03	11.10	11.17	11.25	11.32	11.39	11.47	11.54
11.5	10.03	10.10	10.17	10.25	10.32	10.39	10.47	10.54	10.61	10.68	10.76	10.83	10.90	10.97	11.05	11.12	11.19	11.26	11.34	11.41
12.0	9.91	9.99	10.06	10.13	10.20	10.27	10.35	10.42	10.49	10.56	10.63	10.71	10.78	10.85	10.92	10.99	11.06	11.14	11.21	11.28
12.5	9.80	9.87	9.94	10.02	10.09	10.16	10.23	10.30	10.37	10.44	10.51	10.58	10.66	10.73	10.80	10.87	10.94	11.01	11.08	11.15
13.0	9.69	9.76	9.83	9.90	9.97	10.04	10.11	10.19	10.26	10.33	10.40	10.47	10.54	10.61	10.68	10.75	10.82	10.89	10.96	11.03
13.5	9.59	9.65	9.72	9.79	9.86	9.93	10.00	10.07	10.14	10.21	10.28	10.35	10.42	10.49	10.56	10.63	10.70	10.77	10.84	10.91
14.0	9.48	9.55	9.62	9.69	9.76	9.82	9.89	9.96	10.03	10.10	10.17	10.24	10.31	10.37	10.44	10.51	10.58	10.65	10.72	10.79

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795
14.5	9.38	9.44	9.51	9.58	9.65	9.72	9.78	9.85	9.92	9.99	10.06	10.13	10.19	10.26	10.33	10.40	10.47	10.53	10.60	10.67
15.0	9.27	9.34	9.41	9.48	9.54	9.61	9.68	9.75	9.81	9.88	9.95	10.02	10.08	10.15	10.22	10.29	10.35	10.42	10.49	10.56
15.5	9.18	9.24	9.31	9.38	9.44	9.51	9.58	9.64	9.71	9.78	9.84	9.91	9.98	10.04	10.11	10.18	10.24	10.31	10.38	10.44
16.0	9.08	9.14	9.21	9.28	9.34	9.41	9.47	9.54	9.61	9.67	9.74	9.80	9.87	9.94	10.00	10.07	10.13	10.20	10.27	10.33
16.5	8.98	9.05	9.11	9.18	9.24	9.31	9.37	9.44	9.50	9.57	9.64	9.70	9.77	9.83	9.90	9.96	10.03	10.09	10.16	10.22
17.0	8.89	8.95	9.02	9.08	9.15	9.21	9.28	9.34	9.41	9.47	9.54	9.60	9.66	9.73	9.79	9.86	9.92	9.99	10.05	10.12
17.5	8.80	8.86	8.92	8.99	9.05	9.12	9.18	9.24	9.31	9.37	9.44	9.50	9.57	9.63	9.69	9.76	9.82	9.89	9.95	10.01
18.0	8.70	8.77	8.83	8.90	8.96	9.02	9.09	9.15	9.21	9.28	9.34	9.40	9.47	9.53	9.59	9.66	9.72	9.78	9.85	9.91
18.5	8.62	8.68	8.74	8.80	8.87	8.93	8.99	9.06	9.12	9.18	9.24	9.31	9.37	9.43	9.50	9.56	9.62	9.69	9.75	9.81
19.0	8.53	8.59	8.65	8.72	8.78	8.84	8.90	8.96	9.03	9.09	9.15	9.21	9.28	9.34	9.40	9.46	9.53	9.59	9.65	9.71
19.5	8.44	8.50	8.57	8.63	8.69	8.75	8.81	8.87	8.94	9.00	9.06	9.12	9.18	9.25	9.31	9.37	9.43	9.49	9.55	9.62
20.0	8.36	8.42	8.48	8.54	8.60	8.66	8.73	8.79	8.85	8.91	8.97	9.03	9.09	9.15	9.21	9.28	9.34	9.40	9.46	9.52
20.5	8.28	8.34	8.40	8.46	8.52	8.58	8.64	8.70	8.76	8.82	8.88	8.94	9.00	9.06	9.12	9.18	9.25	9.31	9.37	9.43
21.0	8.19	8.25	8.31	8.37	8.43	8.49	8.55	8.61	8.67	8.73	8.79	8.85	8.92	8.98	9.04	9.10	9.16	9.22	9.28	9.34
21.5	8.11	8.17	8.23	8.29	8.35	8.41	8.47	8.53	8.59	8.65	8.71	8.77	8.83	8.89	8.95	9.01	9.07	9.13	9.19	9.25
22.0	8.04	8.09	8.15	8.21	8.27	8.33	8.39	8.45	8.51	8.57	8.63	8.68	8.74	8.80	8.86	8.92	8.98	9.04	9.10	9.16
22.5	7.96	8.02	8.08	8.13	8.19	8.25	8.31	8.37	8.43	8.48	8.54	8.60	8.66	8.72	8.78	8.84	8.89	8.95	9.01	9.07
23.0	7.88	7.94	8.00	8.06	8.11	8.17	8.23	8.29	8.35	8.40	8.46	8.52	8.58	8.64	8.69	8.75	8.81	8.87	8.93	8.98
23.5	7.81	7.86	7.92	7.98	8.04	8.09	8.15	8.21	8.27	8.33	8.38	8.44	8.50	8.56	8.61	8.67	8.73	8.79	8.84	8.90
24.0	7.73	7.79	7.85	7.90	7.96	8.02	8.08	8.13	8.19	8.25	8.30	8.36	8.42	8.48	8.53	8.59	8.65	8.70	8.76	8.82
24.5	7.66	7.72	7.77	7.83	7.89	7.94	8.00	8.06	8.11	8.17	8.23	8.28	8.34	8.40	8.45	8.51	8.57	8.62	8.68	8.74
25.0	7.59	7.65	7.70	7.76	7.81	7.87	7.93	7.98	8.04	8.10	8.15	8.21	8.26	8.32	8.38	8.43	8.49	8.54	8.60	8.66
25.5	7.52	7.58	7.63	7.69	7.74	7.80	7.85	7.91	7.97	8.02	8.08	8.13	8.19	8.24	8.30	8.35	8.41	8.47	8.52	8.58
26.0	7.45	7.51	7.56	7.62	7.67	7.73	7.78	7.84	7.89	7.95	8.00	8.06	8.11	8.17	8.22	8.28	8.33	8.39	8.44	8.50
26.5	7.38	7.44	7.49	7.55	7.60	7.66	7.71	7.77	7.82	7.88	7.93	7.99	8.04	8.10	8.15	8.20	8.26	8.31	8.37	8.42
27.0	7.32	7.37	7.43	7.48	7.53	7.59	7.64	7.70	7.75	7.81	7.86	7.91	7.97	8.02	8.08	8.13	8.19	8.24	8.29	8.35
27.5	7.25	7.30	7.36	7.41	7.47	7.52	7.57	7.63	7.68	7.74	7.79	7.84	7.90	7.95	8.01	8.06	8.11	8.17	8.22	8.27
28.0	7.19	7.24	7.29	7.35	7.40	7.45	7.51	7.56	7.61	7.67	7.72	7.77	7.83	7.88	7.93	7.99	8.04	8.10	8.15	8.20
28.5	7.12	7.18	7.23	7.28	7.33	7.39	7.44	7.49	7.55	7.60	7.65	7.71	7.76	7.81	7.87	7.92	7.97	8.02	8.08	8.13

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795
29.0	7.06	7.11	7.16	7.22	7.27	7.32	7.38	7.43	7.48	7.53	7.59	7.64	7.69	7.74	7.80	7.85	7.90	7.95	8.01	8.06
29.5	7.00	7.05	7.10	7.15	7.21	7.26	7.31	7.36	7.42	7.47	7.52	7.57	7.62	7.68	7.73	7.78	7.83	7.89	7.94	7.99
30.0	6.94	6.99	7.04	7.09	7.14	7.20	7.25	7.30	7.35	7.40	7.46	7.51	7.56	7.61	7.66	7.71	7.77	7.82	7.87	7.92
30.5	6.88	6.93	6.98	7.03	7.08	7.13	7.19	7.24	7.29	7.34	7.39	7.44	7.49	7.55	7.60	7.65	7.70	7.75	7.80	7.85
31.0	6.82	6.87	6.92	6.97	7.02	7.07	7.12	7.17	7.23	7.28	7.33	7.38	7.43	7.48	7.53	7.58	7.63	7.69	7.74	7.79
31.5	6.76	6.81	6.86	6.91	6.96	7.01	7.06	7.11	7.16	7.21	7.27	7.32	7.37	7.42	7.47	7.52	7.57	7.62	7.67	7.72
32.0	6.70	6.75	6.80	6.85	6.90	6.95	7.00	7.05	7.10	7.15	7.20	7.25	7.30	7.36	7.41	7.46	7.51	7.56	7.61	7.66
32.5	6.64	6.69	6.74	6.79	6.84	6.89	6.94	6.99	7.04	7.09	7.14	7.19	7.24	7.29	7.34	7.39	7.44	7.49	7.54	7.59
33.0	6.59	6.64	6.69	6.74	6.79	6.84	6.89	6.93	6.98	7.03	7.08	7.13	7.18	7.23	7.28	7.33	7.38	7.43	7.48	7.53
33.5	6.53	6.58	6.63	6.68	6.73	6.78	6.83	6.88	6.93	6.98	7.02	7.07	7.12	7.17	7.22	7.27	7.32	7.37	7.42	7.47
34.0	6.48	6.53	6.57	6.62	6.67	6.72	6.77	6.82	6.87	6.92	6.97	7.02	7.06	7.11	7.16	7.21	7.26	7.31	7.36	7.41
34.5	6.42	6.47	6.52	6.57	6.62	6.67	6.71	6.76	6.81	6.86	6.91	6.96	7.01	7.06	7.10	7.15	7.20	7.25	7.30	7.35
35.0	6.37	6.42	6.47	6.51	6.56	6.61	6.66	6.71	6.76	6.80	6.85	6.90	6.95	7.00	7.05	7.09	7.14	7.19	7.24	7.29
35.5	6.32	6.36	6.41	6.46	6.51	6.56	6.60	6.65	6.70	6.75	6.80	6.84	6.89	6.94	6.99	7.04	7.08	7.13	7.18	7.23
36.0	6.26	6.31	6.36	6.41	6.45	6.50	6.55	6.60	6.65	6.69	6.74	6.79	6.84	6.88	6.93	6.98	7.03	7.08	7.12	7.17
36.5	6.21	6.26	6.31	6.35	6.40	6.45	6.50	6.54	6.59	6.64	6.69	6.73	6.78	6.83	6.88	6.92	6.97	7.02	7.07	7.11
37.0	6.16	6.21	6.26	6.30	6.35	6.40	6.44	6.49	6.54	6.59	6.63	6.68	6.73	6.77	6.82	6.87	6.92	6.96	7.01	7.06
37.5	6.11	6.16	6.20	6.25	6.30	6.35	6.39	6.44	6.49	6.53	6.58	6.63	6.67	6.72	6.77	6.81	6.86	6.91	6.95	7.00
38.0	6.06	6.11	6.15	6.20	6.25	6.29	6.34	6.39	6.43	6.48	6.53	6.57	6.62	6.67	6.71	6.76	6.81	6.85	6.90	6.95
38.5	6.01	6.06	6.10	6.15	6.20	6.24	6.29	6.34	6.38	6.43	6.47	6.52	6.57	6.61	6.66	6.71	6.75	6.80	6.84	6.89
39.0	5.96	6.01	6.05	6.10	6.15	6.19	6.24	6.29	6.33	6.38	6.42	6.47	6.52	6.56	6.61	6.65	6.70	6.75	6.79	6.84
39.5	5.91	5.96	6.01	6.05	6.10	6.14	6.19	6.23	6.28	6.33	6.37	6.42	6.46	6.51	6.56	6.60	6.65	6.69	6.74	6.78
40.0	5.87	5.91	5.96	6.00	6.05	6.09	6.14	6.19	6.23	6.28	6.32	6.37	6.41	6.46	6.50	6.55	6.59	6.64	6.69	6.73

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius]

Temp.	Atmospheric pressure, in millimeters of mercury																			
(deg C)	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695
0.0	11.53	11.62	11.72	11.82	11.91	12.01	12.11	12.20	12.30	12.40	12.49	12.59	12.69	12.78	12.88	12.98	13.07	13.17	13.27	13.36
0.5	11.36	11.46	11.56	11.65	11.75	11.84	11.94	12.03	12.13	12.22	12.32	12.41	12.51	12.60	12.70	12.80	12.89	12.99	13.08	13.18
1.0	11.21	11.30	11.39	11.49	11.58	11.68	11.77	11.86	11.96	12.05	12.15	12.24	12.34	12.43	12.52	12.62	12.71	12.81	12.90	12.99
1.5	11.05	11.14	11.24	11.33	11.42	11.52	11.61	11.70	11.79	11.89	11.98	12.07	12.17	12.26	12.35	12.44	12.54	12.63	12.72	12.81
2.0	10.90	10.99	11.08	11.18	11.27	11.36	11.45	11.54	11.63	11.72	11.82	11.91	12.00	12.09	12.18	12.27	12.37	12.46	12.55	12.64
2.5	10.75	10.84	10.93	11.02	11.11	11.20	11.29	11.39	11.48	11.57	11.66	11.75	11.84	11.93	12.02	12.11	12.20	12.29	12.38	12.47
3.0	10.61	10.70	10.79	10.88	10.96	11.05	11.14	11.23	11.32	11.41	11.50	11.59	11.68	11.77	11.86	11.95	12.03	12.12	12.21	12.30
3.5	10.47	10.55	10.64	10.73	10.82	10.91	10.99	11.08	11.17	11.26	11.35	11.43	11.52	11.61	11.70	11.79	11.87	11.96	12.05	12.14
4.0	10.33	10.42	10.50	10.59	10.68	10.76	10.85	10.94	11.02	11.11	11.20	11.28	11.37	11.46	11.54	11.63	11.72	11.81	11.89	11.98
4.5	10.19	10.28	10.36	10.45	10.54	10.62	10.71	10.79	10.88	10.97	11.05	11.14	11.22	11.31	11.39	11.48	11.57	11.65	11.74	11.82
5.0	10.06	10.15	10.23	10.32	10.40	10.48	10.57	10.65	10.74	10.82	10.91	10.99	11.08	11.16	11.25	11.33	11.42	11.50	11.59	11.67
5.5	9.93	10.02	10.10	10.18	10.27	10.35	10.43	10.52	10.60	10.68	10.77	10.85	10.94	11.02	11.10	11.19	11.27	11.35	11.44	11.52
6.0	9.80	9.89	9.97	10.05	10.14	10.22	10.30	10.38	10.47	10.55	10.63	10.71	10.80	10.88	10.96	11.04	11.13	11.21	11.29	11.37
6.5	9.68	9.76	9.84	9.93	10.01	10.09	10.17	10.25	10.33	10.42	10.50	10.58	10.66	10.74	10.82	10.91	10.99	11.07	11.15	11.23
7.0	9.56	9.64	9.72	9.80	9.88	9.96	10.04	10.12	10.20	10.29	10.37	10.45	10.53	10.61	10.69	10.77	10.85	10.93	11.01	11.09
7.5	9.44	9.52	9.60	9.68	9.76	9.84	9.92	10.00	10.08	10.16	10.24	10.32	10.40	10.48	10.56	10.64	10.72	10.80	10.87	10.95
8.0	9.33	9.40	9.48	9.56	9.64	9.72	9.80	9.88	9.95	10.03	10.11	10.19	10.27	10.35	10.43	10.51	10.58	10.66	10.74	10.82
8.5	9.21	9.29	9.37	9.44	9.52	9.60	9.68	9.76	9.83	9.91	9.99	10.07	10.14	10.22	10.30	10.38	10.46	10.53	10.61	10.69
9.0	9.10	9.18	9.25	9.33	9.41	9.48	9.56	9.64	9.71	9.79	9.87	9.95	10.02	10.10	10.18	10.25	10.33	10.41	10.48	10.56
9.5	8.99	9.07	9.14	9.22	9.29	9.37	9.45	9.52	9.60	9.67	9.75	9.83	9.90	9.98	10.05	10.13	10.21	10.28	10.36	10.43
10.0	8.88	8.96	9.03	9.11	9.18	9.26	9.33	9.41	9.49	9.56	9.64	9.71	9.79	9.86	9.94	10.01	10.09	10.16	10.24	10.31
10.5	8.78	8.85	8.93	9.00	9.08	9.15	9.23	9.30	9.37	9.45	9.52	9.60	9.67	9.75	9.82	9.89	9.97	10.04	10.12	10.19
11.0	8.68	8.75	8.82	8.90	8.97	9.04	9.12	9.19	9.26	9.34	9.41	9.48	9.56	9.63	9.71	9.78	9.85	9.93	10.00	10.07
11.5	8.58	8.65	8.72	8.79	8.87	8.94	9.01	9.08	9.16	9.23	9.30	9.38	9.45	9.52	9.59	9.67	9.74	9.81	9.88	9.96
12.0	8.48	8.55	8.62	8.69	8.77	8.84	8.91	8.98	9.05	9.12	9.20	9.27	9.34	9.41	9.48	9.56	9.63	9.70	9.77	9.84
12.5	8.38	8.45	8.52	8.59	8.67	8.74	8.81	8.88	8.95	9.02	9.09	9.16	9.23	9.31	9.38	9.45	9.52	9.59	9.66	9.73
13.0	8.29	8.36	8.43	8.50	8.57	8.64	8.71	8.78	8.85	8.92	8.99	9.06	9.13	9.20	9.27	9.34	9.41	9.48	9.55	9.62
13.5	8.19	8.26	8.33	8.40	8.47	8.54	8.61	8.68	8.75	8.82	8.89	8.96	9.03	9.10	9.17	9.24	9.31	9.38	9.45	9.52
14.0	8.10	8.17	8.24	8.31	8.38	8.45	8.52	8.58	8.65	8.72	8.79	8.86	8.93	9.00	9.07	9.14	9.20	9.27	9.34	9.41

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius]

Temp.	Atmospheric pressure, in millimeters of mercury																			
(deg C)	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695
14.5	8.01	8.08	8.15	8.22	8.29	8.35	8.42	8.49	8.56	8.63	8.69	8.76	8.83	8.90	8.97	9.04	9.10	9.17	9.24	9.31
15.0	7.93	7.99	8.06	8.13	8.20	8.26	8.33	8.40	8.47	8.53	8.60	8.67	8.74	8.80	8.87	8.94	9.00	9.07	9.14	9.21
15.5	7.84	7.91	7.97	8.04	8.11	8.17	8.24	8.31	8.37	8.44	8.51	8.57	8.64	8.71	8.77	8.84	8.91	8.97	9.04	9.11
16.0	7.76	7.82	7.89	7.95	8.02	8.09	8.15	8.22	8.28	8.35	8.42	8.48	8.55	8.61	8.68	8.75	8.81	8.88	8.95	9.01
16.5	7.67	7.74	7.80	7.87	7.93	8.00	8.07	8.13	8.20	8.26	8.33	8.39	8.46	8.52	8.59	8.65	8.72	8.79	8.85	8.92
17.0	7.59	7.66	7.72	7.79	7.85	7.92	7.98	8.05	8.11	8.17	8.24	8.30	8.37	8.43	8.50	8.56	8.63	8.69	8.76	8.82
17.5	7.51	7.58	7.64	7.70	7.77	7.83	7.90	7.96	8.03	8.09	8.15	8.22	8.28	8.35	8.41	8.47	8.54	8.60	8.67	8.73
18.0	7.43	7.50	7.56	7.62	7.69	7.75	7.81	7.88	7.94	8.01	8.07	8.13	8.20	8.26	8.32	8.39	8.45	8.51	8.58	8.64
18.5	7.36	7.42	7.48	7.55	7.61	7.67	7.73	7.80	7.86	7.92	7.99	8.05	8.11	8.18	8.24	8.30	8.36	8.43	8.49	8.55
19.0	7.28	7.34	7.41	7.47	7.53	7.59	7.66	7.72	7.78	7.84	7.90	7.97	8.03	8.09	8.15	8.22	8.28	8.34	8.40	8.47
19.5	7.21	7.27	7.33	7.39	7.45	7.52	7.58	7.64	7.70	7.76	7.82	7.89	7.95	8.01	8.07	8.13	8.20	8.26	8.32	8.38
20.0	7.13	7.20	7.26	7.32	7.38	7.44	7.50	7.56	7.62	7.68	7.75	7.81	7.87	7.93	7.99	8.05	8.11	8.17	8.24	8.30
20.5	7.06	7.12	7.18	7.24	7.31	7.37	7.43	7.49	7.55	7.61	7.67	7.73	7.79	7.85	7.91	7.97	8.03	8.09	8.15	8.21
21.0	6.99	7.05	7.11	7.17	7.23	7.29	7.35	7.41	7.47	7.53	7.59	7.65	7.71	7.77	7.83	7.89	7.95	8.01	8.07	8.13
21.5	6.92	6.98	7.04	7.10	7.16	7.22	7.28	7.34	7.40	7.46	7.52	7.58	7.64	7.70	7.76	7.82	7.88	7.94	7.99	8.05
22.0	6.85	6.91	6.97	7.03	7.09	7.15	7.21	7.27	7.33	7.39	7.45	7.50	7.56	7.62	7.68	7.74	7.80	7.86	7.92	7.98
22.5	6.79	6.85	6.90	6.96	7.02	7.08	7.14	7.20	7.26	7.31	7.37	7.43	7.49	7.55	7.61	7.67	7.72	7.78	7.84	7.90
23.0	6.72	6.78	6.84	6.90	6.95	7.01	7.07	7.13	7.19	7.24	7.30	7.36	7.42	7.48	7.53	7.59	7.65	7.71	7.77	7.82
23.5	6.66	6.71	6.77	6.83	6.89	6.94	7.00	7.06	7.12	7.17	7.23	7.29	7.35	7.40	7.46	7.52	7.58	7.63	7.69	7.75
24.0	6.59	6.65	6.71	6.76	6.82	6.88	6.94	6.99	7.05	7.11	7.16	7.22	7.28	7.33	7.39	7.45	7.51	7.56	7.62	7.68
24.5	6.53	6.59	6.64	6.70	6.76	6.81	6.87	6.93	6.98	7.04	7.10	7.15	7.21	7.27	7.32	7.38	7.44	7.49	7.55	7.61
25.0	6.47	6.52	6.58	6.64	6.69	6.75	6.81	6.86	6.92	6.97	7.03	7.09	7.14	7.20	7.25	7.31	7.37	7.42	7.48	7.53
25.5	6.41	6.46	6.52	6.57	6.63	6.69	6.74	6.80	6.85	6.91	6.96	7.02	7.08	7.13	7.19	7.24	7.30	7.35	7.41	7.46
26.0	6.35	6.40	6.46	6.51	6.57	6.62	6.68	6.73	6.79	6.84	6.90	6.95	7.01	7.07	7.12	7.18	7.23	7.29	7.34	7.40
26.5	6.29	6.34	6.40	6.45	6.51	6.56	6.62	6.67	6.73	6.78	6.84	6.89	6.95	7.00	7.06	7.11	7.16	7.22	7.27	7.33
27.0	6.23	6.28	6.34	6.39	6.45	6.50	6.56	6.61	6.67	6.72	6.77	6.83	6.88	6.94	6.99	7.05	7.10	7.15	7.21	7.26
27.5	6.17	6.23	6.28	6.33	6.39	6.44	6.50	6.55	6.60	6.66	6.71	6.77	6.82	6.87	6.93	6.98	7.04	7.09	7.14	7.20
28.0	6.12	6.17	6.22	6.28	6.33	6.38	6.44	6.49	6.54	6.60	6.65	6.70	6.76	6.81	6.87	6.92	6.97	7.03	7.08	7.13
28.5	6.06	6.11	6.17	6.22	6.27	6.33	6.38	6.43	6.49	6.54	6.59	6.64	6.70	6.75	6.80	6.86	6.91	6.96	7.02	7.07

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius]

Temp.	Atmospheric pressure, in millimeters of mercury																			
(deg C)	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695
29.0	6.01	6.06	6.11	6.16	6.22	6.27	6.32	6.37	6.43	6.48	6.53	6.59	6.64	6.69	6.74	6.80	6.85	6.90	6.95	7.01
29.5	5.95	6.00	6.06	6.11	6.16	6.21	6.27	6.32	6.37	6.42	6.47	6.53	6.58	6.63	6.68	6.74	6.79	6.84	6.89	6.95
30.0	5.90	5.95	6.00	6.05	6.11	6.16	6.21	6.26	6.31	6.37	6.42	6.47	6.52	6.57	6.63	6.68	6.73	6.78	6.83	6.88
30.5	5.85	5.90	5.95	6.00	6.05	6.10	6.16	6.21	6.26	6.31	6.36	6.41	6.46	6.52	6.57	6.62	6.67	6.72	6.77	6.82
31.0	5.79	5.85	5.90	5.95	6.00	6.05	6.10	6.15	6.20	6.25	6.31	6.36	6.41	6.46	6.51	6.56	6.61	6.66	6.71	6.77
31.5	5.74	5.79	5.84	5.90	5.95	6.00	6.05	6.10	6.15	6.20	6.25	6.30	6.35	6.40	6.45	6.50	6.55	6.61	6.66	6.71
32.0	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.10	6.15	6.20	6.25	6.30	6.35	6.40	6.45	6.50	6.55	6.60	6.65
32.5	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.09	6.14	6.19	6.24	6.29	6.34	6.39	6.44	6.49	6.54	6.59
33.0	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.09	6.14	6.19	6.24	6.29	6.34	6.39	6.44	6.49	6.54
33.5	5.54	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.09	6.14	6.19	6.24	6.28	6.33	6.38	6.43	6.48
34.0	5.50	5.54	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.08	6.13	6.18	6.23	6.28	6.33	6.38	6.43
34.5	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.98	6.03	6.08	6.13	6.18	6.23	6.28	6.32	6.37
35.0	5.40	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.88	5.93	5.98	6.03	6.08	6.13	6.18	6.22	6.27	6.32
35.5	5.35	5.40	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.88	5.93	5.98	6.03	6.08	6.12	6.17	6.22	6.27
36.0	5.31	5.36	5.40	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.79	5.83	5.88	5.93	5.98	6.02	6.07	6.12	6.17	6.22
36.5	5.26	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.93	5.97	6.02	6.07	6.12	6.16
37.0	5.22	5.27	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.93	5.97	6.02	6.07	6.11
37.5	5.17	5.22	5.27	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.92	5.97	6.02	6.06
38.0	5.13	5.18	5.22	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.60	5.64	5.69	5.73	5.78	5.83	5.87	5.92	5.97	6.01
38.5	5.09	5.13	5.18	5.22	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.83	5.87	5.92	5.97
39.0	5.04	5.09	5.13	5.18	5.23	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82	5.87	5.92
39.5	5.00	5.05	5.09	5.14	5.18	5.23	5.27	5.32	5.37	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82	5.87
40.0	4.96	5.00	5.05	5.09	5.14	5.18	5.23	5.28	5.32	5.37	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000
0.0	1.0000	0.9961	0.9922	0.9882	0.9843	0.9804	0.9764	0.9724	0.9684	0.9644	0.9604	0.9564	0.9524	0.9483	0.9443
1.0	1.0000	0.9961	0.9923	0.9884	0.9845	0.9805	0.9766	0.9727	0.9687	0.9648	0.9608	0.9568	0.9528	0.9488	0.9448
2.0	1.0000	0.9962	0.9923	0.9885	0.9846	0.9807	0.9768	0.9729	0.9690	0.9651	0.9611	0.9572	0.9532	0.9493	0.9453
3.0	1.0000	0.9962	0.9924	0.9886	0.9847	0.9809	0.9770	0.9732	0.9693	0.9654	0.9615	0.9576	0.9536	0.9497	0.9458
4.0	1.0000	0.9962	0.9925	0.9887	0.9849	0.9811	0.9772	0.9734	0.9696	0.9657	0.9618	0.9579	0.9541	0.9502	0.9462
5.0	1.0000	0.9963	0.9925	0.9888	0.9850	0.9812	0.9774	0.9736	0.9698	0.9660	0.9622	0.9583	0.9545	0.9506	0.9467
6.0	1.0000	0.9963	0.9926	0.9889	0.9851	0.9814	0.9776	0.9739	0.9701	0.9663	0.9625	0.9587	0.9549	0.9510	0.9472
7.0	1.0000	0.9963	0.9927	0.9890	0.9853	0.9816	0.9778	0.9741	0.9703	0.9666	0.9628	0.9590	0.9552	0.9514	0.9476
8.0	1.0000	0.9964	0.9927	0.9891	0.9854	0.9817	0.9780	0.9743	0.9706	0.9669	0.9631	0.9594	0.9556	0.9519	0.9481
9.0	1.0000	0.9964	0.9928	0.9892	0.9855	0.9819	0.9782	0.9745	0.9708	0.9672	0.9634	0.9597	0.9560	0.9523	0.9485
10.0	1.0000	0.9964	0.9928	0.9893	0.9856	0.9820	0.9784	0.9747	0.9711	0.9674	0.9637	0.9601	0.9564	0.9527	0.9489
11.0	1.0000	0.9965	0.9929	0.9893	0.9858	0.9822	0.9786	0.9750	0.9713	0.9677	0.9640	0.9604	0.9567	0.9530	0.9494
12.0	1.0000	0.9965	0.9930	0.9894	0.9859	0.9823	0.9787	0.9752	0.9716	0.9680	0.9643	0.9607	0.9571	0.9534	0.9498
13.0	1.0000	0.9965	0.9930	0.9895	0.9860	0.9825	0.9789	0.9754	0.9718	0.9682	0.9646	0.9610	0.9574	0.9538	0.9502
14.0	1.0000	0.9965	0.9931	0.9896	0.9861	0.9826	0.9791	0.9756	0.9720	0.9685	0.9649	0.9613	0.9578	0.9542	0.9506
15.0	1.0000	0.9966	0.9931	0.9897	0.9862	0.9827	0.9793	0.9758	0.9723	0.9687	0.9652	0.9617	0.9581	0.9545	0.9510
16.0	1.0000	0.9966	0.9932	0.9898	0.9863	0.9829	0.9794	0.9760	0.9725	0.9690	0.9655	0.9620	0.9584	0.9549	0.9513
17.0	1.0000	0.9966	0.9932	0.9898	0.9864	0.9830	0.9796	0.9761	0.9727	0.9692	0.9657	0.9622	0.9587	0.9552	0.9517
18.0	1.0000	0.9967	0.9933	0.9899	0.9865	0.9831	0.9797	0.9763	0.9729	0.9695	0.9660	0.9625	0.9591	0.9556	0.9521
19.0	1.0000	0.9967	0.9933	0.9900	0.9866	0.9833	0.9799	0.9765	0.9731	0.9697	0.9663	0.9628	0.9594	0.9559	0.9524
20.0	1.0000	0.9967	0.9934	0.9901	0.9867	0.9834	0.9800	0.9767	0.9733	0.9699	0.9665	0.9631	0.9597	0.9562	0.9528
21.0	1.0000	0.9967	0.9934	0.9902	0.9868	0.9835	0.9802	0.9769	0.9735	0.9701	0.9668	0.9634	0.9600	0.9566	0.9531
22.0	1.0000	0.9968	0.9935	0.9902	0.9869	0.9836	0.9803	0.9770	0.9737	0.9704	0.9670	0.9636	0.9603	0.9569	0.9535
23.0	1.0000	0.9968	0.9935	0.9903	0.9870	0.9838	0.9805	0.9772	0.9739	0.9706	0.9672	0.9639	0.9605	0.9572	0.9538
24.0	1.0000	0.9968	0.9936	0.9904	0.9871	0.9839	0.9806	0.9774	0.9741	0.9708	0.9675	0.9642	0.9608	0.9575	0.9541
25.0	1.0000	0.9968	0.9936	0.9904	0.9872	0.9840	0.9808	0.9775	0.9743	0.9710	0.9677	0.9644	0.9611	0.9578	0.9545
26.0	1.0000	0.9968	0.9937	0.9905	0.9873	0.9841	0.9809	0.9777	0.9744	0.9712	0.9679	0.9647	0.9614	0.9581	0.9548
27.0	1.0000	0.9969	0.9937	0.9906	0.9874	0.9842	0.9810	0.9778	0.9746	0.9714	0.9681	0.9649	0.9616	0.9584	0.9551
28.0	1.0000	0.9969	0.9938	0.9906	0.9875	0.9843	0.9812	0.9780	0.9748	0.9716	0.9684	0.9651	0.9619	0.9586	0.9554
29.0	1.0000	0.9969	0.9938	0.9907	0.9876	0.9844	0.9813	0.9781	0.9750	0.9718	0.9686	0.9654	0.9621	0.9589	0.9557

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	15000	16000	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000
0.0	0.9402	0.9361	0.9321	0.9280	0.9239	0.9198	0.9157	0.9116	0.9074	0.9033	0.8992	0.8950	0.8909	0.8867	0.8826
1.0	0.9408	0.9367	0.9327	0.9286	0.9246	0.9205	0.9164	0.9124	0.9083	0.9042	0.9001	0.8960	0.8918	0.8877	0.8836
2.0	0.9413	0.9373	0.9333	0.9293	0.9252	0.9212	0.9172	0.9131	0.9091	0.9050	0.9009	0.8969	0.8928	0.8887	0.8846
3.0	0.9418	0.9378	0.9339	0.9299	0.9259	0.9219	0.9179	0.9139	0.9099	0.9058	0.9018	0.8978	0.8937	0.8897	0.8856
4.0	0.9423	0.9384	0.9345	0.9305	0.9266	0.9226	0.9186	0.9146	0.9107	0.9067	0.9027	0.8986	0.8946	0.8906	0.8866
5.0	0.9428	0.9389	0.9350	0.9311	0.9272	0.9233	0.9193	0.9154	0.9114	0.9075	0.9035	0.8995	0.8955	0.8915	0.8875
6.0	0.9433	0.9395	0.9356	0.9317	0.9278	0.9239	0.9200	0.9161	0.9122	0.9082	0.9043	0.9004	0.8964	0.8924	0.8885
7.0	0.9438	0.9400	0.9361	0.9323	0.9284	0.9246	0.9207	0.9168	0.9129	0.9090	0.9051	0.9012	0.8973	0.8933	0.8894
8.0	0.9443	0.9405	0.9367	0.9329	0.9290	0.9252	0.9213	0.9175	0.9136	0.9098	0.9059	0.9020	0.8981	0.8942	0.8903
9.0	0.9447	0.9410	0.9372	0.9334	0.9296	0.9258	0.9220	0.9182	0.9143	0.9105	0.9067	0.9028	0.8989	0.8951	0.8912
10.0	0.9452	0.9415	0.9377	0.9340	0.9302	0.9264	0.9226	0.9188	0.9150	0.9112	0.9074	0.9036	0.8998	0.8959	0.8921
11.0	0.9457	0.9419	0.9382	0.9345	0.9308	0.9270	0.9233	0.9195	0.9157	0.9119	0.9082	0.9044	0.9006	0.8968	0.8929
12.0	0.9461	0.9424	0.9387	0.9350	0.9313	0.9276	0.9239	0.9201	0.9164	0.9126	0.9089	0.9051	0.9014	0.8976	0.8938
13.0	0.9465	0.9429	0.9392	0.9355	0.9319	0.9282	0.9245	0.9208	0.9171	0.9133	0.9096	0.9059	0.9021	0.8984	0.8946
14.0	0.9470	0.9433	0.9397	0.9361	0.9324	0.9287	0.9251	0.9214	0.9177	0.9140	0.9103	0.9066	0.9029	0.8992	0.8954
15.0	0.9474	0.9438	0.9402	0.9366	0.9329	0.9293	0.9257	0.9220	0.9183	0.9147	0.9110	0.9073	0.9036	0.8999	0.8962
16.0	0.9478	0.9442	0.9406	0.9370	0.9334	0.9298	0.9262	0.9226	0.9190	0.9153	0.9117	0.9080	0.9044	0.9007	0.8970
17.0	0.9482	0.9446	0.9411	0.9375	0.9340	0.9304	0.9268	0.9232	0.9196	0.9160	0.9123	0.9087	0.9051	0.9014	0.8978
18.0	0.9486	0.9451	0.9415	0.9380	0.9345	0.9309	0.9273	0.9238	0.9202	0.9166	0.9130	0.9094	0.9058	0.9022	0.8985
19.0	0.9490	0.9455	0.9420	0.9385	0.9349	0.9314	0.9279	0.9243	0.9208	0.9172	0.9136	0.9101	0.9065	0.9029	0.8993
20.0	0.9493	0.9459	0.9424	0.9389	0.9354	0.9319	0.9284	0.9249	0.9214	0.9178	0.9143	0.9107	0.9071	0.9036	0.9000
21.0	0.9497	0.9463	0.9428	0.9394	0.9359	0.9324	0.9289	0.9254	0.9219	0.9184	0.9149	0.9114	0.9078	0.9043	0.9007
22.0	0.9501	0.9467	0.9432	0.9398	0.9363	0.9329	0.9294	0.9260	0.9225	0.9190	0.9155	0.9120	0.9085	0.9049	0.9014
23.0	0.9504	0.9470	0.9436	0.9402	0.9368	0.9334	0.9299	0.9265	0.9230	0.9196	0.9161	0.9126	0.9091	0.9056	0.9021
24.0	0.9508	0.9474	0.9440	0.9406	0.9372	0.9338	0.9304	0.9270	0.9236	0.9201	0.9167	0.9132	0.9097	0.9063	0.9028
25.0	0.9511	0.9478	0.9444	0.9411	0.9377	0.9343	0.9309	0.9275	0.9241	0.9207	0.9172	0.9138	0.9104	0.9069	0.9034
26.0	0.9515	0.9481	0.9448	0.9415	0.9381	0.9347	0.9314	0.9280	0.9246	0.9212	0.9178	0.9144	0.9110	0.9075	0.9041
27.0	0.9518	0.9485	0.9452	0.9419	0.9385	0.9352	0.9318	0.9285	0.9251	0.9217	0.9183	0.9149	0.9115	0.9081	0.9047
28.0	0.9521	0.9488	0.9455	0.9422	0.9389	0.9356	0.9323	0.9289	0.9256	0.9222	0.9189	0.9155	0.9121	0.9087	0.9053
29.0	0.9524	0.9492	0.9459	0.9426	0.9393	0.9360	0.9327	0.9294	0.9261	0.9228	0.9194	0.9161	0.9127	0.9093	0.9060

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	30000	31000	32000	33000	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000
0.0	0.8784	0.8742	0.8701	0.8659	0.8617	0.8575	0.8533	0.8491	0.8449	0.8407	0.8365	0.8323	0.8281	0.8239	0.8197
1.0	0.8795	0.8753	0.8712	0.8670	0.8629	0.8587	0.8546	0.8504	0.8462	0.8421	0.8379	0.8337	0.8296	0.8254	0.8212
2.0	0.8805	0.8764	0.8723	0.8682	0.8641	0.8599	0.8558	0.8517	0.8476	0.8434	0.8393	0.8351	0.8310	0.8268	0.8227
3.0	0.8815	0.8775	0.8734	0.8693	0.8652	0.8611	0.8570	0.8529	0.8488	0.8447	0.8406	0.8365	0.8324	0.8283	0.8242
4.0	0.8825	0.8785	0.8745	0.8704	0.8664	0.8623	0.8582	0.8542	0.8501	0.8460	0.8419	0.8379	0.8338	0.8297	0.8256
5.0	0.8835	0.8795	0.8755	0.8715	0.8675	0.8635	0.8594	0.8554	0.8513	0.8473	0.8433	0.8392	0.8351	0.8311	0.8270
6.0	0.8845	0.8805	0.8766	0.8726	0.8686	0.8646	0.8606	0.8566	0.8526	0.8485	0.8445	0.8405	0.8365	0.8325	0.8284
7.0	0.8855	0.8815	0.8776	0.8736	0.8697	0.8657	0.8617	0.8577	0.8538	0.8498	0.8458	0.8418	0.8378	0.8338	0.8298
8.0	0.8864	0.8825	0.8786	0.8746	0.8707	0.8668	0.8628	0.8589	0.8549	0.8510	0.8470	0.8431	0.8391	0.8351	0.8311
9.0	0.8873	0.8834	0.8796	0.8757	0.8718	0.8678	0.8639	0.8600	0.8561	0.8522	0.8482	0.8443	0.8404	0.8364	0.8325
10.0	0.8882	0.8844	0.8805	0.8766	0.8728	0.8689	0.8650	0.8611	0.8572	0.8533	0.8494	0.8455	0.8416	0.8377	0.8338
11.0	0.8891	0.8853	0.8815	0.8776	0.8738	0.8699	0.8661	0.8622	0.8583	0.8545	0.8506	0.8467	0.8428	0.8389	0.8351
12.0	0.8900	0.8862	0.8824	0.8786	0.8748	0.8709	0.8671	0.8633	0.8594	0.8556	0.8517	0.8479	0.8440	0.8402	0.8363
13.0	0.8908	0.8871	0.8833	0.8795	0.8757	0.8719	0.8681	0.8643	0.8605	0.8567	0.8529	0.8490	0.8452	0.8414	0.8375
14.0	0.8917	0.8879	0.8842	0.8804	0.8767	0.8729	0.8691	0.8654	0.8616	0.8578	0.8540	0.8502	0.8464	0.8426	0.8388
15.0	0.8925	0.8888	0.8851	0.8813	0.8776	0.8739	0.8701	0.8664	0.8626	0.8588	0.8551	0.8513	0.8475	0.8437	0.8400
16.0	0.8933	0.8896	0.8859	0.8822	0.8785	0.8748	0.8711	0.8674	0.8636	0.8599	0.8561	0.8524	0.8486	0.8449	0.8411
17.0	0.8941	0.8905	0.8868	0.8831	0.8794	0.8757	0.8720	0.8683	0.8646	0.8609	0.8572	0.8535	0.8497	0.8460	0.8423
18.0	0.8949	0.8913	0.8876	0.8840	0.8803	0.8766	0.8730	0.8693	0.8656	0.8619	0.8582	0.8545	0.8508	0.8471	0.8434
19.0	0.8957	0.8921	0.8884	0.8848	0.8812	0.8775	0.8739	0.8702	0.8666	0.8629	0.8592	0.8556	0.8519	0.8482	0.8445
20.0	0.8964	0.8928	0.8892	0.8856	0.8820	0.8784	0.8748	0.8711	0.8675	0.8639	0.8602	0.8566	0.8529	0.8493	0.8456
21.0	0.8972	0.8936	0.8900	0.8864	0.8828	0.8793	0.8757	0.8720	0.8684	0.8648	0.8612	0.8576	0.8539	0.8503	0.8467
22.0	0.8979	0.8943	0.8908	0.8872	0.8837	0.8801	0.8765	0.8729	0.8693	0.8658	0.8622	0.8585	0.8549	0.8513	0.8477
23.0	0.8986	0.8951	0.8915	0.8880	0.8845	0.8809	0.8774	0.8738	0.8702	0.8667	0.8631	0.8595	0.8559	0.8523	0.8487
24.0	0.8993	0.8958	0.8923	0.8888	0.8853	0.8817	0.8782	0.8747	0.8711	0.8676	0.8640	0.8605	0.8569	0.8533	0.8497
25.0	0.9000	0.8965	0.8930	0.8895	0.8860	0.8825	0.8790	0.8755	0.8720	0.8685	0.8649	0.8614	0.8578	0.8543	0.8507
26.0	0.9006	0.8972	0.8937	0.8903	0.8868	0.8833	0.8798	0.8763	0.8728	0.8693	0.8658	0.8623	0.8588	0.8552	0.8517
27.0	0.9013	0.8979	0.8944	0.8910	0.8875	0.8841	0.8806	0.8771	0.8736	0.8702	0.8667	0.8632	0.8597	0.8562	0.8527
28.0	0.9019	0.8985	0.8951	0.8917	0.8883	0.8848	0.8814	0.8779	0.8745	0.8710	0.8675	0.8641	0.8606	0.8571	0.8536
29.0	0.9026	0.8992	0.8958	0.8924	0.8890	0.8856	0.8821	0.8787	0.8753	0.8718	0.8684	0.8649	0.8615	0.8580	0.8545

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	45000	46000	47000	48000	49000	50000	51000	52000	53000	54000	55000	56000	57000	58000	59000
0.0	0.8155	0.8112	0.8070	0.8028	0.7986	0.7944	0.7901	0.7859	0.7817	0.7775	0.7733	0.7691	0.7648	0.7606	0.7564
1.0	0.8170	0.8128	0.8086	0.8045	0.8003	0.7961	0.7919	0.7877	0.7835	0.7793	0.7751	0.7709	0.7668	0.7626	0.7584
2.0	0.8185	0.8144	0.8102	0.8061	0.8019	0.7978	0.7936	0.7894	0.7853	0.7811	0.7770	0.7728	0.7686	0.7645	0.7603
3.0	0.8200	0.8159	0.8118	0.8077	0.8035	0.7994	0.7953	0.7911	0.7870	0.7829	0.7788	0.7746	0.7705	0.7664	0.7623
4.0	0.8215	0.8174	0.8133	0.8092	0.8051	0.8010	0.7969	0.7928	0.7887	0.7846	0.7805	0.7764	0.7723	0.7682	0.7641
5.0	0.8230	0.8189	0.8148	0.8108	0.8067	0.8026	0.7986	0.7945	0.7904	0.7863	0.7823	0.7782	0.7741	0.7700	0.7660
6.0	0.8244	0.8204	0.8163	0.8123	0.8082	0.8042	0.8002	0.7961	0.7921	0.7880	0.7840	0.7799	0.7759	0.7718	0.7678
7.0	0.8258	0.8218	0.8178	0.8138	0.8098	0.8057	0.8017	0.7977	0.7937	0.7897	0.7857	0.7816	0.7776	0.7736	0.7696
8.0	0.8272	0.8232	0.8192	0.8152	0.8112	0.8073	0.8033	0.7993	0.7953	0.7913	0.7873	0.7833	0.7793	0.7753	0.7713
9.0	0.8285	0.8246	0.8206	0.8167	0.8127	0.8088	0.8048	0.8008	0.7969	0.7929	0.7889	0.7850	0.7810	0.7770	0.7731
10.0	0.8299	0.8259	0.8220	0.8181	0.8141	0.8102	0.8063	0.8023	0.7984	0.7945	0.7905	0.7866	0.7826	0.7787	0.7748
11.0	0.8312	0.8273	0.8234	0.8195	0.8156	0.8117	0.8077	0.8038	0.7999	0.7960	0.7921	0.7882	0.7843	0.7804	0.7764
12.0	0.8324	0.8286	0.8247	0.8208	0.8170	0.8131	0.8092	0.8053	0.8014	0.7975	0.7936	0.7898	0.7859	0.7820	0.7781
13.0	0.8337	0.8299	0.8260	0.8222	0.8183	0.8145	0.8106	0.8067	0.8029	0.7990	0.7952	0.7913	0.7874	0.7836	0.7797
14.0	0.8349	0.8311	0.8273	0.8235	0.8197	0.8158	0.8120	0.8082	0.8043	0.8005	0.7966	0.7928	0.7890	0.7851	0.7813
15.0	0.8362	0.8324	0.8286	0.8248	0.8210	0.8172	0.8134	0.8095	0.8057	0.8019	0.7981	0.7943	0.7905	0.7867	0.7828
16.0	0.8374	0.8336	0.8298	0.8260	0.8223	0.8185	0.8147	0.8109	0.8071	0.8033	0.7995	0.7958	0.7920	0.7882	0.7844
17.0	0.8385	0.8348	0.8310	0.8273	0.8235	0.8198	0.8160	0.8123	0.8085	0.8047	0.8010	0.7972	0.7934	0.7896	0.7859
18.0	0.8397	0.8360	0.8322	0.8285	0.8248	0.8210	0.8173	0.8136	0.8098	0.8061	0.8023	0.7986	0.7948	0.7911	0.7873
19.0	0.8408	0.8371	0.8334	0.8297	0.8260	0.8223	0.8186	0.8149	0.8112	0.8074	0.8037	0.8000	0.7963	0.7925	0.7888
20.0	0.8419	0.8383	0.8346	0.8309	0.8272	0.8235	0.8198	0.8161	0.8124	0.8087	0.8050	0.8013	0.7976	0.7939	0.7902
21.0	0.8430	0.8394	0.8357	0.8321	0.8284	0.8247	0.8211	0.8174	0.8137	0.8100	0.8064	0.8027	0.7990	0.7953	0.7916
22.0	0.8441	0.8405	0.8368	0.8332	0.8296	0.8259	0.8223	0.8186	0.8150	0.8113	0.8076	0.8040	0.8003	0.7967	0.7930
23.0	0.8451	0.8415	0.8379	0.8343	0.8307	0.8271	0.8234	0.8198	0.8162	0.8126	0.8089	0.8053	0.8016	0.7980	0.7943
24.0	0.8462	0.8426	0.8390	0.8354	0.8318	0.8282	0.8246	0.8210	0.8174	0.8138	0.8102	0.8065	0.8029	0.7993	0.7957
25.0	0.8472	0.8436	0.8400	0.8365	0.8329	0.8293	0.8257	0.8222	0.8186	0.8150	0.8114	0.8078	0.8042	0.8006	0.7970
26.0	0.8482	0.8446	0.8411	0.8375	0.8340	0.8304	0.8269	0.8233	0.8197	0.8162	0.8126	0.8090	0.8054	0.8018	0.7983
27.0	0.8491	0.8456	0.8421	0.8386	0.8350	0.8315	0.8280	0.8244	0.8209	0.8173	0.8138	0.8102	0.8066	0.8031	0.7995
28.0	0.8501	0.8466	0.8431	0.8396	0.8361	0.8326	0.8290	0.8255	0.8220	0.8184	0.8149	0.8114	0.8078	0.8043	0.8007
29.0	0.8510	0.8476	0.8441	0.8406	0.8371	0.8336	0.8301	0.8266	0.8231	0.8196	0.8160	0.8125	0.8090	0.8055	0.8019

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000
30.0	1.0000	0.9969	0.9939	0.9908	0.9877	0.9845	0.9814	0.9783	0.9751	0.9720	0.9688	0.9656	0.9624	0.9592	0.9560
31.0	1.0000	0.9970	0.9939	0.9908	0.9877	0.9846	0.9815	0.9784	0.9753	0.9721	0.9690	0.9658	0.9626	0.9595	0.9563
32.0	1.0000	0.9970	0.9939	0.9909	0.9878	0.9847	0.9817	0.9785	0.9754	0.9723	0.9692	0.9660	0.9629	0.9597	0.9565
33.0	1.0000	0.9970	0.9940	0.9909	0.9879	0.9848	0.9818	0.9787	0.9756	0.9725	0.9694	0.9662	0.9631	0.9600	0.9568
34.0	1.0000	0.9970	0.9940	0.9910	0.9880	0.9849	0.9819	0.9788	0.9757	0.9727	0.9696	0.9665	0.9633	0.9602	0.9571
35.0	1.0000	0.9970	0.9940	0.9911	0.9880	0.9850	0.9820	0.9790	0.9759	0.9728	0.9698	0.9667	0.9636	0.9605	0.9573

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	15000	16000	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000
30.0	0.9527	0.9495	0.9463	0.9430	0.9397	0.9364	0.9332	0.9299	0.9266	0.9232	0.9199	0.9166	0.9133	0.9099	0.9066
31.0	0.9530	0.9498	0.9466	0.9434	0.9401	0.9369	0.9336	0.9303	0.9270	0.9237	0.9204	0.9171	0.9138	0.9105	0.9071
32.0	0.9533	0.9501	0.9469	0.9437	0.9405	0.9373	0.9340	0.9308	0.9275	0.9242	0.9209	0.9176	0.9143	0.9110	0.9077
33.0	0.9536	0.9505	0.9473	0.9441	0.9409	0.9376	0.9344	0.9312	0.9279	0.9247	0.9214	0.9181	0.9149	0.9116	0.9083
34.0	0.9539	0.9508	0.9476	0.9444	0.9412	0.9380	0.9348	0.9316	0.9284	0.9251	0.9219	0.9186	0.9154	0.9121	0.9088
35.0	0.9542	0.9511	0.9479	0.9448	0.9416	0.9384	0.9352	0.9320	0.9288	0.9256	0.9224	0.9191	0.9159	0.9126	0.9094

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	30000	31000	32000	33000	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000
30.0	0.9032	0.8998	0.8964	0.8931	0.8897	0.8863	0.8829	0.8795	0.8760	0.8726	0.8692	0.8658	0.8623	0.8589	0.8554
31.0	0.9038	0.9005	0.8971	0.8937	0.8904	0.8870	0.8836	0.8802	0.8768	0.8734	0.8700	0.8666	0.8632	0.8597	0.8563
32.0	0.9044	0.9011	0.8977	0.8944	0.8910	0.8877	0.8843	0.8809	0.8776	0.8742	0.8708	0.8674	0.8640	0.8606	0.8572
33.0	0.9050	0.9017	0.8984	0.8950	0.8917	0.8884	0.8850	0.8817	0.8783	0.8749	0.8716	0.8682	0.8648	0.8614	0.8580
34.0	0.9056	0.9023	0.8990	0.8957	0.8923	0.8890	0.8857	0.8824	0.8790	0.8757	0.8723	0.8690	0.8656	0.8622	0.8588
35.0	0.9061	0.9028	0.8996	0.8963	0.8930	0.8897	0.8864	0.8830	0.8797	0.8764	0.8731	0.8697	0.8664	0.8630	0.8597

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	45000	46000	47000	48000	49000	50000	51000	52000	53000	54000	55000	56000	57000	58000	59000
30.0	0.8520	0.8485	0.8450	0.8416	0.8381	0.8346	0.8311	0.8276	0.8241	0.8207	0.8172	0.8137	0.8102	0.8066	0.8031
31.0	0.8529	0.8494	0.8460	0.8425	0.8391	0.8356	0.8321	0.8287	0.8252	0.8217	0.8182	0.8148	0.8113	0.8078	0.8043
32.0	0.8537	0.8503	0.8469	0.8435	0.8400	0.8366	0.8331	0.8297	0.8262	0.8228	0.8193	0.8159	0.8124	0.8089	0.8054
33.0	0.8546	0.8512	0.8478	0.8444	0.8410	0.8375	0.8341	0.8307	0.8272	0.8238	0.8204	0.8169	0.8135	0.8100	0.8066
34.0	0.8555	0.8521	0.8487	0.8453	0.8419	0.8385	0.8351	0.8317	0.8282	0.8248	0.8214	0.8180	0.8145	0.8111	0.8077
35.0	0.8563	0.8529	0.8496	0.8462	0.8428	0.8394	0.8360	0.8326	0.8292	0.8258	0.8224	0.8190	0.8156	0.8122	0.8087

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SPECIFIC ELECTRICAL CONDUCTANCE 6.3

By D.B. Radtke, J.V. Davis, and F.D. Wilde

Tables

SPECIFIC ELECTRICAL CONDUCTANCE 6.3

By **D.B. Radtke, J.V. Davis, and F.D. Wilde**

Electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity.

The USGS reports conductivity in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

SPECIFIC ELECTRICAL CONDUCTANCE (CONDUCTIVITY)—a measure of the electrical conductance of a substance normalized to unit length and unit cross section at a specified temperature.

EQUIPMENT AND SUPPLIES 6.3.1

The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Many conductivity instruments are available, including multiparameter instruments that include conductivity sensors. This section provides detailed information on the use of conductivity-specific instruments only, although instructions regarding conductivity standards and measurement methods are applicable in general. Users must be familiar with the instructions provided by the manufacturer. Every conductivity (or multiparameter) instrument must have a log book in which repairs and calibrations are recorded, along with manufacturer make and model description and serial or property number.

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Table 6.3–1. Equipment and supplies used for measuring conductivity[1]
[°C, degrees Celsius; ≤ , less than or equal to; >, greater than; µS/cm, microsiemens per centimeter at 25 degrees Celsius; L, liter]

- ✓ Conductivity instrument and conductivity sensor
  - Battery powered Wheatstone bridge
  - Direct readout
  - Temperature range at least –5 to +45°C
  - Temperature compensating (25°C)
  - Accuracy: Conductivity ≤100 µS/cm, within 5 percent of full scale
    Conductivity >100 µS/cm, within 3 percent of full scale
- ✓ Thermistor thermometer sensor (for automatic temperature-compensating models)
- ✓ Thermometer, liquid-in-glass or thermistor
- ✓ Extra sensors (if possible) and batteries, or backup instrument
- ✓ Conductivity standards at conductivities that approximate and bracket field values
- ✓ Compositing and splitting device for surface-water samples
- ✓ Flowthrough chamber or downhole instrument for ground-water measurements
- ✓ Plastic beakers (assorted sizes)
- ✓ Soap solution, nonphosphate (1 L)
- ✓ Hydrochloric acid solution, 5 percent volume-to-volume (1 L)
- ✓ Deionized water, 1 L, maximum conductivity of 1 µS/cm
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Brush (small, soft)
- ✓ Waste disposal container
- ✓ Minnow bucket with tether (or equivalent) for equilibrating buffer solutions to sample temperature
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

[1]Modify this list to meet the specific needs of the field effort.

As soon as possible after delivery to the office, label conductivity standards with the date of expiration. Discard standards that have expired, been frozen, have begun to evaporate, or that were decanted from the storage container. Quality-controlled conductivity standards ranging from 50 to 50,000 µS/cm at 25°C can be obtained by USGS personnel through "One Stop Shopping." Order standards outside this range from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water.

CONDUCTIVITY SENSORS 6.3.1.A

Conductivity sensors are either contacting-type sensors with electrodes or electrodeless-type sensors.

- **Contacting-type sensors with electrodes.** Three types of cells are available: (1) a dip cell that can be suspended in the sample, (2) a cup cell that contains the sample, or (3) a flow cell that is connected to a fluid line. Choose a cell constant on the basis of expected conductivity (table 6.3–2). The greater the cell constant, the greater the conductivity that can be measured. The cell constant is the distance between electrodes (in centimeters) divided by the effective cross-sectional area of the conducting path (in square centimeters).
- **Electrodeless-type sensors.** These operate by inducing an alternating current in a closed loop of solution, and they measure the magnitude of the current. Electrodeless sensors avoid errors caused by electrode polarization or electrode fouling.

Table 6.3–2. Example of cell constants for contacting-type sensors with electrodes and corresponding conductivity ranges

Conductivity range, in microsiemens per centimeter	Cell constant, in 1/centimeter
0.005 – 20	.01
1 – 200	.1
10 – 2,000	1.0
100 – 20,000	10.0
1,000 – 200,000	50.0

CAUTION: Before handling conductivity standards or acids, refer to Material Safety Data Sheets (MSDS) for safety precautions.

6.3.1.B EQUIPMENT MAINTENANCE

Maintenance of conductivity equipment includes periodic office checks of instrument operation. To keep equipment in good operating condition:

- Protect the conductivity system from dust and excessive heat and cold.
- Keep all cable connectors dry and free of dirt.
- Protect connector ends in a clean plastic bag.

Sensor cleaning and storage

Conductivity sensors must be clean to produce accurate results; residues from previous samples can coat surfaces of sensors and cause erroneous readings. Refer to the manufacturer's instructions regarding long- and short-term storage of the sensor.

- Clean sensors thoroughly with deionized water (DIW) before and after making a measurement (this is sufficient cleaning in most cases).
- Remove oily residue or other chemical residues (salts) with a detergent solution. Sensors can soak in detergent solution for many hours without damage.
- If oil or other residues persist, dip the sensor in a dilute hydrochloric acid solution. **Never leave the sensor in contact with acid solution for more than a few minutes.** Check the manufacturer's recommendations before using acid solutions.
- Clean carbon and stainless steel sensors with a soft brush. Never use a brush on platinum-coated sensors.
- Sensors may be temporarily stored in deionized water between measurements and when the system is in daily use.
- For long-term storage, store sensors clean and dry.

CALIBRATION 6.3.2

Conductivity systems must be calibrated before every water-quality field trip and again at each site before samples are measured. Calibration readings are recorded in the instrument log book and on field forms at the time the instrument is calibrated. Remember, the temperature sensor on the conductivity sensor must be District certified within the past 4 months.

Calibration and operating procedures differ, depending on instrument and sensor type.

- Some conductivity sensors may need to be soaked overnight in deionized water before use—Check the manufacturer's instructions.
- Some analog instruments require an initial mechanical zero adjustment of the indicator needle.
- For a cup-type cell, calibration and measurement procedures described for the dip-type cell apply; the only difference is that standards are poured directly into the cup-type cell.
- When using a dip-type cell, do not let the cell rest on the bottom or sides of the measuring container.

Calibrate at your field site— bring standards to sample temperature.

Conductivity systems normally are calibrated with at least two standards. Calibrate sensors against a standard that approximates sample conductivity and use the second standard as a calibration check. The general procedures described in steps 1 through 15 below apply to most instruments used for field measurements—check the instrument manual for specific instructions.

1. Inspect the instrument and the conductivity sensor for damage. Check the battery voltage. Make sure that all cables are clean and connected properly.
2. Turn the instrument on and allow sufficient time for electronic stabilization.

3. Select the correct instrument calibration scale for expected conductivity.
4. Select the sensor type and the cell constant that will most accurately measure expected conductivity.
5. Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired.
6. Equilibrate the standards and the conductivity sensor to the temperature of the sample.
   - Put bottles of standards in a minnow bucket, cooler, or large water bath that is being filled with ambient water.
   - Allow 15 to 30 minutes for thermal equilibration. Do not allow water to dilute the standard.
7. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
   - **First**, rinse the sensor, the thermometer, and the container three times with deionized water.
   - **Next**, rinse the sensor, the thermometer, and the container three times with the standard to be used.
8. Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard.
9. Measure water temperature. **Accurate conductivity measurements depend on accurate temperature measurements or accurate temperature compensation.**
   - If the sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If using a manual instrument without a temperature display or temperature compensation, adjust the instrument to the temperature of the standard using a calibrated liquid-in-glass or a thermistor thermometer.
10. Agitate a submersible-type conductivity sensor up and down under the solution surface to expel air trapped in the sensor. Read the instrument display. Agitate the sensor up and down under the solution surface again, and read the display. Repeat the procedure until consecutive readings are the same.

11. Record the instrument reading and adjust the instrument to the known standard value.
    - For nontemperature-compensating conductivity instruments, apply a temperature-correction factor to convert the instrument reading to conductivity at 25°C.
    - The correction factor depends to some degree on the specific instrument used—use the temperature-correction factor recommended by the manufacturer. If this is not available, use correction factors from table 6.3–3.
    - If an instrument cannot be adjusted to a known calibration standard value, develop a calibration curve. After temperature compensation, if the percentage difference from the standard exceeds 5 percent, refer to the troubleshooting guide (section 6.3.4).
12. Record in the instrument log book and on field forms:
    - The temperature of the standard solution.
    - The known and the measured conductivity of the standard solution (including ± variation).
    - The temperature-correction factor (if necessary).
13. Discard the used standard into a waste container. Thoroughly rinse the sensor, thermometer, and container with deionized water.
14. Repeat steps 7 through 13 with the second conductivity standard.
    - The purpose for measuring a second standard is to check instrument calibration over the range of the two standards.
    - The difference from the standard value should not exceed 5 percent.
    - If the difference is greater than 5 percent, repeat the entire calibration procedure. If the second reading still does not come within 5 percent of standard value, refer to the troubleshooting guide in section 6.3.4 or calibrate a backup instrument.
15. Record in the instrument log book and on field forms the calibration data for the second standard.

Do not use expired standards.
Never reuse standards.

Table 6.3–3. Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

[Use of potassium-based constants on non-potassium-based waters generally does not introduce significant errors for general purpose instruments used to measure conductivity]

Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	0.99
6.0	1.58	16.0	1.21	26.0	0.98
6.5	1.56	16.5	1.19	26.5	0.97
7.0	1.54	17.0	1.18	27.0	0.96
7.5	1.52	17.5	1.16	27.5	0.95
8.0	1.49	18.0	1.15	28.0	0.94
8.5	1.47	18.5	1.14	28.5	0.93
9.0	1.45	19.0	1.13	29.0	0.92
9.5	1.43	19.5	1.12	29.5	0.91
10.0	1.41	20.0	1.11	30.0	0.90

To extend the temperature range shown in table 6.3–3, consult the manufacturer's guidelines. If these are unavailable, use the following equation:

$$C_{25} = \frac{C_m}{1 + 0.02(t_m - 25)}$$

where,
C_{25}= corrected conductivity value adjusted to 25°C;
C_m = actual conductivity measured before correction; and
t_m = water temperature at time of C_m measurement.

MEASUREMENT 6.3.3

In situ measurement generally is preferred for determining the conductivity of surface water; downhole or flowthrough-chamber measurements are preferred for ground water. Be alert to the following problems if conductivity is measured in an isolated (discrete) sample or subsample:

- The conductivity of water can change over time as a result of chemical and physical processes such as precipitation, adsorption, ion exchange, oxidation, and reduction—Do not delay making conductivity measurements.
- Field conditions (rain, wind, cold, dust, direct sunlight) can cause measurement problems—Shield the instrument to the extent possible and perform measurements in a collection chamber in an enclosed vehicle or an on-site laboratory.
- For waters susceptible to significant gain and loss of dissolved gases, make the measurement within a gas-impermeable container (Berzelius flask) fitted with a stopper—Place the sensor through the stopper and work quickly to maintain the sample at ambient surface-water or ground-water temperature.
- Avoid contamination from the pH electrode filling solution—Measure conductivity on a separate discrete sample from the one used for measuring pH; in a flowthrough chamber, position the conductivity sensor upstream of the pH electrode.

Conductivity must be measured at the field site.

Document the precision of your measurements. Precision should be determined about every tenth sample or more frequently, depending on study objectives. Successive measurements should be repeated until they agree within 5 percent at conductivity ≤ 100 µS/cm or within 3 percent at conductivity > 100 µS/cm.

The conductivity measurement reported must account for sample temperature. If using an instrument that does not automatically temperature compensate to 25°C, record the uncompensated measurement in your field notes, along with the corrected conductivity value. Use correction factors supplied by the instrument manufacturer if available; otherwise, refer to table 6.3–3.

6.3.3.A SURFACE WATER

Surface-water conductivity should be measured in situ, if possible; otherwise, determine conductivity in discrete samples collected from a sample splitter or compositing device. Filtered samples may be needed if the concentrations of suspended material interfere with obtaining a stable measurement.

In situ measurement

Conductivity measurements in flowing surface water should represent the cross-sectional mean or median conductivity at the time of observation (see step 7, below). Any deviation from this convention must be documented in the data base and with the published data.

First:

- Take a cross-sectional conductivity profile to determine the degree of system variability. A submersible sensor works best for this purpose.
- Refer to NFM 6.0 for criteria to help decide which sampling method to use.

Next, follow the 7 steps listed below:

1. Calibrate the conductivity instrument system at the field site after equilibrating the buffers with stream temperature.
2. Record the conductivity variation from a cross-sectional profile on a field form and select the sampling method.
   - **Flowing, shallow stream—**wade to the location(s) where conductivity is to be measured.
   - **Stream too deep or swift to wade—**lower a weighted conductivity sensor from a bridge, cableway, or boat. Do not attach weight to the sensor or the sensor cable.
   - **Still-water conditions—**measure conductivity at multiple depths at several points in the cross section.
3. Immerse the conductivity and temperature sensors in the water to the correct depth and hold there (no less than 60 seconds) until the sensors equilibrate to water conditions.
4. Record the conductivity and corresponding temperature readings without removing the sensors from the water.
   - Values should stabilize quickly to within 5 percent at conductivity ≤100 µS/cm and within 3 percent at conductivity >100 µS/cm.
   - Record the median of the stabilized values on field forms.
   - If the readings do not meet the stability criterion after extending the measurement period, record this difficulty in the field notes along with the fluctuation range and the median value of the last five or more readings.
5. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 and 4. Record on field forms the mean (or median, if appropriate) value for each subsection measured.
6. When the measurement is complete, remove the sensor from the water, rinse it with deionized water, and store it.
7. Record the stream conductivity on the field forms:
   - **In still water—median** of three or more sequential values.
   - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
   - **EWI—mean or median** of all subsections measured (see NFM 6.0).

Subsample measurement

Representative samples are to be collected and split or composited according to approved USGS methods (NFM 4). Measure the conductivity of samples as soon as possible after collection. If the sample cannot be analyzed immediately, fill a bottle to the top, close it tightly, and maintain the sample at stream temperature until measurement.

Reported conductivity values normally are determined on an unfiltered sample. Large concentrations of suspended sediment can be a source of measurement error—record such conditions in the field notes.

- If sediment concentrations are heavy, measure conductivity on both unfiltered and filtered subsamples and record both values on the field form.
- If the conductivity value differs significantly between the filtered and unfiltered samples, report the filtered value as sample conductivity and identify it as a "filtered sample."

1. Calibrate the conductivity instrument system at the field site.
2. Select the sampling method (see NFM 6.0) and collect a representative sample.
3. Withdraw a homogenized subsample from a sample splitter or compositing device. Rinse the sample bottles three times with the sample—rinse them with sample filtrate, for filtered samples.
4. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
    a. First, rinse the sensor, the thermometer, and the container three times with deionized water.
    b. Next, rinse the sensor, the thermometer, and the container using sample water.
5. Allow the sensors to equilibrate to sample temperature, then discard the used sample water. Pour fresh sample water into a container holding the sensor and the thermometer. **When using a dip-type sensor, do not let the sensor touch the bottom or sides of the measuring container.**

6. Measure water temperature.
   - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If the instrument is not temperature compensating, use a calibrated thermistor or a liquid-in-glass thermometer.
   - Adjust the instrument to the sample temperature (if necessary) and remove the thermometer.
7. Measure conductivity.
   a. Remove any air trapped in the sensor by agitating the sensor up and down under the water surface.
   b. Read the instrument display.
   c. Agitate the sensor up and down under the water surface, and read the display again.
   d. Repeat the procedure until consecutive readings are the same.
8. Record the conductivity and the sample temperature on field forms.
   - If the instrument is not temperature compensating, record the raw data and convert the values to conductivity at 25°C using temperature-correction factors provided by the manufacturer.
   - Report the median of the readings to three significant figures on the field forms.
   - Discard the sample into a waste container and dispose according to regulations.
9. **Quality control—**
   - Repeat steps 3 through 8 with at least two fresh subsamples, rinsing the instruments once only with sample water.
   - Subsample values should be within ±5 percent for conductivity ≤100 µS/cm, or ±3 percent for conductivity >100 µS/cm.
   - If criteria cannot be met: filter the samples, report the median of 3 or more samples, and record this difficulty in field notes.
10. Rinse the sensor, the thermometer, and the container with deionized water. If another measurement is to be made within the next day or two, store the sensor in deionized water. Otherwise, store the sensor dry.

6.3.3.B GROUND WATER

Measurements of ground-water conductivity must represent aquifer conditions. Temperature changes resulting from transporting a well sample to land surface can affect conductivity.

- To minimize the effect from temperature changes, measure conductivity as close to the source as possible, using either a downhole or flowthrough-chamber sampling system (refer to NFM 6.0 for details).
- Bailed or other methods for collecting discrete samples isolated from the source are not recommended as standard practice, although such methods are sometimes called for owing to site characteristics or other study requirements.
- The well should be purged or in the process of purging before sample conductivity is determined and recorded.

Downhole and flowthrough-chamber measurement

1. Calibrate the conductivity instrument system on site.
   - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
     a. Check the temperature of the water flowing into the bucket against that of standards.
     b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
   - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.
2. Install the conductivity and temperature sensors.
   - **Downhole system—**Lower the conductivity and temperature sensors to the sampling point, followed by the pump.

a. Remove any air from the system by agitating the conductivity sensor up and down under the water; read the instrument display.
b. Repeat this procedure until rapid consecutive readings are approximately the same.

- **Flowthrough-chamber system—**Install the chamber system as close to the well as possible and shield the system from direct sunlight.

a. Position the conductivity sensor upstream from the pH electrode.
b. Direct flow to the chamber after an initial discharge to waste to clear sediment from sample line.
c. Release any air trapped in the chamber.
d. Agitate the conductivity sensor up and down under the water to remove air from system. Rapid consecutive readings should be about the same.

3. During purging (table 6.0–1 in NFM 6.0):
   - Keep flow constant and laminar.
   - Allow the sensors to equilibrate with ground-water temperature for 5 minutes or more at the flow rate to be used for collecting all other samples.
4. Measure conductivity and associated temperature at regular intervals throughout purging; record the conductivity values and the associated temperature in the field notes.
   - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If the instrument is not temperature compensating, install a calibrated thermometer in the flowthrough chamber, record raw data, and apply correction factors.
5. Check the variability of the conductivity values toward the end of purging.
   - The stability criterion is met when five readings taken at regularly spaced intervals of 3 to 5 minutes or more are within
     ±5 percent for conductivity ≤100 µS/cm
     ±3 percent for conductivity >100 µS/cm

- When readings fluctuate rapidly, record the median of three or more readings within about 60 seconds as the value for a specific time interval.
- If the criterion is not met, extend the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals. Record this difficulty on the field forms.

6. Report conductivity.
   - Record the final five values on field forms.
   - Report the median value of the final five measurements as the sample conductivity.
   - If values exceed the stability criterion, report the range of values observed for the time interval, along with the median of the final five or more values.

Subsample measurement

Conductivity measurements reported from bailed or other discrete samples need to be identified in the data base, indicating the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

1. Calibrate the conductivity instrument system onsite.
   - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
     a. Check the temperature of the water flowing into the bucket against that of standards.
     b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
   - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.

2. Draw off subsamples for measurement.
    - **Quality control—Collect three subsamples to check precision.**
    - If samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles—fill to the brim, cap tightly, and maintain at ambient ground-water temperature. Measure conductivity as soon as possible.
3. Follow procedures described in steps 4 through 10 for "Subsample measurement" of surface water (6.3.3.A).

> **TECHNICAL NOTE:** If the sample is measured in an open container and readings do not stabilize within several minutes, the cause may be CO_2 degassing—use a closed system to measure the sample. Filter the conductivity sample if the settling of clay particles appears to interfere with the stability of the readings.

TROUBLESHOOTING 6.3.4

Contact the instrument manufacturer if the actions suggested in table 6.3–4 fail to resolve the problem.

- If available, use a commercial, electronic calibrator to check the function of conductivity instruments.
- Check the voltage of batteries. Always have good batteries in instruments and carry spares.

Table 6.3–4. Troubleshooting guide for conductivity measurement
[HCl, hydrochloric acid; ºC, degrees Celsius]

Symptom	Possible cause and corrective action
Will not calibrate to standards	• Standards may be old or contaminated—use fresh standards. • Electrodes dirty—clean with a detergent solution, then with 5 percent HCl. Before using any acid solution to remove resistant residues, check manufacturer's guidelines. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Weak batteries—replace. • Temperature compensation incorrect—ensure that thermometer is operating properly and is calibrated. • Sensor constant incorrect—replace sensor.
Erratic instrument readings	• Loose or defective connections—tighten or replace. • Broken cables—repair or replace. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Rapid changes in water temperature—measure in situ. • Outgassing of ground-water sample—use a downhole instrument; if unavailable, use a flowthrough chamber. • Broken sensor—replace.
Instrument requires frequent recalibration	• Temperature compensator not working—measure conductivity of a solution. Place solution in a water bath and raise solution temperature to about 20ºC. Measure conductivity again, allowing sufficient time for temperature of conductivity sensor to equilibrate to temperature of solution. If the two values differ by 5 percent or more, replace conductivity sensor.

REPORTING 6.3.5

Report routine conductivity measurements to three significant figures, whole numbers only, in microsiemens per centimeter at 25°C.

- Record the accuracy range of the instrument system in the data base, if possible, and always report it with published values.
- Enter field-determined conductivity measurements on the NWQL Analytical Services Request form using the correct parameter code.

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pH 6.4

Revised by George F. Ritz and Jim A. Collins

Illustrations

Tables

pH 6.4

Revised by **George F. Ritz and Jim A. Collins**

pH is a primary factor governing the chemistry of natural water systems and is measured routinely in U.S. Geological Survey (USGS) studies of water quality. The pH of water directly affects physiological functions of plants and animals and is, therefore, an important indicator of the health of a water system.

pH: A mathematical notation defined as the negative base-ten logarithm of the hydrogen-ion activity, measured in moles per liter of a solution.

The pH of an aqueous system can be understood as an estimation of the activity, or effective concentration,[1] of hydrogen ions (H^+) affecting that system. The theoretical basis of H^+ activity and measurement are described in greater detail in Hem (1989) and in Pankow (1991).

By definition,

$$pH = -log_{10}[H^+], \text{ and}$$

$$[H^+] = 10^{-pH}.$$

- Logarithmic units are used to express H^+ activity because the concentration of H^+ in most environmental waters is usually too low to be expressed as milligrams per liter, micrograms per liter, or moles per liter, in contrast to most other chemical species (Hem, 1989).
- pH is reported on a scale that most commonly is shown to range from 0 to 14 (see TECHNICAL NOTE below). The pH scale is related directly to H^+ and hydroxide (OH^-) concentrations at a given temperature.
  - A solution is defined as having a neutral pH (pH = 7.00 at 25°C) when the H^+ concentration is equal to the OH^- concentration.
  - A solution is defined as acidic if the H^+ activity (concentration) is greater than that of the OH^- ion (pH is less than 7 at 25°C).
  - A solution is defined as basic, or alkaline, when the OH^- concentration is greater than the H^+ concentration (pH is greater than 7 at 25°C).

[1]The majority of natural freshwater systems for which water-quality data are routinely collected by the USGS are considered to be dilute; that is, the volume of dissolved solids is less than 50 milligrams per liter and the ionic strength of the solution (the strength of the electrostatic field caused by the ions) is less than 10^{-4}. For dilute solutions, activity values can be assumed to be equal to measured ion concentrations (Hem, 1989). Therefore, throughout the text of this section, the terms "activity" and "concentration," as they relate to the hydrogen ion, are used interchangeably.

- Temperature affects the chemical equilibria of ionic activities in aqueous solutions, including that of H^+ (Hem, 1989). For example, neutral pH for pure water at 30°C is calculated to be 6.92, whereas at 0°C, neutral pH is 7.48. The pH of pure water at 25°C is defined as 7.00. Therefore, the temperature of the solution must be taken into account when measuring and recording pH.

TECHNICAL NOTE: Although pH commonly is reported on a scale ranging from 0 to 14, pH values of less than 0 can be measured in highly acidic solutions, and pH values greater than 14 can be measured in concentrated base solutions (Nordstrom and Alpers, 1999; Hem, 1989).

6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH consists of a pH meter, sensor(s) (a pH electrode and often a temperature sensor), and buffer solutions (table 6.4–1). Since a variety of instrument systems are available from manufacturers (multiparameter instruments, for example, are described in NFM 6.8), the procedures described in this section may not be applicable or may need to be modified, depending on the specific instrument system being used. Field personnel should:

- Be thoroughly familiar with the information provided in the manufacturer's user manual.
- Adhere to USGS protocols for quality control and assurance of pH measurements.
- Test the meter and electrode before each field trip.

Temperature affects the operation of pH meters, electrodes, and buffer solutions.

Table 6.4–1. Equipment and supplies used for measuring pH[1]

[mL, milliliters; mV, millivolt; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; +, plus: ±, plus or minus; MSDS, Material Safety Data Sheets]

✓	pH meter and pH electrodes Battery powered, solid state, with automatic temperature compensation (for multiparameter instruments, see NFM 6.8) Range of at least 2 to 12 pH, preferably 0 to 14 pH Accuracy of at least ±0.01 units Temperature range of at least 0 to +45°C Millivolt readout with accuracy of ±1.0 mV
✓	pH electrodes, gel-filled or liquid-filled, as appropriate, for study objectives and site conditions
✓	pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
✓	pH electrode storage solution
✓	Thermistor (or thermometer), calibrated
✓	Buffer solutions for pH 4, 7, and 10; temperature correction chart(s) for buffers; labeled with expiration dates
✓	Stand for holding pH electrode
✓	Bottle, delivery (squeeze), to dispense deionized water
✓	Deionized water, maximum conductivity of 1 µS/cm
✓	Beakers or measurement vessels, polyethylene or Teflon® preferable, assorted volumes of 50 to 150 mL, clean but not acid rinsed
✓	Flowthrough chamber (for ground-water measurements)
✓	Minnow bucket (or mesh bag) with tether or equivalent, used for temperature equilibration of buffer solutions
✓	Waste-disposal container
✓	pH-meter/electrode logbook for recording calibrations, maintenance, and repairs
✓	MSDS for all pH buffers and other reagents to be used

[1]This list pertains to single-parameter instruments for measuring pH. Refer to NFM 6.8 for information on and general use of multiparameter instruments. This list may be modified to meet the specific needs of the field effort.

CAUTION: Keep Material Safety Data Sheets (MSDS) readily available and refer to them to ensure that pH buffers or other chemicals are handled safely.

6.4.1.A pH METERS

A pH meter is a high-impedance voltmeter that measures the very small, direct current potential (in millivolts (mV)) generated between a glass pH electrode and a pH reference electrode. The potentiometric measurement is displayed as a pH value. The meter uses potentiometric differences to generate these pH values and is programmed with (1) the ideal Nernstian response relating hydrogen-ion activity (concentration) and electrical response (59.16 mV/unit pH), and (2) an automatic temperature compensation (ATC) factor. Since the ideal Nernstian slope response from the electrode varies with temperature, the meter's software adjusts the slope to be in accordance with the Nernst equation at the corresponding environmental temperature during calibration and measurement (refer to section 6.4.3 for an explanation of the Nernst equation).

6.4.1.B pH ELECTRODES

The pH electrode is a special type of ion selective electrode (ISE) that is designed specifically for the measurement of hydrogen-ion concentration in a dilute aqueous solution.

- Diodes or triodes (combination electrodes) are used in most USGS field studies.
  - Combination electrodes are housed either in a glass or an epoxy body. Diodes contain a pH reference electrode and pH measurement electrode. Triodes contain the reference and measurement electrodes plus a thermistor. In either case, the basic electrode operation is the same (IC Controls, 2005a).
  - All combination pH electrodes have a glass membrane, a reference and a measurement electrode, an ionic (filling) solution, and a reference junction (shown on fig. 6.4–1); these are described below.

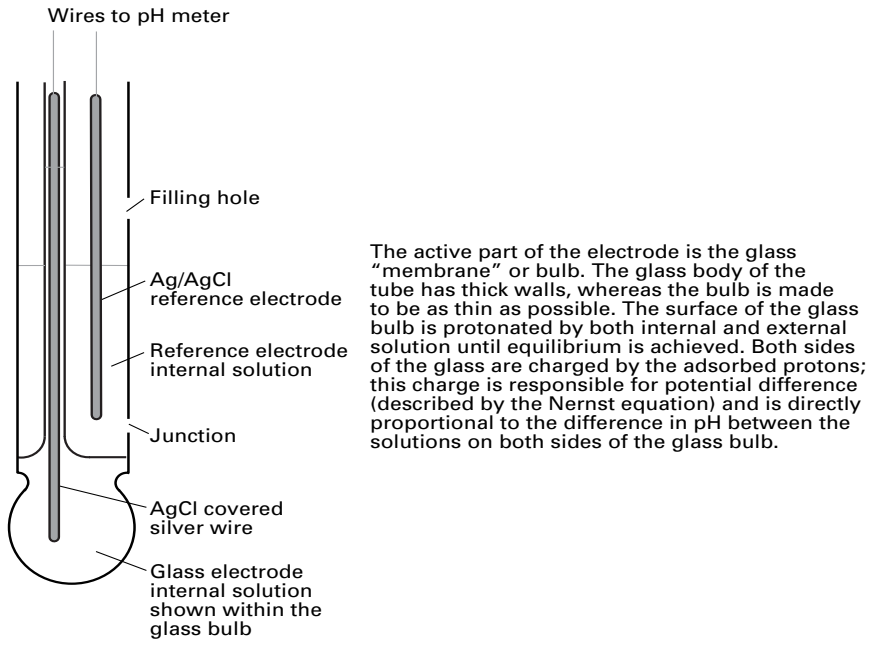

Figure 6.4–1. Diagram of a combination (single-junction) pH electrode. Modified from pH-meter.info (2005).

- Electrode performance naturally degrades over time with normal use. However, field personnel need to be alert to those chemical environments that can cause serious and more rapid degradation of electrode performance (IC Controls, 2005a). Many such environments are coincident with industrial, mined, and urban areas (table 6.4–2).
  - Field personnel should be aware of the effect on the pH measurement when deploying the electrode in such environments: document field conditions on field forms.
  - When measuring pH under specific adverse chemical conditions, the use of electrodes with properties designed to withstand such conditions is recommended (table 6.4–2).

Table 6.4–2. pH electrodes recommended for water having elevated concentrations of sodium and other monovalent major cations, sulfide, cyanide, and ferric chloride.

[H^+, hydrogen ion; Na^+, sodium ion; >, greater than; ≥, greater than or equal to]

Chemical condition	Description of water	Degradation effect on a common combination pH electrode	Recommended pH electrode
Basic ions dominant in solution	pH high (>10 pH units); low H^+ activity results in measurement of other monovalent ions in solution.	Sluggish response to changes in pH, resulting from dehydration of the glass membrane.	Glass pH electrode designed for measuring high values of pH.
	Sodium effect: Elevated Na^+ at pH ≥11.0, H^+ activity is low. The electrode senses Na^+ activity as if it were H^+ because of the similar charge and structure of the Na^+ and H^+ ions.	The pH measurement is negatively biased.	Glass pH electrode designed for measuring high values of pH.
Elevated concentrations of sulfide or cyanide	Elevated concentrations of sulfides or cyanides are found in industrial, mined, or urban areas.	Sulfide or cyanide contamination of the internal reference electrode.	Double-junction electrodes and plasticized reference electrodes.
Elevated concentration of ferric chloride	Ferric chloride is used as a flocculating agent in wastewater treatment plants, for example.	Ferric chloride attacks the glass membrane of the pH electrode, deactivating many of the sensing sites on the glass surface.	Consult the manufacturer for (1) selecting pH electrodes that can withstand this environment; and (or) (2) specific cleaning procedures for the glass membrane.

Glass membrane. The most essential and vulnerable element of the pH electrode is the sensitive glass membrane, which permits the sensing of hydrogen-ion activity in most natural waters. When the pH electrode is immersed in a solution (for example, a calibration buffer or a sample solution), ions from the glass diffuse into a thin layer on the outside of the membrane, while hydrogen ions diffuse through this layer until an equilibrium is reached between the internal and external ionic concentrations. In this way, an electrical potential is developed across the sensing surface, which is proportional to the concentration of hydrogen ions in the surrounding solution (pH-meter.info, 2005).

A clean, undamaged glass membrane is necessary for performing an accurate measurement of pH.

Reference and measurement electrodes. Contained within the pH-sensor body are a reference electrode (that generates a constant electrical potential) and a pH-measurement electrode. The measurement electrode generates a separate electrical potential that is proportional to the concentration of hydrogen ions in the sample solution. The electrodes together form a complete electrical circuit; when the diffusion of hydrogen ions reaches equilibrium, no electrical current is present, and the difference in electrical potential that exists between the reference and the measurement electrodes is an indication of the hydrogen-ion concentration in the solution. The pH meter, sensing this minute difference in electrical potentials, converts this difference into a pH value based on the latest calibration of the pH electrode.

Ionic (filling) solutions. An ionic solution used to fill the space within the pH electrode is the source of mobile, chemical ions that serve to complete the electrical circuit between the internal reference and pH-measurement electrodes.The pH electrode may be filled either with an ionic liquid solution (liquid-filled pH electrode) or an ionic gel solution (gel-filled pH electrode). Typically, these ionic solutions contain a chloride salt (usually silver or potassium) of a known and specific molarity (strength). For liquid-filled electrodes, maintaining a sufficient volume and the correct molarity of the filling solution within the electrode is very important to achieving meaningful measurements. Most standard pH electrodes are designed to function well when the electrode filling solution strength is similar to the sample ionic strength, typically having a relatively high ionic strength of 3 molar (M) or greater. Using low ionic-strength or high ionic-strength pH electrodes and a filling solution of appropriate composition and molarity—as recommended by the electrode manufacturer—is recommended when working with environmental samples having conductivities less than 100 µS/cm or greater than 20,000 µS/cm, respectively.

Reference junction. The liquid reference junction (sometimes called the "salt bridge") is an electrically conductive bridge within the pH electrode, between the reference ionic solution and the sample being measured. This junction is necessary for the proper functioning of the pH-sensing electrical cell; it must allow free movement of electrons, but at the same time, isolate the ionic solution from the bulk environmental sample. Typically, this junction is made of a porous material such as ceramic, Teflon, or glass fiber, and may clog and malfunction if not maintained properly. The function of the reference junction is characterized by a chemical memory. In a correctly functioning pH electrode, a small amount of time lapses before the appropriate ionic bridge is formed between the electrode reference ionic solution and the external environmental sample or external calibration-buffer solution. The length of time necessary for the establishment of this ionic equilibrium is a primary reason for the requirement that pH be measured in a quiescent sample solution. (Sections 6.4.4 and 6.4.5 provide further discussion.)

Remember to check that the junction on the pH electrode is not clogged; a clogged electrode will not function properly.

Electrode performance naturally deteriorates over time under normal operating conditions. However, use of the electrode in severe chemical environments can cause more rapid deterioration (table 6.4–2). Many of these environments are coincident with industrial and urban locations: immersing a pH electrode in such environments should be avoided or minimized to the extent possible (IC Controls, 2005a). Whenever the pH electrode is exposed to conditions such as those listed on table 6.4–2, this information should be recorded in the pH-meter/electrode logbook and documented in field notes.

pH BUFFER SOLUTIONS 6.4.1.C

pH buffer solutions (buffers) are ionic solutions that are used to calibrate the pH instrument system. Buffers maintain constant pH values because of their ability to resist changes to the specific pH value for which they are produced. **Measurements of pH are only as accurate as the buffers used to calibrate the electrode.**

- Use only buffers that have been certified traceable to an NIST standard reference material.
- Select the buffer molarity that is appropriate for the ionic strength of the water to be measured and the instrument system that will be used.
  - For pH measurements of dilute waters with conductivities less than 100 µS/cm, use of buffers having lower-than-standard molarity and a low ionic-strength pH electrode is recommended (refer to section 6.4.3.B).
  - For pH measurements in high ionic-strength waters with conductivities greater than 20,000 µS/cm, use of buffers having a higher-than-standard molarity is recommended (refer to section 6.4.3.C).
- Label pH buffer containers with the acquisition date and the expiration date. Copy the expiration date and the buffer lot number onto any reagent containers into which the buffer is transferred. Copy the temperature-correction information onto the respective buffer container or keep a copy of this information with the buffers being transported to the field.
- **Discard the pH buffer on its expiration date**. The pH of a buffer can be altered substantially because of temperature fluctuation, carbon dioxide (CO_2) absorption, mold growth, or evaporation.

Use the following precautions and protocols to help ensure the accuracy of the pH measurement *(modified from Busenberg and Plummer, 1987):*

- Cap buffer bottles firmly after use to prevent evaporation and contamination from atmospheric CO_2. The pH 10 buffer has the greatest sensitivity to CO_2 contamination, whereas the pH 4 buffer is the least sensitive. Buffers are stable for the short exposure time during electrode calibration.
- Never pour used buffer back into a bottle containing the stock buffer solution.
- Do not insert an electrode or other material into a bottle containing stock buffer solution — **always pour the buffer into a separate container** and discard the solution after use.
- Take care not to contaminate the buffer with another buffer or with other fluids.
- **Do not let the buffer become diluted** (this can happen, for example, if deionized water used to clean the electrode drips into the buffer).
- **Protect buffers against wide temperature variations**, whether in transit, during use, or in storage. Never expose buffers to extreme heat or freezing temperatures. If buffers experience these conditions, their pH values can no longer be assumed to be valid. Discard buffer solutions and any other reagents appropriately.
- Before using buffers in the calibration sequence, bring them to the temperature of the sample solution as much as possible. Since buffer composition differs among manufacturers; check the temperature-correction factors provided by the manufacturer in order to assign the correct pH value to the buffer for the temperature of the buffer at the time of calibration.

In order of greatest to least sensitivity of standard buffers to CO_2 contamination: pH 10 buffer > pH 7 buffer > pH 4 buffer. In order of greatest to least variation of buffer pH with change in temperature: pH 10 buffer > pH 7 buffer > pH 4 buffer.

6.4.2 MAINTENANCE OF pH INSTRUMENTS

Proper care of pH meters, and particularly of the electrode, is essential for maintaining the accuracy and precision required for pH measurements and promotes the longevity of the equipment. pH instrument maintenance includes adhering to the manufacturer's instructions for the use and care of the instrument, and routine use of appropriate electrode cleaning, reconditioning, and storage requirements. As always, follow the manufacturer's instructions for the specific type of electrode in use.

Electrode performance must be monitored before every water-quality field trip and again while at the field site.

6.4.2.A ELECTRODE CARE AND CLEANING

USGS field personnel should integrate the following guidance for the care and cleaning of pH electrodes into their routine field-measurement procedures.

- Never handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with the design characteristics of the glass membrane and affect subsequent pH measurements.
- Inspect the electrode and electrode cable for physical damage. For example, check for
  - Cut or frayed cable(s).
  - Broken connectors and mismatched or missing parts.
  - A visibly scratched or broken bulb, cracked electrode body, and broken or damaged internal electrode (reference and measurement electrodes).
- Gel-filled electrodes do not require filling and typically require less maintenance than liquid-filled electrodes. Do not store gel-filled electrodes in dilute water, even temporarily, as salts may leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.

To prepare and care for liquid-filled electrodes:

1. Remove salt crystal deposits from the electrode, membranes, and junctions by rinsing with deionized water (DIW). Visually check that the reference junction is not blocked or caked with salt. Thorough rinsing with DIW should remove these deposits. Be sure to unplug the fill hole before making pH measurements, as suction pressure may affect the proper movement of ions in the filling solution and the correct operation of the reference junction. Re-plug the fill hole after use.
   - If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the electrode in the air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet the junction.
   - After 15 minutes, visually inspect the junction for liquid or new salt accumulation. Ensure that the filling solution is flowing freely. Refer to the manufacturer's instructions.
2. Check the filling solution level and replenish it if necessary. The solution should reach the bottom of the fill hole. **Filling solutions differ in molarity and composition—always check that the correct filling solution required by the manufacturer for a particular electrode is being used.**
3. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (check the manufacturer's recommendations).
4. Keep a record of the electrode and meter operation and maintenance and repairs in the pH-meter/electrode logbook.
   - Record in the calibration logbook the operational history of each pH electrode.
   - Record the Nernst slope reading and the millivolt readings at pH 4, 7, 10, or other pertinent pH buffer values (based on field study objectives) during calibration. Properly working electrodes should give 95 to 102 percent response of that expected from the theoretical Nernst relationship (Busenberg and Plummer, 1987).

     TECHNICAL NOTE: The theoretical Nernst response is 59.16 mV/pH unit at 25°C, but varies based on temperature. Adequate adjustment of the Nernstian relation requires manual or automatic temperature compensation (ATC). Most modern pH meters have the ATC feature. A slope of 95 percent or less signals probable electrode deterioration and the need to monitor closely any further decline in slope percent. Consider replacing the electrode if calibration slope values cannot be brought to greater than 95 percent. **Do not use an electrode with a slope of less than 95 percent.**
5. Keep the electrode bulb moist and capped when not in use. Use only the wetting solution recommended by the manufacturer.

For routine cleaning of the pH electrode:

Keeping electrodes clean and the liquid junction free-flowing is necessary for producing accurate pH measurements. Because of the variety of electrodes available, check the manufacturer's instructions for specific tips and precautions.

1. **Before and after each use—**rinse the electrode body thoroughly, using only DIW. Dispense the DIW from a squeeze bottle.
2. Do not wipe or wick moisture from electrodes with paper towels or ChemWipes® as these can scratch the pH glass membrane. Wiping the electrode body with paper also may cause a static charge (polarization) on the exterior of the pH electrode, which can also adversely affect the pH measurement.

6.4.2.B RECONDITIONING OF LIQUID-FILLED ELECTRODES

If problems persist during calibration of a liquid-filled electrode, or if there is reason to doubt that the electrode is in good working condition, check the manufacturer's instructions for how to test and recondition the electrode. Reconditioning procedures should be implemented only if the electrode's slope response has deteriorated to less than 95 percent. Document in the pH-meter/electrode logbook if the electrode has been reconditioned or replaced.

The following general procedures can be used to attempt to bring the liquid-filled electrode back into proper working condition:

1. Remove the old filling solution from the electrode.
   a. Place the needle of a 1- or 3-milliliter (mL) syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).
   b. Tilt the pH electrode until the filling solution is near the fill hole and the needle tip is covered with the filling solution.
   c. Pull back on the syringe plunger until the syringe is full.
   d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode.
2. Flush the pH electrode with DIW.
   a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with DIW.
   b. With a syringe, remove the DIW from the pH electrode chamber.
   c. As a result of changes in pressure, temperature, and evaporation, visible crystals may form in the pH electrode. If these are present, continue to flush with DIW until all the crystals have been dissolved and removed from the pH electrode.
3. Fill the electrode with fresh filling solution. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
   a. Partially fill the pH electrode chamber with the filling solution.
   b. Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
   c. Remove and discard the filling solution to a waste container.
   d. Refill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. **Be sure to use the appropriate type and molarity of filling solution.**
   e. Rinse any excess filling solution from the outside of the electrode with DIW.
4. After following the reconditioning procedures, retest the electrode**. If the procedures fail to remedy the problem, discard the electrode.**

ELECTRODE STORAGE 6.4.2.C

Electrodes must be clean before they are stored for any length of time. Refer to the manufacturer's instructions for the proper short-term (used daily or weekly) and long-term (2 to 4 months) storage requirements of the electrode.

General guidelines for short-term storage:

1. Storage solutions are specific to the type of electrode; check the manufacturer's manual for each electrode. **Do not store glass hydrogen-ion electrodes in DIW** unless instructed to do so by the manufacturer.
2. Storage solutions have a limited shelf life. Label storage solution containers with the expiration date and discard expired solutions on that date and in a proper manner.
3. Do not place a small piece of cotton or paper towel in the electrode cap to help keep it moist, as this can scratch the glass membrane sensor.
4. Store liquid-filled pH electrodes upright.
5. Store liquid-filled electrodes wet between uses to maximize their accuracy and response time.
   - The glass membrane (bulb) should be fully immersed in the proper electrode storage solution.
   - Between field sites, replace the plug on the fill hole and cover the electrode bulb with the cap.
   - Fill the cap with enough storage solution to keep the bulb wet.
6. Gel-filled electrodes should be stored according to the manufacturer's instructions.

General guidelines for long-term storage:

1. Liquid-filled electrodes may need to be drained of filling solution; follow the manufacturer's instructions.
2. Clean the electrode contacts and connector (with alcohol, if necessary). Allow the contacts to dry and seal and store them in a plastic bag.
3. Store every component of the pH measuring system in an area that is clean, dry, and protected from extremely hot or cold temperatures.

6.4.3 CALIBRATION OF THE pH INSTRUMENT SYSTEM

Proper calibration of the pH instrument system is crucial to accurate pH measurement of environmental samples. During calibration, the pH electrodes are immersed in buffer solutions of known pH (section 6.4.1.C). The buffers are designed to produce a corresponding electrical response potential (usually in millivolts) for the specific pH buffer (for example, pH = 4, 7, or 10 buffer solution) within the pH electrode. These potentials are measured by the pH meter. The Nernst equation gives the expected (theoretical) response potential of the pH buffer at the specific temperature of the calibration (Hem, 1989; see TECHNICAL NOTE below). Note that the measured temperature must be programmed into the pH meter unless the meter has incorporated automatic temperature compensation. The calibration returns the actual, measured potential.

TECHNICAL NOTE: pH electrodes operate on the principle that differing concentrations of the H^+, in buffers or environmental samples, produce differing potentiometric responses (measured in millivolts). The Nernst equation is used to establish the calibration of the pH instrument system by determining the slope of electrical potential versus pH at a given temperature. At 25°C, this Nernstian relation (the slope along any two points on the line plotted for electrical potential versus pH) is known to be 59.16 mV/pH units. To calculate the slope between two points along the line of measured potentials versus pH:

$$E=E^0- S(pH)$$

where

S = slope

E = electrode pair potential, in mV, and

E^0 = standard potential, in mV.

Thus, using two buffers of known pH (pH_1 and pH_2),

$$E_1=E^0- S(pH_1) \quad and \quad E_2=E^0- S(pH_2).$$

Rearrange as:

$$s = \frac{E_2 - E_1}{pH_1 - pH_2}$$

The theoretical slope is temperature dependent; the theoretical slope (in mV) can be calculated as:

$$S_t=0.19841(273.15 + t)$$

where

t = temperature in degrees Celsius, and

S_t = slope at a given temperature.

The primary concept in accurate calibration of the pH electrode is to select pH buffers with values that bracket the expected pH of the environmental sample; this is known as a two-point calibration. Before field calibration of the pH instrument system, it is useful to estimate (or to anticipate from historical site data, if available) the pH and conductivity of the waters to be encountered at the field sites. If no data are available from which to estimate sample pH, then pH indicator paper can be used onsite as a gross indicator of the pH of the system. (**Under no circumstances should a pH value from indicator paper be recorded as site pH.)** For three-point or other multipoint calibrations, follow the manufacturer's instructions for (a) which buffers to use and (b) the sequence of buffer use.

> **EXAMPLE:** When measuring pH in a stream that is within the normal range of specific electrical conductivity,
>
> a. If pH values are expected to be between 7 and 8, then the standard pH 7 and pH 10 buffers should be selected.
>
> b. If pH values are expected to be less than 7, then the standard pH 7 and pH 4 buffers should be selected.
>
> c. If the anticipated pH range in pH is large, a check of electrode performance using a third standard buffer value is advisable.

The following guidelines and standard procedures apply in general whenever a pH instrument system is to be calibrated. Because calibration and operating procedures can differ with differing instrument systems, check the manufacturer's recommended calibration procedures and calibration solutions. Digital pH meters automatically compensate for buffer temperatures and indicate appropriate Nernst values (in millivolts). When using these instruments, follow the manufacturer's calibration instructions precisely—**do not take shortcuts**.

- Before each field trip and field calibration, check pH meter/electrode logbook records for electrode performance. **Remember—**any noted calibration slope of 95 percent or less indicates probable electrode deterioration; at 94-percent slope or less, the electrode should not be used.
- Use at least two pH buffer solutions of documented, traceable pH value for adequate calibration of the pH instrument system.
- Pour the amount needed of each buffer from the source container into a clean, polyethylene bottle dedicated for the respective buffer, and label the bottle with the buffer's pH value, lot number, expiration date, and the temperature-adjusted pH values provided by the manufacturer for that buffer.
- The temperature of the buffer solutions should be near the same temperature as the water to be sampled. A calibration check of the temperature sensor must be performed at least annually (NFM 6.1).

> **TECHNICAL NOTE:** Temperature has two effects on the pH measurement of a sample—temperature can affect meter and electrode potentials (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect) within the sample. The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample will be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

Do not use pH buffers that have exceeded their date of expiration.

6.4.3.A CALIBRATION PROCEDURE UNDER STANDARD AQUEOUS CONDITIONS

"Standard aqueous conditions" refers to environmental water with an ionic strength that is within the range in which a standard buffer solution and combination pH electrode can be appropriately used to achieve an accurate pH measurement. For routine USGS water-quality measurements, ionic strengths ranging from 100 to 20,000 µS/cm are considered standard.

When calibrating the pH electrode:

1. Bring the pH buffers to the ambient temperature of the stream or ground water to be measured, to the degree possible under the prevailing field conditions. The temperature sensor (liquid-in-glass or thermistor thermometer), measurement vessel, and electrode also should be at or near the ambient temperature of the environmental sample. **Maintain each buffer as close to sample temperature as possible when calibrating the electrode.**
   - Surface water and ground water—When equilibrating the buffer temperature to ambient surface-water temperature, one method is to place the buffer bottles in a minnow bucket or mesh bag and suspend them in the body of surface water. Alternatively, place the buffers into a bucket or insulated cooler (a) containing surface water, or (b) being filled with ground water.
   - **When immersing buffer bottles in water, ensure that the bottle is firmly capped and that the water level remains below the cap so that water cannot enter the bottle and contaminate the buffer**.
2. Inspect the pH electrode.
   a. Check for damage to the electrode bulb, body, or cables.
   b. Rinse any mineral precipitate off the electrode with DIW.
   c. Uncover (unplug) the fill hole.
   d. If you can visually see small bubbles within the electrode solution, **gently** tap the electrode body to dislodge them. Bubbles trapped in the sensing tip of the electrode will affect the physical conditions necessary for correct operation of the electrode. **Do not wipe moisture from the electrode.**
3. Power up the pH meter. The meter will perform an internal self-test. Note any discrepancies displayed by the meter and record these in the pH-meter/electrode logbook. Malfunctioning meters usually require manufacturer attention; do not try to fix malfunctioning meters in the field. Having backup meters for field trips is necessary for this reason.
4. Record in the ph-meter/instrument logbook the internal self-test information displayed by the pH meter. A calibration log is **mandatory** for all calibrations.

5. Initiate the calibration process by pushing the required calibration display sequences for the particular pH meter and electrode. **Standard USGS procedure for calibration of a single-parameter pH meter-and-electrode system requires a two- or three-point calibration.**
   - Some types of pH-instrument systems may use a different multipoint calibration procedure; in such cases, follow the instructions provided in the instrument manual.
   - A single-point calibration, recommended by some manufacturers, is not acceptable for USGS field measurement of pH.
6. Record in the pH-meter/electrode logbook: pH value, measured temperature, lot number, and expiration date of the first buffer. Typically, the meter will initially indicate the pH 7 buffer (isoelectric point).
7. Begin calibration procedures:
   a. Note that the electrode and thermistor must be rinsed with DIW at least three times between uses of each buffer.
   b. Rinse the electrode twice with the first buffer (usually the pH 7 buffer). Do not allow the glass membrane of the electrode to come in contact with the sides or bottom of the beaker or other measurement vessel.
      i. **First rinse—**Pour enough buffer into a small beaker or other vessel so that it covers the electrode reference junction; swirl the buffer to rinse the electrode body from above the reference junction to the bottom of the bulb. Discard buffer appropriately.

      ii. **Second rinse—**Pour the next aliquot of buffer into the vessel and immerse the electrode in the buffer for 1 minute. Discard buffer appropriately.
   c. Pour another aliquot of buffer into the vessel. Immerse the electrode for 1 minute, without swirling the buffer solution.
   d. Record the pH measurement shown on the meter display in the pH meter/electrode logbook, along with the buffer temperature reading and the pH value from the buffer and temperature table.
      - For pH meters displaying millivolt values, the meter will display the value associated with the pH 7 buffer, as compensated for the buffer temperature.
      - **For properly functioning electrodes, the pH 7 millivolt value should be between +10 and -10 mV. Record the millivolt data in the pH-meter/electrode logbook.**
   e. Press “Cal” or other display instructions to lock in the pH 7 calibration.

> **TECHNICAL NOTE:** During the calibration sequence, after the DIW and buffer rinses and when the specific buffer value is ready to be locked in to the calibration, some meters provide the opportunity to adjust the initially displayed pH value to a corrected pH value for that buffer solution.
>
> - **If this adjustment is equal to or less than 0.05 pH units**, proceed with the adjustment, but specifically note this in the pH meter/electrode logbook.
>
> - **If the adjustment would exceed 0.05 pH units**, the pH electrode is not functioning optimally; consider reconditioning the electrode or using another electrode until the cause of the substandard performance can be determined.

8. **Return to step 6 above, followed by step 7**, repeating each of the procedures just followed but using either the pH 4 or pH 10 buffer, whichever buffer solution, along with the pH 7 buffer, brackets the pH values of the environmental water to be sampled. Record all the calibration data, including the millivolt data, in the pH meter/electrode logbook (see step 7 to test the adequacy of the calibration using the slope test or millivolt test).

9. **At this point, the electrode should be calibrated**. Check the adequacy of the calibration and that the electrode is functioning properly, using the slope test or (and) the millivolt test. Some instruments have the capability to display the slope value; this datum should be recorded in the pH-meter/electrode logbook.

   - **The slope test.** Values ranging from 95 to 102 percent slope are acceptable—if the slope-percent value is outside of this range: clean the electrode and check the level of the filling solution, that the fill hole is open, and that the junction is free-flowing; then, recalibrate.

     TECHNICAL NOTE: Since the theoretical Nernstian relation between electrical response and pH at the calibration temperature is programmed into the pH meter software, the calibration process provides the Nernstian response from the electrode/meter system being calibrated. The actual calibration slope is calculated and the **displayed slope value** represents the actual slope of the electrical potential (millivolt)– pH line that this calibration has produced.

   - **The millivolt test.** For pH meters that display and store only millivolt readings (do not display the slope percent), use the following guidelines to ascertain adequate calibration:
     - pH 7 buffer: Displays between -10 to +10 mV
     - pH 4 buffer: Displays between +165 to +195 mV
     - pH 10 buffer: Displays between -165 to -195 mV
   - If using buffers other than the standard pH 4, 7, and 10 buffers, refer to the information provided with the specific buffer lot to determine the correct, temperature-compensated millivolt potential for that buffer.

10. **Replace the electrode** if, after recalibration, the slope remains outside the acceptable range of 95 to 102 percent or if the acceptable range of the millivolt response is not met at any of the calibration points.

CALIBRATION FOR LOW IONIC-STRENGTH WATER 6.4.3.B

Calibration of pH instrument systems with standard buffers does not guarantee accurate and (or) timely pH measurement in low ionic-strength waters (conductivity less than 100 µS/cm) and in very low ionic-strength waters (conductivity less than 50 µS/cm). As sample ionic strength decreases, the efficiency of the standard pH instrument system also decreases. Low or very low ionic-strength waters have little buffering capacity and may readily absorb atmospheric CO_2, resulting in the formation of carbonic acid in the sample. A continuous change in pH values can occur from the varying reaction rates of the sample water with CO_2, resulting in an unstable measurement.

Standard pH electrodes do not respond well in waters with low ionic strength.

- Standard combination pH electrodes respond more slowly, the response is characterized by continual drift, and calibration is difficult to maintain. Equilibration with the sample water may not be completely achieved or the equilibration time may be on the order of hours.
- Standard pH electrodes exhibit a jumpy response and are more sensitive to conditions of flow and agitation, and measurement accuracy decreases (Wood, 1981).

When preparing to measure pH in low ionic-strength waters, the response time, accuracy, and reproducibility of the measurement can be improved by modifying the type of electrode and buffer.

To measure pH in water of low ionic strength:

1. Use a specific, low ionic-strength electrode. The pH electrode for low ionic-strength solutions typically is characterized by
   - A thin, responsive glass membrane;
   - A reference junction that allows rapid electrolyte flow; and
   - A pH-neutral ionic additive within the reference filling solution.
2. Use corresponding low ionic-strength pH buffers.
   - The low ionic-strength buffer should contain the same type of pH-neutral ionic additive as that in the electrode reference filling solution (the amount of pH neutral ionic additive must be the same in the electrode and buffer, so that the net pH effect is standardized).
   - Low ionic-strength buffers may not be of the standard pH buffer values (pH = 4, 7, 10). Check that your pH meter can accept these “nonstandard” buffer values for calibration.

Calibration of the pH instrument system and measurements made in low ionic-strength solutions should involve a specific combination of low ionic-strength buffers and low ionic-strength electrodes.

6.4.3.C CALIBRATION FOR HIGH IONIC-STRENGTH WATER

USGS studies increasingly involve pH measurement and sampling of high ionic-strength waters (ionic strength greater than 3 *M* or conductivity greater than 20,000 µS/cm) from sources such as industrial effluent (for example, from paper mills, oil refineries, carbonate processing or other mining activities that have corrosive properties), combined sewer/storm water from urban systems, seawater, and brines. Using standard buffers or standard equipment may not yield an accurate pH measurement for such waters.

- The high ionic strength of some industrial effluents or brines often are of greater or equal ionic strength than that of the filling solution in the standard pH electrode. This results in an ionic gradient toward the reference junction and into the pH electrode, which compromises the design parameters of the electrode and therefore the soundness of the calibration and the pH measurement.
- Standard buffers are not of an ionic strength that approximates or exceeds the ionic strength of the sample solution, and standard filling solutions in pH electrodes similarly may have too low of an ionic strength to be calibrated properly for measurement of pH in high ionic-strength waters.

When selecting the measurement system to be used to determine the pH of high ionic-strength waters, consider the following options:

1. Obtain high ionic-strength (conductivity greater than 20,000 µS/cm) pH buffer solutions from commercial sources, if available. Follow the guidelines for maintenance and use of pH buffers previously described in section 6.4.1.C, paying close attention to the effect of temperature on buffer values.
2. Obtain high ionic-strength pH glass electrodes, if available. These may be characterized by filling solutions of greater than 3 *M* ionic strength and more solution-specific glass sensors. Note specific uses recommended by the manufacturer and follow the manufacturer's instructions.
3. If no suitable pH glass electrode/buffer system is available for pH measurement in high ionic-strength environments, investigate the suitability of alternative instrumentation and methods, such as those that employ spectrophotometric or optical methods, with respect to the site-specific conditions to be encountered and study data-quality objectives (Bellerby and others, 1995; Farquharson and others, 1992; Sedjil and Lu, 1998).
    - Spectrophotometric methods typically involve the constant-rate introduction of acid-base indicator dyes into the sample; pH measurement is accomplished by measurement of the resultant spectra of the dye. An important limitation to this system is that acid-base indicator dyes are typically sensitive over very narrow pH ranges (Raghuraman and others, 2006).
    - Spectrophotometric measurement of pH in environmental samples is a methodology designed for specific environments; follow the guidelines provided by the equipment manufacturer.
    - As part of USGS studies, any pH data obtained by spectrophotometry or other nontraditional pH measurement method must be entered under the unique parameter and (or) method code designated in the USGS National Water Information System (NWIS) water-quality database.

CALIBRATION FOR THE pH SENSOR IN MULTIPARAMETER INSTRUMENTS 6.4.3.D

Before beginning calibration of the pH electrode in a multiparameter instrument sonde, read and follow carefully the instrument manual and manufacturer's instructions. Guidelines that incorporate USGS protocols for pH calibration and measurement are described in NFM 6.8.

General procedures for calibration of the pH sensor in a multiparameter sonde:

1. Select the pH 7 and one additional buffer solution that will bracket the anticipated pH of the sample. Equilibrate the temperature of the buffers to the temperature of the environmental sample.
2. Rinse the sonde and electrode thoroughly three times with DIW before and between use of each buffer solution.
3. Rinse the pH and temperature sensors three times with separate aliquots of the first pH buffer, using the "pour-swirl-discard, pour-sit-discard, pour-sit-measure" method described in section 6.4.3.A. Allow enough time for the sensors to equilibrate to buffer temperature before locking in the first calibration point.
4. Repeat step 3, using the second pH buffer, and lock in the second calibration point. (Depending on site conditions and study objectives, it might be useful to check the calibration range of the pH sensor using a third buffer; if appropriate, lock in a value.)
5. Always record temperature information with calibration information in the pH-meter/electrode logbook and on the field sheet.

MEASUREMENT 6.4.4

The pH of sample water is to be measured as soon as possible after removal of the sample from its environmental source. The pH of a water sample can change substantially within hours or even minutes after sample collection as a result of temperature change; degassing (loss of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); in-gassing (gain of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); mineral precipitation (formation of calcium carbonate, iron hydroxides); metabolic respiration by microorganisms; and other chemical, physical, and biological reactions (Hem, 1989). Field conditions, including rain, wind, cold, dust, direct sunlight, and direct exposure to vehicle exhaust can cause measurement problems.[2] Always protect the instrument system and the measurement process from the effects of harsh weather and transportation damage.

The pH value of an aqueous system should be determined by taking the median of three or more separate and stable measurements that are recorded in a quiescent sample. Recording a median value ensures that the reported pH value represents a true measurement, instead of a computed measurement, and avoids the mathematical procedure required to compute a mean pH from logarithmic operations.

[2]The effects of field conditions on the quality of field measurements, water-quality samples, and data integrity must be anticipated by field personnel and protocols to minimize sample contamination as described in NFM 4 and 5 are to be implemented as standard operating procedure.

TECHNICAL NOTE: The pH value of a given sample always is recorded in the USGS database as a median of a series of stable measurements. For applications that require reporting pH over time (for example, an annual average pH) or space, however, computation of the mean of the hydrogen ion activity may be useful. To compute a series of pH measurements collected over time or space:

a. Take the antilog of each pH measurement, using the following equation: Activity = 10^{-pH}.
b. Add all the antilog values and divide the sum by the total number of values.
c. Convert the calculated mean activity back to pH units, using the equation, pH = (-log10) (mean H^+ activity).

If reporting pH as a computed mean, document this information and the procedure used. **Do not enter a mean pH value in the USGS NWIS database under the parameter code for a median or direct determination of pH.**

6.4.4.A pH MEASUREMENT IN SURFACE WATER

When using a single-parameter pH electrode/meter instrument system, the pH of surface water is determined ex situ, from a quiescent, non-stirred sample that is withdrawn from a churn or cone splitter or other approved sample-compositing device. Although referred to as a single-parameter method, most modern pH meters are equipped with a thermistor used to determine the temperature of the sample. Each pH measurement must be accompanied with a concurrent temperature measurement.

- It is not advisable to immerse the pH electrode into flowing surface water for the following reasons:
  - Placing the pH electrode into moving water risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. In addition, proper functioning of the glass membrane is affected when ionic equilibrium is not achieved with the surrounding sample solution.
  - Calibration of the electrode was accomplished in a quiescent sample, not in flowing or stirred water. Adequate calibration of the instrument system cannot be assumed to extend to moving water.
  - USGS methodology in surface-water measurement usually involves the collection of depth- and width-integrated samples. In situ measurements of pH in a moving water system, either at a singular point in the waterway or across a section, do not meet these requirements.
  - Reference-junction equilibrium cannot be achieved in moving water; thus, correct electrode functioning will again be inhibited.
  - It is difficult to have electrode temperature come to equilibrium with sample temperature in moving water; correct pH instrument system functioning will be inhibited.
- The determination of pH in situ, using a multiparameter instrument system, is described in NFM 6.0 and 6.8. The system selected depends on the data-quality objectives of the study and on site-specific conditions.

Before collecting the sample and making ex situ measurements, it is advisable to determine the range of pH values in the cross section, or estimate the magnitude of lateral mixing of the waterway at the field site, using an in situ measurement method (for example, with a multiparameter sonde).

When making an ex situ pH measurement:

Set up the pH instrument system close to the sampling site in order to minimize the time lapse between sample collection and pH measurement.

1. The glass membrane of the electrode should not contact the sides or bottom of the beaker or other measurement vessel. Use only a clean measurement vessel.
2. Fill the measurement vessel with sufficient sample to ensure that the electrode reference junction is fully immersed, taking care not to aerate the sample.
3. After calibration (or measuring the pH of a different sample), rinse the electrode and thermistor three times with DIW. This crucial step must always be completed between differing solutions.
4. **Rinse the electrode and thermistor sensors two times with the sample**, as follows:
    a. **First rinse—**Pour an aliquot of sample onto the sensors and swirl the sample water around the electrode sensors. Discard the sample appropriately.
    b. **Second rinse—**Pour an aliquot of sample onto the sensors and allow the sensors to sit in the solution for 1 minute (do not swirl). Discard the sample appropriately.
5. **Measure pH**, as follows:
    a. Pour a third aliquot of sample into the vessel. **Allow the sensors to sit in a quiescent sample** for 1 minute or until the pH value stabilizes within the established criterion. Record the pH value on the electronic or paper field-notes form.
    b. Repeat the procedure in (a) above on at least two additional aliquots of the sample, recording the pH measurement for each aliquot on the field form(s).
6. **Calculate a final sample pH as the median** of the values measured for the sample aliquots and document the calculation on field forms.
7. **Record** the final pH value of the sample to the nearest 0.01 pH unit, along with the sample temperature, in paper and (or) electronic field forms, including forms that accompany samples being shipped to the laboratory.
8. The pH value should be reported to the nearest 0.1 pH unit when published and when recorded in the NWIS database.

Always record the temperature of the sample concurrently with each pH measurement.

6.4.4.B pH MEASUREMENT IN GROUND WATER

The pH of ground water should be measured under no-flow (quiescent sample) conditions. When using a single-parameter meter, the measurement can be made either with the pH electrode and temperature sensor inserted (a) into an airtight flowthrough cell or chamber to which the sample is pumped, or (b) in a vessel that contains an aliquot of sample either collected from pump discharge or withdrawn from a sampling device, such as a bailer (figs. 6.4–2 and 6.4–3, respectively). (See NFM 6.8 for pH measurement using a multiparameter sonde).

The central concept for measuring pH in ground water is to use equipment that minimizes aeration, chemical change, and temperature change. If possible, operate equipment in a manner that helps to mitigate losses and gains of dissolved gases in solution.

- The flowthrough cell/chamber method yields accurate pH data when implemented appropriately.
- Bailed or other methods for collecting discrete samples for pH measurement must be implemented carefully to avoid temperature change, turbulence, and sample aeration from decanting and mixing of the bailed water.
- Downhole deployment of a submersible sensor or sonde risks losing the equipment if it becomes lodged in the well.

Document on electronic or paper field forms the methodology used to obtain samples for pH measurement.

Unless specifically required by study objectives or environmental constraints, in situ measurement of pH by putting the sensor system directly into the well (downhole method) should be avoided for the following reasons:

- Placing the pH electrode directly into the borehole risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. Any accretions or coatings on the inside of the borehole may be transferred to the pH sensor and damage, or alter, the membrane.
- Pumps, wiring, and (or) other equipment within the borehole may damage or degrade the pH sensor and the sonde.
- Any static electrical charge on the inside of the well casing or borehole may be transferred to the pH electrode, a condition sometimes referred to as a “ground loop,” which also compromises accurate pH measurement.

Always measure and record sample temperature concurrently with pH measurements.

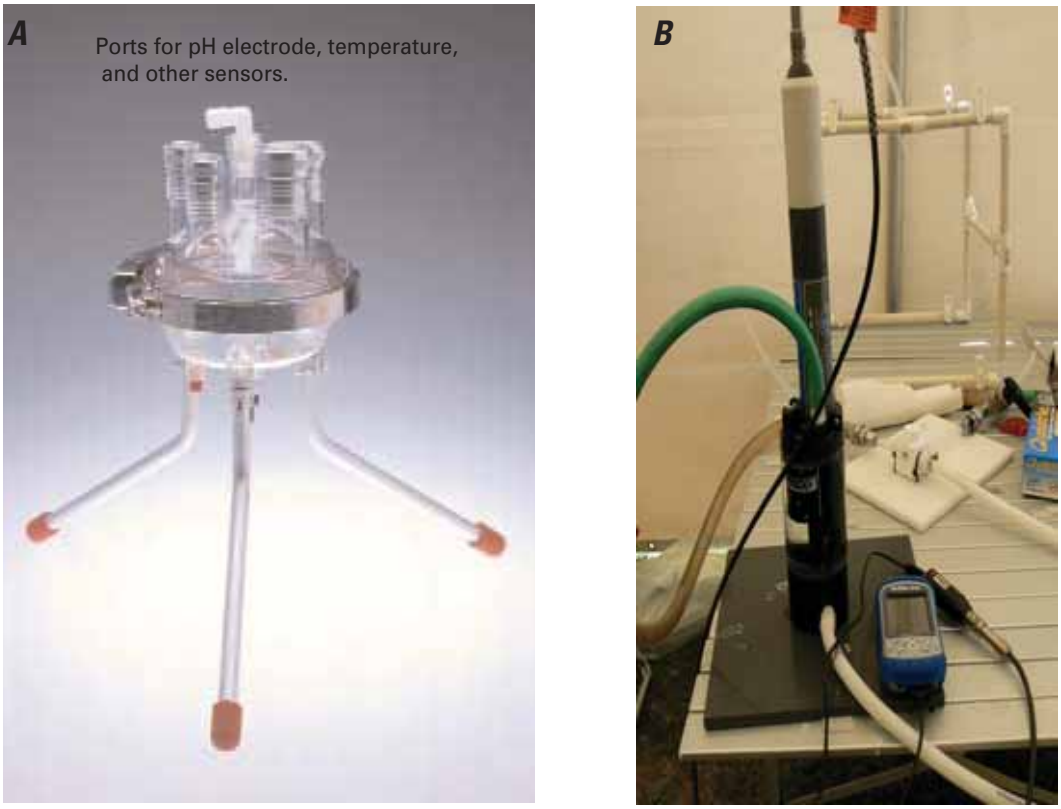

Figure 6.4–2. Photographs of (***A***) a flowthrough cell/chamber for use with single-parameter field-measurement sensors, shown without sensors installed; and (***B***) a flowthrough cell attached to a multiparameter sonde. Photograph ***A*** courtesy of Geotech Environmental. Photograph ***B*** is a USGS stock image.

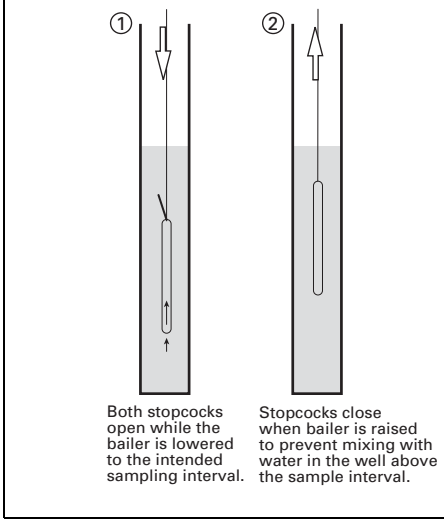

Figure 6.4–3. Use of a dual-valve (double stop-cock) Teflon bailer.

Referring to figure 6.4–2, ground water is pumped directly from the well through tubing and into an airtight flowthrough cell/chamber containing either a calibrated pH electrode and other sensors (typically, dissolved oxygen, specific electrical conductance, and temperature sensors (fig. 6.4–2A), or a multiparameter sonde (fig. 6.4–2B).

After successful calibration of the pH instrument system on site, pH measurement of sample water may proceed either on discrete samples obtained from a bailer, or on pumped ground water circulated through a flowthrough cell/chamber.

- Use of the bailer to obtain ground-water samples is analogous to the approved use of samplers in a surface-water situation, as described below.
- Use of a flowthrough cell/chamber has the advantage of concurrent monitoring of ground-water field measurements in addition to pH, as described below.

To make a pH measurement using a flowthrough cell/chamber system instrumented with single-parameter sensors (fig. 6.4–2):

1. Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight.
2. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged.
3. Check for and eliminate any backpressure condition.
4. Monitor pH variation during purging:
    a. Keep the flow constant and laminar.
    b. Allow the sensors to equilibrate with the ground water for 5 minutes or more, at the flow rate to be used for collecting all of the other samples.
    c. Record pH values at regularly spaced time intervals throughout purging (consult NFM 6.0 for detailed guidance). Compare the variability of pH values toward the end of purging. The stability of pH values is assumed when three to five readings made at regularly spaced intervals are constant. If readings continue to fluctuate, continue to monitor, or, if site conditions are demonstrably variable (degassing, in-gassing, rapid thermal changes from water at depth), select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
5. Determine sample pH toward the end of purging (for example, during removal of the final purge volume) as follows:
    a. Divert flow from the chamber to allow the sample contained within the chamber to become quiescent (after recording the other field measurements). Record the pH value under quiescent conditions to the nearest 0.01 pH unit.
    b. Determine the median of the pH values recorded under quiescent conditions and report this value as sample pH.
    c. If field personnel have reason to suspect an electrode malfunction, a calibration check at the end of sampling is recommended.

To make a pH measurement on a bailed sample (fig. 6.4–3):

1. Withdraw subsamples from the well and transfer each bailed sample to a churn, cone splitter, or other appropriate compositing device (NFM 2).
2. Remove an aliquot from the sample composite for measurement of pH.

TROUBLESHOOTING 6.4.5

Consult the instrument manufacturer for recommended troubleshooting actions for specific single-parameter and multiparameter pH instrument systems.

- Nearly all problems encountered during pH calibration and measurement can be attributed directly to the condition and responsiveness of the pH electrode (table 6.4–3).
- For any problem, first test that the instrument batteries are fully charged. Keep spare batteries on hand that are fully charged.

Table 6.4–3. Troubleshooting guide for pH measurement.

[DIW, deionized water]

Symptom	Possible cause—Corrective action
Instrument system will not calibrate to full scale	• Buffers may be contaminated or old—Use fresh buffers. • Faulty electrode—Recondition or replace electrode (see section 6.4.2). • Weak batteries—Replace with new or fully charged batteries.
Slow response	***For liquid-filled electrodes:*** • Weak or incorrect solution—Change filling solution to correct molarity. • No or low filling solution—Add fresh solution of correct molarity. • Dirty tip (for example, visible chemical deposits or organic or biological matter on the electrode)—Rinse tip with DIW; if residue persists, use solution and cleaning method recommended by the manufacturer. **Take care not to scratch the electrode tip.** • Clogged or partially clogged junction—Follow the manufacturer's instructions to unclog the junction). • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B). • Sluggish response to pH changes; pH measurement is biased negatively—Refer to table 6.4–2. ***For gel-filled electrodes:*** • Dirty bulb—Rinse bulb carefully with DIW. If organic/inorganic/biological residue persists, consult the manufacturer's recommendations. • Visibly clogged junction—Follow the manufacturer's instructions to unclog the junction • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B).
Erratic readings	• Loose or defective connections—Tighten, clean, or replace connections. • Broken or defective cable—Repair or replace cable. • Static charge—Polish face of meter with antistatic solution. • Loose battery connection—Tighten. • Air bubbles in the electrode bulb—Shake electrode gently. • Too much pressure in flowthrough chamber—Release and reduce pressure. • Weak batteries—Replace with new, fully charged batteries.

6.4.6 REPORTING

Due to the rapidity of pH reactions in environmental samples, the effect of temperature on the operation of the pH instrument system, and chemical and microbiological equilibria within the sample, pH measurements must be completed and recorded as soon as possible after removing the sample from the environmental medium. When entering the pH value for the site into the NWIS database, ensure that the method code selected correctly corresponds to the method that was used for the pH measurement.

- On field forms (electronic or paper) and in the pH-meter/electrode logbook, record pH calibration and environmental measurements to 0.01 standard pH units.
- In the USGS NWIS database, report pH values to the nearest 0.1 standard pH unit, unless study and data-quality objectives dictate otherwise and equipment of the appropriate precision and accuracy has been used.

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6.5 REDUCTION-OXIDATION POTENTIAL (ELECTRODE METHOD)

By D.K. Nordstrom and F.D. Wilde

Illustrations

Tables

REDUCTION-OXIDATION POTENTIAL (ELECTRODE METHOD) 6.5

In contrast to other field measurements, the determination of the reduction-oxidation potential of water (referred to as redox) should not be considered a routine determination. Measurement of redox potential, described here as Eh measurement, is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement (see "Interferences and Limitations," section 6.5.3.A).

REDUCTION-OXIDATION POTENTIAL (*as* Eh)—A measure of the equilibrium potential, relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode and an aqueous solution containing electroactive redox species.

- Eh measurement may show qualitative trends but generally cannot be interpreted as equilibrium values.
- Determinations of redox using the platinum (or other noble metal) electrode method (Eh) are valid only when redox species are (a) electroactive, and (b) present in the solution at concentrations of about 10^{-5} molal and higher. Redox species in natural waters generally do not reach equilibrium with metal electrodes.

Procedures for equipment calibration (test procedures) and Eh measurement are described in this section for the platinum electrode only. Although the general guidance given here applies to other types of redox electrodes (such as gold and glassy carbon electrodes), it is necessary to consult the manufacturer's instructions for correct use of the specific electrode selected. Concentrations of redox species can be determined by direct chemical analysis instead of using the electrode method (Baedecker and Cozzarelli, 1992).

6.5.1 EQUIPMENT AND SUPPLIES

The equipment and supplies needed for making Eh measurements using the platinum electrode method and stand-alone millivolt or pH meter are listed in table 6.5–1.

Table 6.5–1. Equipment and supplies used for Eh measurements[1]

[mV, millivolt; ±, plus or minus; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Millivolt meter or pH meter with millivolt reading capability, preferably with automatic temperature compensator; 0.1-mV sensitivity; scale to at least ±1,400 mV; BNC connector (see instrument specifications for pH meters, 6.4.1 in NFM 6.4
- ✓ Redox electrodes, either (a) platinum and reference electrode (calomel or silver:silver-chloride) or (b) combination electrode
- ✓ Electrode filling solutions (refer to manufacturer's specifications)
- ✓ Thermometer (liquid-in-glass or thermistor type), calibrated (see NFM 6.1 for selection and calibration criteria)—for use with millivolt meters without temperature compensator
- ✓ Flowthrough cell with valves, tubing, and accessories impermeable to air (for use with pump system)
- ✓ Sampling system: (1) in situ (downhole) measurement instrument, or (2) submersible pump (used with closed-system flowthrough cell). Pump tubing must be "impermeable" to oxygen.
- ✓ ZoBell's solution
- ✓ Aqua regia or manufacturer's recommended electrode-cleaning solution
- ✓ Liquid nonphosphate laboratory-grade detergent
- ✓ Mild abrasive: crocus cloth or 400- to 600-grit wet/dry Carborundum™ paper
- ✓ Deionized water (maximum conductivity of 1.0 µS/cm)
- ✓ Bottle, squeeze dispenser for deionized water
- ✓ Safety equipment: gloves, glasses, apron, chemical spill kit
- ✓ Paper tissues, disposable, lint free
- ✓ Waste-disposal container

[1]Modify this list to meet specific needs of the field effort.

This report does not provide guidance or instructions for redox determination using an oxidation-reduction-potential (ORP) sensor connected to a multiparameter instrument. Eh equipment must be tested before each field trip and cleaned soon after use. Every instrument system used for Eh measurement must have a log book in which all the equipment repairs and calibrations or equipment tests are recorded, along with the manufacturer make and model numbers and serial or property number.

ELECTRODE SELECTION 6.5.1.A

Select either a redox-sensing combination electrode or an electrode pair (a platinum and reference electrode). **Use of the correct electrolyte filling solution is essential to proper measurement and is specified by the electrode manufacturer**. Orion Company, for example, recommends selection of a filling solution to best match the ionic strength of the sample solution, in order to minimize junction potentials.

- Silver:silver-chloride or calomel reference electrodes are the redox electrodes in common use.
- The Orion™ combination electrodes are platinum redox and silver:silver-chloride reference electrodes in one body (the Orion™ brand is used for purposes of illustration only).

CAUTION: The standard hydrogen reference electrode (SHE) can be dangerous and is not recommended for field use.

ZOBELL'S SOLUTION 6.5.1.B

ZoBell's is the standard solution for testing redox instruments. ZoBell's solution can be obtained from a commercial supplier or it can be prepared fresh (see below). Quinhydrone solution is sometimes used but is not recommended because it is significantly less stable above 30°C and its temperature dependence is not as well defined as that of ZoBell's.

ZoBell's solution consists of a 0.1 molal KCl solution containing equimolal amounts of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. ZoBell's is reported stable for at least 90 days if kept chilled at 4°C.

To prepare ZoBell's solution:

1. Weigh the chemicals (dry chemicals should be stored overnight in a desiccator before use).
   1.4080 g $K_4Fe(CN)_6 \bullet 3H_20$ (Potassium ferrocyanide)
   1.0975 g $K_3Fe(CN)_6$ (Potassium ferricyanide)
   7.4557 g KCl (Potassium chloride)

2. Dissolve these chemicals in deionized water and dilute solution to 1,000 mL.
3. Store the solution in a dark bottle, clearly labeled with its chemical contents, preparation date, and expiration date. Keep the solution chilled.

CAUTION: ZoBell's solution is toxic—handle with care.

6.5.1.C EQUIPMENT MAINTENANCE

Refer to 6.4.1 of NFM 6.4 on pH for general guidelines on meter and electrode maintenance, cleaning, and storage. Follow the manufacturer's guidelines on the operation and maintenance of the meters and electrodes, and keep a copy of the instruction manual with each instrument system. Keep the meters and electrodes clean of dust and chemical spills, and handle them with care.

Maintenance

Keep the surface of noble electrodes clean of coatings or mineral deposits. A brightly polished metal surface prevents deterioration of electrode response. The billet tip is more easily cleaned than the wire tip on the platinum electrode. Condition and maintain the Eh electrodes as recommended by the manufacturer.

Electrode Cleaning

Keep the O-ring on electrodes moist during cleaning procedures.

- To remove precipitate that forms on the outside wall or tip of the reference or combination electrode, rinse the outside of the electrode with deionized water.
- If particulates or precipitates lodge in the space between the electrode sleeve and the inner cone of sleeve-type electrode junctions, clean the chamber by flushing out the filling solution (the precise procedure to be followed must come from the electrode manufacturer).

- To remove oily residues, use a liquid nonphosphate detergent solution and polish the surface with mild abrasive such as coarse cloth, a hard eraser, or 400- to 600-grit wet/dry Carborundum™ paper (Bricker, 1982).
- To recondition the Eh electrode, immerse the electrode in warm aqua regia (70°C) for about 1 minute. **Do not immerse the electrode for longer than 1 minute** because aqua regia dissolves the noble metal as well as foreign matter and leads to an erratic electrode response (Bricker, 1982). Soak the electrode several hours in tap water before use.

> **TECHNICAL NOTE:** Disassembly of the electrode is not recommended for routine cleaning and should only be used when absolutely needed. Additional cleaning and reconditioning procedures are discussed in NFM 6.4 and in American Public Health Association and others (1992), American Society for Testing and Materials (1990), Edmunds (1973), Adams (1969), and Callame (1968).

Aqua regia

Aqua regia can be used for cleaning the Eh electrode (check the electrode manufacturer's recommendations). Prepare the aqua regia at the time of use—do not store it. To prepare the aqua regia, mix 1 volume concentrated nitric acid with 3 volumes of concentrated hydrochloric acid.

Electrode storage

For short-term storage, immerse the electrode in deionized water to above the electrode junction and keep the fill hole plugged to reduce evaporation of the filling solution. The recommended procedures for long-term storage of electrodes vary with the type of electrode and by manufacturer. The Orion™ combination electrodes are stored dry after rinsing precipitates from outside of the electrode, draining the filling solution from the chamber, and flushing it with water (consult the manufacturer's cleaning instructions). The ends of the electrode connector must be kept clean. Clean them with alcohol, if necessary. Store the connector ends in a plastic bag when not in use.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.

6.5.2 EQUIPMENT TEST PROCEDURE

Eh measuring systems can be tested for accuracy but they cannot be adjusted. Eh equipment must be tested, either in the laboratory or in the field, against a ZoBell's standard solution before making field measurements. In general, field testing with ZoBell's is not required, but the protocol used will depend on study needs.

- Before using, check that the ZoBell's solution has not exceeded its shelf life.
- Test the Eh equipment using the ZoBell's solution **before and after** field use.
- Be aware that:
  - — ZoBell's is toxic and needs to be handled with care.
  - — ZoBell's reacts readily with minute particles of iron, dust, and other substances, making field use potentially difficult and messy.

The Eh measurements are made by inserting a platinum electrode coupled with a reference electrode into the solution to be measured. The resulting potential, read directly in millivolts from a potentiometer (such as a pH meter), is corrected for the difference between the standard potential of the reference electrode being used at the solution temperature and the potential of the standard hydrogen electrode (table 6.5–2).

> **TECHNICAL NOTE:** E_{ref} is the whole-cell potential of the reference electrode in ZoBell's solution.
>
> E_{ref} = 238 mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the silver:silver-chloride (Ag:AgCl) electrode;
>
> E_{ref} = 185.5 mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the calomel ($Hg:HgCl_2$) electrode;
>
> E° = 430 mV is the standard electrode potential of ZoBell's solution measured against the hydrogen electrode at 25°C.

Half-cell potentials for the calomel, silver:silver chloride, and combination electrodes are shown in table 6.5–2. Table 6.5–3 provides the theoretical Eh of ZoBell's solution as a function of temperature. For those temperatures not shown on tables 6.5–2 and 6.5–3, interpolate the values. Add the value corresponding to the solution temperature to the measured potential electromotive force (emf measurement).

Table 6.5–2. Standard half-cell potentials of selected reference electrodes as a function of temperature and potassium chloride reference-solution concentration, in volts

[Liquid-junction potential included—multiply volts by 1,000 to convert to millivolts; KCl, potassium chloride; Temp °C, temperature in degrees Celsius; M, molar; —, value not provided in reference]

Temp °C	Silver:silver chloride			Calomel [1]				Orion™ 96-78 combination electrode [3,4]
	3*M* KCl [1]	3.5*M* KCl [2]	Saturated KCl [2]	3*M* KCl [2]	3.5*M* KCl [2]	4*M* KCl [2]	KCl saturated [2]	
10	0.220	0.215	0.214	0.260	0.256	—	0.254	0.256
15	0.216	0.212	0.209	—	—	—	0.251	0.253
20	0.213	0.208	0.204	0.257	0.252	—	0.248	0.249
25	0.209	0.205	0.199	0.255	0.250	0.246	0.244	0.246
30	0.205	0.201	0.194	0.253	0.248	0.244	0.241	0.242
35	0.202	0.197	0.189	—	—	—	0.238	0.238
40	0.198	0.193	0.184	0.249	0.244	0.239	0.234	0.234

[1]Modifed from Langmuir (1971).
[2]Modifed from Bates (1973).
[3]Nordstrom (1977) and D.K. Nordstrom, U.S. Geological Survey, written commun., 1995; the half-cell potentials calculated from Nordstrom (1977) are recommended rather than the values from Chateau (1954) cited in the instrument manual provided by the Orion Company because Nordstrom's values were developed specifically for the Orion™ 96-78 redox electrode and provide greater accuracy and precision.
[4]Orion™ manufacturer recommends that for sample solutions with total ionic strength exceeding 0.2 molar (for example, seawater), use a 4*M* KCI-saturated filling solution (usually supplied with the Orion™ model 97-78 electrode) and the half-cell potentials shown above for the silver:silver chloride saturated KCI reference electrode.

Table 6.5–3. Eh of ZoBell's solution as a function of temperature

[From Nordstrom (1977); °C, degrees Celsius; mV, millivolts]

Temperature °C	Eh(mV)	Temperature °C, (continued)	Eh(mV), (continued)
10	467	26	428
12	462	28	423
14	457	30	418
16	453	32	416
18	448	34	407
20	443	36	402
22	438	38	397
24	433	40	393
25	430		

To test Eh equipment, complete the following 7 steps and record results on the Eh data record form for the equipment test procedure (fig. 6.5–1):

1. Follow the manufacturers' recommendations for instrument warm up and operation.
   - Set the scale to the desired millivolt range.
   - Record the type of reference electode being used.
2. Unplug the fill hole. Shake the electrode gently to remove air bubbles from the sensing tip of the electrode. Check the level of the filling solution and replenish to the bottom of the fill hole.
   - The filling solution level must be at least 1 in. above the level of solution being measured.
   - Use only the filling solution specified by the manufacturer.
3. Rinse the electrode, thermometer, and measurement beaker with deionized water. **Blot (do not wipe) excess moisture from the electrode.**
4. Pour ZoBell's solution into a measurement beaker containing the electrode and temperature sensor.
   - The Eh electrode must not touch the bottom or side of the container.
   - Add enough solution to cover the reference junction.
   - Allow 15 to 30 minutes for the solution and sensors to equilibrate to ambient temperature.
5. Stir slowly with a magnetic stirrer (or swirl manually) to establish equilibrium between the electrode(s) and solution. Switch the meter to the millivolt function, allow the reading to stabilize (±5 mV), and record the temperature and millivolt value.
6. Look up the half-cell reference potential for the electrode being used (table 6.5–2). Add this value to the measured potential to obtain the Eh of ZoBell's at ambient temperature.
   - If the value is within 5 mV of the ZoBell Eh given on table 6.5–3, the equipment is ready for field use. (See the example below.)
   - Refer to section 6.5.4 if the value is not within 5 mV of the ZoBell Eh.
7. Rinse off the electrodes and the thermometer thoroughly with deionized water. Store the test solution temporarily for possible verification.

EXAMPLE:

Example of the equipment test procedure using a silver:silver chloride-saturated KCl (Ag:AgCl) electrode.

$$Eh = emf + E_{ref}$$

where:

Eh is the potential (in millivolts) of the sample solution relative to the standard hydrogen electrode,

emf or $E_{measured}$ is the electromotive force or potential (in millivolts) of the water measured at the sample temperature,

E_{ref} is the reference electrode potential of the ZoBell's solution corrected for the sample temperature (table 6.5–2).

a. Follow steps 1–5 (above). For this example,

   - Measured temperature = 22°C
   - *emf* = 238 mV.

b. Check table 6.5–2. The interpolated reference potential = 202 mV for Ag:AgCl–saturated KCl at 22°C.

c. From $Eh = emf + E_{ref}$

   Eh (ZoBell's) = 238 mV + 202 mV = 440 mV.

d. Check table 6.5–3. The test value of 440 mV is within ± 5 mV of 438 mV from table 6.5–3. Thus, the equipment is functioning well and ready for field use.

Check the date on Zobell's solution—do not use solution past its expiration date.

Eh Data Record

Equipment Test Procedure

Equipment description and identification (model and serial and/or W number):

Meter _____

Eh electrode _____ Reference electrode _____

ZoBell's solution: Lot # _____ Date: prepared _____ expired _____

		Before sample Eh:	After sample Eh:
1. Temperature of ZoBell's solution: (after equilibration to ambient temperature)	T =	_____	_____
2. Observed potential (in millivolts) of ZoBell's relative to measuring electrode, at ambient temperature ($E_{measured}$ or *emf*):	*emf* =	_____	_____
3. Reference electrode potential (in millivolts) at ambient temperature from table 6.5–2 (E_{ref}):	E_{ref} =	_____	_____
4. Calculate Eh of ZoBell's: Eh = *emf* + E_{ref}	Eh =	_____	_____
5. Theoretical potential (in millivolts) of ZoBell's at ambient temperature from table 6.5–3:	Eh (theoretical) =	_____	_____
6. Subtract calculated Eh from Eh theoretical (Zobell's)(step 4 minus step 5)	ΔEh =	_____	_____
7. Check: is ΔEh within ± 5 mV?	Observations:	_____	

Figure 6.5–1. Eh data record: equipment test procedure.

MEASUREMENT 6.5.3

To obtain accurate results, it is necessary to prevent losses and gains of gases dissolved in the sample. Consult NFM 6.0 for information on precautions and general procedures used in sample collection and NFM 6.2 for a description of the flowthrough cell used in dissolved-oxygen determination (the spectrophotometric method).

- Chemical, physical, and biological reactions can cause the Eh of water to change significantly within minutes or even seconds after the collection of a sample.
- Water samples cannot be preserved and stored for the Eh measurement.
- Use equipment that eliminates sample aeration and operate the equipment to meet this goal. Measure Eh in situ with a submersible instrument or use an airtight flowthrough system.
- If using a flowthrough chamber or cell:
  - — Use tubing that is impermeable (relatively) to oxygen.
  - — Channel the sample flow throught an airtight cell (closed system) constructed specifically to accommodate redox or ion-specific electrodes, temperature, and other sensors.
  - — Connections and fittings must be airtight
  - — Purge atmospheric oxygen from the sample tubing and associated flow channels before measuring Eh.

Do not use pumping systems in which inert gas contacts and lifts the sample to the surface: the gas could strip gaseous redox species from the water.

Before measuring Eh:

1. Record the type of reference-electrode system being used (fig. 6.5–1).
2. Check for the correct electrode filling solution. If working in very hot or boiling waters, change the reference electrode filling solution daily.
3. Keep the electrode surface brightly polished.

TECHNICAL NOTE: Temperature determines the Eh reference potential for a particular solution and electrode pair, and may affect the reversibility of the redox reactions, the magnitude of the exchange current, and the stability of the apparent redox potential reading. The observed potential of the system will drift until thermal equilibrium is established. **Thermal equilibrium can take longer than 30 minutes but it is essential before beginning the measurements.**

Measure the Eh and complete the field form (fig. 6.5–2):

1. Select an in situ or closed-system sampling method. Immerse the electrodes and temperature sensors in the sample water.
   - **In situ (or downhole)**—Lower the sensors to the depth desired and follow the manufacturer's recommendations.
   - **Closed-system flow cell**—Check that the connections and sensor grommets do not leak, and that the water being pumped fills the flowthrough cell.
2. Allow the sensors to reach thermal equilibrium with the aqueous system being measured and record the time lapsed.
   - It is essential that platinum electrodes be flushed with large volumes of sample water to obtain reproducible values.
   - Record the pH and temperature of the sample water.
3. Switch the meter to the millivolt function.
   - Allow the reading to stabilize (±5 mV).
   - Record the value and temperature (see the **TECHNICAL NOTE** that follows step 7, below).
   - **Stabilization should occur within 30 minutes.**
4. Take readings of the sample temperature and potential (in millivolts) every few minutes for the first 15 to 20 minutes.
   - It is best to stop the flow of the sample while the reading is being taken to prevent streaming-potential effects.
   - After 15 to 20 minutes, begin to record the time, temperature, and potential in plus or minus millivolts about every 10 minutes. Continue until 30 minutes have passed from the initial measurement and until the measurements indicate a constant potential.

5. After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized water.

   If field calibration is required for a study,

   a. Place the electrode(s) and other sensors in ZoBell's solution that has been equilibrated to the temperature of the aqueous system to be measured. The electrode(s) must not touch the container, and the solution must cover the reference junction.

   b. Allow the electrode to reach thermal equilibrium (15 to 30 minutes).

   c. Record the potential reading.

   d. Follow steps 5 through 7 of the equipment test procedure in section 6.5.2.

6. Record all data and calculate Eh (see **EXAMPLE**, section 6.5.2). Fill out the Eh data record form for field measurements fig. 6.5–2).

7. **Quality control**—Repeat the measurement.

Eh Data Record

Field Measurements

		Field Eh	Field Eh[1]
1. Temperature and pH of system measured:	T =	_____	_____
	pH=	_____	_____
2. Time to thermal equilibration:			
	Measurement began at	_____	_____
	Measurement ended at	_____	_____
3. Measured potential of water system (mV): *emf* =		_____	_____
4. Reference electrode potential mV of ZoBell's at sample temperature:	E_{ref} =	_____	_____
5. Calculate sample Eh: *emf* + E_{ref} (add step 3 + step 4):	Eh =	_____	_____

6. Field measurements should agree within about 10 mV.

Observations: _____

[1]The second measurement is necessary for quality control.

Figure 6.5–2. Eh data record: field measurements.

TECHNICAL NOTE: The response of the Eh measurement system may be considerably slower than that of the pH system and that response also may be asymmetrical: the time required for stabilization may be longer when moving from an oxidizing to reducing environment or vice versa. If the readings do not stabilize within about 30 minutes, record the potential and its drift; assume a single quantitative value is not possible. If an estimate of an asymptotic final (hypothetical) potential in such a drifting measurement is desired, refer to the method used by Whitfield (1974) and Thorstenson and others (1979).

6.5.3.A INTERFERENCES AND LIMITATIONS

Measurements should not be carried out without an awareness of the interferences and limitations inherent in the method.

- Organic matter and sulfide may cause contamination of the electrode surface, salt bridge, or internal electrolyte, which can cause drift or erratic performance when reference electrodes are used (American Public Health Association and others, 2001).
- Hydrogen sulfide can produce a coating on the platinum electrode that interferes with the measurement if the electrode is left in sulfide-rich water for several hours (Whitfield, 1974; Sato, 1960).
- The platinum single and combination redox electrodes may yield unstable readings in solutions containing chromium, uranium, vanadium, or titanium ions and other ions that are stronger reducing agents than hydrogen or platinum (Orion Research Instruction Manual, written commun., 1991).
- Do not insert redox electrodes into iron-rich waters directly after the electrode(s) contact ZoBell's. An insoluble blue precipitate coats the electrode surface because of an immediate reaction between ferro- and ferricyanide ions in ZoBell's with ferrous and ferric ions in the sample water, causing erratic readings.

Many elements with more than one oxidation state do not exhibit reversible behavior at the platinum electrode surface and some systems will give mixed potentials, depending on the presence of several different couples (Barcelona and others, 1989; Bricker, 1982, p. 59–65; Stumm and Morgan, 1981, p. 490–495; Bricker, 1965, p. 65). Methane, bicarbonate, nitrogen gas, sulfate, and dissolved oxygen generally are not in equilibrium with platinum electrodes (Berner, 1981).

TECHNICAL NOTE: Misconceptions regarding the analogy between Eh (pe) and pH as master variables and limitations on the interpretation of Eh measurements are explained in Hostettler (1984), Lindberg and Runnells (1984), Thorstenson (1984), and Berner (1981). To summarize:

(1) Hydrated electrons do not exist in meaningful concentrations in most aqueous systems—in contrast, pH represents real activities of hydrated protons. Eh may be expressed as pe (the negative logarithm of the electron activity), but conversion to pe offers no advantage when dealing with measured potentials.

(2) Do not assume that redox species coexist in equilibrium. Many situations have been documented in which dissolved oxygen coexists with hydrogen sulfide, methane, and ferrous iron.

- The practicality of Eh measurements is limited to iron in acidic mine waters and sulfide in waters undergoing sulfate reduction.

- Other redox species are not sufficiently electroactive to establish an equilibrium potential at the surface of the conducting electrode.

(3) A single redox potential cannot be assigned to a disequilibrium system, nor can it be assigned to a water sample without specifying the particular redox species to which it refers. Different redox elements (iron, manganese, sulfur, selenium, arsenic) tend not to reach overall equilibrium in most natural water systems; therefore, a single Eh measurement generally does not represent the system.

6.5.3.B INTERPRETATION

A rigorous quantitative interpretation of an Eh measurement requires interactive access to an aqueous speciation code. Exercise caution when interpreting a measured Eh using the Nernst equation. The Nernst equation for the simple half-cell reaction $(M^{I}_{(aq)} = M^{II}_{(aq)} + e^{-})$ is

$$Eh = E^{0} + 2.303RT/nF \log (a^{II}_{M(aq)} / a^{I}_{M(aq)})$$

where:

R = gas constant;
T = temperature, in degrees kelvin;
n = number of electrons in the helf-cell reaction;
F = Faraday constant; and

$a^{I}_{M(aq)}$ and $a^{II}_{M(aq)}$ = thermodynamic activities of the free ions $M^{I}_{(aq)}$ and $M^{II}_{(aq)}$ and not simply the analytical concentrations of total M in oxidation states I and II, respectively.

Measurements of Eh are used to test and evaluate geochemical speciation models, particularly for suboxic and anoxic ground-water systems. Eh data can be useful for gaining insights on the evolution of water chemistry and for estimating the equilibrium behavior of multivalent elements relative to pH for an aqueous system. Eh can delineate qualitatively strong redox gradients; for example, those found in stratified lakes and rivers with an anaerobic zone, in an oxidized surface flow that becomes anaerobic after passing through stagnant organic-rich systems, and in mine-drainage discharges.

TROUBLESHOOTING 6.5.4

Contact the instrument manufacturer if the suggestions in table 6.5–4 fail to resolve the problem.

- Check the voltage of the batteries.
- Always start with good batteries in the instruments and carry spares.

Table 6.5–4. Troubleshooting guide for Eh measurement

[±, plus or minus; mV, millivolts; *emf*, electromotive force]

Symptom	Possible corrective action
Eh of ZoBell's solution exceeds theoretical by ±5 mV Excessive drift Erratic performance	Check meter operation: • Use shorting lead to establish meter reading at zero mV. • Check/replace batteries. • Check against backup meter.
Poor response when using paired electodes	Check electrode operation: • Check that electrode reference solution level is to the fill hole. • Plug questionable reference electrode into reference electrode jack and another reference electrode in good working order of the same type into the indicator electrode jack of the meter; immerse electrodes in a potassium chloride solution, record mV, rinse off and immerse electrodes in ZoBell's solution. The two mV readings should be 0 ± 5 mV. If using different electrodes (Ag:AgCl and Hg:$HgCl_2$), reading should be 44 ± 5 mV for a good reference electrode. • Polish platinum tip with mild abrasive (crocus cloth, hard eraser, or a 400–600-grit wet/dry Carborundum™ paper), rinse thoroughly with deionized water. Use a Kimwipe™ if these abrasives are not available. • Drain and refill reference electrolyte chamber. • Disconnect reference electrode. Drain and refill electrolyte chamber with correct filling solution. Wipe off connectors on electrode and meter. Use backup electrode to check the *emf*. • Read *emf* with fresh aliquot of ZoBell's solution; prepare fresh ZoBell's solution if possible. • Recondition electrode by cleaning with aqua regia and renewing filling solution—**this is a last resort.**

6.5.5 REPORTING

Report the calculated Eh in mV to two significant figures.

Potentials are reported to the nearest 10 mV, along with the temperature at which the measurement was made, the electrode system employed, and the pH at time of measurement.

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6.6 Alkalinity and Acid Neutralizing Capacity

Revised by S.A. Rounds

Figures

Tables

6.6 Alkalinity and Acid Neutralizing Capacity

Alkalinity and acid neutralizing capacity (ANC) are measures of the ability of a sample to neutralize strong acid. They are determined using identical electrometric procedures involving the acidimetric titration of a sample; the only difference is that the alkalinity sample is filtered, whereas the ANC sample is not filtered (raw, or unfiltered). The terms alkalinity, ANC, and carbonate alkalinity are used in this manual as follows:

- **Alkalinity** is the acid neutralizing capacity of solutes in a water sample, reported in milliequivalents or microequivalents per liter. Alkalinity consists of the sum of titratable carbonate and noncarbonate chemical species in a **filtered water sample** (filter membrane of 0.45-micrometer (µm) pore size or smaller).[1]

- **ANC** is the acid-neutralizing capacity of solutes plus particulates in an **unfiltered water sample**, reported in milliequivalents or microequivalents per liter. ANC is equivalent to alkalinity for samples without titratable particulate matter.

- **Carbonate alkalinity** is the acid-neutralizing capacity attributable to carbonate solutes (bicarbonate and carbonate), reported either in milliequivalents or microequivalents per liter, or in milligrams per liter as a carbonate species, and titrated on a **filtered water sample**. In many aqueous systems, alkalinity is controlled primarily by carbonate chemistry and most commonly is attributable to bicarbonate (HCO_3^-) and less frequently to carbonate (CO_3^{2-}).

ALKALINITY: the capacity of solutes in an aqueous system to neutralize acid.

ACID NEUTRALIZING CAPACITY (ANC): the capacity of solutes plus particulates in an aqueous system to neutralize acid.

Alkalinity is used routinely to check the charge balance of a solution and to gain insights regarding the evolution of aqueous systems. Alkalinity and ANC provide information on the suitability of water for uses such as irrigation, for determining the efficiency of wastewater processes and the presence of contamination by anthropogenic wastes, and for maintaining ecosystem health.

Any substance in the water sample that reacts with strong acid titrant can contribute to the acid neutralizing capacity of the water body being sampled.

- The primary contributors to alkalinity and ANC typically are bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}).

[1] In standard USGS practice, a filtered sample is operationally defined as having passed through a 0.45-µm pore filter membrane without clogging the filter.

- Important noncarbonate contributors may include organic ligands (especially acetate and propionate) as well as hydroxide, silicate, borate, and less commonly ammonia and sulfide (Hem, 1985). When found in unusually high concentrations, phosphate and arsenate also may contribute to the ANC of a sample (Stumm and Morgan, 1996).

- Except for unusual natural waters and waters substantially affected by human activity, noncarbonate ionized contributors generally are not present in large enough quantities to affect alkalinity or ANC determinations.

- Particulate matter can be an important contributor and must be removed by filtration before titrating the sample for an alkalinity determination.

Alkalinity is determined on a filtered sample.

ANC is determined on an unfiltered sample.

TECHNICAL NOTE: Alkalinity and ANC are measured relative to a solution of carbon dioxide in water; therefore, they are independent of any exchange of carbon dioxide or other common gases between the sample and the atmosphere. However, atmospheric gas exchange can alter the concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter—this may alter the alkalinity, especially in water systems closed to the atmosphere under ambient conditions.

6.6.1 Equipment and Supplies

Equipment and supplies for the electrometric method for determining alkalinity and ANC are listed in table 6.6–1. The equipment must be tested before each field trip and cleaned immediately after each use.

Buret, micrometer buret, and digital titrator

The buret provides good accuracy and precision when used by a trained operator.

- Micrometer burets provide better accuracy and precision than burets—acid can be delivered in increments to 0.0001 milliliter (mL) and are available commercially (for example, Gilmont® micrometer burets).

- The digital titrator is popular because it is more convenient and less fragile than a buret and keeps the acid in a virtually closed system. Empty titrant cartridges also are available. (The Hach® brand is used as an example in this document.) **Delivery tubes of clear (instead of red) plastic should be used.**

Volumetric pipet, graduated cylinder, and digital balance

The volumetric pipet is used only for dispensing the correct volume of filtered sample for the alkalinity determination.

- Use only class A "TD" pipets. TD is a calibration designation meaning "To Deliver" (TD is distinguished from "TC" or "To Contain" pipets).

- Class A pipets should not be used to aspirate or dispense solutions containing suspended particles—the small bore of this pipet tends to reject particles during aspiration and retain them during delivery (C.J. Patton, U.S. Geological Survey, written commun., 1995).

The graduated cylinder and digital balance are used only for measuring the correct volume of unfiltered sample for the ANC determination. The digital balance yields higher precision than the graduated cylinder.

Sulfuric acid titrant

Sulfuric acid is the titrant used routinely by the U.S. Geological Survey (USGS). The normality of sulfuric acid titrant is subject to change with time; proper storage and standardization of the acid titrant are essential. Reagents should be stored in a cool (less than 25–30 degrees Celsius (°C)), dry, dark place to ensure maximum shelf life. Check label for expiration date.

- 0.1600 *Normal (N)* or 1.600*N* sulfuric acid solutions in prefilled cartridges for the Hach® digital titrator should be obtained by USGS personnel from the National Field Supply Services (NFSS) One-Stop Shopping Web site. The National Water Quality Laboratory (NWQL) has calculated a correction factor of 1.01 (see section 6.6.5.A) necessary to compensate for cartridge manufacturing anomalies and (or) variations in the reported acid normality. The Hach Company provides an online certificate of analysis and expiration date for the specific lot number of the prefilled sulfuric acid cartridge. Expiration dates also are printed on each cartridge.

- 0.01639*N* sulfuric acid solution for the buret system is available from a vendor of scientific products. Alternatively, a sulfuric acid solution of similar normality may be prepared by following the procedure described in section 6.6.2. **Check the normality of the 0.01639*N* titrant solution each month.**

- Acid solutions of other normality may be needed, depending on the sample chemistry or ionic strength. Prepare the solution under a fume hood. Check the normality monthly.

TECHNICAL NOTE: For samples vulnerable to precipitation reactions, a Berzelius beaker can help minimize gas exchange. Select a size of Berzelius beaker that fits the sample volume and associated titrating equipment and yet minimizes headspace above the sample. Fit the Berzelius beaker with a two- or three-hole stopper to accommodate the electrode(s), the thermometer, and the digital or buret titrator. Another option is to work in a glove box filled with an inert gas atmosphere. Oceanographers use a closed cell with an expanding plunger to avoid gas exchange (Almgren and others, 1977).

Table 6.6–1. Equipment and supplies used for alkalinity or ANC titrations.[1]

[TD, to deliver; mL, milliliters; ANC, acid neutralizing capacity; g, gram; µS/cm, microsiemens per centimeter at 25 degrees Celsius; *N*, normal; NFM, U.S. Geological Survey National Field Manual]

Equipment and supplies needed when using either a digital titrator or a buret
✓ pH meter, preferably with automatic temperature compensator (see NFM 6.4 for selection and associated supplies)
✓ pH electrode, calibrated, combination or equivalent, and appropriate filling solution, if required
✓ Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
✓ Stirrer, magnetic (battery operated)
✓ Stirring bars, Teflon® coated, smallest size (always carry spare bars)
✓ Volumetric pipets, class A "TD" (for alkalinity)—25 mL, 50 mL, and 100 mL
✓ Graduated cylinder (for ANC). For higher precision, use a digital balance, 0.1-g accuracy, 200-g capacity, pocket-sized, battery operated
✓ Pipet squeeze bulb or pipet pump
✓ Sample bottles, 250 mL, acid rinsed or deionized-water rinsed
✓ Beakers, glass—50 mL, 100 mL, and 150 mL
✓ Beaker, Berzelius, 300 mL, tall form, spoutless, with two- or three-hole stopper
✓ Deionized water (DIW) (maximum conductivity of 1 µS/cm)
✓ Dispenser bottle, squeeze, for deionized water
✓ Filtration unit, in-line disposable capsule or disc (for the alkalinity sample)
✓ Sodium carbonate (Na_2CO_3) standard solution
✓ Safety gloves, glasses, acid spill kit, and apron
✓ Paper tissues, disposable, soft and lint free
Additional equipment and supplies needed when using a digital titrator
✓ Digital titrator and mounting assembly
✓ Delivery tube, 90 degree or straight with "J"-hook, colorless, transparent
✓ Titrant solution: sulfuric acid (H_2SO_4) solution, 0.1600*N* and 1.600*N* (empty or prefilled cartridges are available for use with the Hach® system)
Additional equipment and supplies needed when using a buret
✓ Calibrated buret, 25-mL capacity with 0.05-mL graduations and Teflon® stopcock
✓ Calibrated buret, 10-mL capacity with 0.02-mL graduations and Teflon® stopcock
✓ Micrometer buret (alternative to standard burets, for greater accuracy)
✓ Titrant solution: sulfuric acid solution, 0.01639*N*
✓ Buret stand and clamp
✓ Wire pen cleaner (for cleaning buret tip)
✓ Buret cap
✓ Buret meniscus reader
✓ Acid bottle, pump (for filling buret)

[1] Modify this list to meet the specific needs of the field effort.

CAUTION: Use the safety precautions on the Material Safety Data Sheets (MSDS) when handling chemicals.

6.6.1.A Maintenance, Cleaning, and Storage

Proper maintenance, cleaning, and storage of the pH instrument are critical for ensuring the accuracy of alkalinity or ANC determinations; guidance is provided in the *National Field Manual* section on pH (NFM 6.4).

Clean the volumetric pipets, beakers, bottles, burets, and stirring bars with hot water and nonphosphate detergent. Rinse them copiously with tap water followed by deionized water. If oily or chemical residues are difficult to remove, soak the glassware and nonmetal equipment in a mild (5 percent by volume) hydrochloric acid solution (see Horowitz and others, 1994), and repeat the detergent wash. Store cleaned equipment wrapped or bagged in plastic until ready for use.

Reagents must not exceed their shelf life and should be stored, as appropriate, in a dust-free cabinet, desiccator, or refrigerator. When chemicals to be used for preparation of reagents are received, mark the dates of receipt and expiration on the container. When a reagent is prepared, label the container with the contents, date of preparation, expiration date, and preparer's initials. Store the 0.01639*N* standard sulfuric acid solution and filled Hach® titrant cartridges in a cool, dark place (a storage cabinet or frost-free refrigerator). Seal the filled cartridges in plastic bags to avoid moisture loss or gain.

If using a digital titrator, perform a calibration check of its accuracy and precision at least annually by using either reference samples or by comparing the results of an alkalinity or ANC measurement with those determined by performing a buret titration on the same sample. If results show an equipment calibration problem, contact the manufacturer for repair or replacement.

Some of the recommended procedures for equipment operation may be out of date if the equipment being used is different from that described or if the equipment incorporates more recent technological advances—follow the manufacturer's instructions.

6.6.2 Calibration and Standardization

Calibration is required for the pH instrument—follow the instructions in NFM 6.4.

Alkalinity and ANC determinations require the use of an acid titrant with a known concentration. **Accurate standardization of the acid titrant is essential.**

- The normality of locally prepared titrant or 0.01639*N* solution must be tested once a month. The acid is checked against a fresh standard solution of sodium carbonate, as described below.

- Record on field notes any correction factors necessary to compensate for cartridge manufacturing anomalies and (or) variations in the stated acid normality for the lot of prefilled cartridges to be used.

CAUTION: When diluting concentrated acids, always:
"Do as you 'oughter' and add acid to water."

Prepare a sulfuric acid titrant solution:

To prepare your own acid titrant for the buret system, follow the procedure below (adapted from Fishman and Friedman, 1989).

1. Cautiously add 0.5 mL concentrated H_2SO_4 (specific gravity 1.84 grams per milliliter) to approximately 950 mL of fresh deionized water (DIW).

2. Mix thoroughly; dilute with DIW to the 1-liter (L) mark.

This recipe results in an acid concentration of roughly 0.018*N*. To determine the actual acid concentration, the solution must be standardized as described below. If a concentration of exactly 0.01639*N* is desired, the standardized solution may be diluted with DIW and restandardized.

Prepare the standard solution:

To prepare a fresh standard solution of 0.01639*N* sodium carbonate (Na_2CO_3):

1. Dry 1.0 gram (g) primary standard Na_2CO_3 at 150 to 160 °C for 2 hours.

2. Cool in a desiccator; weigh out 0.8686 g Na_2CO_3; add to a 1-L volumetric flask.

3. Dilute with DIW to the 1-L mark.

Standardize the sulfuric acid:

1. Calibrate the pH system following instructions in NFM 6.4.

2. Pipet 25 mL of sodium carbonate standard solution into a 100-mL beaker, and titrate with the sulfuric acid solution. Record the pH and volume of titrant added, following the procedure in section 6.6.4.A.

3. Determine the equivalence point of the titration using the inflection point method (section 6.6.4.B). The equivalence point is the point at which the change in pH per volume of titrant added is maximized, and generally will be found near pH 4.5.

4. Determine the normality of the acid as follows:

$$C_a = \frac{(25\ mL)\left(\frac{0.8686\ g\ Na_2CO_3}{1.0\ L}\right)\left(\frac{1\ mole\ Na_2CO_3}{105.989\ g\ Na_2CO_3}\right)\left(\frac{2\ eq}{1\ mole\ Na_2CO_3}\right)}{V_a} = \frac{(25\ mL)\left(0.01639\ \frac{eq}{L}\right)}{V_a}$$

where

C_a is acid normality, in equivalents (eq) per liter, and
V_a is volume of sulfuric acid added to reach the equivalence point, in milliliters.

5. Store the acid solution in a tightly sealed 1-L glass bottle. Label the bottle with its contents, normality, date of preparation, expiration date, and the preparer's initials and store it in a cool, dark place.

6.6.3 Collection and Processing

Collect and process the water samples in a manner that ensures that they represent environmental concentrations at the time of collection. Minimize the effects of wind, rain, cold, dust, and sun on the samples. Collect and (or) process the samples in a chamber to protect them from airborne particulates.

Before collecting or processing the sample, clean the samplers, compositing and splitting devices, sample bottles, measurement vessels, and other equipment that contacts the sample (for detailed procedures refer to NFM 3 and NFM 4).

- In the office laboratory, prerinse the sample bottles with deionized water and store them in sealable plastic bags until ready for field sampling (acid-rinsed sample bottles are recommended, especially for samples with low alkalinity or ANC).

► Field rinse the bottle(s) three times with the water to be sampled (sample filtrate for the alkalinity sample). If the amount of sample is limited or the triple rinse will cause the total field rinse volume to exceed 100 mL, DIW of appropriate quality may be substituted for the first 2 rinses.

► Do not field rinse the measurement vessels. Volumetric pipets and graduated cylinders should be clean and dry before use.

To collect and process the sample:

1. Filter the samples along with other anion samples, if determining alkalinity. The 0.45-µm flowthrough disposable filter capsule is the standard unit used by the USGS. Record on field forms if a different unit or membrane is used, as this can affect the determination.

2. Fill and securely cap two 250-mL sample bottles (instead of one 500-mL bottle) with the sample (filtrate for alkalinity) to ensure that there is sufficient volume to (a) repeat the titration, (b) preserve the integrity of the second aliquot after the first has been opened, and (c) accommodate any losses from spillage.

3. Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulfide, ferrous iron, and manganous manganese, and to prevent precipitation of mineral phases.

    - Loss of carbon dioxide (CO_2) from the sample, or addition of CO_2 to the sample, will not change the alkalinity or ANC determination, but chemical or physical reactions can cause concentrations of bicarbonate and carbonate to change within minutes.
    - Begin the titration as soon as possible, as there is less chance of chemical precipitation once acidification begins. If the titration is delayed, maintain the samples at the temperature of their ambient environment.
    - If there is a tendency for mineral precipitation, collect and process the sample under an inert gas atmosphere.

Surface water

Collect and process a representative sample according to USGS-approved methods (see NFM 4.1, 5.0, 5.1, and 5.2).

► Most USGS water-quality programs require filtration of alkalinity samples through a 0.45-µm membrane.

► To collect and process samples from anoxic lake or reservoir depth intervals, adapt procedures described below for groundwater and the procedures for suboxic or anoxic water described in NFM 4.0.2, "Preventing sample contamination."

Groundwater

Collect the sample as close to the source as possible, minimize aeration of the sample, and take the precautions described in step 3 above. See NFM 4.0.2, 4.2, 5.0, 5.1, and 5.2 for groundwater sample collection and filtration methods.

- Purge the well (NFM 4.2) and connect the filter unit in-line with the pump.
- Flush and fill the sample lines and filter unit with sample water so as to exclude air.

6.6.4 Measurement

Alkalinity, ANC, and concentrations of bicarbonate, carbonate, and hydroxide species are most commonly determined by analyzing acidimetric-titration data with either the inflection point titration method (section 6.6.4.B) or the Gran function plot method (section 6.6.4.C).

- **The Inflection Point Titration (IPT) method**, also called the incremental titration method, is adequate for most waters and study needs. Difficulty in identifying the inflection points using the IPT method increases as the ratio of organic acids to carbonate species increases and (or) as the alkalinity decreases.
- **The Gran function plot (Gran) method** is recommended for water in which the alkalinity or ANC is expected to be less than about 0.4 milliequivalents per liter (meq/L) (20 milligrams per liter (mg/L) as $CaCO_3$), or in which conductivity is less than 100 microsiemens per centimeter (µS/cm), or if there are appreciable noncarbonate contributors or measurable concentrations of organic acids.

The Fixed Endpoint method (titration to pH 4.5) rarely is used and is no longer recommended by the USGS for determining alkalinity values because it is less accurate than the IPT and Gran methods. This decrease in accuracy is evident particularly for low concentrations of total carbonate species and for water with significant organic and other noncarbonate contributors to alkalinity or ANC.

Titrate a filtered sample if checking the charge balance or if reporting results as carbonate alkalinity.

6.6.4.A Titration Systems and Procedures

Titration procedures are identical for surface-water and groundwater determinations on filtered or unfiltered aliquots of fresh to saline water samples. Become familiar with the information and detailed instructions for the buret and digital titration systems and the IPT and Gran methods before proceeding with the titration.

Titration system

Select the titration system to be used.

- The digital titration system is convenient but may be less precise and less accurate than the buret system because of mechanical inadequacies. Good technique is necessary to produce acceptable results.

- The buret system can be cumbersome and fragile in the field, and using the system requires experience to execute with precision and accuracy.

- A micrometer buret can achieve accuracy to 0.1 mg/L (determinations are reported to whole numbers if the result is greater than or equal to 100 mg/L as $CaCO_3$).

The buret system can yield better accuracy than the digital titrator.

Sample volume and acid normality

The methods as presented in this manual require electrometric titration of a sample with incremental additions of a strong acid (commonly H_2SO_4) of known normality. Suggested combinations of titrant normality and sample volume for various ranges of alkalinity or ANC values are given in table 6.6–2. These ranges can overlap at the thresholds indicated and should not be interpreted as absolute. Generally, 1.600*N* acid is too strong for most samples and only is used when alkalinity or ANC is greater than 4.0 meq/L (200 mg/L as $CaCO_3$). A more dilute acid (0.01639*N*) commonly is used with the buret system.

Select the size of the delivery and measurement vessels according to the volume of sample needed. Use a volumetric pipet for an alkalinity sample and a graduated cylinder or digital balance for an ANC sample. When selecting the measurement vessel:

- 50 mL of sample in a 100-mL beaker is typical for most routine work.
- Use 100 mL (or more) of sample in a 150-mL (or larger) beaker for samples with low alkalinity or ANC.
- Use 25 mL or less of a sample in a 50-mL beaker for samples with high alkalinity or ANC. Larger volumes of sample may be used in combination with higher normality titrant.

Table 6.6–2. Suggested sample volume and titrant normality for approximate ranges of alkalinity or ANC.

[ANC, acid neutralizing capacity as determined on an unfiltered sample; meq/L, milliequivalents per liter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; mL, milliliter; >, greater than]

ANC or alkalinity (meq/L)	ANC or alkalinity (mg/L as $CaCO_3$)	Sample volume (mL)	Titrant normality
0–1.0	0–50	100 (or larger)	0.1600 (or lower)
1.0–4.0	50–200	50	0.1600
4.0–20	200–1,000	100	1.600
>20	>1,000	50	1.600

To achieve greater accuracy, use lower normality titrant, decrease the volume of acid increments, or use a larger sample volume.

To pipet the sample for alkalinity determination:

A small volume of sample will remain in the tip of class A "TD" volumetric pipets—do not blow or shake it out.

1. Suspend the pipet tip vertically in a beaker, touching neither the walls nor the contents of the receiving vessel.

2. Allow the sample to drain freely until the liquid it contains reaches the bottom of the pipet.

3. Touch the pipet tip to the beaker wall until the flow from the pipet stops—leave the tip in contact with the beaker wall for an additional 10 seconds after the flow stops.

Stirring method

When titrating, stirring helps to establish a uniform mixture of sample and titrant, as well as the equilibrium between sensors and sample. Select a stirring method and use a consistent technique.

- **If using a magnetic stirrer, stir the sample slowly and continuously,** using a small stir bar; avoid creating a vortex and large streaming potentials. If using a digital titrator, keep the delivery tube immersed throughout the procedure but keep the aperture of the tube away from the stir bar to avoid bleeding acid from the tube to the sample between titrant additions.

- If swirling the sample to mix, make the pH measurement as the sample becomes quiescent, after each addition of titrant.

- Avoid splashing the sample out of the beaker or onto the beaker walls. Droplets on the beaker walls can be rinsed down with deionized water. If you splash the sample out of the beaker, you must start over.

- Allow sufficient time between titrant additions for the pH value displayed on the instrument to equilibrate. Emphasis should be placed on maintaining a consistent technique (titrant additions every 15 to 30 seconds) rather than waiting for the instrument to "lock on" to a particular pH value.

Titration methods

Select and plan your method of titration.

- **IPT method.** Titrate cautiously on both sides of the expected equivalence points (fig. 6.6–1).
  - **If concentrations of contributing carbonate species will be determined and the initial pH is greater than 8.1:** Using small increments of acid, titrate carefully to a pH of about 8.0. The data to pH 8.0 are important in determining the carbonate equivalence point.
  - **If concentrations of contributing carbonate species will not be determined:** Titrate rapidly at first, adding relatively large acid increments to bring the pH to about 5.5. Do not skip the pH range above 5.5 completely, or you may pass the equivalence point.
  - **If a pH is below 5.5:** Titrate slowly, using small increments of acid. This region is important in determining the bicarbonate equivalence point. Titrate to a pH of 4.0 or lower (3.5 if the sample alkalinity or ANC range is unknown or if the sample contains high concentrations of noncarbonate contributors, such as organic acids).
- **Gran method.** Collect data between and beyond the expected equivalence points (fig. 6.6–1).
  - **If concentrations of contributing carbonate species will be determined:** Record titration points throughout the entire pH range of the titration. A good rule of thumb is to collect data along the titration curve roughly every 0.2 to 0.3 pH units. The points on the titration curve that are somewhat removed from the carbonate and bicarbonate equivalence points are used by the Gran method (Pankow, 1991).
  - **If concentrations of contributing carbonate species will not be determined:** It is not necessary to develop incremental titration points above a pH of about 5.5.
  - **Titrate to a pH of 3.5 or lower** (3.0 or less if the sample alkalinity or ANC range is unknown). A sufficient number of titration points beyond the equivalence point are needed to ensure accuracy.

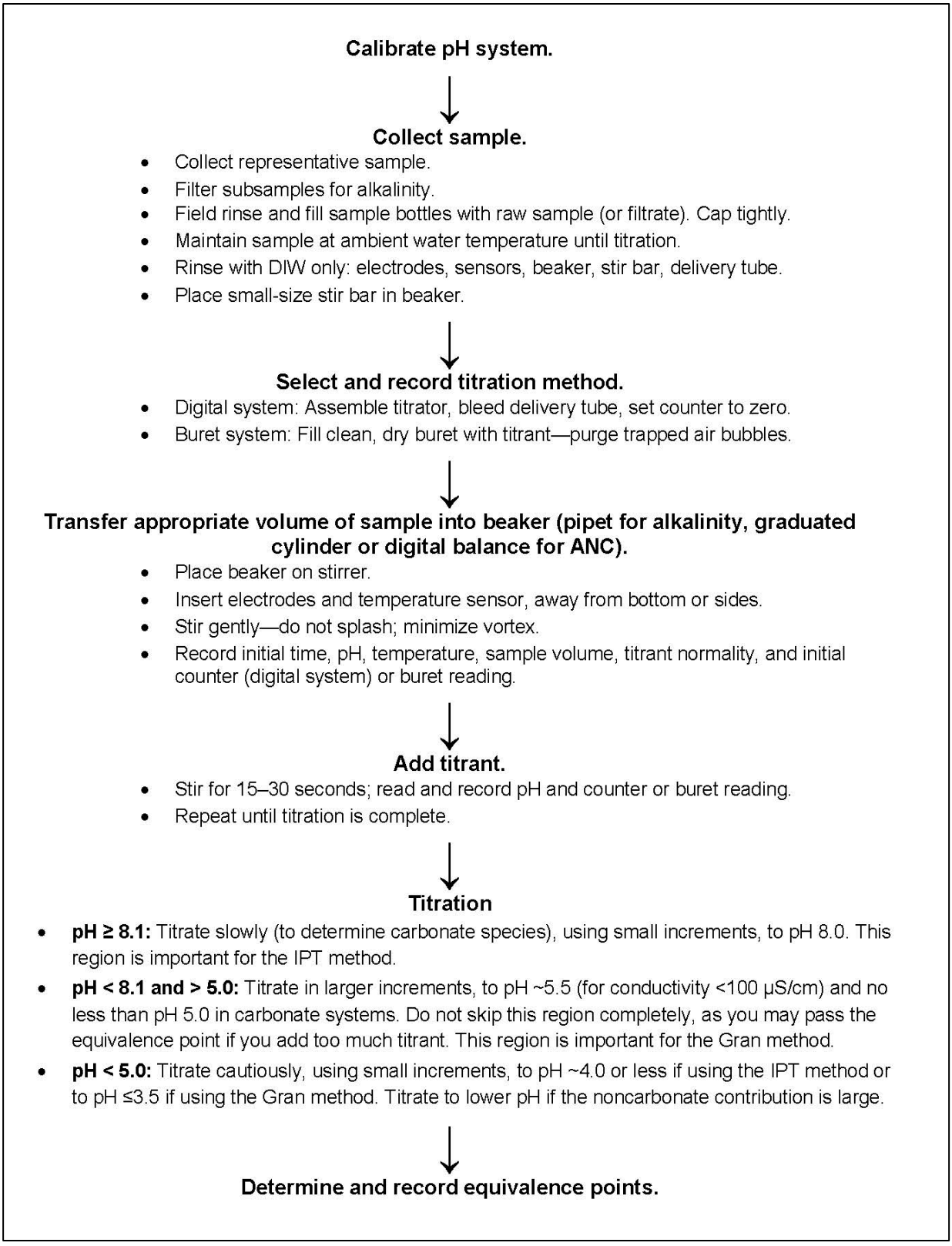

Figure 6.6–1. Summary of alkalinity or ANC titration procedures.

Quality-control (QC) procedures

► Verify your accuracy and ability to reproduce the alkalinity or ANC determinations by using reference samples and repeating the titration periodically on duplicate or triplicate samples. The frequency and distribution of QC determinations are established by study requirements, and whenever the accuracy or precision of the digital titrator is in question. See guidance in 6.6.1.A on maintenance of the digital titrator.

RULE OF THUMB:

QC samples should be collected and titrated no less than every tenth sample. The determination on a filtered sample should be reproducible within ±5 percent when titrating a duplicate aliquot from the same batch of sample filtrate.

- For filtered samples with alkalinity less than 0.4 meq/L (20 mg/L as $CaCO_3$), reproducibility should be between 5 and 10 percent.

- If the alkalinity is about 0.02 meq/L or less, differences between duplicate samples are likely to exceed 10 percent because of rounding errors alone. Such rounding errors may be reduced by using a larger sample volume or a lower normality of titrant.

► **Compare ANC with alkalinity values**—When interferences are absent, titration of an unfiltered sample may result in a determination identical to or within 5 percent of the filtered sample and can be used as a QC check.

– If filtered and unfiltered values fail the ±5-percent criterion, perform the QC check on duplicate filtered samples.

– Reproducibility of the ANC determination to within 5 percent on duplicate unfiltered samples can be problematic when the sample has large amounts of particulate matter—extend the quality-assurance criterion to ±10 percent.

To obtain the most accurate results for carbonate species, titrate while at the field site, without delay.

Digital titrator

Be thoroughly familiar with the operation of the digital titrator before field use. The procedures in this section describe the use of a Hach® digital titrator. A plunger in the digital titrator forces acid from the titrant cartridge through the delivery tube. The plunger is controlled by a main-drive screw, which in turn is controlled by rotation of the delivery knob. The delivery knob controls the volume of titrant delivered through the delivery tube, as indicated by a digital counter (800 counts = 1 mL).

To use the digital titrator:

1. Equilibrate titrant temperature to sample temperature.

2. Assemble the digital titrator.

    - Depress the plunger-release button and retract the plunger.
    - Insert the titrant cartridge into the titrator and twist the cartridge one-quarter turn to lock it into position.
    - Carefully depress the plunger-release button and push the plunger forward until it makes contact with the Teflon® seal inside the cartridge.

3. Remove the vinyl cap from the cartridge (save the cap) and insert the straight end of the delivery tube into the cartridge.

    - Do not push the delivery tube beyond the cartridge tip. Do not alter the delivery tube.
    - Use a new delivery tube for each assembly of the titrator. Discard the tube after use.
    - Reuse of the delivery tube is not recommended. If reuse becomes necessary: rinse it with DIW; store in a clean sealable plastic bag; only reuse with the same titrant normality; do not reuse if it shows wear.

4. To ensure that no air bubbles or water are in the delivery tube, hold the titrator with the cartridge tip up and turn the delivery knob to force a few drops of titrant through the end of the delivery tube. Rinse the exterior of the tube with DIW and blot acid or water droplets from the tube before inserting it into the sample.

5. Set the digital counter to zero using the counter-reset knob (taking care not to turn the delivery knob).

6. Transfer the selected volume of the sample (pipet for alkalinity, graduated cylinder or digital balance for ANC) to a clean beaker. If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before transferring the sample to the beaker. Do not use a magnetic stirrer if sample conductivity is less than 100 µS/cm. Place the beaker on the stirrer.

7. Rinse the pH and temperature sensors with DIW. Gently blot with lint-free paper any water droplets adhering to the sensors.

8. Insert the sensors into the beaker.

    - Do not let sensors touch the bottom or wall of the beaker.
    - The amount of sample in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.

9. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.

    - Do not splash sample onto the beaker wall or out of the beaker.
    - Minimize the vortex caused by magnetic stirring, and ensure that the stir bar does not hit the pH electrodes.
    - Record on the field form the pH and temperature values, the initial counter reading (it should read "0000"), the titrant normality, the time, and the sample volume. If available, record the sample conductivity.

10. Immerse the end of the titrant delivery tube in the sample. To prevent bleeding of the titrant from the delivery tube, keep the aperture of the delivery tube away from the stir bar.

11. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow a consistent 15 to 30 seconds after each addition for equilibration, then record the pH and counter readings.

    - **pH ≥ 8.1** —To determine the carbonate equivalence point using the IPT method, slowly add the titrant in small (but no less than three digital-count) increments until sample pH is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
    - **pH < 8.1 and ≥ 5.0** —If using the IPT method, titrate with larger increments to pH ~5.0 (5.5 for sample alkalinity or ANC <0.4 meq/L (<20 mg/L as $CaCO_3$) or sample conductivity <100 µS/cm). Do not skip this pH region entirely; the equivalence point might be passed if too much acid is added. If using the Gran method, collect data points every 0.2 to 0.3 pH units in this region.
    - **pH < 5.0** —To determine the bicarbonate equivalence point with the IPT method, cautiously add the titrant in small (but no less than three digital-count) increments from pH 5.0 to ≤ 4.0. (The most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters.) If using the Gran method, extend the titration to pH ≤ 3.5 (≤ 3.0 for samples high in organic acids or other noncarbonate contributors, or when the alkalinity or ANC range is unknown). The Gran method relies on these low pH points beyond the equivalence point.

To reduce errors in the delivery of acid titrant, add the acid in minimum increments of three digital counts.

12. After completing the titration, remove the digital titrator from the sample; depress the plunger release, retract the plunger, and remove the titrant cartridge. Immediately replace the vinyl cap on the cartridge tip. Rinse the delivery tube with DIW or discard.

13. Analyze the titration data to determine the carbonate and bicarbonate equivalence points using the IPT method (section 6.6.4.B) and (or) the Gran method (section 6.6.4.C).

14. Calculate the sample alkalinity or ANC and the concentrations of the carbonate species from the equivalence points, as described in section 6.6.5.

Buret titrator

When using a buret, exercise caution to ensure that the acid does not evaporate or become contaminated with extrinsic matter or moisture. The titrant temperature should be equilibrated to the sample temperature before use. Always empty the buret after each use. Never reuse the titrant solution; dispose of the solution properly.

To titrate with a buret:

1. Fill a clean, dry buret with sulfuric acid titrant (0.01639*N* or other known concentration).

    - Use a 10-mL semimicroburet with 0.05-mL graduations and a Teflon® stopcock for samples with alkalinity or ANC less than 4 meq/L (200 mg/L as $CaCO_3$).
    - Use a 25-mL buret with 0.1-mL graduations and a Teflon® stopcock for samples with alkalinity or ANC of 4 meq/L (200 mg/L as $CaCO_3$) or greater and when the sample pH exceeds 8.1.
    - If greater accuracy is desired, use a Gilmont®-type micrometer buret.

2. Make sure no air bubbles are trapped in the buret or the buret stopcock. Record on field forms the sulfuric acid normality and initial buret reading.

3. Transfer the selected volume of sample (pipet for alkalinity, graduated cylinder or digital balance for ANC) to a clean beaker. **Do not pipet by mouth.**

    - If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before transferring the sample to the beaker. Place the beaker on a magnetic stirrer.
    - Do not use a magnetic stirrer if sample conductivity is <100 µS/cm.

4. Rinse the pH and temperature sensors with DIW. Gently blot water droplets adhering to the sensors with lint-free paper (residual DIW will not affect the determination).

5. Insert the sensors into the beaker.

   - Do not let sensors touch the bottom or wall of the beaker.
   - Sample depth in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.

6. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.

   - Do not splash the sample onto the beaker wall or out of the beaker.
   - Minimize the vortex caused by magnetic stirring, and ensure that the stir bar does not hit the pH electrodes.
   - Record on the field form the pH and temperature values, the initial buret reading, the titrant normality, the time, and the sample volume. If available, record the sample conductivity.

7. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow a consistent 15 to 30 seconds after each addition for equilibration, then record the pH and buret readings.

   - **pH ≥ 8.1** —To determine the carbonate equivalence point using the IPT method, add the titrant drop by drop in 0.01-mL increments until the pH is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
   - **pH < 8.1 and ≥ 5.0** —If using the IPT method, titrate with larger increments to pH ~5.0 (5.5 for sample with alkalinity or ANC <0.4 meq/L (<20 mg/L as $CaCO_3$) or with sample conductivity <100 µS/cm). Do not skip this pH region entirely; the equivalence point might be passed if too much acid is added. If using the Gran method, collect data points every 0.2 to 0.3 pH units in this region.
   - **pH < 5.0** —To determine the bicarbonate equivalence point with the IPT method, cautiously add the titrant drop by drop in 0.01-mL increments from pH 5.0 to ≤4.0. (The most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters.) If using the Gran method, extend the titration to pH ≤3.5 (≤3.0 for samples high in organic acids or other noncarbonate contributors, or when the alkalinity or ANC range is unknown). The Gran method relies on these low pH points beyond the equivalence point.

TECHNICAL NOTE: 0.01 mL of a standard 0.05-mL drop of titrant tends to remain on the buret tip. To dispense a 0.01-mL titrant drop, quickly rotate the stopcock through 180 degrees (one-half turn) and then rinse the titrant from the buret tip into the beaker with a small quantity of DIW.

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8. Analyze the titration data to determine the carbonate and bicarbonate equivalence points using the IPT method (section 6.6.4.B) and (or) the Gran method (section 6.6.4.C).

9. Calculate the sample alkalinity or ANC and the concentrations of the carbonate species from the equivalence points, as described in section 6.6.5.

6.6.4.B Inflection Point Titration Method

The inflection point titration (IPT) method, also known as the incremental titration method, uses the inflection points of the titration curve to determine equivalence points. For many natural water samples, these equivalence points are near pHs of 8.3 and 4.5, but it is more accurate to calculate their exact locations from the titration data.

Inflection points are the points of maximum rate of change in pH per volume of titrant added. **Near equivalence points, rapid pH changes occur with small additions of titrant. For this reason, the titration must be performed slowly and cautiously near the expected equivalence points, using small incremental additions of titrant.** The relative error of the determinations can be within ±4 percent if the equivalence point is recognizable within ±0.3 pH unit of the true equivalence point.

To determine the inflection point(s), you can construct a titration curve either by (1) plotting the change in pH divided by the change in titrant volume against the volume of titrant added to the sample; (2) calculating such values in a table or spreadsheet; or (3) using a titration-curve analyzer such as the USGS Alkalinity Calculator or PCFF program (see section 6.6.5.C).

- Graphing the titration curve always is advisable. Such plots are helpful in uncovering data-entry errors and spurious maxima that might confuse the detection of the inflection point(s).

- More than one inflection point in close proximity indicates that the true inflection point has been missed. If this occurs, titrate a duplicate sample using smaller acid increments near the inflection point or use a Gran plot. Note that if the acid increments are too small, the location of the inflection points may become masked by noise in the data.

- If the maximum rate of change in pH per volume of titrant occurs at two or more points near an equivalence point (two or more points are “tied” for the maximum value), then determine the location of the equivalence point as the middle of the range where ties were produced. For example, if the maximum rate occurs at digital counts 120, 122, and 126, then the calculated location of the equivalence point is at digital count 123.

- If no clear inflection point(s) can be determined easily, interferences from weak organic acids are likely—use the Gran method.

The example that follows for IPT–1A shows the results of an IPT analysis of a typical titration using a digital titrator. The example for IPT–1B shows similar results using a buret titration. Each of these titrations has inflection points at both the carbonate and bicarbonate equivalence points.

Example IPT–2 shows the results of the IPT method applied to a low alkalinity sample. Note that this sample has only one inflection point.

Example IPT–1A: IPT method using the digital titrator

A titration was performed on a natural water sample from the South Diamond Canal inflow to the Donner und Blitzen River, Oregon. The data are plotted in figure 6.6–2 and listed in table 6.6–3. Using the IPT method, the maximum rates of change of pH per volume of titrant added occur at pH 8.27 and 4.50 (at counts 186 and 1014). Because these slopes represent changes between two points, the actual inflection points are located between counts 183 and 186 for the carbonate equivalence point and between 1011 and 1014 for the bicarbonate equivalence point. Thus, the calculated digital-counter values for the inflection points are 184.5 (185) and 1012.5 (1013). The error in using 1014 rather than 1013 typically is insignificant but the larger the increments used, the greater the error. Calculation of the correct inflection point results in smaller errors.

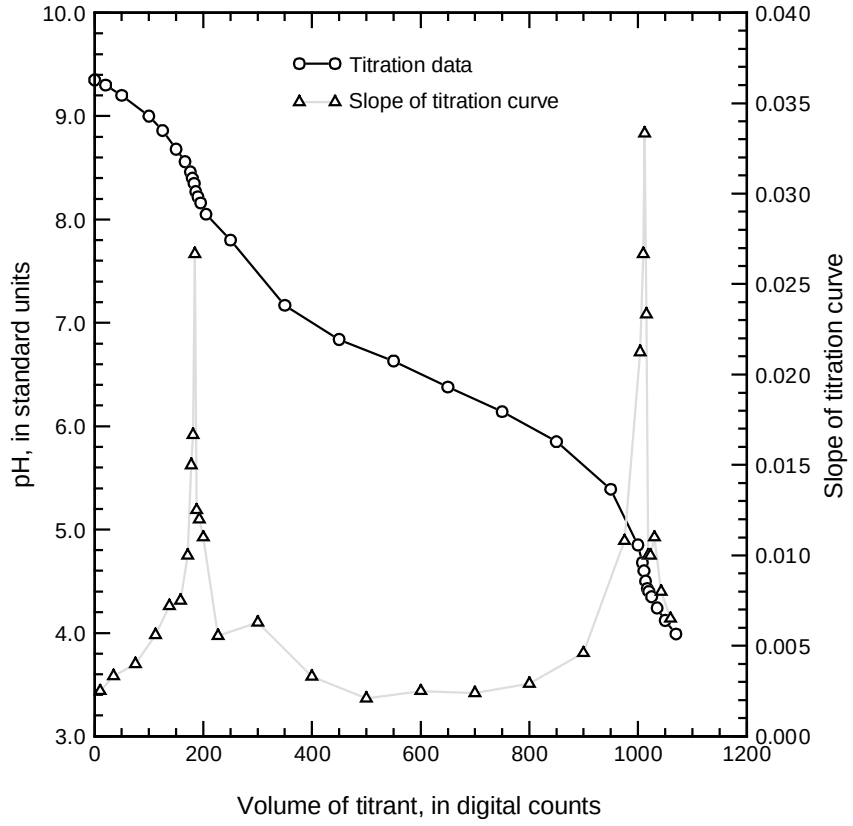

Figure 6.6–2. Plot of data for an inflection point titration using a digital titrator (Example IPT–1A).

Table 6.6–3. Typical inflection point titration data using a digital titrator (Example IPT–1A).

[—, no data. The shaded rows indicate where the maximum rates of change of pH per digital count occur (at pH 8.27 and 4.50 in this sample)]

pH (standard units)	Change in pH (standard units)	Counter reading (counts)	Change in counter (counts)	Change in pH per change in counter
9.35	—	0	—	—
9.30	0.05	20	20	0.0025
9.20	.10	50	30	.0033
9.00	.20	100	50	.0040
8.86	.14	125	25	.0056
8.68	.18	150	25	.0072
8.56	.12	166	16	.0075
8.46	.10	176	10	.0100
8.40	.06	180	4	.0150
8.35	.05	183	3	.0167
8.27	**.08**	**186**	**3**	**.0267**
8.22	.05	190	4	.0125
8.16	.06	195	5	.0120
8.05	.11	205	10	.0110
7.80	.25	250	45	.0056
7.17	.63	350	100	.0063
6.84	.33	450	100	.0033
6.63	.21	550	100	.0021
6.38	.25	650	100	.0025
6.14	.24	750	100	.0024
5.85	.29	850	100	.0029
5.39	.46	950	100	.0046
4.85	.54	1000	50	.0108
4.68	.17	1008	8	.0213
4.60	.08	1011	3	.0267
4.50	**.10**	**1014**	**3**	**.0333**
4.43	.07	1017	3	.0233
4.40	.03	1020	3	.0100
4.35	.05	1025	5	.0100
4.24	.11	1035	10	.0110
4.12	.12	1050	15	.0080
3.99	.13	1070	20	.0065

Example IPT–1B: IPT method using the buret system

If the sample in Example IPT–1A had been titrated with the buret system, the titration data would be similar to that plotted in figure 6.6–3 and given in table 6.6–4. Using the IPT method, the maximum rates of change of pH per volume of titrant added occur at pH 8.27 and 4.50 (at 1.86 and 10.14 mL of acid added). Because these slopes are changes between two points, the actual inflection points are located between 1.83 and 1.86 mL for the carbonate equivalence point, and between 10.11 and 10.14 mL for the bicarbonate equivalence point. The calculated titrant volumes for the inflection points, therefore, are 1.85 and 10.13 mL.

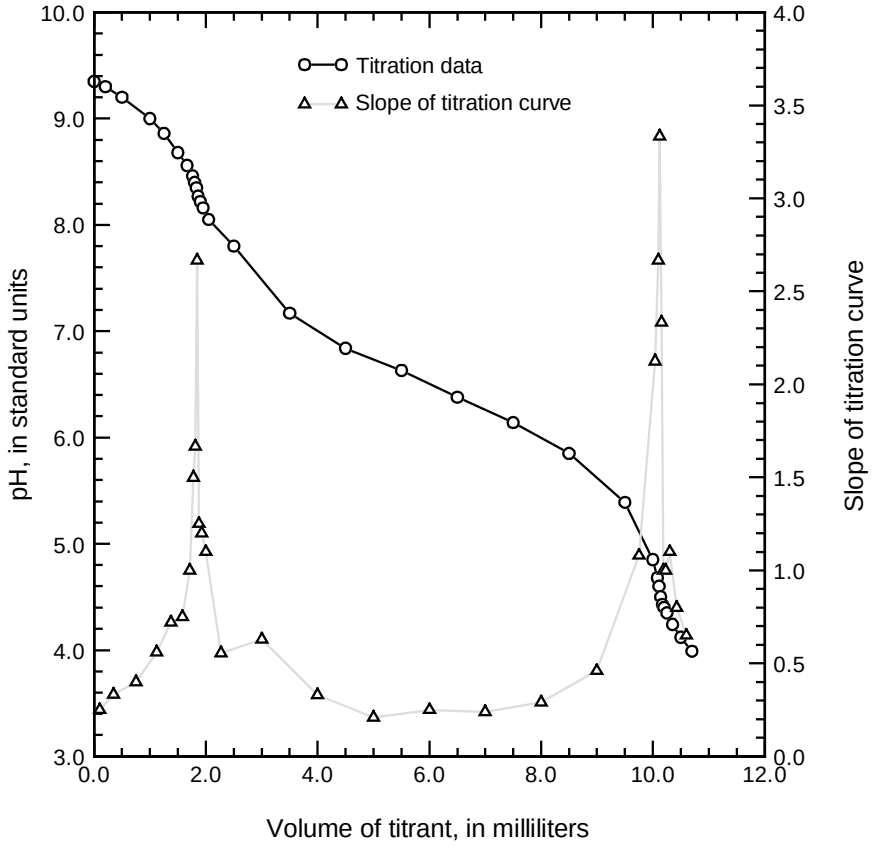

Figure 6.6–3. Plot of data for an inflection point titration using a buret (Example IPT–1B).

Table 6.6–4. Typical inflection point titration data using a buret (Example IPT–1B).

[—, no data. The shaded rows indicate where the maximum rates of change of pH per volume of titrant occur (at pH 8.27 and 4.50 in this sample); mL, milliliter]

pH (standard units)	Change in pH (standard units)	Buret reading (mL)	Titrant volume (mL)	Change in volume (mL)	Change in pH per change in volume
9.35	—	1.20	0.00	—	—
9.30	0.05	1.40	.20	0.20	0.250
9.20	.10	1.70	.50	.30	.333
9.00	.20	2.20	1.00	.50	.400
8.86	.14	2.45	1.25	.25	.560
8.68	.18	2.70	1.50	.25	.720
8.56	.12	2.86	1.66	.16	.750
8.46	.10	2.96	1.76	.10	1.000
8.40	.06	3.00	1.80	.04	1.500
8.35	.05	3.03	1.83	.03	1.667
8.27	**.08**	**3.06**	**1.86**	**.03**	**2.667**
8.22	.05	3.10	1.90	.04	1.250
8.16	.06	3.15	1.95	.05	1.200
8.05	.11	3.25	2.05	.10	1.100
7.80	.25	3.70	2.50	.45	.556
7.17	.63	4.70	3.50	1.00	.630
6.84	.33	5.70	4.50	1.00	.330
6.63	.21	6.70	5.50	1.00	.210
6.38	.25	7.70	6.50	1.00	.250
6.14	.24	8.70	7.50	1.00	.240
5.85	.29	9.70	8.50	1.00	.290
5.39	.46	10.70	9.50	1.00	.460
4.85	.54	11.20	10.00	.50	1.080
4.68	.17	11.28	10.08	.08	2.125
4.60	.08	11.31	10.11	.03	2.667
4.50	**.10**	**11.34**	**10.14**	**.03**	**3.333**
4.43	.07	11.37	10.17	.03	2.333
4.40	.03	11.40	10.20	.03	1.000
4.35	.05	11.45	10.25	.05	1.000
4.24	.11	11.55	10.35	.10	1.100
4.12	.12	11.70	10.50	.15	.800
3.99	.13	11.90	10.70	.20	.650

Example IPT–2: IPT method for a low alkalinity sample

A water sample collected from Little Abiqua Creek near Scotts Mills, Oregon, provides a good example for a low-alkalinity titration. In this titration, 200 mL of filtered sample were titrated with 0.16*N* titrant and analyzed by the IPT method. The results are shown in figure 6.6–4 and table 6.6–5. The bicarbonate equivalence point was found near a pH of 5.25, between digital counts 134 and 137. The correct digital-counter value at the inflection point, therefore, is 136 (135.5) counts. This results in a calculated alkalinity of 6.8 mg/L as $CaCO_3$.

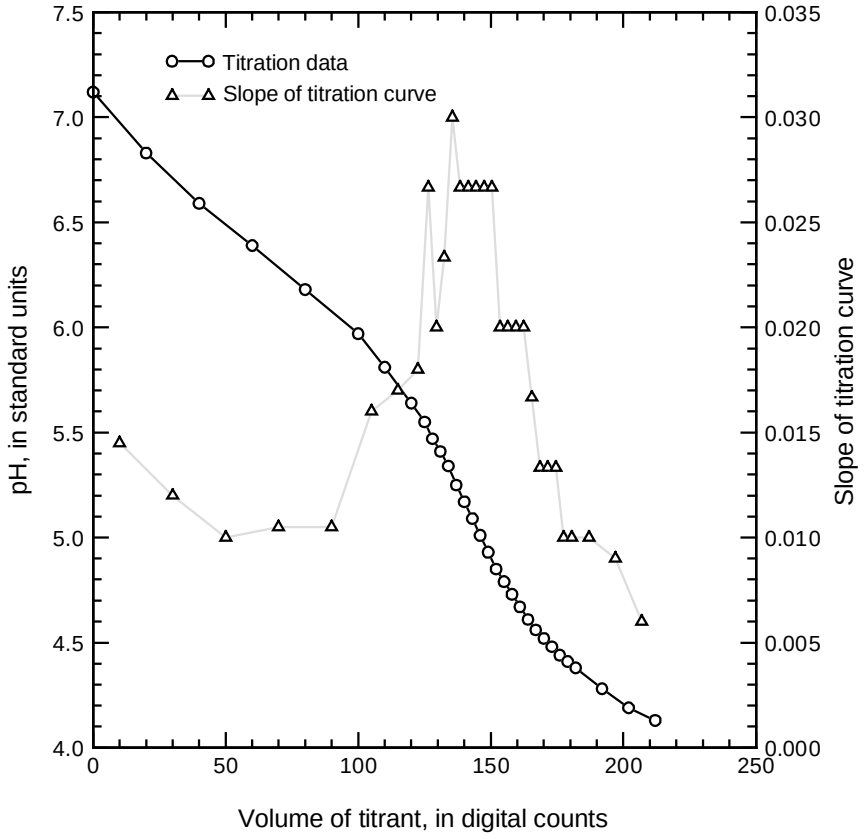

Figure 6.6–4. Plot of data for an inflection point titration of a low-alkalinity sample (Example IPT–2).

Table 6.6–5. Inflection point analysis for a low-alkalinity sample (Example IPT–2).

[—, no data. The shaded row indicates where the maximum rate of change of pH per digital count occurs (at pH 5.25 in this sample)]

pH (standard units)	Change in pH (standard units)	Counter reading (counts)	Change in counter (counts)	Change in pH per change in counter
7.12	—	0	—	—
6.83	0.29	20	20	0.0145
6.59	.24	40	20	.0120
6.39	.20	60	20	.0100
6.18	.21	80	20	.0105
5.97	.21	100	20	.0105
5.81	.16	110	10	.0160
5.64	.17	120	10	.0170
5.55	.09	125	5	.0180
5.47	.08	128	3	.0267
5.41	.06	131	3	.0200
5.34	.07	134	3	.0233
5.25	**.09**	**137**	**3**	**.0300**
5.17	.08	140	3	.0267
5.09	.08	143	3	.0267
5.01	.08	146	3	.0267
4.93	.08	149	3	.0267
4.85	.08	152	3	.0267
4.79	.06	155	3	.0200
4.73	.06	158	3	.0200
4.67	.06	161	3	.0200
4.61	.06	164	3	.0200
4.56	.05	167	3	.0167
4.52	.04	170	3	.0133
4.48	.04	173	3	.0133
4.44	.04	176	3	.0133
4.41	.03	179	3	.0100
4.38	.03	182	3	.0100
4.28	.10	192	10	.0100
4.19	.09	202	10	.0090
4.13	.06	212	10	.0060

6.6.4.C Gran Function Plot Method

Gran function plots commonly are used to determine alkalinity and ANC in low ionic-strength water, water with low carbonate concentrations, and water with measurable concentrations of titratable organic compounds. Gran's method does not rely on the presence of inflection points in the titration curve; therefore, it particularly is useful for waters with low alkalinity.

Using the known chemistry of carbonic acid and some simplifying assumptions, Gran's method linearizes a set of functions that describe parts of the titration curve (Gran, 1952). The linearizing assumptions used by Gran's method are valid only for data that are some distance away from the equivalence points (Pankow, 1991).

- Collect titration points throughout the entire pH range of the titration. A good rule of thumb is to collect data along the titration curve roughly every 0.2 to 0.3 pH unit.

- Titrate to a pH of 3.5 or lower (3.0 or less if the alkalinity or ANC range is unknown for the waters sampled). A sufficient number of titration points beyond the bicarbonate equivalence point are needed to ensure the accuracy of the calculation.

In contrast to the IPT method, the Gran function plot method uses data that are somewhat removed from the equivalence points.

Gran Functions

During an alkalinity titration (carbonate system), the hydrogen ions added convert carbonate to bicarbonate and then bicarbonate to carbonic acid. The titration continues until no more species are reacting. When this process is complete, additional hydrogen ions will be in excess in the solution. **The F_1 Gran function plot identifies the point at which all alkalinity has been titrated and hydrogen ions begin to be in excess.** Beyond the bicarbonate equivalence point, the shape of the curve is determined by hydrogen ions in excess of all hydrogen ion acceptors in the sample. Similar relations are used with the Gran functions in other parts of the titration curve.

Two Gran functions can be calculated for each equivalence point in the titration. Including the equivalence points for hydroxide, carbonate, and bicarbonate, six Gran functions (F_1 through F_6) are useful for analyzing titration data from natural water samples. The functions for the hydroxide equivalence point, however, commonly are not used. Derivations of these Gran functions are available (Stumm and Morgan, 1996).

For an acidimetric titration, the six Gran functions are

$$F_1 = (V_o + V_t)(10^{-pH})/\gamma = (V_t - V_s)C_a$$
$$F_2 = (V_s - V_t)10^{-pH} = (V_t - V_w)K_1'$$
$$F_3 = (V_t - V_w)10^{pH} = (V_s - V_t)/K_1'$$
$$F_4 = (V_s - 2V_w + V_t)10^{pH} = (V_w - V_t)/K_2'$$
$$F_5 = (V_w - V_t)10^{-pH} = (V_t - V_x)K_2'$$
$$F_6 = (V_o + V_t)10^{pH} = (V_x - V_t)C_a/K_w'$$

where

V_o is initial volume of the sample;
V_t is volume of acid titrant added;
V_s is titrant volume at the bicarbonate equivalence point;
V_w is titrant volume at the carbonate equivalence point;
V_x is titrant volume at the hydroxide equivalence point;
C_a is the normality of the acid titrant;
γ is the activity coefficient for H^+;
K_1' is the first acid dissociation constant for H_2CO_3, corrected for the activity of carbonate species;
K_2' is the second acid dissociation constant for H_2CO_3, corrected for the activity of carbonate species; and
K_w' is the acid dissociation constant for water, corrected for the activity of hydroxide.

Note that if these functions are calculated in the correct sequence, the function value on the left side of each equation will consist of known values. By extrapolating these function values to zero, the right side of each equation can be set to zero and can be used to solve for a previously unknown equivalence point.

- The F_1 function, followed by F_2, is the most commonly used Gran function.

- The Gran functions F_1 and F_3 are useful in determining the bicarbonate equivalence point because F_1 and F_3 are zero when $V_t = V_s$. Similarly, F_2 and F_4 are used to determine the carbonate equivalence point ($V_t = V_w$), whereas F_5 and F_6 can be used to determine the hydroxide equivalence point ($V_t = V_x$).

Gran Function Plots

Gran function plots are made by plotting each of the Gran functions against titrant volume (V_t) and fitting a line through the data points for each function in a particular pH region.

- The F_1 function is valid for the pH range just below the bicarbonate equivalence point. The F_1 data only become linear somewhat beyond the bicarbonate equivalence point; therefore, it is often necessary to titrate the sample down to a pH between 3.5 and 3.0. For systems with measurable concentrations of organic acids, titrate to pH 2.5 (Baedecker and Cozzarelli, 1992).

- Functions F_2 and F_3 are valid in the pH range between the carbonate and bicarbonate endpoints.

- Functions F_4 and F_5 are valid for pH values between the carbonate and hydroxide endpoints.

- Function F_6 is valid for pH values higher than the hydroxide endpoint.

Equivalence points are found by extrapolating each function to where it crosses the x-axis. An idealized Gran analysis would result in a plot such as that shown in figure 6.6–5. The F_1 and F_2 functions are the most commonly used Gran functions.

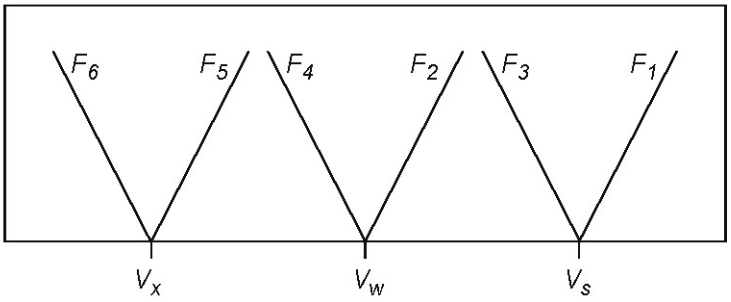

Figure 6.6–5. An idealized Gran function plot, showing six Gran functions.

The F_1 function must be calculated first. In order to calculate F_2, one needs to know the location of the bicarbonate equivalence point, V_s, which is obtained from the solution of F_1.

Similarly, the value of V_w from an analysis of F_2 is necessary to plot and analyze F_3. Function F_4 requires both V_s and V_w from the results of F_2 and either F_1 or F_3. Function F_5 requires a value for V_w from the results of either F_2 or F_4.

TECHNICAL NOTE: The Gran functions also can be used to extract useful information from their fitted slopes, such as the values of acid-titrant concentration (C_a) and the various acid dissociation constants. Further explanation can be found in Stumm and Morgan (1996) and Pankow (1991).

To prepare a Gran function plot:

1. **Bicarbonate equivalence point (Gran function F_1).** Plot $(V_o + V_t)\ 10^{-pH}$ against the titrant volume, V_t. (This formulation ignores activity corrections, setting $\gamma = 1.0$.)

   - When developing this function, V_o and V_t must be in the same units (probably mL).
   - The value of V_t on the x-axis can be in either milliliter or digital counts.

2. Extrapolate a straight line through the data in the region beyond the bicarbonate equivalence point to where it meets the x-axis at $F_1 = (V_o + V_t)\ 10^{-pH} = 0$ or $V_t = V_s$. That point is the bicarbonate equivalence point. See **Example Gran–1** for an illustration of steps 1 and 2.

3. **Carbonate equivalence point (Gran function F_2).** Using the value of V_s from step 2, plot $(V_s - V_t)\ 10^{-pH}$ against the titrant volume, V_t, in the region between the carbonate and bicarbonate equivalence points. Make sure to use the same units for V_t and V_s in developing this function.

4. Extrapolate a straight line through the data in this region to where it meets the x-axis at $F_2 = (V_s - V_t)\ 10^{-pH} = 0$ or $V_t = V_w$. That point is the carbonate equivalence point.

Skip steps 5 and 6 (F_5 and F_6 Gran functions) if the initial sample pH is less than approximately 10.3.

5. **Hydroxide equivalence point (Gran function F_5).** Using the value of V_w from step 4, plot $(V_w - V_t)\ 10^{-pH}$ against the titrant volume, V_t, in the region above the carbonate equivalence point. Use the same units for V_t and V_w in developing this function.

6. Extrapolate a straight line through the data in the region between the carbonate and hydroxide equivalence points to where it meets the x-axis at $F_5 = (V_w - V_t)\ 10^{-pH} = 0$ or $V_t = V_x$. That point is the hydroxide equivalence point.

At this point, you can either stop, or try to verify your values of V_s, V_w and V_x by plotting additional Gran functions. To continue plotting, follow these optional steps:

7. In the region between the carbonate and bicarbonate equivalence points, plot $(V_t - V_w)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_3.

8. Extrapolate a straight line in this region to where it meets the x-axis at $F_3 = (V_t - V_w)\ 10^{pH} = 0$ or $V_t = V_s$ to get another estimate of the bicarbonate equivalence point.

9. In the region between the carbonate and hydroxide equivalence points, plot $(V_s - 2V_w + V_t)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_4.

10. Extrapolate a straight line in this region to where it meets the x-axis at $F_4 = (V_s - 2V_w + V_t)\ 10^{pH} = 0$ or $V_t = V_w$ to obtain another estimate of the carbonate equivalence point.

11. In the region above the hydroxide equivalence point, plot $(V_o + V_t)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_6.

12. Extrapolate a straight line in this region to where it meets the x-axis at $F_6 = (V_o + V_t)\ 10^{pH} = 0$ or $V_t = V_x$ to obtain another estimate of the hydroxide equivalence point.

Depending on the number of points used to develop each of the Gran functions, the equivalence points from each pair of functions (F_1 and F_3, F_2 and F_4, F_5 and F_6) may not be identical.

- If both functions appear to fit the data well and use a sufficient number of points, then average the estimates for that equivalence point.
- If one of the functions (F_3, for example) clearly has a poorer fit to the data or uses far fewer points than does its partner (F_1, in this case), then choose the equivalence point calculated from the other Gran function (F_1). Example Gran–1 illustrates the use of Gran function F_1 while Example Gran–2 illustrates use of Gran functions F_1 through F_4.

Gran function plots are easy to prepare with a spreadsheet or computer program (see section 6.6.5.C).

Example Gran–1: Gran function plot of F_1 only

Gran function plots are useful for samples with low alkalinity. Using the titration data obtained from a sample of Little Abiqua Creek near Scotts Mills, Oregon (from Example IPT–2), a Gran function plot is easily prepared. The necessary calculations are shown in table 6.6–6. The results are plotted in figure 6.6–6. In the region beyond the equivalence point in figure 6.6–6, a straight line results. Extrapolation of this straight line to $(V_o+V_t)10^{-pH} = 0$ locates the equivalence point. The extrapolated straight line intercept at $(V_o+V_t)\ 10^{-pH} = 0$ on figure 6.6–6 is at 139.5 digital counts of titrant added, corresponding to a bicarbonate equivalence point at a pH of approximately 5.18. The calculated alkalinity by this method is 7.0 mg/L as $CaCO_3$, in excellent agreement with the value of 6.8 mg/L as $CaCO_3$ calculated by the IPT method in Example IPT–2.

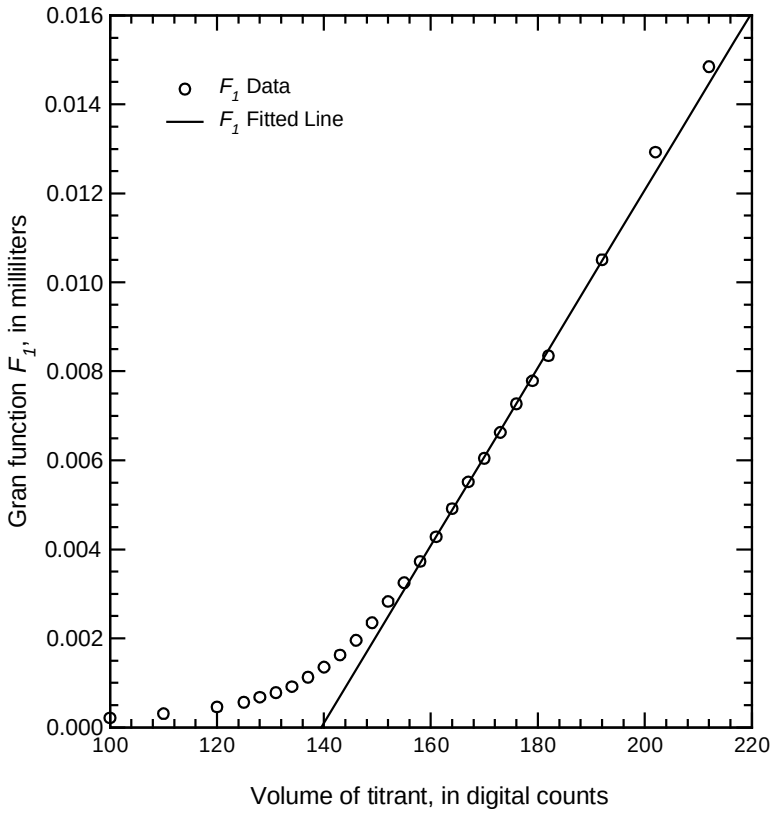

Figure 6.6–6. Example of a Gran function plot using F_1 to determine the bicarbonate equivalence point.

Table 6.6–6. Gran function plot analysis for a low-alkalinity sample—calculation of Gran function F_1 for Example Gran–1.

[V_o, volume of sample; V_t, volume of titrant; mL, milliliters]

pH (standard units)	Counter reading (counts)	Titrant volume, V_t (mL)	V_o+V_t (mL)	10^{-pH}	$(V_o+V_t)10^{-pH}$ (mL)
7.12	0	0.000	200.000	$7.586x10^{-08}$	$1.517x10^{-05}$
6.83	20	.025	200.025	$1.479x10^{-07}$	$2.959x10^{-05}$
6.59	40	.050	200.050	$2.570x10^{-07}$	$5.142x10^{-05}$
6.39	60	.075	200.075	$4.074x10^{-07}$	$8.151x10^{-05}$
6.18	80	.100	200.100	$6.607x10^{-07}$	$1.322x10^{-04}$
5.97	100	.125	200.125	$1.072x10^{-06}$	$2.144x10^{-04}$
5.81	110	.138	200.138	$1.549x10^{-06}$	$3.100x10^{-04}$
5.64	120	.150	200.150	$2.291x10^{-06}$	$4.585x10^{-04}$
5.55	125	.156	200.156	$2.818x10^{-06}$	$5.641x10^{-04}$
5.47	128	.160	200.160	$3.388x10^{-06}$	$6.782x10^{-04}$
5.41	131	.164	200.164	$3.890x10^{-06}$	$7.787x10^{-04}$
5.34	134	.168	200.168	$4.571x10^{-06}$	$9.149x10^{-04}$
5.25	137	.171	200.171	$5.623x10^{-06}$	$1.126x10^{-03}$
5.17	140	.175	200.175	$6.761x10^{-06}$	$1.353x10^{-03}$
5.09	143	.179	200.179	$8.128x10^{-06}$	$1.627x10^{-03}$
5.01	146	.183	200.183	$9.772x10^{-06}$	$1.956x10^{-03}$
4.93	149	.186	200.186	$1.175x10^{-05}$	$2.352x10^{-03}$
4.85	152	.190	200.190	$1.413x10^{-05}$	$2.828x10^{-03}$
4.79	155	.194	200.194	$1.622x10^{-05}$	$3.247x10^{-03}$
4.73	158	.198	200.198	$1.862x10^{-05}$	$3.728x10^{-03}$
4.67	161	.201	200.201	$2.138x10^{-05}$	$4.280x10^{-03}$
4.61	164	.205	200.205	$2.455x10^{-05}$	$4.914x10^{-03}$
4.56	167	.209	200.209	$2.754x10^{-05}$	$5.514x10^{-03}$
4.52	170	.213	200.213	$3.020x10^{-05}$	$6.046x10^{-03}$
4.48	173	.216	200.216	$3.311x10^{-05}$	$6.630x10^{-03}$
4.44	176	.220	200.220	$3.631x10^{-05}$	$7.270x10^{-03}$
4.41	179	.224	200.224	$3.890x10^{-05}$	$7.790x10^{-03}$
4.38	182	.228	200.228	$4.169x10^{-05}$	$8.347x10^{-03}$
4.28	192	.240	200.240	$5.248x10^{-05}$	$1.051x10^{-02}$
4.19	202	.253	200.253	$6.457x10^{-05}$	$1.293x10^{-02}$
4.13	212	.265	200.265	$7.413x10^{-05}$	$1.485x10^{-02}$

Example Gran–2: Gran function plot using F_1 through F_4

In this example, the same titration data that were used in Example IPT–1A in section 6.6.4.B are analyzed using the Gran method. The sample pH (9.35) was not high enough to justify the use of Gran functions F_5 and F_6, so only functions F_1 through F_4 are used.

The results are shown in figure 6.6–7, and indicate a bicarbonate equivalence point at 1005 counts (from F_3, only 2 data points could be used for F_1), and a carbonate equivalence point at about 209 counts (F_2 estimated the equivalence point at 214, F_4 at 204). Although this is not an ideal data set for Gran function analysis (the titration did not extend to pH values lower than about 4.0), the Gran method was able to provide reasonable estimates of the equivalence points.

Using a bicarbonate equivalence point of 1005 counts as determined by the Gran method, an acid titrant normality of 0.16*N*, and a sample volume of 100 mL, the calculated alkalinity of this sample is 100.5 mg/L as $CaCO_3$ (see section 6.6.5). Using an equivalence point of 1013 counts for this sample from the analysis in Example IPT–1A (inflection point method), the calculated alkalinity would be 101.3 mg/L as $CaCO_3$. The agreement between these two methods is very good, producing a discrepancy of less than 1 percent. Results from either method would be reported as 101 mg/L as $CaCO_3$.

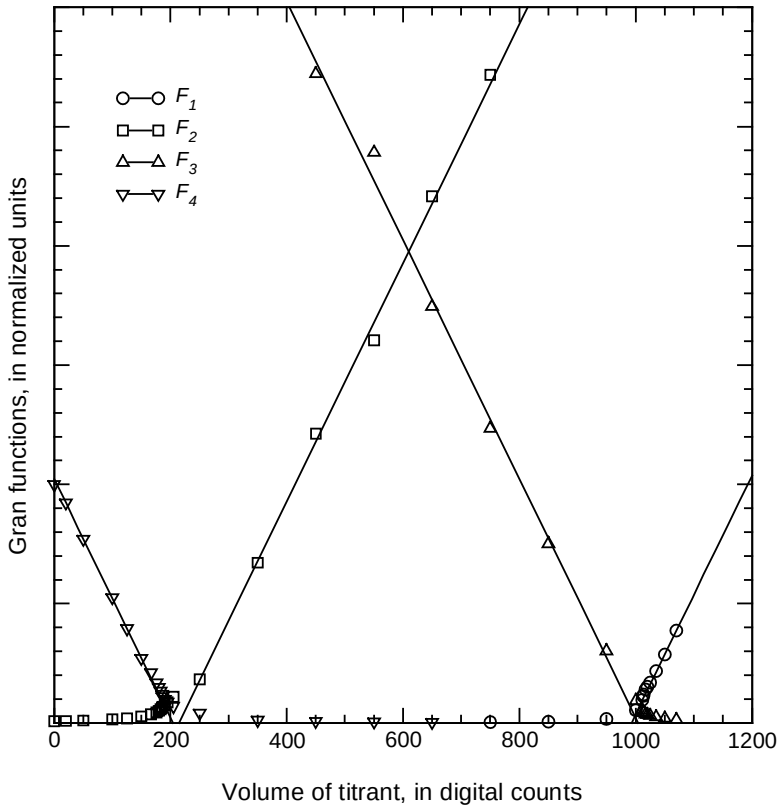

Figure 6.6–7. Example of a Gran function plot using F_1, F_2, F_3, and F_4 to determine carbonate and bicarbonate equivalence points.

6.6.5 Calculations

Concentrations of alkalinity or ANC and carbonate species can be calculated by hand or in a spreadsheet (sections 6.6.5.A and 6.6.5.B), or by using a computer program (section 6.6.5.C). For hand calculations, first determine the equivalence points using the IPT (section 6.6.4.B) or Gran function (section 6.6.4.C) method. The equations below are valid for buret or digital titration equipment, and any acid concentration and sample volume.

6.6.5.A Alkalinity or ANC

Calculation of alkalinity or ANC is a simple accounting of the amount of acid used to neutralize the sample to the bicarbonate equivalence point:

$$Alk\left(\frac{meq}{L}\right) = \frac{B(mL) \times C_a\left(\frac{meq}{mL}\right) \times CF}{V_s(mL) \times \left(\frac{1\ L}{1000\ mL}\right)} = 1000(B)(C_a)(CF)/V_s$$

and

$$Alk\left(\frac{mg}{L}\ \text{as}\ CaCO_3\right) = Alk\left(\frac{meq}{L}\right) \times \frac{1\ mmol\ CaCO_3}{2\ meq} \times \frac{100.087\ mg\ CaCO_3}{1\ mmol\ CaCO_3}$$

$$= 50044(B)(C_a)(CF)/V_s$$

where

Alk is the alkalinity or ANC of the sample.

B is the volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters.
To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts).

C_a is the concentration of acid titrant, in milliequivalents (*meq*) per milliliter (same as equivalents per liter, or normality *N*).

CF is a correction factor (see below).

V_s is the volume of sample, in milliliters.

mmol is millimoles, in this case for calcium carbonate.

The correction factor *CF* is equal to 1.01 when using the Hach digital titrator cartridges, as determined by the NWQL and resulting from a bias caused by the configuration of those cartridges. For other titration methods, CF is equal to 1.0.

6.6.5.B Carbonate-Speciation Equations

For samples in which the alkalinity or ANC is due primarily to bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide (OH^-), the concentrations of those constituents in the sample can be determined directly from the sample's pH and alkalinity or ANC with the following equations:

$$[HCO_3^-]\left(\frac{meq}{L}\right) = \left(\frac{Alk - K_w' \times 10^{pH} + \frac{10^{-pH}}{\gamma}}{1 + 2K_2' \times 10^{pH}}\right) \times \left(\frac{1000\ meq}{1\ mol}\right)$$

$$[CO_3^{2-}]\left(\frac{meq}{L}\right) = \left(\frac{Alk - K_w' \times 10^{pH} + \frac{10^{-pH}}{\gamma}}{2 + \frac{10^{-pH}}{K_2'}}\right) \times \left(\frac{2000\ meq}{1\ mol}\right)$$

$$[OH^-]\left(\frac{meq}{L}\right) = (K_w' \times 10^{pH}) \times \left(\frac{1000\ meq}{1\ mol}\right)$$

where

Alk is the computed sample alkalinity or ANC in equivalents per liter (eq/L)—divide value in meq/L by 1000 to obtain eq/L;
pH is the initial sample pH;
K_w' is the acid dissociation constant for water, corrected for the activity of hydroxide;
K_2' is the second acid dissociation constant for H_2CO_3, corrected for the activity of carbonate species; and
γ is the activity coefficient for H^+.

To convert concentrations in meq/L to mg/L, multiply the bicarbonate result by 61.0171, the carbonate result by 30.0046, and the hydroxide result by 17.0073.

These equations are valid for any sample pH and account for activity corrections—deviations from ideal chemical behavior typically caused by the presence of other ions. The calculation and application of activity coefficients is an advanced topic that is not covered here, but is addressed by some of the tools described in section 6.6.5.C.

In dilute freshwater systems, activity corrections may be neglected, allowing the activity coefficients (γ) to be set to 1.0 and the "infinite-dilution" acid dissociation constants (K_w, K_1, K_2) to be used in place of values that include activity corrections (K_w', K_1', K_2'). The nominal values of these constants in dilute freshwater at 25 °C are $K_w = 10^{-14.0}$, $K_1 = 10^{-6.35}$, and $K_2 = 10^{-10.3}$. Values at other temperatures can be computed with the following equation:

$$\log_{10}(K) = a_1 + a_2 T + \frac{a_3}{T} + a_4 \log_{10}(T) + \frac{a_5}{T^2}$$

where T is the absolute water temperature in Kelvin (T = t(°C)+273.15) and the coefficients are given in Table 6.6–7.

Table 6.6–7. Coefficients to compute the temperature dependence of acid dissociation constants for water and carbonic acid, as tabulated by Stumm and Morgan (1996).

Acid Dissociation Constant	Coefficient				
	a_1	a_2	a_3	a_4	a_5
K_w	-283.971	-0.05069842	13323.0	102.24447	-1119669.0
K_1	-356.3094	-0.06091964	21834.37	126.8339	-1684915
K_2	-107.8871	-0.03252849	5151.79	38.92561	-563713.9

TECHNICAL NOTE: Prior to 2012, NFM included equations for the calculation of bicarbonate and carbonate concentrations based on the volumes of titrant required to reach the carbonate and bicarbonate equivalence points. That "simple speciation" method assumed that only carbonate ions were titrated in the pH range above the carbonate equivalence point, and only bicarbonate ions were titrated in the pH range below the carbonate equivalence point. The result was a set of equations that were easy to apply but suffered from two problems.

First, the method did not account for the effects of hydroxide, which resulted in significant errors for samples with pH values higher than 9.2. Second, the method ignored the fact that small concentrations of bicarbonate ions exist at pHs above the carbonate equivalence point, and small concentrations of carbonate ions exist at pHs below the carbonate equivalence point. Because of these limitations and the availability of a more general and accurate method (included in this version of NFM), the older "simple speciation" method has been discontinued.

Important points to remember:

- The equations to compute concentrations of bicarbonate, carbonate, and hydroxide shown above are valid for any sample pH, but the equations for bicarbonate and carbonate are only valid if these three species are the only significant contributors to the sample alkalinity or ANC.

- If the sample contains other titratable species such as ammonia, borate, silicic acid, or humic and fulvic acids that contribute significantly to alkalinity or ANC, then the equations for bicarbonate and carbonate shown here no longer apply, and use of a full geochemical model such as PHREEQC (Parkhurst and Appelo, 1999) is recommended.[2] Versions of PHREEQC may be obtained at no cost from the USGS at *http://water.usgs.gov/software*.

- Double-check your calculations!

6.6.5.C Computer-Program Analysis of Titration Data

USGS computer programs are available to simplify alkalinity or ANC plotting and calculation tasks. Two such tools are described here:

Alkalinity Calculator

The Web-based or stand-alone **Alkalinity Calculator** is a publically available tool that helps to analyze titration data and determine alkalinity or ANC using several different methods, including:

- The inflection point (IPT) method,

- The Gran function plot method, and

- A theoretical carbonate titration curve method.

The Calculator's methods are valid for the full range of pH measured in natural waters and provide a simple means for performing the alkalinity and carbonate-speciation calculations described in sections 6.6.5.A and 6.6.5.B, including activity corrections and temperature adjustments.

[2] A description of such geochemical models is beyond the scope of this manual.

The IPT and Gran methods implemented by the Alkalinity Calculator are as described in this manual. The carbonate titration curve method attempts to fit the titration data with a theoretical titration curve derived solely from the chemistry of carbonic acid. This method shows the user whether the chemistry of carbonic acid alone can account for the shape of the entire titration curve. If the fit is poor, it is likely that more than just bicarbonate, carbonate, and hydroxide were titrated in the sample. An excellent fit with this method is evidence that the titration curve is dominated by bicarbonate and carbonate, providing useful feedback for reporting and using the results.

A link to the Alkalinity Calculator is available at *http://water.usgs.gov/owq/methods.html* [3] or can be accessed directly at *http://or.water.usgs.gov/alk.*[3]

The methods used by the Alkalinity Calculator are documented at *http://or.water.usgs.gov/alk/methods.html.*[3]

Personal Computer Field Form (PCFF)

The PCFF software provides another means for USGS users to analyze titration data in the field using the methods described in this manual. This software can determine alkalinity or ANC from titration data using the IPT or Gran function plot methods, and applies the carbonate-speciation calculations as shown in section 6.6.5.B. More information about PCFF can be obtained by USGS users only from *http://water.usgs.gov/usgs/owq/pcff.html.*[3]

6.6.6 Troubleshooting

The major difficulties with equipment used to measure alkalinity or ANC are the same as for pH measurement—refer to NFM 6.4. Particulate materials, including algae or other biota, can interfere with the stability and reproducibility of pH readings. Such difficulties normally are eliminated by filtering the sample.

When the sample has low ionic strength, or when dissolved organic compounds or noncarbonate inorganic species are present that can interfere with the titration (note color, odor, or previous chemical analysis), the Gran function determination is recommended to avoid some of these problems.

[3] The URLs shown were accessed on 8/24/2012.

6.6.7 Reporting

Report and publish results from filtered samples as alkalinity. Titration values from unfiltered samples are to be entered and published as ANC.

Alkalinity and ANC should be reported in milliequivalents per liter (or microequivalents per liter), if possible. If this option is not available in the data base, calculate alkalinity and ANC in milligrams per liter, assigning all neutralizing capacity to the carbonate system (typically mg/L as $CaCO_3$). For measurements made using section 6.6.4 procedures, when calculating ANC, alkalinity, bicarbonate, or carbonate in milligram units, report:

- Less than (<) 1,000 mg/L and equal to (=) or greater than (>) 100 mg/L to whole numbers; however, to the tenths place if <100 mg/L.
- 1,000 mg/L and above, to three significant figures.
- Carbonate alkalinity usually is reported in the data base in milligrams per liter as calcium carbonate.
- Do not report hydroxide, carbonate, or bicarbonate concentration as 0.0 mg/L; instead, report values less than 0.1 mg/L as <0.1 mg/L.
- Hydroxide, carbonate, and bicarbonate concentration values cannot be negative.
- Alkalinity and ANC values may be negative; report negative values with the same number of significant figures that would be used if the values were positive.
- Be sure that the titration method and speciation methods are documented correctly in the data base.
    - The carbonate speciation equations in section 6.6.5.B are collectively called the "advanced speciation method." Appropriate method codes for the advanced speciation method are ASM01 through ASM12. Information on when each code should be used is provided at *http://or.water.usgs.gov/alk/reporting.html*.
    - Parameter and method codes for field measurements are available at *http://water.usgs.gov/usgs/owq/Forms/Fieldmeasurement_parametersmethods.doc*.[4]

[4] For turbidity, parameter and method codes can be accessed at *http://water.usgs.gov/owq/turbidity_codes.xls*.

Conversion factors listed below are taken from Hem (1985) and were verified independently by the author of this document.

Multiply	By	To obtain
Alkalinity (mg/L as HCO_3^-)	0.8202	Alkalinity (mg/L as $CaCO_3$)
Alkalinity (mg/L as HCO_3^-)	0.4917	Alkalinity (mg/L as CO_3^{2-})
Alkalinity (mg/L as $CaCO_3$)	0.01998	Alkalinity (meq/L)
Bicarbonate (mg/L as HCO_3^-)	0.01639	Bicarbonate (meq/L)
Bicarbonate (mg/L as HCO_3^-)	16.389	Bicarbonate (µeq/L)
Carbonate (mg/L as CO_3^{2-})	0.03333	Carbonate (meq/L)
Hydroxide (mg/L as OH^-)	0.05880	Hydroxide (meq/L)

Report the average value for duplicate samples or the median when more than two replicate samples are used for quality control and the value falls within the appropriate quality-assurance criterion for variability.

USGS data entry into the National Water Information System: use the correct parameter code to indicate (1) the method of titration or calculation and (2) a filtered or unfiltered sample. A summary of parameter and method codes for alkalinity titration results is available at *http://or.water.usgs.gov/alk/reporting.html*.

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Acknowledgments

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TURBIDITY 6.7

By Chauncey W. Anderson

Illustrations

Tables

TURBIDITY 6.7

Turbidity, which can make water appear cloudy or muddy, is caused by the presence of suspended and dissolved matter, such as clay, silt, finely divided organic matter, plankton and other microscopic organisms, organic acids, and dyes (ASTM International, 2003a). The color of water, whether resulting from dissolved compounds or suspended particles, can affect a turbidity measurement.

TURBIDITY–an expression of the optical properties of a liquid that causes light rays to be scattered and absorbed rather than transmitted in straight lines through a sample.

— ASTM, 2003a

Although turbidity is not an inherent property of water, as is temperature or pH (Davies-Colley and Smith, 2001), the recognition of turbidity as an indicator of the environmental health of water bodies has increased over the past decade, resulting in a growing demand for high-quality and objective turbidity measurements. To meet this demand, relatively inexpensive, yet sophisticated instruments have been developed that allow for nearly continuous monitoring and data logging of turbidity in natural waters. Gray and Glysson (2003) note the following examples of disparate uses for turbidity data:

- Regulating and maintaining drinking water clarity.
- Determining water clarity for aquatic organisms.
- Indicating visual impairment in water.
- Real-time monitoring that indicates watershed conditions.
- Developing surrogates for concentration of suspended sediment (SSC) and other constituents.
- Monitoring the effects of land development and related human activities and subsequent management of natural resources.
- Determining transport of contaminants associated with suspended materials.

Although technological advances in turbidity measurement have produced a variety of instrument types to meet one or more of these differing objectives, turbidity instruments of different designs commonly do not yield identical or equivalent results. Moreover, the mixing of different source waters or dilutions of environmental samples may not produce linear results when measuring for turbidity because of the variety of factors that contribute to and can have an effect on turbidity. Selection of the appropriate turbidity instrument requires, therefore, consideration of project objectives, data requirements, and the physical and chemical properties of the water body.

This section on turbidity provides protocols and guidelines for selecting appropriate field and laboratory instruments and procedures for instrument calibration and maintenance, turbidity measurement, data storage, and quality assurance that meet stated objectives for U.S. Geological Survey (USGS) data-collection efforts.[1] The use of consistent procedures and instruments within and among projects or programs for which turbidity data will be compared over space and time is crucial for the the success of the data-collection program.

Select instruments carefully after reviewing project objectives and after consulting with cooperating agencies.

- **Report turbidity on the basis of the individual instrument design.**
- **Use identically prepared calibration solutions.**
- **Use consistent techniques and instrumentation throughout a data-collection program.**

[1]For additional procedures related to continuous, dynamic monitoring of environmental waters, refer to Wagner and others (2000).

EQUIPMENT 6.7.1

When selecting an appropriate instrument for measuring turbidity, consider the potential effects that may result from the various properties of different water bodies. In addition, ensure that the measurement method, instrument design, and the data output are appropriate for the purpose and objectives for which these data are to be collected.

INTERFERENCES AND INSTRUMENT DESIGN 6.7.1.A

A variety of water properties can affect the measurement of turbidity (table 6.7-1). These include the color of dissolved constituents in the water matrix and particulate materials, particle size, and density. Sensor fouling, such as biological growth or scratches on the optical surface of the instrument, tends to produce a negative bias when light beams are blocked, but can produce a positive bias if scratches increase the scatter of the sensor's light beam (table 6.7-2). Likewise, bubbles or gases in the water can cause apparent turbidity (positive bias), and might require special sample preparation or handling to eliminate without changing the particle characteristics of the original sample (consult manufacturer’s recommendations).

To account for the effects of properties of water or interferences on turbidity, many types of instruments have been designed (table 6.7-3), many with multiple light beams or detectors (fig. 6.7-1). For example, although stray light can cause a positive bias in turbidity measurement because of apparent additional reflectance, many newer instruments, particularly those used for dynamic monitoring, are designed to minimize stray light.

For a valid comparison of turbidity data over time, between sites, and among projects, use instruments with identical optical and data-processing configurations.

Table 6.7-1. Properties of water matrices and their expected effect on turbidity measurement

[Negative, a negative effect produces a disproportionately low measurement; IR, infrared; nm, nanometers; positive, a positive effect produces a disproportionately high measurement; ~, approximately. See table 6.7-3 for descriptions of instrument designs.]

Properties of water matrix	Effect on the measurement	Direction of effect on the measurement	Instrument designs to compensate for effect
Colored particles	Absorption of light beam	Negative	• Near IR (780-900 nm) light source • Multiple detectors
Color, dissolved (in the matrix)	Absorption of light beam (if the incident light wavelengths overlap the absorptive spectra within the sample matrix)	Negative	• Near IR (780-900 nm) light source • Multiple detectors
Particle size:	*Wavelength dependent.*		
Large particles	• Scatter long wavelengths of light more readily than small particles	• Positive (for near IR light source, ~820-900 nm)	• White light (broad spectrum) light source
Small particles	• Scatter short wavelengths of light more efficiently than long wavelengths	• Positive (for broad spectrum light source, such as white light)	• Near IR (780-900 nm) light source
Particle Density	Increases forward and backward scattering of light at high densities	Negative	• Multiple detectors • Backscattering

Table 6.7-2. Sampling interferences and their expected effect on turbidity measurement

[Positive, a positive effect produces a disproportionately high measurement; Negative, a negative effect produces a disproportionately low measurement.]

Interference	Effect on the measurement	Direction of effect on the measurement
Stray light	Increases apparent light scatter	Positive
Bubbles from entrained gases	Increases apparent light scatter	Positive
Contamination of calibrants	Increases apparent light scatter	Positive
Optical sensor fouling or scratching	*Particularly with dynamic instruments.* • Possible beam blockage • Possible scratches on optical surfaces	• Negative • Positive
Bubbles	Increases apparent light scatter	Positive
Scratches on cuvette glass	Increases apparent light scatter	Positive

Table 6.7-3. Summary of instrument designs and capabilities, current reproducible technologies, appropriate applications, and approximate limits

[Indicated ranges are for example only and do not exclude the possibility that manufacturers can develop instruments under each design that surpass these ranges. Abbreviations: EPA 180.1, U.S. Environmental Protection Agency (1993) method 180.1; Regulatory, range complies with EPA regulations (unless specified "non-US"); IR, infrared; ISO 7027, International Organization for Standardization (1999) method 7027; nm, nanometers; US, United States]

Design	Prominent feature and application	Typical instrument capability range (nm)	Suggested application range (nm)
Nephelometric non-ratiometric	White light turbidimeters – Complies with EPA 180.1 for low-level monitoring.	0 to 40	0 to 40 Regulatory
Ratiometric white-light turbidimeters	Complies with EPA 180.1 for low-level monitoring. Uses a nephelometric detector as the primary detector, but contains other detectors to minimize effects of color and noise. Can be used for both low- and high-level measurement.	0 to 4,000	0 to 40 Regulatory 0 to 4,000
Nephelometric, near-IR turbidimeters, non-ratiometric	Complies with ISO 7027 – The wavelength (780-900 nm) is less susceptible to effects of color. Good for samples with color and good for low-level monitoring.	0 to 1,000	0 to 11 Regulatory (non-US) 0 to 1,000
Nephelometric near-IR turbidimeters, ratiometric	Complies with ISO 7027. Contains a ratio algorithm to monitor and compensate for variability and color.	0 to 4,000	0 to 40 Regulatory 0 to 4,000
Surface-scatter turbidimeters	Not applicable for regulatory purposes. Turbidity is determined through light scatter from or near the surface of a sample. The detection angle is still nephelometric, but interferences are not as substantial as nephelometric non-ratiometric measurements. This is primarily used in high-level turbidity applications.	10 to 10,000	10 to 10,000
Backscatter/ ratiometric technology	Not applicable for regulatory purposes. Backscatter detection for high levels and nephelometric detection for low levels. Backscatter is common with probe technology and is best applied in high turbidity samples.	10 to 10,000	10 to 10,000
Light attenuation (spectro-photometric)	Not applicable for regulatory purposes. Wavelength 860 nm. Highly susceptible to interferences; best applied at low to medium turbidity levels.	20 to 1,000	20 to 1,000
Multiple-beam turbidimeters	Multiple light sources and multiple detectors are used to provide both reference and active signals, with at least four independent measurements being made. The final signal is determined with a ratio algorithm.	0 to 40	0 to 40 Regulatory 0 to 1,000

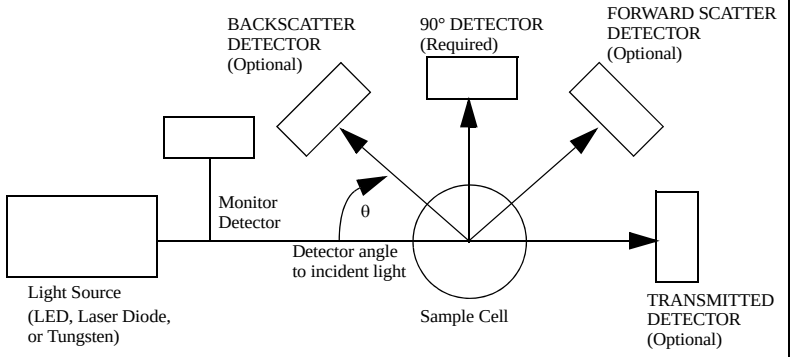

Figure 6.7-1. Photoelectric nephelometer (single-beam design) showing optional additional detectors for ratiometric, backscatter, or transmitted determination of turbidity. [Modified from Sadar (1998)].

One outcome of the availability of different instrument designs is that **turbidity measured using instruments with different optical designs can differ by factors of two or more for the same environmental sample, even with identically calibrated instruments**. Thus, raw data from differently designed instruments should not be considered directly interchangeable—the resultant data are inherently incomparable without additional work to establish relations between instruments over the range of the environmental conditions present.

Such complications underscore the need to clearly determine study objectives before selecting a turbidimeter, and to understand the limitations of the instrument selected. In addition, a carefully planned quality-assurance (QA) protocol is required to identify errors associated with different aspects of the turbidity measurement process. For additional information on turbidity measurement, see Sadar (1998), U.S. Environmental Protection Agency (1999), and the literature provided by instrument manufacturers.

TECHNICAL NOTE (1): Variability in measurements caused by instability in light sources, high particle densities, or color can be reduced by the use of multiple detectors at different angles. Such "ratiometric" instruments compute the turbidity value using a ratio of the light received by the different detectors. Furthermore, because turbidity is an optical measurement, the absorption of light by colored particles or by a colored matrix can cause a reduction in the apparent turbidity. The negative effect from color is minimized by using near-infrared light frequencies as the light source (tables 6.7-1, 6.7-3) or ratiometric techniques.

DATA STORAGE 6.7.1.B

To ensure that USGS turbidity data can be understood and interpreted properly within the context of the instrument used and site conditions encountered, data from each instrument type will be stored and reported in the National Water Information System (NWIS) using parameter codes and measurement reporting units that are specific to the instrument type, with specific instruments designated by the method code. The respective measurement units, most of which also are in use internationally, are listed and defined in table 6.7-4.

- The designations NTU, NTRU, BU, AU, and NTMU signify the use of a broad spectrum incident light in the wavelength range 400-680 nanometers (nm).
- The designations FNU, FNRU, FBU, FAU, and FNMU generally signify an incident light in the range between 780-900 nm.[2]

These reporting units are equivalent when measuring a calibration solution (for example, formazin or polymer beads—see section 6.7.2), but their respective instruments may not produce equivalent results for environmental samples. **Information for specific instruments is maintained at: http://water.usgs.gov/owq/turbidity_codes.xls**

The term "turbidity unit," as used in this manual, refers generically to turbidity measured by instruments of undefined design. Note that manufacturers might, for the foreseeable future, retain the general use of the measurement unit "NTU" when referring to calibrants and equipment.

> **TECHNICAL NOTE (2):** Historically, reporting units included Jackson Turbidity Units (JTU) and Formazin Turbidity Units (FTU). Neither unit is still in common use, due to lack of precision (JTU) and lack of specificity about instrumentation type (FTU).

[2]ISO 7027 specifically defines the light source for FNU measurements as having a wavelength of 860 nm, with a bandwidth of 60 nm. The angle of the detector must be 90 degrees from incident light, plus or minus 2.5 degrees.

Table 6.7-4. Reporting units corresponding to turbidity instrument designs

[Parameter code numbers begin with a "P"; nm, nanometers; °, degree; ±, plus or minus; K, kelvin]

Detector geometry	Light wavelength	
	White or broadband (with a peak spectral output of 400-680 nm)	Monochrome (spectral output typically near infrared, 780-900 nm)
Single illumination beam light source		
At 90° to incident beam	Nephelometric Turbidity Unit (NTU)[1] (P63675)	Formazin Nephelometric Unit (FNU)[2] (P63680)
At 90° and other angles. An instrument algorithm uses a combination of detector readings, which may differ for values of varying magnitude.	Nephelometric Turbidity Ratio Unit (NTRU) (P63676)	Formazin Nephelometric Ratio Unit (FNRU) (P63681)
At 30° ± 15 to incident beam (backscatter)	Backscatter Unit (BU) (P63677)	Formazin Backscatter Unit (FBU) (P63682)
At 180° to incident beam (attenuation)	Attenuation Unit (AU) (P63678)	Formazin Attenuation Unit (FAU) (P63683)
Multiple illumination beam light source		
At 90° and possibly other angles to each beam. An instrument algorithm uses a combination of detector readings, which may differ for values of varying magnitude.	Nephelometric Turbidity Multibeam Unit (NTMU) (P63679)	Formazin Nephelometric Multibeam Unit (FNMU) (P63684)

[1]EPA Method 180.1 defines the optical geometry for NTU measurements. The detector angle must be 90° ± 30 to the incident light beam. The light source must be a tungsten lamp with color temperature 2,200 - 3,000 K. (Source: U.S. Environmental Protection Agency, 1993)

[2]ISO 7027 defines the optical geometry for FNU measurements. The detector angle must be 90° ± 2.5 to the incident light beam. The light source must be a light-emitting diode (LED) with wavelength 860 ± 60 nm. (Source: International Organization for Standardization, 1999).

INSTRUMENT SELECTION AND MAINTENANCE 6.7.1.C

Owing to potential differences in turbidity readings resulting from different instrument types, it is critical that when selecting turbidimeters, investigators carefully consider the objectives of the study and the uses of the resulting data. Considerations include:

- Whether the program will be regulatory in nature (typically applies in a drinking water context).
- The expected range in turbidity and the portions of that range that will be the most important to measure with accuracy.
- The need for consistency of method and comparability among data sources (whether data from one site need to be comparable with data from another site or with historical data).
- Which potential interferences are the most important to quantify or otherwise take into account (tables 6.7-1 through 6.7-4).

Within the United States, turbidity is regulated by the U.S. Environmental Protection Agency (USEPA) only for water that is intended for use as drinking water. In some cases, States use turbidity for regulations associated with the Clean Water Act (U.S. Environmental Protection Agency, 2002a). To date, the USEPA has approved the following three methods to measure turbidity in drinking water: (1) EPA Method 180.1 (U.S. Environmental Protection Agency, 1993), based on white-light nephelometric instrument designs; (2) GLI Method 2 (U.S. Environmental Protection Agency, 1999; Great Lakes Instrument Company, undated), which uses a dual-beam and dual detector technology with an 860 nm light-emitting diode (LED) light source to compensate for color and reduce erratic readings; and (3) Hach Method 10133 (U.S. Environmental Protection Agency, 2002b), an inline process-stream method that is unlikely to be used within USGS. Owing to a nonlinear response of these technologies at high turbidities, their applicable range in drinking water is from 0 to 40 turbidity units. Instrument designs that conform to EPA Method 180.1 or GLI Method 2 may perform poorly (including nonlinear responses) at turbidities that commonly occur in surface-water bodies (greater than 40 turbidity units). Also, white-light instruments typically consume more power than monochrome instruments, so access to the regional power grid is commonly required. For these methods, waters with turbidities greater than 40

must be diluted before measuring. **For studies involving the measurement of turbidity in finished drinking water, either EPA Method 180.1, GLI Method 2, or Hach Method 10133 must be used**. (This requirement commonly is applied when determining ground-water turbidity in water from wells used for human consumption.)

> **TECHNICAL NOTE (3)**: One other method, ISO 7027 (International Organization for Standardization, 1999), has been defined for waters with low turbidity and is in use in Europe and elsewhere; however, as of 2003, ISO 7027 had not been accepted by USEPA for compliance with drinking-water regulations in the United States.

USEPA-approved methods generally are not required when providing data for regulatory purposes in accordance with the Clean Water Act (U.S. Environmental Protection Agency, 2002a). For example, nonregulatory methods can be used to determine changes in turbidity of surface water resulting from resource management actions, or to correlate turbidity with regulated constituents such as suspended sediment (Uhrich and Bragg, 2003), nutrients, or bacteria (Christensen and others, 2000). For such data-collection efforts, it may be possible to use alternative instrument designs that are targeted towards specific study objectives and that will accommodate the range of natural conditions that occur in the water body. **Before selecting a methodology and the corresponding instrumentation, determine if USEPA-compliant methodologies are necessary.** Given the breadth of applications for measuring turbidity, no particular sampling consideration can be defined as the most important in all cases; however, **consistency of instrument types and calibration procedures within monitoring programs or among individual projects is one of the most important aspects to consider when designing a data-collection program that will include turbidity.**

Nephelometry: the measurement of light scattering using a light detector 90 degrees from the incident light (USEPA, 1999).

Decision Considerations for Instrument Selection

Numerous factors are involved when deciding on the type(s) of equipment that are appropriate for a given study. A major consideration in the selection of a turbidity instrument is whether turbidity will be measured under **static** or **dynamic** conditions. Water samples that are removed from the source and are measured with benchtop meters are considered static. Submersible sensors allow turbidity measurement under dynamic water conditions, using either instantaneous profiling techniques or a deployed instrument for continuous monitoring.

Measurements taken under static conditions compared to those taken under dynamic conditions differ primarily because static-measurement techniques do not completely account for particle settling, whereas dynamic-measurement techniques more accurately reflect the dynamic nature of particle movement within the water body. Such differences are particularly pronounced when coarse silt or sand-sized particles are present. Also, temperature changes in the sample during transport from source water to laboratory can cause differences between measurements taken on a static sample (benchtop instrument) and measurements taken under dynamic (in situ or pumped) conditions. Some benchtop instruments do, however, provide flowthrough chambers that keep the sample in motion to approximate the dynamic conditions in the original water body.

As discussed previously, instrument selection begins with a thorough consideration of study objectives, and continues with questions about the use of the data, the type of water body and its sources of turbidity, and the way in which the data will be collected and stored. A decision tree (fig. 6.7-2) is provided below to help guide the selection process. In the decision process described below, numbers 1 through 3 pertain to information in fig. 6.7-2; numbers 4 and 5 provide additional guidance.

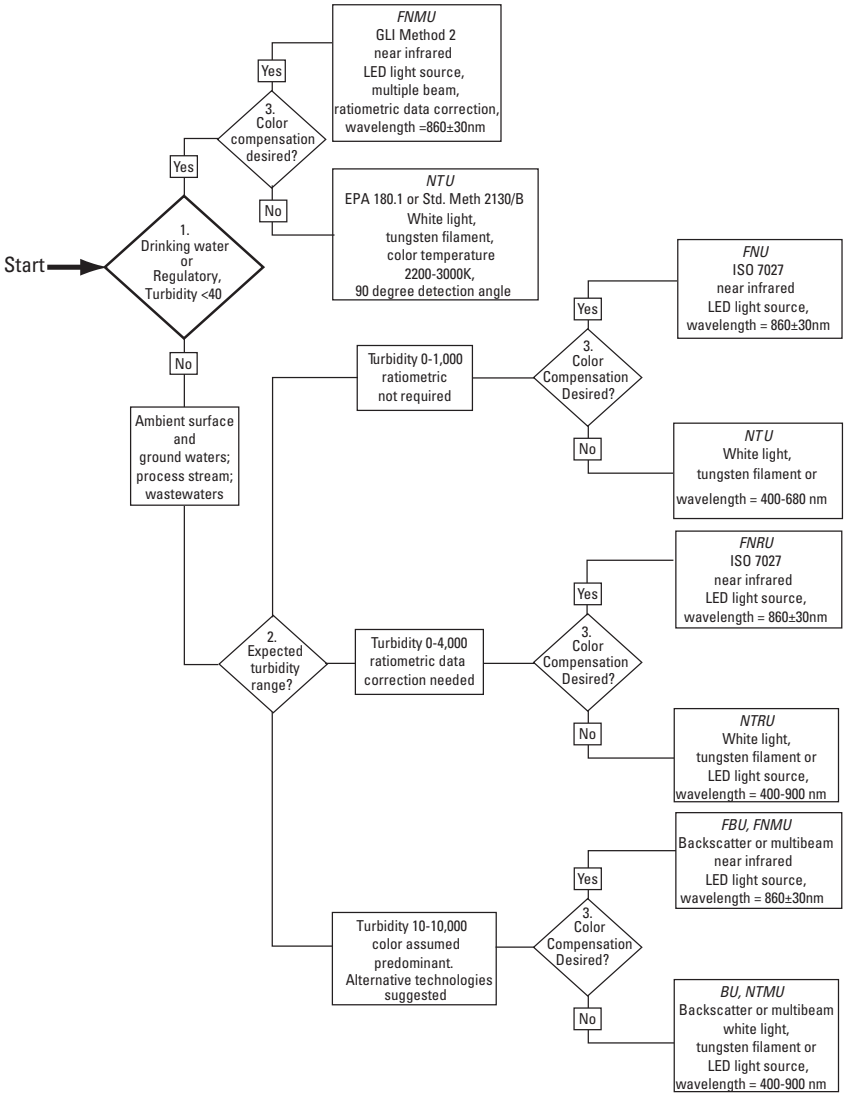

Figure 6.7-2. Decision tree to determine appropriate instrumentation designs for intended turbidity measurements.

Decision Considerations (considerations 4 and 5 are not shown in fig. 6.7-2)**:**

1. **Is the study regulatory in nature?**
   If "Yes," go to step **3 (**fig. 6.7-2).
   If "No," continue to step **2** (fig. 6.7-2).

   If the study involves regulation of drinking water, the instrument choices are limited by the methods accepted by the USEPA for drinking water. If the study involves State regulations (for example, those proposed under provisions of the Clean Water Act), the regulations may require the use of one or more specific instrument designs, which cannot be anticipated in this protocol.

   If the study does not involve turbidity in drinking water or other specially designated instrument types, consider using instrument designs that accommodate a broader range of environmental conditions.

2. **What is the expected range in turbidity, or what part of the range is most important to measure accurately?**

   For turbidities in the range of 0-1,000 units, single-detector nephelometric measurement may work adequately if the instrument is calibrated in the same range as the sample. As particle densities increase, however, the backward scattering of light particles increases to the point that it can cause interference with single-detector nephelometry, resulting in a negative effect on the measurement or an unstable reading (table 6.7-1). Multiple detectors at different angles can be used, with the turbidity value determined by a ratio of the light received by the different detectors. Ratioing helps to reduce noise in the turbidity signal, especially at ultra-low turbidities or when particle densities are high. Instruments that utilize backscatter detection also can help compensate for such effects at high turbidities. Backscatter is particularly important above 1,000 units. The effect of particle size should be considered too. Positive effects on turbidities for water sources with predominantly large or small particle sizes can be minimized with careful consideration of the study objectives, the water source, and instrument requirements.

3. Is the water source colored by dissolved or particulate materials, and should the color be part of the measured turbidity?

Color in water samples, from dissolved or particulate materials (or both), can cause a negative effect (Sutherland and others, 2000) on measured turbidity (table 6.7-1). In some cases, it could be desirable to quantify this decrease by using an instrument with a broad-spectrum or white-light source that would be sensitive to color changes. Alternatively, when measuring changes in turbidity that are unrelated to color, instruments with a near-infrared light source should be used.

4. Will the measurement be done by dynamic means or by a benchtop measurement of samples removed from the source?

In most cases, it is preferable to measure turbidity directly within the water source or in a pumped sample (dynamically), rather than taking a sample from which an aliquot must then be measured using a benchtop (static) method. Dynamic measurement is preferred to static measurement because of problems with representative subsampling, settling of solids and temperature changes in static samples, and interferences such as condensation or scratches on sample cuvettes. Dynamic techniques usually are required for continuous monitoring, and the sensors often can be combined with other sensors that measure additional properties, such as temperature, specific conductance, dissolved oxygen, and pH. In some cases, however, dynamic readings are not feasible or desired (for example, if a measurement is needed of a composite sample or in a laboratory setting). Most instruments used for static measurements are not capable of being used for dynamic measurements; whereas some instruments used for dynamic measurements can be immersed in a water sample and the measurement taken statically.

5. What resolution is required in the resulting data?

For turbidity data that primarily will be in the low (less than 5 turbidity units) or ultra-low (less than 1 unit) ranges, the necessary resolution may be down to the 100th or 10th decimal place, whereas for turbidities greater than 40 units, resolution to the nearest 5, 10, or even 100 reporting units might be adequate. After determining the primary instrument design requirements, consult literature or online sources of individual instrument manufacturers for information on available resolution.

Once a particular instrument design and set of reporting units (table 6.7-4) have been selected, the user evaluates the literature and cost information from instrument manufacturers to decide on the most appropriate model. Although rapid changes in optical and sensor technology preclude the inclusion of specific manufacturers' models in figure 6.7-2, the turbidity parameter and methods codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005) provides a partial list of available models according to instrument design and reporting units, which can be used in combination with figure 6.7-2 to narrow the options for the choice of an instrument to meet a specific set of study objectives.

Figure 6.7-2 shows that differences among instrument designs have resulted in a wide array of options for measuring turbidity. Although these options provide flexibility and the capability to tailor the data-collection program to the needs of each particular study, they also present problems for data comparison among studies with differing objectives or water sources, particularly if different equipment is used in the studies. When data are to be compared among different programs or studies, sending duplicate samples to a laboratory such as the National Water Quality Laboratory (NWQL) provides a reference for quality-assurance purposes and is recommended (the NWQL, for example, simulates dynamic measurement using a flowthrough chamber with its benchtop meters). If a dynamic measurement is used for determining field turbidities, it can be useful to compare these data with results obtained from a laboratory-analyzed sample, as long as the properties contributing to the sample turbidity do not degrade during storage and transit (see section 6.7.3).

Dynamic measurement is the preferred method for determining the turbidity of a water body, provided that this method is consistent with study objectives and other study protocols. Dynamic measurement more accurately reflects surface-water conditions than static determination because particle settling in cuvettes is avoided.

Signal-Processing Options

Because turbidity measurements can be highly variable, a range of signal-processing options may be available with different instruments. Some instruments can provide statistics such as the maximum, minimum, mean, median, range, and variance of many readings over a timespan of a few seconds. These statistics can be useful for reducing variability in recorded turbidities, for understanding sources of turbidity, or for diagnostic purposes. Instruments that use proprietary algorithms can provide functions intended to reduce spikes in instantaneous data, sometimes employing user-defined variables such as time constants and spike thresholds. Such algorithms can provide a smoother signal than simple instantaneous measurements; however, because the algorithms may not be published, these data must be used with care and in consideration of the data-quality objectives of the study. Note that if the instrument uses signal averaging to smooth the data output, the instrument response to changes in turbidity readings can be slowed. **Select the output you desire in accordance with study objectives and data-storage and transmittal requirements.**

Maintenance of Turbidity Instruments

The equipment and supplies commonly used for field measurement of turbidity are listed in table 6.7-5. These include supplies generally needed for the maintenance, storage, and cleaning of the selected instrument. Routine maintenance of turbidity instrumentation is critical, particularly for continuously deployed, dynamic applications.

Table 6.7-5. Equipment and supplies used for measuring turbidity

[Modify this list to meet the specific needs of the field effort. Abbreviations: ≤, less than or equal to; mm, millimeter; mL, milliliter]

- Turbidimeter, spectrophotometer, or submersible-sensor instrument (such as a multiparameter instrument with a turbidity sensor).[1]
- Calibration turbidity stock solutions and standards
  - Formazin stock suspension, commercially obtained or prepared from scratch with hydrazine sulfate and hexamethelenetetramine chemicals, or
  - Instrument-specific polymer solutions containing styrene divinylbenzene beads.
- Sample cells (cuvettes), clear colorless glass (supplied from instrument manufacturer).
- Inert (dry) gas (for example, nitrogen) and gas-delivery apparatus; tanks must be fitted with regulators and filter.
- Sample bottle (preferably an amber bottle that does not sorb suspended material).
- Silicon oil, optical grade (with same index of refraction as sample cells; supplied by instrument manufacturer).
- Paper tissues, extra lint free.
- Turbidity-free water, deiononized water filtered through a ≤ 0.2 mm filter membrane with precision-sized pores.
- Bottle to hold turbidity-free water, cleaned and rinsed three times with filtered water.
- Volumetric flask, Class A, 100 mL or 500 mL.
- Volumetric pipet, Class A, 5.0 mL and pipet filler.

[1]See text, figure 6.7-2, and table 6.7-3 for description of appropriate instrument types.

- Before field use of water-quality instruments, become familiar with the manufacturer's instructions for calibration, operation, and maintenance.
- The maintenance program must include:
  - Regular cleaning of optical surfaces. Use a lint-free cloth, soft toothbrush, or paintbrush and deionized water for cleaning optical surfaces. Exercise care so as not to damage optical surfaces. Optical surfaces of some instruments may be more easily damaged than others — check manufacturer's recommendations before proceeding with cleaning and use.
  - For deployed, dynamic monitoring, the cleaning frequency should be approximately every 2 to 4 weeks. More frequent cleaning is necessary where biofouling is particularly apparent.
  - Verification that wipers are operational. Change wiper pads when they are excessively dirty or worn; avoid hindering or forcing wiper movement, or scratching optical surfaces.
  - Washing sample cuvettes after each use (wear powderless, disposable laboratory gloves and use a lint-free cloth).
  - Regular calibration or verification against secondary calibration solutions.
  - Examination of collected data for indication of instrument malfunction.
- Test all field instruments in an office or laboratory before use. Record all maintenance and repairs in the instrument logbook.

CALIBRATION 6.7.2

To ensure the collection of reliable turbidity data, carefully follow the standard calibration procedures described below and the instructions from the instrument manufacturer. Even identically calibrated turbidimeters can produce significantly different readings of native-water sources for instruments of different designs. All turbidity instruments are designed to produce equivalent responses to "scratch" formazin (prepared in the office laboratory), the accepted reference solution, despite differences among the designs. The calibration process provides a common point for standardization, and if turbidity were an inherent physical property, then measurements of environmental waters would be expected to have similar numerical values for any instrument. However, the varying particle and color characteristics of environmental waters differ fundamentally from formazin crystals. This has led manufacturers to develop calibration solutions that in some cases are tailored to specific instruments, potentially increasing the magnitude of error if solutions are used improperly. **Where turbidity data are to be compared within or among data-collection projects, the consistent use of sampling, calibration, and measurement equipment and techniques is necessary.**

The USGS follows conventions for turbidity determination established by ASTM International (2003a), which defines three levels of calibration solutions (calibrants): "Reference Turbidity" solutions, "Calibration Turbidity" solutions, and "Calibration Verification" solutions or solids.

- The **Reference Turbidity** solution is a calibrant that a skilled analyst synthesizes reproducibly from traceable raw materials. All other calibrants are traced back to this solution. The reference standard for turbidity is formazin made from scratch (see below for preparation instructions), a polymer with repeating units of $C_2H_4N_2$.
- **Calibration Turbidity** solutions are those that are used to adjust instrument readout, and must be traceable and equivalent to the reference turbidity calibrant to within accepted statistical errors.

TECHNICAL NOTE (4): Acceptable calibration turbidity solutions include dilutions of formazin made from scratch (scratch formazin), commercially prepared stabilized formazin (such as StablCal®, available from Hach Company in formulations of 4,000 turbidity units and lower)[3], and styrene divinylbenzene beads (SDVB) (such as AMCO-AEPA-1® polymer)[3]. Although stabilized formazin calibrants have a much longer shelf life than solutions diluted from scratch formazin, settling of formazin crystals can still be observed when they sit unused. Calibrants made from SDVB have a more uniform grain size than formazin and tend to settle less over time, but often are custom developed for specific instruments and must be purchased accordingly.

- **Calibration Verification** calibrants are those used to perform instrument checks in the field. Calibration verification calibrants may include but are not limited to calibration turbidity solutions. Sealed or solid materials should not be used to adjust instrument performance.

Calibration turbidity solutions and calibration verification calibrants can be instrument specific. Be careful to check the manufacturer's instructions. Use of calibrants with instruments for which they are not designed can introduce significant errors.

All evidence indicates that formazin and stabilized formazin are safe to use as primary turbidity standards when good laboratory practices are followed (Sadar and others, 1998). Standard safety procedures, including wearing laboratory coats, glasses, and gloves, are considered adequate protection for routine use of formazin. The primary hazard from the formazin solution is physical irritation. Of the components in formazin, only formaldehyde will evaporate and

[3]The use of brand names in this report is for example purposes only and does not constitute an endorsement by the U.S. Geological Survey.

cause exposure through the air; however, its concentration in this mixture is well below what is considered to be a health risk. Concentrations in formazin solutions diluted below 4,000 turbidity units will result in exposures that are reduced even further. For more information, see the Material Safety Data Sheet (http://www.ilpi.com/msds/index.html#Internet) or Sadar and others (1998).

TECHNICAL NOTE (5): The raw materials used in the synthesis of scratch formazin do present potential safety concerns. These materials, specifically hydrazine sulfate and hexamethylenetetramine (hexamine), are currently (2004) listed as a suspected carcinogen and an experimental mutagen, respectively. Hydrazine sulfate also is a strong reducing agent and as such requires standard laboratory safety precautions (avoid inhalation, ingestion, and contact with skin, and work in a fume hood). In water, it separates into free hydrazine and sulfuric acid. An excess of hexamethylenetetramine reacts with acid to produce formaldehyde at neutral pH. The formaldehyde then reacts with dissolved hydrazine to produce the formazin polymer. The final product, 4,000 turbidity-unit formazin suspension, contains 3.2 parts per million hydrazine sulfate, 0.1 percent formaldehyde, 0.2 percent formazin, 0.5 percent ammonium sulfate, and 4.7-percent hexamethylenetetramine. Laboratory rats were fed 4,000-NTU formazin at 5,000 mg/kg body weight with no toxic effect (Sadar and others, 1998)

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Avoid inhalation and ingestion of or skin contact with hydrazine sulfate when preparing formazin solutions. Work in a fume hood.

6.7.2.A CALIBRATION SOLUTION: USE, PREPARATION, AND DILUTION

A stock formazin solution may be prepared in the laboratory or may be purchased from a manufacturer. Serial dilutions are made to achieve the desired calibration interval. **Commercially prepared calibration turbidity solutions are recommended for routine instrument calibration to avoid any safety and quality-assurance concerns.**

Under circumstances in which study personnel need to prepare a stock turbidity suspension, precise laboratory practices are required in order to achieve consistent results.

- Always use turbidity-free water (deionized water passed through a filter media of less than or equal to 0.2 μm) at 20-25ºC for mixing dilutions or suspensions.
- Prepare the stock turbidity suspension monthly and calibrant dilutions immediately prior to instrument calibration. **Calibrant solutions made from diluted scratch formazin are stable for only a few hours to a few days, depending on the concentration** (ASTM, 2003b)**. With the exception of 4,000 NTU formazin, commercial calibration solutions such as StablCal® or AMCO-AEPA-1® must not be diluted because changes will occur in the suspension matrix that will render the dilutions nonlinear.**
- Store reagents, as appropriate, in a dust-free cabinet or refrigerator.

Inconsistent techniques used to dilute calibrants and variable temperatures can add significant measurement error.

To prepare a 4,000 turbidity-unit formazin stock suspension[4]:

1. Wearing laboratory powderless disposable gloves, quantitatively transfer 5.0 g of reagent-grade hydrazine sulfate $[(NH_2)_2 \bullet H_2SO_4]$ into approximately 400 mL of turbidity-free water in a 1-L volumetric flask.
2. Quantitatively transfer 50.0 g of reagent-grade hexamethylenetetramine $[(CH_2)_6N_4]$ into approximately 400 mL of turbidity-free water in a separate, clean flask; stopper and swirl until the $(CH_2)_6N_4$ is completely dissolved. Filter through a 0.2-µm filter into a clean flask.
3. Quantitatively transfer the filtered hexamethylenetetramine into the flask containing hydrazine sulfate (from step 1). Dilute solution to the 1-L mark with turbidity-free water. Stopper and mix for at least 5 minutes, but no more than 10 minutes.
4. Let stand for 24 hours at 25º ± 1ºC to develop the 4,000 turbidity-unit suspension.
5. Transfer the solution to an opaque, light-blocking, polyethylene bottle and store refrigerated. The 4,000 turbidity-unit stock suspension is stable for about a year, if stored at 20 to 25ºC in amber polyethylene bottles.

To prepare 500 mL of a 400 turbidity-unit calibrant solution, dilute the 4,000 turbidity-unit stock solution by a 1:10 ratio as follows:

1. Mix 50 mL of the 4,000 turbidity-unit stock solution in a 500-mL flask.
2. Dilute to the mark with turbidity-free water and mix.
3. Transfer the solution to an opaque, light blocking, polyethylene bottle and store refrigerated. The 400 turbidity-unit stock solution is stable only for about one day.

[4]Refer to ASTM International (2003a) for detailed instructions.

To prepare a 40 turbidity-unit calibrant solution, dilute the 400 turbidity-unit solution by a 1:10 ratio as follows:

1. Mix 10 mL of the 400 turbidity-unit stock solution in a 100-mL flask.
2. Dilute to the mark with turbidity-free water and mix.
3. Transfer the solution to an opaque, light-blocking, polyethylene bottle. **Prepare the calibrant suspension on the day the calibrant is needed, use it immediately after preparation, and discard unused calibrant. The 40 turbidity-unit stock solution is stable only for about 1 day.**

When chemicals to be used for preparation of reagents are received, mark the dates of receipt and expiration on the container. When a calibrant is prepared, label the container with the contents, date of preparation, expiration date, and preparer's initials. Store formazin in a cool, dark place (a storage cabinet or frost-free refrigerator). After use, pour waste calibration solutions into a labeled glass or plastic container for proper disposal.

Reagents and calibrants must not exceed their shelf life.

6.7.2.B CALIBRATION PROCEDURES

Although calibration principles are similar whether using static or dynamic sensors, in practice the steps taken can be different.

- Benchtop meters use a small, 15- to 25-mL sample holding cell, or "cuvette," which is inserted into the measurement chamber. This results in a static measurement unless additional flowthrough equipment is used.
  - Values must be read from the meter before particle settling can affect the measured turbidity.
  - If particle settling of sand or silt occurs before the measurement can be completed, the sample results must be recorded in the database to reflect the possible bias in the

data. (For input to the USGS NWIS database, the results would be coded with an "E" remark, indicating the value is an "Estimate" only.)

— The cuvettes used for calibrating static turbidimeters are identical to those used in the meter when taking a turbidity reading.

▶ Submersible meters collect data by immersing a turbidity sensor in the sample media, but are calibrated using a separate chamber that allows the sensor to be immersed in the calibrant.

Benchtop (static) turbidimeter calibration

The calibration instructions and procedures that follow are general and should be modified to apply to the instrument being used—check manufacturer's instructions. Refer to table 6.7–5 for a list of supplies commonly used for turbidity measurement.

To calibrate a benchtop turbidimeter:

1. Prepare formazin suspensions as described above.
   - Allow stock solutions to come to room temperature.
   - Calibrate each instrument range using at least two calibrant concentrations, and three or more if the instrument allows it. Use calibrant solutions that bracket the range of the turbidity anticipated in the sample solution.
   - Prepare dilute calibrant fresh from the stock at the time of use—after dilution, the stock suspension is stable only for a few hours.
   - Formazin-based calibrants should be resuspended by inverting the calibrant 25 times (1-second inversion cycle), followed by a 2- to 10-minute wait to allow for bubble removal. Calibrants of 40 turbidity units or less will remain suspended for up to 30 minutes; calibrants greater than 40 turbidity units may require more frequent resuspension.
   - **Do not use calibrants with flocculated suspensions**.
2. Turn on the turbidimeter and allow it to warm up. (Check manufacturer's instructions for equipment startup.)

3. Select the desired turbidity range. Use a calibration range to equal the high value of calibrant for the range of interest.

4. Rinse a clean, dry, scratch-free cell with the highest concentration of the calibrant for the instrument range setting or range of interest. Index-mark the cell to ensure consistent orientation within the instrument. (See manufacturer's instructions for index-marking the cell.)

    a. Hold the sample cell by the rim (top lip), not beneath the lip.
    b. Pour calibrant into the sample cell to the fill mark.
    c. Wipe the exterior of the cell using a soft, lint-free cloth or tissue to remove moisture (condensation) from cell walls.
    d. Apply a thin layer of silicon oil onto the exterior of the cell to reduce condensation on the cell and to mask slight scratches and nicks. Apply silicon oil uniformly onto the blank cell if it will be used on the cell filled with calibrant (follow manufacturer's recommendations).
    e. Before inserting the cell containing calibrant into the instrument, ensure that no air bubbles are present in the cell. If necessary, degas the sample according to manufacturer's instructions. Air bubbles can cause significant positive bias in turbidity measurements (table 6.7-1).

5. Orient the calibration cell in the cell holder according to the index marks—**the calibration cell and sample cell must have identical orientation** when in the instrument-measurement chamber.

6. In the instrument logbook, record the instrument value for each calibrant. Most modern turbidimeters contain calibration curve-fitting capabilities specific to that instrument, allowing the instrument to produce sample readings that may be used directly. If the meter does not have this capability, you will need to construct a calibration curve to correct sample readings to the calibrated turbidity. To determine turbidity using a calibration curve (see American Public Health Association, 2001, for more details on this procedure):

a. Record the instrument response to a range of calibration solutions bracketing the expected turbidity of the sample.
b. Create a graph showing the value of the instrument response (x-axis) against the turbidity value of the calibration solutions (y-axis).
c. Using linear regression, plot a line that encompasses the plotted values.
d. For water samples, input the instrument reading on the x-axis and read the corresponding corrected turbidity value from the y-axis, or determine the corrected y-value from the regression equation on the instrument reading.

7. Adjust the calibration control until the value on the meter equals the value of the calibrant used.

8. Repeat steps 4 through 7 as recommended by the instrument manufacturer for calibration solutions bracketing the range of expected turbidities. Use calibrants representing at least two different turbidities, including the expected maximum and minimum. Ensure that calibrants are within the linear portion of the instrument's operating range.

Submersible (dynamic) turbidity sensor calibration

Most dynamic turbidimeters and multiparameter instruments with turbidity sensors are microprocessor based, with the calibration parameters stored in instrument memory. Turbidity values of the calibrants are user selectable in some instruments, but others have internally established calibration ranges that cannot be changed.

- Check calibrants in the 1 to 5 turbidity-unit (low-level) range to assess the actual performance of the instrument near the detection limit; **instrument reliability often decreases at turbidities less than 2 turbidity units—**consult the manufacturer's specification for the expected accuracy of the measurement.

- Refer to Wagner and others (2000) for instructions on record keeping when cleaning and calibrating continuously deployed instruments, and for acceptable tolerances. Monitor the output carefully to ensure that turbidity readings are stable before confirming the calibration.
- **Calibrate the instrument using calibration turbidity solutions before leaving for the field**. While in the field, check instrument performance periodically using a calibration or verification calibrant and turbidity-free water.
- The optical surface of the sensor must be clean before beginning the calibration procedure. In deployed, continuous monitoring situations, pipes or other structures that house the sensor also may require periodic cleaning.

To calibrate a submersible turbidity sensor *(modify the general instructions that follow as necessary so that they are compatible with the manufacturer's instructions)**:***

1. Prepare a sufficient volume of the selected calibration solution or verification calibrant, as described previously. The volume of calibrant required could be 500 mL for some instruments, particularly if the entire sonde bundle will be immersed.
2. **Select Procedure (A) or (B).** The same procedure, once tested and selected, also should be applied to instruments used in future studies against which the data could be compared.

   Procedure A. Immersion of the entire sonde (bundle of field-measurement sensors, including the turbidity sensor) requires larger volumes of calibrant; calibrant is vulnerable to contamination and dilution. The sonde sensor guard may need to be removed.

   Procedure B. Immersion of turbidity sensor only—depending on sonde configuration, isolation of the turbidity sensor and achieving a bubble-free optical surface could be difficult. This technique minimizes the volume of calibrant required for calibration.
3. Determine the number of calibration points to be used (a minimum of two, but three is preferred) and configure the instrument for this number of points, if applicable.

4. For a zero turbidity-unit calibrant (or turbidity-free water):
   a. Rinse sonde/sensor with deionized water, followed by a portion of the turbidity calibrant.
   b. Immerse sensor in calibrant, or add enough calibrant to cover the sensor in the calibration chamber.
   c. Agitate the sonde/sensor repeatedly to remove bubbles from the optical surface (activate mechanical wiper, if present).
   d. Set sensor vertically on a flat surface or use a ringstand to hold it.
   e. Monitor turbidity readings for 1 to 2 minutes or longer to ensure that readings are stable (consult manufacturer's recommendations and signal-processing information). Record the pre-calibration value in the instrument logbook or on the field sheet.
   f. Confirm the calibration value or adjust the instrument calibration using the manufacturer's instructions.
   g. Remove the sonde/sensor and dry thoroughly to minimize dilution or contamination of the next calibrant.
   h. Discard the calibrant into a labeled waste container and hold for proper disposal.
   i. If measurement of color-derived turbidity is not desired, filter (using a 0.2-µm pore-size filter) an aliquot of the sample water and use the filtered water in place of turbidity-free water.

5. Using a second calibrant with a value near the maximum of the expected turbidity range, repeat steps 4(a-i). Repeat again with a third calibrant near the middle of the expected range if increased accuracy is desired and instrument software permits. If the software does not permit a three-point calibration, the third calibrant can nonetheless be used to document the accuracy of the calibrated instrument near the middle of the expected range. If an "out of range" error is displayed, verify the intended calibrant value and start again with the first (zero) calibrant solution. Repeat the calibration procedure if the measurement is not within the specification. Record all calibration and verification measurements in the instrument logbook.

6. On a one-time basis, determine the maximum value that can be reported by the instrument by holding a lint-free cloth over the optical sensor and recording the turbidity. Use this value as an indicator that turbidity might have been greater than the range of the instrument during measurements in a water body.

Spectrophotometric turbidimeter calibration

Spectrophotometric turbidity measurements, sometimes referred to as absorbtometric or attenuation turbidity, are useful to indicate relative values or to monitor changes in turbidity with time. Spectrophotometers, however, measure light transmission (rather than light scattering) using a narrow, short-wavelength light source, are inaccurate for absolute turbidity measurement, and are unrated for instrument sensitivity. Most of the spectrophotometers used for measuring turbidity are benchtop or portable instruments, so sample handling is similar to that described for benchtop (static) turbidimeters.

- Use spectrophotometry as an indication of optical properties in water only upon careful review of study objectives and alternative available technology.
- Instrument response is negative (that is, the detector response decreases) with increasing turbidity, which is the opposite of traditional turbidity and backscatter instrument responses. Report results in Attenuation Units (AU) or Formazin Attenuation Units (FAU), depending on the light source (table 6.7-4). (The overwhelming majority of available spectrophotometric turbidity instruments use FAU.)

Spectrophotometers commonly have a stored program for turbidity that has been factory calibrated and that can be verified but not adjusted. Check the instrument output against that of a different instrument every few weeks while the instrument is in use. Check the relative accuracy of the turbidity measurement before leaving for the field by inserting calibration turbidity solutions covering the FAU range needed. Accounting for a change in reporting units, calibration steps for spectrophotometric determination are identical to those for static measurement of turbidity, including the possible need for constructing a calibration curve (see instructions under **Benchtop (static) turbidimeter calibration**, steps 1 through 8).

MEASUREMENT 6.7.3

Three methods for field-measurement determinations of turbidity are described in this section: static (or benchtop) determination (6.7.3.A); dynamic (submersible) determination (6.7.3.B); and spectrophotometric (absorptometric) determination (6.7.3.C). Procedures for the use of turbidity instruments are similar for various surface-water and ground-water applications. The sampling methods used and the considerations needed for accurate representation of the intended water conditions, however, depend on the objectives and intended data use of the study and on site type and conditions. Routine sampling of streams by the USGS typically involves isokinetic, depth-integrated sampling methods (NFM 4.1; NFM 6.0.2). Much of the routine sampling of ground water at wells by the USGS involves well purging (NFM 4.2; NFM 6.0.3).

- Before making a turbidity determination, ensure that the instrument to be used has been cleaned and calibrated properly, and that the calibration process has been accurately documented (section 6.7.2).
- Biased or erroneous readings can result from numerous factors, including unmatched cell orientation, colored sample solutions, gas bubbles, condensation, and scratched or dirty sample cells (see tables 6.7–1 and 6.7–2). Condensation on the sample cell commonly occurs when the water sample is much colder than the air temperature.
- **Turbidity measurement is time sensitive and therefore should be completed on-site (preferably in situ)** to avoid effects from (a) biodegradation, growth, settling, or sorption of particulates in the sample; or (b) precipitation of humic acids and minerals (carbonates and hydroxides, for example) caused by changes in sample pH during transport and holding.
- If temporary storage of samples is necessary, collect samples in clean amber bottles, keep out of sunlight, and chill at or below 4°C to prevent biodegradation of solids or biological growth. The holding time must not exceed 24 hours (ASTM International, 2003a).

Turbidities in surface waters can range widely, even within the same water body, depending on local hydrology, sources of sediment or colored materials, and disturbance regimes. Although drinking-water sources often have background turbidities of less than 1 turbidity unit, it is not unusual to measure turbidities of 1,000 or greater, depending on stream and weather conditions (Uhrich and Bragg, 2003). Protocols for determining turbidities in surface waters typically must account for making reliable measurements that span turbidities over one to three orders of magnitude. Use either a dynamic or static method, employing either discharge-weighted, pumped-sample, or grab-sample procedures, as appropriate for site characteristics and study objectives (NFM 6.0). Repeat the measurement three to five times to ensure accuracy and replication within the precision of the instrument.

6.7.3.A STATIC (BENCHTOP) DETERMINATION

The methods described below encompass both white-light nephelometry that meets USEPA specifications for drinking water, and other static methods (for example, ISO 7027) that do not meet USEPA specifications. EPA Method 180.1 is applicable in the range of turbidity from 0 to 40 NTU without dilution, and from about 40 to 1,000 NTU with dilution (U.S. Environmental Protection Agency, 1993). **Note that dilution of environmental samples that contain particulate materials or exhibit other nonlinearity properties can introduce significant errors from subsampling; therefore, dilution is discouraged.** Reporting units will vary with the instrument type used: Consult table 6.7–3 and the turbidity parameter and methods codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005). The static method assumes the turbidimeter recently has been calibrated properly with a calibration or verification solution (section 6.7.2).

Benchtop determination of turbidity is especially susceptible to negative bias from particle settling. Visually check for the presence of coarse material (sand or coarse silt) in the sample. Gently agitate the sample, then set it down. **If particles rapidly settle to the bottom (within 3-5 seconds), then coarse materials are present and the sample cannot be measured accurately using the static method.** Static measurements made on such samples therefore must be coded to indicate that accuracy is qualified when being entered into a database. In the USGS NWIS database, for example, the results should be entered with an “E” remark code.

Preliminary steps for benchtop turbidity determination:

1. Warm up the turbidimeter according to the manufacturer's instructions. Put on powderless laboratory gloves.
2. Rinse a clean, dry, scratch-free, index marked cell with a turbidity calibrant within the range of interest.
3. Gently agitate the calibrant, pour the calibrant into the sample cell to the fill mark, and dry the cell exterior with a lint-free cloth.When using a meter recently calibrated with an acceptable calibrant turbidity solution (formazin or styrene-divinylbenzene polymer—see section 6.7.2), a verification calibrant may be used for this check measurement.
4. Follow the manufacturer's instructions for readout of turbidity value and record the turbidity of the calibrant used and the turbidity value measured in the calibration logbook. If readings are not within specifications for the indicated range, recalibrate the instrument for the turbidimeter using accepted calibration turbidity solutions.

Most turbidimeters will correct initial sample readings directly into a final reading based on the stored calibration. If the meter does not have this capability, take the values from a previously constructed calibration curve.

For samples with turbidity less than 40 turbidity units:

1. Measure sample turbidity immediately or as soon as possible upon sample withdrawal.
   a. If discrete subsamples are to be taken from a churn splitter or other sample-compositing device, remove samples for turbidity measurement along with other whole water samples. Avoid pouring the sample into a cuvette from a bottle, if possible. If not possible, then invert the bottle 25 times using a 1-second inversion cycle and pour off the sample immediately to capture suspended particles.

b. For drinking water, use an instrument that complies with EPA Method 180.1 or GLI Method 2. Measurements are reported in NTU or NTRU for EPA 180.1, or in FNMU for GLI Method 2. (See table 6.7–4 to select the appropriate parameter code.)

2. Rinse a freshly cleaned cell with the sample to be tested.
3. For a **discrete (static) sample**, complete the following sequence of steps (through step 4a) without hesitation (skip to step 4 for flowthrough cell measurement).
   a. Gently invert—do not shake—the sample 25 times (ASTM, written commun., undated) to completely disperse the solids, taking care not to entrain air bubbles. Allow air bubbles to disappear before filling the sample cell.
   b. Rapidly pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers.
   c. Remove condensation from the cell with a clean, soft, lint-free cloth or tissue. If condensation continues, apply a thin coating of silicon oil to the outside of the cell about every third time the cell is wiped dry of moisture. Allow samples to equilibrate to ambient temperature, if necessary, before subsampling to help minimize condensation problems. Note: warming the sample may change particle associations in the water matrix.
   d. Before inserting the sample cell into the meter, ensure that no air bubbles are present in the cell. If necessary, degas the sample according to the manufacturer's instructions. Air bubbles can cause significant positive bias in turbidity measurements (table 6.7–1).
   e. Orient the calibration cell in the cell holder according to the index marks—the calibration cell and sample cell must have identical orientation when in the instrument measurement chamber.

Be sure that sample cells are index marked to indicate orientation. Match orientation so that cells yield the same value when light passes through.

4. Determine the measured turbidity value of the sample directly from the instrument scale or by using the instrument value and calibration curve, as is appropriate for the instrument being used. For samples with less than 1 turbidity unit, see **TECHNICAL NOTE (6)** under step 4d.
   a. Record the very first readings after placement of the sample cell in the measurement chamber. If readings are unstable, then particle settling may be occurring. If so, gently re-invert the cell 25 times and record at least three readings over a short, defined time interval (for example, 30 seconds to 1 minute).
   b. Repeat at least twice with fresh sample, until three or more sample values fall within ±10 percent.
   c. Samples that contain significant color should be diluted if using EPA Method 180.1 (for samples with turbidity greater than 40 units see below *"For samples, including drinking water, with turbidity greater than 40 turbidity units," step 3)*. **Results of diluted samples must be qualified with a "d" in the "Value Qualifier Code" field for data entered into the USGS NWIS database.**
   d. Report the median of the three or more sequential readings that fall within ±10 percent.

> **TECHNICAL NOTE (6):** When using low-level reporting scales, you may need to subtract a correction factor from the reading to correct for stray light. For example, the Hach Company reports the correction for the 0.2-NTU scale to be on the order of 0.04 NTU for the Hach 2100P. The stray-light correction is determined by reading turbidity from an empty instrument (without cuvette).

5. Record the data in reporting units described in table 6.7–4, using the method code that describes the specific instrument in use: Consult table 6.7–3 and the turbidity parameter and methods codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005). If particle settling or instability in initial readings was a problem, the results must be qualified as an estimate by using an "E" remark code for data entered into NWIS QWDATA.

For samples, including drinking water, with turbidity greater than 40 turbidity units:

1. Select an appropriate instrument. (See table 6.7–4 to select the appropriate USGS parameter code.)
   - For drinking water, use EPA Method 180.1, a compliant instrument, and NTU or NTRU reporting units; alternatively, select the GLI Method 2, a compliant instrument, and FNMU reporting units. Reporting units for these methods must be remarked with an "E" code in NWIS for turbidities greater than 40.
   - For study objectives other than drinking water, choose instruments according to information provided in figure 6.7–2 and table 6.7–3.
2. Obtain a discrete sample.
   - For drinking-water samples, proceed to step 3.
   - For non-drinking-water samples, skip to step 4.
3. For drinking-water samples, dilution is required to comply with USEPA regulations.
   a. Dilute the sample with one or more equal volumes of turbidity-free water until turbidity is less than 40 turbidity units after mixing and degassing.
   b. Record the volume of turbidity-free water used for dilution. Follow steps 1-5 from the previous section for samples with turbidity less than 40 turbidity units.
   c. Skip to step 5, below
4. For non-drinking-water samples (where USEPA compliance is not required), with 100 and 1,000 turbidity-unit ranges only — place a cell riser (if available) into the cell holder before inserting the sample cell. This decreases the length of the light path in order to improve the linearity of measurements. **Do not use the cell riser for the lower turbidity ranges.**
   a. For turbidimeters with adjustable ranges and signal-processing capabilities (for instance, ratio mode to compensate for high particle densities), select the desired configuration (table 6.7–3) and operate according to manufacturer's recommendations. Some instruments will automatically switch to different modes (for example, ratio mode) or to a different light source. Record instrument mode on field sheets.
   b. Select the desired range on the turbidimeter.

Dilutions can introduce errors if coarse material is present or if the sample matrix changes with the addition of diluant. When making dilutions, perform at least three at approximately 80, 50, and 20 percent of the original concentration. Record the turbidity of each dilution and determine if they are linear and correlate positively with the percentage diluted. If the response is nonlinear, alternative instrument designs that better compensate for interferences should be considered. Do not forget to adjust the turbidity value of diluted samples using the dilution factor.

5. Fill the cell with sample water:
   a. Hold the cell by the rim (top lip), not beneath the lip.
   b. Gently agitate the sample 25 times. Without hesitation, carefully but rapidly pour sample water into the cell to the fill mark.
   c. Wipe the exterior of the cell using a soft, lint-free cloth or tissue to remove moisture (condensation) from cell walls.
   d. If necessary, apply a thin layer of silicon oil (table 6.7–1) onto the exterior of the cell to reduce condensation on the cell and mask slight scratches and nicks.
   e. If rapid particle settling is occurring, steadily invert the cell 25 times, taking care not to shake too vigorously, which could entrain gases in the sample.

6. Record the sample turbidity.

Most modern turbidimeters will adjust initial sample readings directly into a final reading based on the previous calibration. If the meter does not have this capability, you will need to read values from a calibration curve constructed previously. See step 6 under "Benchtop (static) turbidimeter calibration" for instructions on constructing and using calibration curves.

a. Record the very first readings after placement of the sample cell in the measurement chamber. If readings are unstable, particle settling may be occurring: gently re-invert the cell 25 times and record at least three readings over a defined time interval (for example, 30 seconds to 1 minute).
b. Repeat at least twice with fresh sample until three or more sample values fall within ±10 percent.
c. Samples that contain significant color should be diluted if using EPA Method 180.1. **Results of diluted samples must be qualified with a "d" in the "Value Qualifier Code" field for data entered into the USGS NWIS database.**
d. Report the median of the three or more sequential readings that fall within ±10 percent.

For diluted water samples, the measured turbidity must be converted based on the amount of dilution, according to the following equation:

$$T_s = T_d \times \frac{(V_o + V_s)}{V_s},$$

where T_s= turbidity of the environmental sample, T_d=turbidity of the diluted sample, V_o = volume of turbidity-free water in the diluted mixture, and V_s= volume of the environmental sample in the diluted mixture.

EXAMPLE: If five volumes of turbidity-free water were added to one volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample is computed as 180 units.

e. Report turbidity as follows, using method codes as described in http://water.usgs.gov/owq/turbidity_codes.xls (accessed 9/30/2005)[5]:
   - For EPA Method 180.1, use NTU or NTRU.
   - For GLI Method 2, use FNMU.
   - For non-diluted, non-USEPA-compliant measurements, use the reporting units described in table 6.7–4.

In contrast to surface waters, natural turbidity in ground water generally is less than 5 turbidity units. Natural ground-water turbidity of up to 19 turbidity units has been reported for some environmental settings (Nightingale and Bianchi, 1977; Strausberg, 1983; Puls and Powell, 1992). Contaminated ground-water systems, however, can have considerably higher turbidity (Wells and others, 1989; Gschwend and others, 1990; Puls and Powell, 1992; Backhus and others, 1993). Measuring turbidity in ground water requires special considerations and procedures. For effervescent ground water, a degassing apparatus may be required; follow manufacturer's instructions.

- **During well development—**Monitor turbidity caused by well installation, recording consecutive measurements to document decreases in turbidity as development proceeds.
- **During well purging—**Monitor changes in turbidity by taking sequential readings until purging criteria are met (NFM 6.0). The final stabilized turbidity value should be equal to or less than the value recorded at the end of well development. A decrease in turbidity values during purging can indicate mitigation of subsurface disturbance caused by well installation and by deployment of data-collection equipment in the well.
- **For dynamic measurement—**Report the median of the three or more sequential measurements that meet the ±10-percent criterion for stability (NFM 6.0).
- **For discrete-sample measurement using a turbidimeter or spectrophotometer:**
  - **Bailers are not recommended** for collecting turbidity samples, as bailer deployment can increase turbidity.
  - Do not collect the discharge passing through the flowthrough chamber in which pH, conductivity, or other field-measurement sensors are installed.

[5]Diluted samples must be qualified with a "d" in the "Value Qualifier Code" field when entering data into NWIS.

— **Pump the ground-water sample** directly from the sample discharge line into a precleaned glass or polyethylene sample-collection bottle.

— Subsample into a cuvette and measure turbidity according to instructions for static determination (steps 3 through 5 above).

Multiparameter instruments can be used with a flowthrough chamber (instead of being deployed in situ) for monitoring ground-water field measurements. See the section below on dynamic determination of turbidity.

6.7.3.B DYNAMIC (SUBMERSIBLE-SENSOR) DETERMINATION

Determination of turbidity using a submersible sensor or sensor in a multiparameter sonde is useful for site-specific water-quality studies. Such turbidity data can be used for watershed investigations; for example, for determination of visual impairment (Davies-Colley and Smith, 2001), for correlation with concentrations of suspended sediment, total phosphorus, or other chemical constituents, and indicator bacteria (Christensen and others, 2000; Uhrich and Bragg, 2003), and for long-term monitoring. Turbidity sensors for these applications utilize a variety of different light sources and other options to compensate for interferences (fig. 6.7–2, table 6.7–3).

Multiparameter instruments with internal batteries and memory can be used in surface-water studies that require long-term deployment. Guidelines for long-term instrument deployment fall under the topic of continuous monitors, and are beyond the scope of this section—refer to the manufacturer's instructions and recommendations, and to guidance documents such as Wagner and others (2000).

Some submersible turbidity sensors can be adjusted to operate within differing turbidity ranges. For example, although the maximum turbidity based on factory settings is just over 1,000 FNU, the YSI 6026 can be factory adjusted to read turbidities up to 4,000 FNU, allowing readings to be obtained that would otherwise be off scale. The adjustment, however, is specific to the individual instrument, with calibration being non-linear between 1,000 and 4,000 FNU; hence,

readings in this high range are not reproducible between instruments (M. Lizotte, YSI Environmental, written commun., May 2003). Any such adjustments made to an instrument's operating range must be documented in the instrument's logbook and in applicable field notes.

Dynamic determination generally reflects the dynamic conditions in a water body more accurately than static measurements of discrete samples because it avoids problems of particle settling. Instrumentation of this type, however, is not approved by the USEPA for evaluating drinking water.

The following procedures apply to in situ determination and to determination of turbidity in a flowthrough chamber:

1. Calibrate the instrument in the laboratory or office using a calibration solution before leaving for the field (see section 6.7.2).
2. At the field site, verify that the instrument has retained its calibration within 5 percent. If it fails verification, then the instrument must be recalibrated.
3. Follow procedures for selection of surface-water and ground-water sampling locations and for dynamic (**Procedure A**) or flowthrough-chamber (**Procedure B**) field measurements, as described in NFM 6.0.

   Procedure A: Dynamic measurement—Immerse the multi-parameter sonde or single turbidity sensor in the water body.

   Procedure B: Flowthrough chamber (ground water only)—Secure chamber cover over sonde/sensor to form an air-tight and water-tight seal. Discharge the first sample aliquot to waste, then open the connection to the flowthrough chamber and pump a sample from the water source to the flowthrough chamber according to instructions in NFM 6.0.3.

4. Activate the instrument to display turbidity values in real time.
5. Agitate the turbidity sensor to remove bubbles from the optical surface: move the sensor up and down or in a circular pattern and (or) activate the wiper mechanism, if available.
6. Monitor turbidity readings as described for other field measurements in NFM 6.0.
    - Allow at least 2 minutes before recording the required number of sequential readings. Some instruments may require as much as 10-20 minutes warmup time.
    - Stability is reached if values for three (for in situ procedure) to five (for flowthrough-chamber procedure) or more sequential readings, spaced at regular time increments, are within 10 percent.
7. Record turbidity readings on the field form and in field notes, including the instrument manufacturer and model. Use reporting units appropriate for the instrument, as described in tables 6.7–3 and 6.7–4.
8. **Surface-water sites—**Repeat steps 5–7 for dynamic measurements (**Procedure A**) at each vertical to be measured. Determine the number of vertical locations; refer to NFM 6.0.2.A and NFM 4.1.
9. Before leaving the field, clean the sonde/sensor with a thorough rinse of deionized water and place it in the storage vessel. Most instruments require a small amount of deionized water to be stored in the storage vessel with the sensors. **Follow the manufacturer's recommendations for storage of sondes/sensors.**
10. Record data in the database in reporting units as described in table 6.7–4, using method codes specific to the instrument in use (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005).
11. If turbidities are higher than the instrument range, dilutions will be necessary. Turbidity will need to be measured with static methods. Take a representative sample and dilute it with one or more equal volumes of turbidity-free water, recording the volume of water used for dilution. In such cases, **qualify the resulting data with a "d" in the "Value Qualifier Code" field in NWIS**.
12. **Quality control.** Periodically check instrument performance by placing a primary or secondary calibration solution in the instrument storage vessel and comparing the standard value with the reading displayed. Record in the instrument maintenance logbook all the readings obtained.

SPECTROPHOTOMETRIC DETERMINATION 6.7.3.C

The attenuation method described below uses a field spectrophotometer to provide a relative measure of the sample turbidity. The spectrophotometer directs a beam of light through the sample at a specific wavelength and measures the amount of transmitted light reaching the "transmitted" detector (fig. 6.7–1). The decrease in the detected light intensity caused by absorption or scattering in the sample is calibrated to accepted calibration turbidity solutions (see 6.7.1.C). Spectrophotometric measurement of turbidity yields readings in AU or FAU, depending on the light source.

- **This method is not approved by the USEPA** and is subject to many interferences. It is a useful method, for example, if the purpose for the turbidity determination is as an indicator of ambient or "stabilized" conditions during well development or purging.
- **Turbidity values less than 50 FAU—the range for most surface water and ground water—are inaccurate using this method** and the procedure is recommended only as a measure of relative turbidity among different samples.

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An FAU is equivalent to an NTU when measuring formazin, but they are not necessarily equivalent when measuring water samples or other types of standards. Relations among different instrument types are site specific. Be careful to enter absorption-derived turbidity values into the data base using the appropriate reporting units, parameter codes, and method codes according to tables 6.7–3 and the methods and parameter codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls).

To make spectrophotometric determinations of turbidity:

1. Before starting, check operating instructions for the specific instrument in use**.**
2. Enter the stored program number for turbidity, if any. Record the light wavelength used. A wavelength of 860 nm (bandwidth 60 nm) is specified by ISO 7027 for reporting in FAU.
3. Use a set of clean, matched 10-mL sample cells.
4. Calibrate according to instructions in the instrument's operating manual (see section 6.7.2).
5. If recently calibrated, take check measurements using calibration solutions that bracket the range anticipated in the sample solution. **Clean the 10-mL cell after using calibrants.**
6. Fill one cell to the 10-mL mark with turbidity-free water and cap with a stopper. NOTE: If measurement of color-derived turbidity is not desired, filter (using a 0.2-µm pore-size filter) an aliquot of the sample water and use this water in place of turbidity-free water.
7. Place blank sample into the cell holder, close the light shield, and verify a zero reading.
8. Fill the other cell to the 10-mL mark with sample water and cap with a stopper. Gently invert 25 times to suspend all particulates.
9. Carefully place sample into the cell holder and close the light shield. Record this reading in AU or FAU.

QUALITY-ASSURANCE PROCEDURES 6.7.4

Quality-assurance procedures should be developed in accordance with the objectives of the sampling or monitoring plan. The primary emphasis should be on quantifying the sources of variability and bias in turbidity measurements that can affect the utility of the data being collected. **Where turbidity from one water source will be compared with turbidity from another source or against a numerical criterion, the use of consistent procedures, instrumentation, and supplies is critical.**

VARIABILITY 6.7.4.A

Sources of variability include the different instruments in use (even similar models), differing subsampling techniques, different operators, spatial and temporal variations in the water body being measured, and different sampling procedures being used. The data resulting from static turbidity determinations also can be negatively biased from particle settling.

Variability in turbidity can be quantified through repeated measurements of turbidity at different times, using different instrumentation, or using different methods. In some cases it might be useful to compare results of a field-turbidity measurement with that of a laboratory-analyzed sample. Keep in mind, however, that sample properties that affect turbidity can degrade during sample transit and storage (see section 6.7.3). The following are examples of tests that can be performed periodically for quality control of some sources of variability in turbidity determinations.

- **Static determination**
  - **Measurement variability:** For one cuvette with sample and gently agitate to keep particulates in suspension. Measure the turbidity and remove the cuvette from the turbidimeter. Repeat at least three times, using the same cuvette. Record each reading and determine the standard deviation of the measurements. Consider submitting replicate samples for laboratory analysis. These procedures may not adequately characterize measurement variability that is caused by particle settling.

— **Subsampling variability:** For one water sample, agitate the sample, then withdraw an aliquot into the cuvette, measure turbidity, discard the sample, and clean the cuvette. Repeat at least three times. Record each reading and determine the standard deviation of the measurements.

— **Operator variability:** Split one water sample into two or more subsamples using a churn splitter. Have different operators prepare cuvettes and measure turbidity on the subsamples. Consider submitting samples for laboratory analysis.

— **Sampling variability:** Collect at least two independent samples from the source using standard techniques. Prepare turbidity cuvettes for each sample and measure turbidity.

▶ **Dynamic Determination**

— **Cross-sectional variability:** At a field site, measure turbidity at a number of verticals across the stream width (see NFM 4 and 6.0). Compare against measurements at the centroid, stream margins, locations for continuous monitors, different depths, or against a static measurement from a composite sample using a meter that is optically compatible with the dynamic meter. Keep in mind that the static measurement will likely be biased low if sand or coarse silt are present.

— **Measurement variability:** At a field site, repeat turbidity measurements three or more times at the same location, one after another. Record these values after removing the meter from the water. Use the same instrument for each set of measurements. Consider submitting samples for laboratory analysis.

— **Operator variability:** At a field site, have two or more people determine turbidity at the established measurement location. Use the same instrument for each set of measurements, although it can be calibrated by each person independently to incorporate all sources of variability.

If sand or coarse silt are present in the sample, qualify your static-determination data being entered into NWIS with an "E" remark code.

BIAS 6.7.4.B

Sources of bias can include effects on measurements from various properties of water (table 6.7–1), interferences (table 6.7–2), sampling and subsampling techniques, instrument drift, biofouling, sensor damage, different operators, and different protocols being employed. Bias in turbidity is quantified through measurements of turbidity against known calibration solutions, at different times, using different instrumentation, or with different methods. This is particularly important before and after a measurement series, either in a laboratory or when servicing a continuous monitor in the field. Following are examples of quality-assurance tests that can be performed periodically for static or dynamic determinations of turbidity.

- **Instrument Drift**: After a series of measurements and prior to calibration, measure turbidity using known calibrants, including turbidity-free water or zero-turbidity calibration solution and a calibration (or "check") solution near the maximum calibrated range. Record the turbidity before making any adjustments to instrument calibration. Bias is computed as the percent difference between readings before calibration and readings at the same range after calibration. Instrument drift is most important to document in continuous monitoring applications.
- **Fouling**: After a series of measurements and before calibration, measure source-water turbidity using known calibrants, including turbidity-free water or zero-turbidity calibration solution and a calibration (or "check") solution near the maximum calibrated range. Record data. Clean the cuvette or submersible sensor and repeat measurements of source water and calibrants. Record data. Calculate bias as the percent difference between the calibrant reading of the uncleaned sensor and the cleaned sensor.
- **Operator Bias:** Similar to Operator Variability (above), bias can result from inconsistencies in methods among different operators. Split one water sample into two or more subsamples using a churn splitter. Have different operators prepare cuvettes and measure turbidity on the subsamples. Consider submitting samples to a laboratory for analysis. Calculate bias as the percent difference between the turbidity readings obtained by the different operators.

6.7.5 DATA REPORTING AND INTERPRETATION

To minimize comparison of data derived from substantially different instrument designs, USGS turbidity data are stored according to the instrument designs and reporting units indicated in table 6.7–4, with the method codes describing the specific instrument used. **Parameter codes associated with instrument design and reporting units, and method codes associated with individual instruments are detailed in the Excel spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls (accessed 6/15/2012).** Method codes are used with these data to provide information that can be used to understand potential differences in turbidity data.

In some cases, instruments are designed to operate in different modes (for example ratiometric or non-ratiometric). Such instruments are listed multiple times in the spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls (accessed 9/30/2005), corresponding to different parameter codes to distinguish their different settings. Be careful to document all instrument settings and dilution factors, and use parameter codes and method codes appropriate for instrument settings. For data storage in NWIS, samples with noticeable sand or coarse materials that were measured by static techniques must be qualified as Estimates with an "E" in the Remark code, and diluted samples must be entered with a "d" in the Value Qualifier Code field.

- USGS personnel: Do not use parameter codes P00076 and P61028. These codes are reserved for historical turbidity data for which an equipment method cannot be assigned.

Guidelines for reporting turbidity measurements to the nearest acceptable digit according to EPA Method 180.1, GLI Method 2, ASTM, and ISO 7027 methods are listed in table 6.7–6. The indicated values represent the least significant digit in the measurement. Reported turbidity values should be rounded to this level of precision. For example, a value of 43.12 units displayed by an instrument would be reported as 45 under USEPA guidelines, but as 43 under ASTM guidelines. In contrast, a value of 13.42 units displayed by an instrument would be reported as 13 under all the guidelines. For most applications, the USGS will conform to ASTM guidelines unless data were specifically collected for drinking-water compliance (using either EPA Method 180.1, GLI Method 2, or ISO 7027).

Traditionally, the USGS has censored data below 2 NTU as not-detected (less than 2). However, improvements in instrument capabilities have resulted in greater reliability at this low end. Based on input from instrument manufacturers, ASTM has chosen to report data below 1 to the nearest 0.05 unit, and to the nearest 0.1 for data ranging between 1 and 10. Because turbidities in this range should be free of appreciable color or settleable materials, static methods should provide reasonable comparisons with dynamic methods. Before publishing such data, study personnel should consider submitting samples of low-turbidity water to the NWQL or other laboratory for confirmation of low-end resolution and reproducibility.

Additionally, the high end of an instrument's range should be determined. Data greater than this value should be censored as greater than the maximum value. For dynamic sensors on a submersible sonde, cover the optics with a piece of lint-free cloth and record the resulting turbidity. Confirm this value with the manufacturer's recommendations. Qualify data having the maximum value by showing a ">" remark code in NWIS.

Table 6.7–6. Guidelines for reporting turbidity units

[For ASTM and USGS measurements, refer to table 6.7—3 for reporting units based on instrument design. **Abbreviations:** USGS, U.S. Geological Survey; ASTM, ASTM International; EPA 180.1, U.S. Environmental Protection Agency method 180.1 (1993); GLI, Great Lakes Instruments; ISO 7027, International Organization for Standardization method 7027 (1999); NTU, nephelometric turbidity units; FNMU, Formazin Nephelometric Multibeam Units; FNU, Formazin Nephelometric Units; N/A, not applicable;<, less than; ≥, equal to or greater than]

Turbidity Reading	USGS	ASTM	EPA 180.1 (NTU)	GLI Method 2 (FNMU)	ISO 7027 (FNU)
0—<1	0.05	0.05	0.05	0.05	0.01
1—<10	.1	.1	.1	.1	.1
10—<40	1	1	1	1	1
40—<100	1	1	5	5	N/A
100—<400	10	10	10	10	N/A
400–<1,000	10	10	50	50	N/A
≥1,000	50	50	100	100	N/A

6.7.6 TROUBLESHOOTING

Consult the instrument manufacturer for additional guidance if the suggestions shown on table 6.7–7 do not remedy the problem encountered.

Table 6.7–7. Troubleshooting guide for field turbidity measurement

Symptom	Possible cause and corrective action
Erratic reading	• Check voltage of the batteries: replace weak batteries with new batteries. • Condensation on cell wall of static turbidimeter: see "Moisture" symptom. • Bubbles in sampling system or on optical surface of sensor: tap sample line to flowthrough cell or chamber systems to dislodge bubbles; adjust degassing apparatus; remove bubbles on sonde/sensor system by agitating the unit repeatedly or by activating the wiper mechanism.
Unusually high or low turbidity	• Bubbles in sampling system or on optical surface of sensor: see "Erratic reading" symptom. • Fouling of optical surfaces. Clean with lint-free cloth or toothbrush. • Wiper mechanism is "parking" on optical surfaces. Use software to reset wiper, or replace wiper mechanism (may require factory repair). • Inappropriate turbidimeter for environmental conditions. See tables 6.7–1, 6.7–2, and 6.7–3, or figure 6.7–2 to determine most appropriate turbidimeter type.
Calibration value "out of range"	• Contaminated calibrant solution or value entered incorrectly. Verify intended calibrant value and start over. If problem persists, try using a different batch of calibrant solution.
Readings first appear stable, then begin to increase inexplicably	• Check for moisture on cell wall: see "Moisture" symptom.
Moisture condensation on cell wall (static turbidimeter or spectrophotometer)	• Wipe cell dry with soft, lint-free cloth. • Apply a thin veneer of silicon oil (first check instrument manufacturer's instructions). • Add gas sweep to system.
Blank samples or reference material standards do not read accurately	• Check that the cells are oriented as instructed. • Check age/expiration of calibrant solutions. • Check accuracy against that of another instrument.

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* The revised version of this report was "in press" at the time of this writing and is intended to replace Wagner and others (2000) upon publication. The revised report will be referenced as Wagner, R.J., Boulger, R.W., and Smith, B.A., 2005, Revised guidelines and standard procedures for continuous water-quality monitors: Station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods, book 9, chap. B.

USE OF MULTIPARAMETER INSTRUMENTS FOR ROUTINE FIELD MEASUREMENTS 6.8

By Jacob Gibs, Franceska D. Wilde, and Heather A. Heckathorn

Appendix

Tables

The citation for this section (6.8) of NFM 6 is as follows:

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USE OF MULTIPARAMETER INSTRUMENTS FOR ROUTINE FIELD MEASUREMENTS 6.8

By **Jacob Gibs, Franceska D. Wilde, and Heather A. Heckathorn**

The miniaturization of sensors and other technological advances in electronics have resulted in water-quality instruments that house multiple sensors capable of simultaneous readings for various field measurements[1] in environmental waters. With the use of these multiparameter instruments, field measurements can be determined with considerable reduction in the field work that generally is required when using multiple single-parameter instruments (table 6.8–1). This section addresses the short-term or discrete-measurement use of portable multiparameter instruments. Refer to Wagner and others (2006) for long-term or continuous-monitor deployment in surface water.

MULTIPARAMETER INSTRUMENT: An electronic instrument that contains sensors (each specific to the measurement of a given physical, chemical, or biological property) that are bundled in a single housing (a sonde) and deployed in environmental waters.

[1]The term "field measurement(s)" is synonymous in this report with the terms field properties and field parameters. USGS field measurements include, for example, water temperature, pH, specific electrical conductance, turbidity, oxidation-reduction potential, barometric pressure, and calculations such as salinity and percent of dissolved oxygen in milligrams per liter. The term "field parameter" commonly is used in the environmental literature.

Table 6.8–1. Advantages and limitations of multiparameter instruments for field use

Advantages	Limitations
Efficiency is increased. Instruments are easy to clean, calibrate, and deploy. The time required to collect discrete samples for determining field properties is minimized. The time needed to measure and record multiple field properties is reduced. In situ measurement is likely to be more accurate and precise than measurements made in samples removed from their source. Instruments can store data, either in a display device or to internal memory. Instruments may be capable of long-term deployment.	Repair of sensors while working onsite often is not possible. Sensor replacement in the field may be unwieldy or not possible. Sensors must be replaced in a clean, dry environment. Backup field instruments (single parameter or multiparameter) are recommended to prevent data loss and extended field time. Purchase, repair, and replacement costs for multiparameter instruments are higher than for single-parameter instruments.

Quality assurance. To ensure the quality of the data collected, this section of NFM 6 describes standard operating procedures and recommendations that have been developed for routine U.S. Geological Survey (USGS) field studies. The instrument manufacturer is, however, the primary source of information about the maintenance and use of a specific instrument. The protocols and recommendations described in this section are meant to complement and enhance the manufacturer's guidelines, providing the level of quality assurance for which USGS data are held accountable.[2]

[2]USGS personnel should discuss any discrepancies between the protocols and recommendations described in this manual and the instructions provided by the instrument manufacturer with their water-quality specialists or with the USGS Office of Water Quality.

EQUIPMENT AND SUPPLIES 6.8.1

Multiparameter instruments are available for long- or short-term deployment at a stream, lake, reservoir, ground-water well, or other environmental setting, and their sondes[3] are suitable for water that is fresh, brackish, saline, or polluted. Sensor housings (the sonde) of multiparameter instruments generally are available in a range of diameters from about 4 inches (in.) (10 centimeters (cm)) to less than 2 in. (5.1 cm). Small-diameter sondes may be used for downhole measurements in wells and may have more limited sensor capability than the larger diameter sonde. Depending on the manufacturer, some instruments can store instantaneous or continuous measurements to internal or external memory in a format compatible with a hand-held display, personal digital assistant (PDA), or laptop computer.

Advances in technology and design are expanding the sensor[3] capabilities of multiparameter instruments and are improving instrument utility. The configuration and sensors that are available for multiparameter instruments can vary considerably among manufacturers. The procedures required for the maintenance, calibration, and use of these instruments also can change over time as a result of the technological changes being implemented; such information generally is available from the manufacturer, either online or as a manual or other document. **Users must stay current as to how their instrument operates and is maintained.**

- Sensors for the determination of water temperature, specific electrical conductance (SC), pH, dissolved-oxygen concentration (DO)[4], and turbidity commonly are bundled in sondes used for USGS water-quality studies, as these measurements are routine for much USGS work.
- Sensors that determine oxidation-reduction potential (ORP or redox) and barometric pressure, and that calculate salinity, also are commonly included in the sonde.

[3]The term sensor, which is used in this report, is synonymous with the term "probe" that is common in the environmental literature. For multiparameter measurements, the sensors are bundled in a submersible sonde.
[4]DO is calculated as the percent of dissolved-oxygen concentration at saturation.

- For some instruments, sensors are available to measure fluorescence,[5] water depth, and velocity. In some cases, specific-ion electrodes (for example, nitrate, ammonia, ammonium, and chloride) can be incorporated in a sonde. Use of sensors to measure cholorphyll and concentrations of specific nutrient species are becoming more common in USGS work. Some instruments include global positioning systems.
- When making field measurements in surface water, the sondes commonly are immersed in situ (directly within the water body). As an alternative to in situ deployment, a flowthough cell containing the sonde can be set up above land surface, to which sample water is pumped. The flowthrough cell commonly is used to monitor field measurements for ground-water investigations and for calibration of the sensors.

The types and number of sensors that can be bundled in a given sonde depend on the instrument model and manufacturer. When selecting a sensor, consult the manufacturer's recommendations and specifications for the instrument, taking into consideration the environmental conditions to be encountered, the data-quality objectives of the study, and the specific benefit of a particular sensor technology that might be applicable to the anticipated field conditions. The manufacturer is the most knowledgeable source of information for a given instrument. **Consult the manufacturer's maintenance instructions for each instrument model before using the instrument.**

Table 6.8–2 lists the equipment specifications and calibration solutions required when determining field-measurement values using a multiparameter instrument. The ancillary supplies needed for measuring field properties using multiparameter instruments (table 6.8–3) are the same or similar to those required for the calibration and maintenance of single-parameter instruments, and are discussed in greater detail in the individual field-measurement sections (NFM 6.1 through 6.7) of Chapter 6.

[5]Fluorescence sensors indicate different algal pigment concentrations; see NFM 7.4 for additional information.

Table 6.8–2. Specifications and calibration solutions for multiparameter instruments

[±, plus or minus; -, minus; +, plus; °C, degrees Celsius; mV, millivolt; >, greater than; SC, specific electrical conductance; µS/cm, microsiemens per centimeter at 25°C; DO, dissolved oxygen; mg/L, milligrams per liter; ORP, oxidation-reduction (redox) potential; NIST, National Institute of Standards and Technology; L, liter; ≤, less than or equal to; µm, micrometer; mL, milliliter; MSDS, Material Safety Data Sheet; SDVB, styrene-divinylbenzene beads; TDS, total dissolved solids; NFM, *National Field Manual for the Collection of Water-Quality Data*; USGS, U.S. Geological Survey.]

Item[1]	Description[2]
Instrument (sensor) specifications:	Visual display - digital readout.
pH and millivolt	pH sensor - range of at least 2 to 12, preferably 0 to 14, pH units. Accuracy, ±0.2 pH units. Millivolt readout - accuracy, ±1.0 mV.
Temperature	Temperature sensor - thermistor range, at least -5 to +45°C. Accuracy, ±0.2°C.
SC	SC sensor - temperature compensating. Accuracy, the greater of 0.5±0.5 percent of reading or ±2 µS/cm.
DO	**DO polarographic sensor** (amperometric method) - range from 0.05 to 20 mg/L. Accuracy, the greater of ±2 percent of reading or ±0.2 mg/L. **DO optical sensor** (luminescent-sensor method) - range from 0.05 to 20 mg/L. Accuracy, the greater of ±1 percent of reading or ±0.1 mg/L.
Turbidity	Turbidity sensor[3] - range and accuracy depend on the instrument type, manufacturer, and field conditions (see NFM 6.7). Choice of instrument will depend on application. Most multiparameter-instrument turbidity sensors use a monochrome light source with a spectral output typically near infrared (780 to 900 nanometers), usually a light-emitting diode. *Note*: Instrument should include a calibration cup specifically designed by the manufacturer, if available.
ORP[3]	ORP sensors - accuracy, ±20 mV. For guidance on Eh measurements using the platinum electrode, refer to NFM 6, section 6.5 and the manufacturer's instructions.
Air pressure	Select instruments that incorporate an **altimeter/barometer** (measures to the nearest 1 millimeter).
Other sensors[3]	Check the text for this section and the manufacturer's instructions for the availability of other sensors.

Table 6.8–2. Specifications and calibration solutions for multiparameter instruments — *continued*

Item[1]	Description[2]
Sensor-calibration solutions:	(Keep the respective **MSDS guidance** on hand in the laboratory and in the field. Dispose of hazardous waste according to regulations, using a licensed disposal company.)
pH buffers	Standard buffers are pH 4, 7, and 10. Temperature-correction chart(s) supplied by the buffer manufacturer or distributor are required.
SC standards	Use the SC standard(s) recommended by the manufacturer for calibration. NOTE: The manufacturer might require a proprietary calibration solution. For field verification of the calibration, select additional standard(s) that bracket the expected or known sample SC. Do not dilute a concentrated standard to prepare a standard of lower conductivity.
DO standard	Zero DO calibration solution. Dissolve 1 gram of sodium sulfite and a few crystals of cobalt chloride[4] in 1 liter of deionized water (prepared during the week of use). **Cobalt chloride is toxic; check the MSDS for safe handling.**
ORP standard	ZoBell's solution[5] - This solution contains cyanide and may be harmful if absorbed through skin, inhaled, or swallowed. Check the MSDS for safe handling. - Use a dedicated hazardous waste disposal container for ZoBell's solution. **Do not pour ZoBell's solution down the sink drain or onto the ground. Do not mix with acids or combustible materials.**
Turbidity standard	Turbidity standard solutions with various ranges are available commercially. Most sensor manufacturers recommend either formazin-based or SDVB-polymer standards for calibrating their turbidity sensors. **Do not use gels or solids for calibrating instruments** (see sections 6.8.2 and NFM 6.7). - Turbidity-free water (deionized water filtered through a ≤0.2-µm membrane filter). - Formazin stock suspension can be obtained commercially or prepared in-house from hydrazine sulfate and hexamethylenetetramine (safety precautions for handling these chemicals are described in NFM 6.7, section 6.7.2)

[1]Modify this list to meet the specific needs of the field effort and the specific requirements for the multiparameter instrument to be used.

[2]The accuracy specification provided in this table has been generalized, based on a survey of three or more manufacturers with instruments in common use among USGS field studies. Consult the manufacturer's operators' manual for the level of accuracy for a specific instrument.

[3]The turbidity sensor commonly is required or recommended for use (section 6.7). ORP sensors are less commonly used for USGS studies; see the description in section 6.5. Follow the manufacturer's guidance for use of the salinity or TDS option, and for other ion-selective sensors (for example, for nitrogen species and chlorophyll).

[4]Prepare fresh zero DO solution for each use. CAUTION: Use of cobalt chloride is recommended in Standard Methods (American Public Health Association, 2005); however, this is a toxic substance that must be handled with care and disposed of in accordance with prevailingregulations. If possible, prepare a zero-DO solution without using cobalt chloride.

[5]Alternatives to Zobell's are being investigated (January 2008).

EQUIPMENT TRANSPORT 6.8.1.A

Transport the multiparameter instrument in a case that is designed to protect this equipment.

- To avoid damaging the sensitive and expensive field-measurement sensors, keep either the sensor guard or transportation/calibration cup installed. Some manufacturers specify adding a small amount of water to the transportation/calibration cup for transport between field sites; follow the manufacturer's recommendations.
- When packing the instrument for transport, use a case provided by the manufacturer; alternatively, obtain a suitable case, such as a Pelican™ case, Otter® box[6], or a tool box, and modify it as needed.
  - — Cases must be padded to absorb shock, using material that does not absorb water.
  - — Pelican and Otter boxes are airtight; the case needs to be vented if using sensors that have a flexible or semi-permeable membrane.
  - — A white or light-colored case should be used to help deflect solar heating of the sonde.

INSTRUMENT MAINTENANCE AND STORAGE 6.8.1.B

Each instrument requires its own (dedicated) log book that accompanies the instrument, in which permanent records of instrument calibrations, bench checks, sensor replacements, general maintenance, and repairs are logged. The following recommendations pertain to maintenance of the multiparameter instrument that is deployed over discrete or short (attended) time intervals. For maintenance of instruments intended for long-term or unattended instrument deployment, refer to Wagner and others (2006) and the instructions provided by the manufacturer.

[6]Examples of transport cases can be found at www.otterbox.com or www.pelican.com (accessed 5/22/2007).

- **Sensor and sonde care and maintenance:**
  - Rinse the sensors immediately after each use with deionized water (DIW).
  - If the multiparameter instrument (handheld display and sensors-containing sonde) is particularly dirty or will be stored for longer than one day, clean it with a mild, nonphosphate detergent solution using a small, nonabrasive brush or cotton swab or cloth, followed by a thorough water rinse.
  - Avoid using organic solvents or other corrosive solutions to clean the sensors.
  - O-rings used for some types of dissolved-oxygen sensors are not very robust; inspect such O-rings before each DO measurement and replace if damaged.
  - **Do not coat the sonde or sensors with protective or anti-fouling paint,** except as specifically instructed by the manufacturer.
  - Manufacturers may have instructions specific to their sensors—**check the manufacturer's operating manual for each instrument that will be in use.**
- **Wiper and wiper-brush maintenance**:
  - Inspect the wiper pad and (or) wiper brush for dirt, deterioration, and damage after each use of the sonde. (Not all instruments have a wiper or wiper-brush mechanism.)
  - Check wiper pads for wear, excessive discoloration, and particle accumulation, and change the pads as needed. Check that the wiper arm is parking properly. Follow the manufacturer's guidance for conditions requiring changing the pads and for wiper maintenance.
  - A soft toothbrush can be used to clean wiper-brush bristles. Rinse with fresh tap water or DIW.
  - Wiper-brush bristles should be kept moist at the start of the operation to prevent them from drying. If the bristles have dried, soak them in DIW and manually loosen them before deploying the sonde.

- **General care of multiparameter instruments:**
  - Do not leave instruments in vehicles for long periods of time during extremes in temperature.
  - At least once a year inspect cables for damage, and electronic connectors and sensor ports for corrosion.
  - Inspect and clean the bulkhead O-rings and grease them with silicone lubricant annually, at a minimum. Replace any damaged O-rings.
  - Store cables in a plastic container only after they are clean, dry, and neatly coiled (no tighter than 6-inch-diameter coils). Use protective plugs when cable connectors are not in use. When in use, protect cables from abrasion or unnecessary tension.
  - Make sure that the instrument is running on software and firmware that is up-to-date. Check for updates from the manufacturer every 6 months or more frequently and follow the download or other installation instructions.
- **General storage recommendations for multiparameter instruments and instrument cases**:
  - For short-term storage, some sensors need a small amount of the storage solution added to the protective (transport) cap or calibration cup; check the manufacturer's instructions.
  - For long-term storage (longer than several weeks), remove the internal batteries; however, be sure to check the instrument manual for guidance before removing all of the batteries.
  - Store multiparameter instruments in a carrying case or plastic container with foam cushioning (for shock protection). Keep the instrument and case out of direct sunlight and protected against extremely hot or cold temperatures.
  - Insert a sensor-port plug into any vacant sensor port to prevent damage to the vacant port during maintenance, operation, or storage.

Table 6.8–3. General supplies related to field-measurement activities

[DO, dissolved oxygen; mL, milliliter; L, liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ASTM, ASTM International Company; NFM, *National Field Manual for the Collection of Water-Quality Data;* USGS, U.S. Geological Survey]

Item[1]	Information
Flowthrough cell	Standard flowthrough cell, obtained from the manufacturer of the instrument. (Commonly used for ground water or other water pumped from the water source to the airtight cell for measurement of field properties.)
Extra sensors and meters	Single-parameter meters and sensors or a multiparameter sonde (as a field backup). Refer to equipment lists and descriptions and instructions provided in NFM 6, sections 6.1 through 6.7.
Membrane-replacement kit for amperometric DO	Membrane-replacement kit (includes membranes or screw-on membrane caps, O-rings, filling solution).
Calibration (laboratory) thermometer	Liquid-in-glass or electronic-thermistor thermometer, either NIST-certified or manufacturer-certified as NIST-traceable. (See NFM 6, section 6.1 for USGS standard specifications.)
Field thermometer	Non-mercury liquid-in-glass or thermistor thermometer that has been office-laboratory certified against a properly certified calibration thermometer. (See NFM 6, section 6.1 for USGS standard specifications.)
Turbidity container and flasks	Bottle for turbidity-free water, cleaned and rinsed three times with filtered water before starting each field trip. Volumetric flask, Class A, 100 mL or 500 mL, if dilution of stock solutions is necessary (see section 6.8.2).
Carrying case	Protective case, vented, white or other reflective color, to hold the multiparameter instrument during transport and storage.
Holding stand[2]	A stand to support the multiparameter sonde during calibration.
Log book(s)[3]	One log book per instrument (multiparameter and single-parameter), for recording instrument calibrations, maintenance, and repairs. Log book travels with the instrument.
Flasks, beakers, and other measurement vessels	Insulated flask or beaker and additional polyethylene or Teflon® preferable beakers for temperature check or other field needs. Assorted sizes, 50 to 150 mL. Beakers must be clean but not acid rinsed.
Deionized water (DIW)	1 L of DIW with a maximum conductivity of 1 µS/cm (ASTM Type 1) for rinsing sensors.
Paper tissues	Laboratory grades (for example, lint free and (for turbidity) extra lint free Kimwipes®), soft, disposable.

Table 6.8–3. General supplies related to field-measurement activities — *continued*

Item[1]	Information
Dispenser (squeeze) bottles	Polyethylene to contain DIW; for rinsing instruments and instrument sensors.
Disposable gloves	Laboratory gloves, disposable, non-powdered and of a material suitable to contact anticipated chemical solutions and environmental waters or wastewater. Keep a supply on hand in the field vehicle.
Brushes for equipment cleaning	Brushes of various sizes, but generally small and soft to prevent scratching the sensor(s) or other surfaces.
Minnow bucket with tether, mesh bag, or equivalent	Used to contain fresh sample water into which tightly capped calibration solutions are immersed for thermal equilibration with the temperature of the sample water before being used for sensor calibration.
Antistatic spray or polish	Used on the digital display screen of a multiparameter instrument.
Cleaning solution	1 L of nonphosphate laboratory detergent (see NFM 3 for solution-concentration guidelines).
Batteries and/or battery pack(s)	Check that batteries are fully charged; bring spares.
Safety equipment	Select safety equipment appropriate for the field effort conditions, such as gloves, eye protection, face mask, apron, chemical spill kit, first-aid kit.
Waste-disposal containers	Appropriate for safe containment of regulated (hazardous or toxic) substances and dedicated to use for the respective waste material (examples: ZoBell's solution, methanol, and acid and turbidity calibration solutions).

[1]Modify this list to meet the specific needs of the field effort.
[2]USGS personnel may check for the availability of instrument stands (HIF # 6103032 or #6103035) at the USGS Hydrologic Instrumentation Facility.
[3]Bound log books with water-resistant pages are available to USGS personnel through the USGS One Stop Shopping store.

6.8.2 CALIBRATION

Multiparameter instruments must be tested and the sensors calibrated before each field use**.** With some exceptions (for example, turbidity calibration), calibrations are performed in the field in preparation for making measurements.

When visiting more than one site for field measurements, the sensors and sonde housing must be cleaned and then the sensor calibration verified for each site. Field calibration should be completed in an area sheltered from wind, dust, and temperature fluctuations. Consult the manufacturer's guidelines before beginning the calibration process and contact the manufacturer's technical support if problems or questions arise.

Ensure that the sensors are properly installed in the sonde. Before beginning the calibration process, check the power source; only use batteries that indicate a full charge.

- Most multiparameter instruments perform best if allowed to warm up for at least 10 minutes after being turned on, or according to the manufacturer's recommendation.
- The following order is recommended for performing calibration or accuracy checks in the field:

1. **Temperature** (using a thermometer that has been calibrated and office-certified, as described in NFM 6.1)
2. **Specific electrical conductance (SC)** (note that the value of the SC standard solution changes by more than 3 percent when the temperature is less than (<) 6°C or greater than (>) 40°C; do not calibrate with standards <6°C or >40°C.
3. **Dissolved oxygen (DO)** (amperometric or luminescent-sensor methods using polarographic or optical sensors, respectively)
4. **pH** (be sure to check and adjust for the buffer pH value at the buffer temperature)
5. **Oxidation-reduction potential (ORP)**
6. **Turbidity** (most manufacturers recommend that the turbidity calibration be performed in a laboratory or other stable environment)
7. **Ion-selective electrodes, followed by chlorophyll-fluorescence and other sensors**.

- Complete the calibration field form during calibration (Appendix 6.8–A). Accurate calibration records must be maintained and entered into the appropriate instrument log book at the time of calibration.[7]
  - Keep a hard copy of the field form in the field or site folder. These records contain vital information that can be referenced if technical or legal questions arise. Interpretation of data analyses or data quality may depend on the documentation regarding instrument performance and the calibration solutions and the methods used, in addition to the results recorded. This record should be checked and verified by a second or third party.
  - The field form documents that a sensor has met the data-quality objectives of the study and that the calibration was performed according to the required standard operating procedures. Lot numbers and expiration dates of calibration solutions are recorded on the electronic or paper field form (Appendix 6.8–A).
  - The instrument log book is the archival document for recording details chronologically, including calibrations, maintenance specific to the sensors, and general repairs. Log book entries should be recorded using black or blue ballpoint ink, preferably on water-resistant paper with the pages consecutively numbered and bound to deter page removal. To ensure the legal viability of the log-book record, a page never should be removed and a single line should be drawn through any erroneous information or data and initialed. (USGS personnel can obtain log books through One Stop Shopping).
- Clean the instrument onsite after each use to reduce the potential for site and sample cross contamination and loss of calibration.

Reagents used for calibration may be hazardous to health and require special handling. Review the MSDS for the reagent of concern. Keep the safety sheets handy.

[7]For USGS studies, the worksheet is included in the electronic (PCFF) and paper national surface-water and ground-water water-quality field-notes forms. Meter-calibration log books are available to USGS personnel through One Stop Shopping.

6.8.2.A STANDARD USGS CALIBRATION PROCEDURES FOR MULTIPARAMETER INSTRUMENTS

The results of sensor calibrations are recorded on a field form at the time of calibration (Appendix 6.8–A provides an example of a field form for recording calibrations and field measurements). In addition, a historical record of calibrations for each sensor used in a given multiparameter instrument must be kept in an instrument log book that accompanies the instrument to the field. This log book also is used to document maintenance, repairs, and sensor replacements for the instrument.

When calibrating multiparameter-instrument sensors:

1. **Follow the manufacturer's instructions** for the instrument model and sensors being used.
   - Become familiar with the operation and setup of the handheld or other display hardware and software. Make sure that the batteries are fully charged, or install fresh batteries.
   - Ensure that the instrument has been set for the appropriate measurement unit, if this option is available.
   - Ensure that the instrument has been warmed up for the amount of time recommended by the manufacturer.
2. **Bring calibration solutions (calibrants) to the temperature of the sample source**, to the degree possible.[8] Note there are exceptions to this protocol for SC and turbidity, as described below. To allow equilibration of the calibration solutions with ambient sample-water temperature, calibrant containers can be partially immersed in the stream being sampled, or in a bucket to which the ground water being sampled is pumped. **Great care must be taken to prevent water from getting close to the top of the calibrant container and contaminating the calibrant.**

Note 3/8/2012: Calibration requirements for field sensors are under review**.**

[8]For calibration of sensors for turbidity and specific electrical conductance, check with the manufacturer for guidance.

- Calibrate the instrument in a temperature-stable environment, out of the wind and direct sunlight.
- Use the calibration cup that comes with the instrument for calibration, unless otherwise instructed by the manufacturer. If a calibration cup is not available, follow the manufacturer's alternative recommendations.
- Use the recommended volume of calibrant when filling the calibration cup. The calibrant must cover the temperature sensor, as most sensors require temperature compensation.
- Be careful not to overtighten the calibration cup. This is especially important for DO calibration. Many calibration cups have vents that allow their equilibration with ambient pressure.
- For SC, do not equilibrate the temperature of the standards to that of the sample source if source temperature is less than 6°C or greater than 40°C, because the value of the SC calibration standard changes significantly (by more than 3 percent) as a function of temperature at these temperature extremes. In such situations, perform the SC calibration inside a room or vehicle in which the ambient temperature of the standards is maintained at a temperature >6°C and < 40°C.
- For turbidity, calibrations should be performed in an environment that is protected from wind and thermal fluctuations.

3. **Rinse sensors thoroughly three times with deionized water after use of each calibrant, followed by three rinses with the next calibrant to be used.**
   - To avoid dilution of calibration solutions, gently shake excess rinse water from sensors.
   - Use a lint-free laboratory tissue (for example, Kimwipes®) to absorb water droplets without touching or wiping the sensor surface; never touch or wipe the transparent surfaces associated with luminescent DO, pH, and turbidity sensors.
4. **Calibrate the SC and DO sensors before calibrating the pH sensor**. This helps prevent contamination of the SC sensor from pH buffer solutions (pH buffers have much higher conductivities than most environmental waters).
5. **Periodic removal and cleaning of sensors** may be needed for any multiparameter sonde that is deployed for long-term monitoring. The time interval between cleanings will depend on site conditions and study requirements.

Bring calibration solutions (standards and buffers) to the ambient temperature of the environmental sample to the degree possible.

6.8.2.B SENSOR-SPECIFIC CALIBRATION TIPS

The following guidelines comprise standard USGS procedures.

- Check sensor ports to be sure that either the ports have a properly installed sensor or that the empty ports are sealed. Sensors from which data are not being collected routinely can be removed from the sonde for safe storage, provided that the sensor is not necessary for the measurements of interest and provided that the empty port is sealed according to the manufacturer's instructions. The temperature sensor should not be removed. All electrical connections must be clean, dry, waterproof, and protected from dust.
- Clean sensors after each use and keep them maintained and stored according to the manufacturer's instructions.
  - Before calibrating and using an instrument in the field, inspect the sensors to be sure that they are clean and are not damaged.
  - Periodic cleaning may be needed for any instrument that is deployed for continuous monitoring (see Wagner and others, 2006).

Temperature (revised, 3/8/2012)

Check to ensure the accuracy of the temperature sensor at least every 3 months if the multiparameter instrument is in frequent use. **The accuracy of pH and other field measurements depends on the accuracy of the temperature measurement.**

1. Verify the accuracy of the temperature sensor against a certified NIST-traceable digital or liquid-in-glass thermometer ~~following the guidelines provided in NFM 6.1 (annual laboratory verification and biannual field checks are mandatory for USGS studies)~~.
   ***Note, 3/8/2012**: NFM 6.1 calibrations guidelines are under review.
   For the calibration check, the NIST thermometer and sonde thermistor should be as close together as possible without touching. For field verification, use a non-mercury thermometer that has been certified as accurate within the past 6 months and is tagged as such by the verifier. When making the field check, record the temperature readings of both the multiparameter instrument and the NIST-traceable thermometer in the instrument log book.
   - If the difference between the readings does not fall within the manufacturer-specified accuracy, return the instrument to the manufacturer for repair or replacement.
   - See NFM 6.1 for a description of the annual and biannual calibration protocol for liquid-in-glass and digital thermometers, which also require calibration checks. *See **Note** above.
2. Make sure that the temperature sensor is completely submerged.
3. Allow at least 1 minute for temperature equilibration and stabilization before recording the temperature value and proceeding with the other measurements.

Specific Electrical Conductance (SC) (see NFM 6.3, section 6.3.2)

1. **Most multiparameter instruments use a one-point calibration** to calibrate the SC sensor. Use a standard having the conductivity recommended by the instrument manufacturer; otherwise, select a standard that is close in conductivity to that of the environmental water.
   - Rinse the calibration cup and sonde using a small amount of standard. **Repeat this two more times** and then fill the cup with the recommended volume of standard.
   - The sensor should be completely submerged in the standard (if a hole exists in the side of the sensor, it must be covered by the standard). Low fluid level can cause an erroneous calibration or may result in an error message on the instrument display.

- The presence of air bubbles in SC electrodes will cause erroneous readings and incorrect calibration.
- Although most SC sensors are shielded from effects caused by proximity to transmission lines and to alternating-current (AC) electrical outlets and radio-frequency noise sources, be aware of the possibility of this interference and check with the instrument manufacturer.

2. Wait for readings to stabilize (approximately 30 seconds under normal conditions) before adjusting and saving the calibration point.

   - The USGS reports SC in units of microsiemens per centimeter (µS/cm). The default SC setting on many multiparameter instruments often is in units of millisiemens per centimeter (mS/cm). Either change the setting to µS/cm (if this option is available) or measure in mS/cm and then convert to µS/cm (multiply mS/cm by 1,000). **To fulfill USGS data protocols, record the SC value in µS/cm on paper or electronic (PCFF) field forms.**
   - Do not override a calibration error message without troubleshooting and correcting the cause of the error. For example, check the fluid level and check for air bubbles in the sensor.

3. To verify that the accuracy of the SC sensor is within the range of the conductivities to be measured:

   - Ensure the linearity of response of the SC sensor at low-conductivity values and check the zero response of the dry sensor in air (Wagner and others, 2006).
   - Select two standards ("check standards") that bracket the expected SC range of your water as closely as possible; a third standard that is at or close to the actual ambient conductivity helps to pinpoint the accuracy of the sensor. Equilibrate the temperature of the standard to that of the water body, unless the water temperature is < 6°C or > 40°C (use of this protocol can depend also on instrument software – consult the manufacturer's guidance). Follow the same procedure as for an actual calibration, but **do not lock in or adjust these readings—this is an accuracy check, not a calibration point.**

Handle conductivity standards in a manner so as to prevent their dilution or contamination.

- **Do not use expired standards.**
- **Do not reuse standard or pour used standard back into the bottle.**

Dissolved Oxygen (DO) (see also NFM 6.2, section 6.2.1.B)

Two sensor options are available for the DO measurement when using multiparameter instruments: the polarographic (or Clark cell) sensor or the luminescent (optical) sensor. Referring to NFM 6.2 on DO measurement methods, the polarographic-sensor option corresponds to the amperometric method, and the optical-sensor option corresponds to the luminescent-sensor method.

General comments:

- Follow the manufacturer's guidelines for care, proper setup, and calibration of the DO sensor for the instrument in use. **For either sensor type, most manufacturers recommend that the sensor be allowed to equilibrate to the temperature of the air-saturated water or water-vapor-saturated air for at least 15 minutes before calibration.**
- Before calibrating for 100-percent saturation of DO, loosen the calibration cup. (It should contain less than 1/8 in. (~0.32 cm) of water, or as recommended by the manufacturer.)
- Remove any water droplets from the thermistor or the DO membrane without wiping the membrane. Water droplets on these surfaces can cause a temperature compensation error in the DO calibration.
- Store and transport the sonde in a padded, vented, white (or light-colored) case to make DO calibration checks quicker and reduce the chance of DO sensor drift (since the instrument is in a more temperature-stable environment and can be calibrated within the cooler).
- Calibrate the DO sensor on the morning of the field day and check the calibration at each measurement station. Enter the barometric pressure (see NFM 6.2 for an explanation of corrected and uncorrected values).

TECHNICAL NOTE: Check the manufacturer's instructions regarding the need to recalibrate amperometric-instrument sensors with changes in altitude. For some instruments, the DO sensor should be recalibrated at each site at which there is a change of approximately 900 ft (~ 300 m) in altitude. Luminescent sensors tend to keep calibration over extended time periods; however, verification of sensor performance with appreciable altitude change is recommended to quality assure and document sensor performance. To convert inches (in.) of mercury (Hg) to millimeters (mm), multiply inches by 25.4.

- **The calibration procedure depends on the type of DO sensor being used.** Note the type of sensor being used—amperometric or optical (luminescent)—and follow the appropriate instructions provided by the manufacturer and as described below. Allow the sensor to equilibrate to the temperature of the solution for at least 15 minutes or as recommended by the manufacturer.
- Always perform a 100-percent saturation calibration before beginning the zero DO calibration.

Amperometric method for DO measurement (polarographic or Clark-cell sensor):

Instrument makes and models can vary considerably; always refer to the manufacturer's instructions for the instrument that is in use. To prevent water damage to the sonde's internal parts, maintain the O-rings and sealing surfaces on the sonde as directed by the manufacturer. Be aware that extreme temperatures and instrument vibrations may cause the DO sensor to drift out of calibration on a day when a series of measurements is made.

1. Inspect the DO sensor anodes and cathodes—if they are not bright and shiny, recondition them as instructed by the manufacturer.
2. Install a new membrane or membrane cap of the desired membrane thickness. If not using the membrane cap, the membrane should be tightly stretched, and have no bubbles, wrinkles, or tears. Replace any worn or stretched (loose) O-rings.
   - Membrane replacement should take place 24 hours before use (USGS standard procedure). Manufacturer guidance generally specifies membrane replacement at least 3 to 4 hours before use (M. Lizotte, YSI and Bruce Wilcox, Hach Environmental, written communs., May 2007).

- A tight-fitting O-ring is critical to good sensor performance.
- Run or power up the newly membraned sensor for 15 minutes.
- Do not allow electrolyte solution to wet the sensor or sonde connector or other O-ring sealed areas. Electrolyte solution is highly conductive and will short out electrical connections.

3. A wet towel can facilitate the water-saturated air calibration of the DO sensor as follows: **wrap the sensor guard with a white towel wetted in field temperature water**, forming an enclosed moist environment around the instrument sensor guard and sonde body. Allow time for the air inside the sensor guard and wet towel to become saturated with water vapor (10 to 15 minutes).

4. **Rinse the DO sensor thoroughly, at least three times, with DIW or tap water after being calibrated in the zero-percent solution,** to avoid cross contamination and faulty readings. Inadequate rinsing will cause negatively biased readings.

Luminescent-sensor method for DO measurement (optical sensor):

Great care is required when calibrating optical DO sensors in the field. Optical DO sensors (like polarographic sensors) can be calibrated in either water vapor-saturated air or in air-saturated water (see NFM 6.2). The air-saturated water method is recommended for calibrating optical sensors. **Temperature equilibration of the sensor with the calibration solution must be achieved before proceeding with the calibration; follow the manufacturer's instructions.**

1. To create an air-saturated water bath, one method is to fill a 5-gallon pail with tap water and aerate the water using a mid-sized aquarium air pump with air stone. Check the manufacturer's recommendations. Some manufacturers have developed their own bath aeration system to help avoid effects from variance of temperature and hydrostatic pressure on the calibration (R. Mooney, In-Situ Inc., written commun., May 2007).

   - The air-saturated water method is faster and guarantees temperature equilibration of the optical DO sensor and calibration medium.
   - If the water bath is kept air-saturated and ready to use, calibration time can be reduced, as there is no need to wait for a calibration cup or wet towel to saturate the air.

2. Aerate the water for at least 1 hour prior to use.
3. When measuring in low DO environments or after replacing a luminescent-sensor membrane, a two-point DO calibration and (or) a zero DO check is needed or required.
   - If the sensor is equipped with a wiper, remove the wiper before starting the calibration (see the warning in step 5 below).
   - Calibrate the saturated and zero DO levels following each manufacturer's specific instructions.
   - To prepare a zero DO calibration solution, dissolve 1 gram of sodium sulfite and a few crystals of cobalt chloride in 1 liter of DIW (prepare this solution during the week of use). Check the Material Safety Data Sheet (MSDS) for handling of cobalt chloride, which is a toxic substance.
4. Observe the readings for DO; when there is no appreciable change for approximately 30 seconds, lock in or adjust the reading.
5. **After calibrating the sensor with the zero-percent solution, take extra care in rinsing the sensor thoroughly** to remove any residue of the solution. Inadequate rinsing will cause negatively biased DO readings and can result in cross contamination, possibly causing faulty SC or pH readings. The three-time tap-water or DIW rinse recommended for the amperometric-instrument sensor may not be sufficient. One manufacturer recommends rinsing the sensor under **running tap water for at least 10 minutes.**

> **WARNING:** On optical sensors equipped with wipers, remove the wiper before beginning the zero-DO calibration to prevent the wiper from soaking up sodium sulfite and thus contaminating the membrane when the wiper is activated.

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pH (see also NFM 6.4, section 6.4.2)

1. **The pH measurement requires a two-point calibration.** Select the pH 7 buffer plus a second pH buffer (for example, pH 4 or pH 10) that brackets the expected range of sample pH.
   - Use historical pH data for the sampling site, if available, to select the correct buffers.

- After performing the calibration, a calibration check with a third buffer can be useful if the pH range is unknown or if sites with differing range in pH value will be measured.
- **Do not use expired buffers**. **Discard decanted buffer after one use**—do not reuse buffers or pour decanted buffer back into the original container.

2. Bring the buffers as close as possible to the ambient temperature of the water being sampled.
3. Normally the sensor is calibrated first against the pH 7 buffer; however, this may differ among manufacturers.
4. Rinse the sensors and calibration cup, first with DIW and then with the buffer.
   a. Before using the first buffer, rinse the pH and temperature sensors and the calibration cup three times with the first buffer.
   b. Fill the calibration cup with enough buffer to completely cover the temperature and pH sensors.
5. Allow time for the pH and temperature sensors to equilibrate to the temperature of the buffer.
6. Record the temperature reading after it has stabilized. The pH value is temperature dependent. **Use the chart provided by the buffer manufacturer to determine the true pH value for the buffer at that temperature.** You will need to adjust the calibration reading to that value. **NOTE: Buffers from different manufacturers can yield somewhat different pH values for a given temperature.**
7. Follow the manufacturer's instructions for calibration with the first buffer.
   a. Record the temperature, pH, and millivolt (if available) readings before and after calibration with the first buffer.
   b. If your instrument does not display the percent slope, then calculate and record the slope of the pH sensor.

> **EXAMPLE**: The acceptable tolerance for the pH 4 buffer is 180±50 mV; for the pH 7 buffer, 0±50 mV; and for the pH 10 buffer, -180±50 mV. If a value of +3 mV were recorded for the pH 7 buffer and -177 mV were recorded for the pH 10 buffer, the slope would be 180 mV. The acceptable range for the slope is from 165 to 180 mV.

8. Repeat steps 4, 5, 6, and 7 using the second buffer.
9. If a third buffer will be used to check the calibration range of the sensor, follow the same general procedures described above for the first and second buffers, **but do not lock in a calibration. The instrument reading should be within ±0.2 pH units** of the theoretical pH value at the buffer temperature.

Oxidation-Reduction Potential (ORP or Eh) (see also NFM 6.5, section 6.5.2)

1. **The pH sensor must be calibrated and working properly before calibrating the ORP sensor,** if the instrument uses a combination pH-ORP electrode.
   - For most multiparameter instruments, the ORP electrode usually is combined with pH electrodes in one sensor body in order to utilize a common reference electrode (usually the silver/silver-chloride electrode).
   - Recommended calibration procedures differ among instrument manufacturers. Follow the manufacturer's recommendations for calibration of the specific instrument and electrodes being used.
2. A one-point calibration at a known temperature generally is used to calibrate the ORP sensor. The ORP measurement should stabilize within 1 to 3 minutes.
   - Table 6.8–4 shows the true readings in millivolts for ZoBell's solution as a function of temperature for the platinum/silver-silver chloride paired electrodes. These values must be converted to a standard hydrogen reference electrode when the field measurements are reported in the USGS National Water Information System (NWIS) QWDATA database. See NFM 6.5 for more detailed information about ORP sensors, data conversion to the standard hydrogen reference electrode, and use of ZoBell's solution.
   - The calibration values should be within a tolerance of ±5 millivolts of the values listed in table 6.8–4.
   - **ZoBell's solution is toxic; handle with care.**[9]
3. Calibration can be affected by static electricity. Avoid touching the sensors during calibration and measurement.

[9]Alternatives to ZoBell's solution are being investigated (January 2008).

4. The ORP sensors of some manufacturers must be oriented near the vertical ±45 degrees for proper operation. Be thoroughly familiar with the manufacturer's instructions before using the instrument.

5. Follow proper procedures for handling and disposal of ZoBell's solution and keep an MSDS for ZoBell's solution with the ORP equipment. Minimize the volume of ZoBell's solution being used and store the spent solution in a separate, dedicated container.

Table 6.8–4. Voltage of ZoBell's solution as a function of temperature for the platinum/silver-silver chloride paired electrodes

[ºC, degrees Celsius; mV, millivolts]

Temperature, in ºC	ZoBell's solution,[1] in mV
-5	270.0
0	263.5
5	257.0
10	250.5
15	244.0
20	237.5
25	231.0
30	224.5
35	218.0
40	211.5
45	205.0
50	198.5

[1]This table is provided as a courtesy by YSI (M. Lizotte, written commun., February 2006). See table 6.5–3 in NFM 6.5 for a chart showing the Eh of ZoBell's solution as a function of temperature.

ZoBell's solution is a toxic solution and considered a hazardous waste. Check with a chemical-substances safety officer and the MSDS for safe handling information and proper and legal disposal of spent ZoBell's solution.

Turbidity (see also NFM 6.7, section 6.7.2)

The methods and standards used for turbidity sensor calibration should be those that are recommended by the instrument manufacturer for the specific instrument type and model, using NFM 6.7 as a guide for USGS work.

Calibration of the turbidity sensor is highly sensitive to environmental fluctuations and should be performed away from wind, sunlight, and temperature fluctuations. (Most manufacturers recommend that the turbidity calibration be performed in a laboratory or other stable environment before departing for the field site. To some extent this is dependent upon the calibrant being used; for example, formazin use is confined to a laboratory environment. USGS protocol stipulates that calibration of the turbidity sensor be verified at each field site. Refer to NFM 6.7 for a detailed explanation.)

- **Calibrants are not necessarily interchangeable**. **Serious calibration errors can result from using the wrong standards.** Three types, or levels, of standard turbidity solutions (calibrants) are used to calibrate and (or) verify the accuracy of turbidity sensors (section 6.7.2). Use only those calibrants that are prescribed for the sensor by the instrument manufacturer. Refer to NFM 6.7 for detailed information on turbidity calibrants and for turbidity units of measurement as operationally assigned according to instrument type by the USGS.[10] The following terminology, taken from ASTM Method D6855, is used by the USGS to distinguish among classes of turbidity standards (C.W. Anderson, U.S. Geological Survey, written commun., December 2006; ASTM International, 2003):
  - Reference standard: 4000 NTU formazin solution, obtained commercially or prepared in-house (“from scratch”).
  - Calibration standard: Diluted scratch formazin, StablCal® or styrene-divinylbenzene (SDVB) polymer.
  - Verification standard: Gels, solids, or diluted SDVB or StablCal.

[10]The guidelines for reporting turbidity units described in NFM 6.7 were developed jointly by the USGS, ASTM International, and participating instrument manufacturers.

- **Diluting a reference standard for turbidity calibration can result in erroneous data and, in general, is not recommended.**
  - Precise laboratory technique is essential for dilutions and should be performed only by experienced personnel. If not handled carefully, the dilutions can become unstable and particle suspension may be lost.
  - Discard a diluted scratch formazin calibration standard within 24 hours of preparation.
- **The quality of the turbidity measurement is dependent on the type of standard (that is, on the particulate matter contained in the suspension)** that is used to prepare instrument calibration curves.
  - Turbidity-free water, used as a zero-turbidity standard and for the preparation of standard solutions, dilutions, and equipment rinsing, is prepared as described in NFM 6.7.
  - Formazin-based calibration standards are freshly prepared by diluting a 4,000 NTU reference standard, using the dilution formula provided in NFM 6.7. Because the dilution process is subject to preparation errors, document that a calibration standard was used and report it as "calibration standard, prepared by dilution of a 4,000 NTU standard." **A calibration standard must be prepared on the day of use and be discarded on the same day.**
    - Record the source of the 4,000 NTU reference standard. The 4,000 NTU standard has a shelf life not to exceed 1 year.
    - The diluted scratch formazin (calibration standard) has a shelf life of less than 24 hours.
    - Do not use expired standards (American Public Health Association, 2005, Method 2130B, p. 2–9 to 2–11).
  - **Do not dilute SDVB polymer or StablCal standard for use as a calibration standard**. Although a diluted polymer-suspension (less than 10:1) sometimes is used as a verification or calibration check (verification standard), this is not recommended by the USGS and should not be used for USGS studies.
    - Store the verification standards out of sunlight and in PVC bottles.
    - Handle verification standards carefully to maintain the stability of the suspension.

- Check the turbidity standards for expiration before performing a dilution, calibration, or calibration verification. Note that higher range formazin standards tend to settle and thus are less stable than lower range formazin standards.

The following summary of turbidity sensor calibration does not replace the more detailed information to be found throughout NFM 6.7, and specifically in section 6.7.2.

1. **If the sonde includes a wiper brush and (or) pad for cleaning the DO, pH, and SC sensors, this brush must be removed before calibrating the turbidity sensor**. If the wiper occupies a sensor port, be sure to plug the open port before starting the calibration.

2. **Perform the turbidity-sensor calibration in a protected environment, away from wind and thermal fluctuations**. Standard USGS procedure is to calibrate sensors onsite, but in a location in which stable environmental conditions can be maintained.

   - Prevent disturbance to the standard solutions that might result in forming bubbles, and prevent exposure of these standards to direct sunlight.
   - Verify calibration of the turbidity sensor in an environment in which stable readings can be obtained.
   - If the calibration is performed in a laboratory just before departing for the field site, use a verification standard onsite to check the sensor calibration.

3. **Use only the recommended calibration standards for actual calibration of the sensors.** A verification standard may be used to check the calibration in the field.

4. **Use the manufacturer-supplied calibration (or storage) cup with a non-reflective endcap**.

   - Do not use plastic beakers or containers when working with sensors that use infrared light; clear plastics can reflect the infrared light beam and cause errors.
   - Clear glassware may be used with the sensor guard installed on the sonde.
   - Do not use small-diameter or small-volume containers (for example, 35-mm film-storage containers) for this purpose.

5. **Inspect the instrument carefully**.

   a. Check the instrument—ensure that all submerged parts of the multiparameter instrument are clean before beginning turbidity calibration. Sediment or other particulates from the sonde, wiper, or other parts can contaminate the standard, leading to an incorrect calibration and measurement.

   b. Check the optical ports—the optical surface of the turbidity sensor must be clean and free of bubbles, fingerprints, scratches, or other interferences.

   c. Check the wiper—if your turbidity sensor has a wiper with a pad or brush, inspect the condition of the pad/brush and replace it if necessary. Check that the wiper is parking properly and is operational.

   d. If the sensor is without a mechanical wiper (for example, during discrete sampling), take extra care to maintain a clean, bubble- and solid-material-free optical face. To remove bubbles from the optical face during calibration or field measurement, agitate the sonde by moving it in a vertical or circular motion.

6. Check the manufacturer's instructions for the minimum distance between the sensor face and the bottom of the calibration chamber, before and during the calibration process. Take care to avoid interference from the bottom of the calibration vessel.

7. **Note that if the sensor is equipped with a wiper (or brush), the wiper (or brush) needs to be activated immediately before the calibration data are acquired.**

8. When verifying the turbidity-sensor calibration, a three-point check is recommended before deciding to adjust the calibration.

   - If the sensor readings exceed the established calibration criteria for project data-quality objectives (for example, the greater of ±5 percent of the measured value or 0.5 turbidity units) during the inspection process, the sensor requires calibration.
   - If instrument calibration allows only a two-step process, use two calibration standards that cover the expected turbidity range and check for linearity using a third midpoint standard. If the instrument calibration requires only turbidity-free water and one calibration standard, select a midpoint standard to check for linearity.

TECHNICAL NOTE: The range of standards recommended for verification of turbidity-sensor calibration varies, depending on the manufacturer and the linearity of the instrument being used.

9. Perform multipoint calibrations in the order of increasing turbidity.

   a. First rinse the calibration cup, turbidity sensor (and sensor guard) three times, each time using a small amount of zero-turbidity solution.

   b. Using the zero-turbidity solution, carefully fill the calibration cup along the inside surface, so as to avoid aerating the solution. Set the multiparameter instrument on top of the calibration cup (do not engage the threads). Verify that there are no air bubbles on the sensor face; then run the wiper (if present) at least once before accepting the first calibration point. Record the first calibration point. Use 2 Formazin Nephelometric Units (FNU) as the low-end calibration point.

      TECHNICAL NOTE: Consult the instrument manufacturer if the accuracy and precision of measurements below 2 FNU are important for the study, as calibration procedures within the 0 to 2 FNU range can differ depending on the instrument. Some manufacturers advise that instruments can be better calibrated to 2 or to 10 FNU than to 0 FNU.

   c. Before using the next standard, re-rinse the calibration cup, sensor guard (if present), and sensor three times with the zero-turbidity solution. Repeat this rinse between each new standard.

   d. To assess the actual performance of the instrument near the detection limit, periodically check using standards in the 1 to 5 turbidity-unit (low-level) range.

   e. Calibrate at the second point, again removing air bubbles and wiping the sonde or sensor at least once before accepting the value.

f. Monitor each output carefully to ensure that turbidity readings are stable before confirming the calibration value. Report the measurements in the proper units, as specified in NFM 6.7, table 6.7–4.

g. **Never override a calibration-error message without fully troubleshooting the cause of the problem.** Calibration-error messages usually indicate that a problem exists that will result in incorrect field readings.

10. While in the field, check instrument performance periodically using either a calibration standard (StablCal, SDVB polymer, or diluted scratch formazin) or a verification standard (gels, solids, or diluted SDVB or StablCal) and turbidity-free water.

TECHNICAL NOTE: Field experience is the best guide as to how often the turbidity sensor will benefit from recalibration. The need for recalibration depends on the condition of the optical windows, which in turn depends on the environment in which the instrument is deployed. Instruments deployed in biologically active environments, for example, require frequent cleaning and calibration checks. Periodic checks of the sensor against calibrants can be beneficial for indicating how well the sensor is holding its calibration.

WARNING: Contamination of the zero turbidity standard (from inadequately cleaned equipment) often is the cause of negative turbidity readings in clear environmental waters. Contact the instrument manufacturer for recommendations if negative turbidity readings cannot be eliminated.

6.8.3 MEASUREMENT

The field-measurement procedures implemented depend on the type of water body for which the chemical and physical properties are being determined, onsite characteristics and conditions at the time of measurement, and on the study objectives and data-quality requirements of the project. Refer to the respective sections of this chapter for detailed information regarding field measurement of temperature, specific electrical conductance, dissolved-oxygen concentration, pH, oxidation-reduction potential, and turbidity.

- Record a description of site conditions and any anomalies at the time of sampling.
- Allow time for the readings on the display to stabilize within the criteria shown on table 6.8–5.
- Record all required and targeted field measurements on the appropriate paper or electronic field forms, laboratory analytical request forms, project log books, chain-of-custody logs, and other documentation that might be required for the study (Appendix 6.8–A). Note on the appropriate forms any onsite conditions that could have affected the quality of the data.

Table 6.8–5. Standard criteria for stabilization of common multiparameter-instrument sensors

[±, plus or minus; ºC, degrees Celsius; %, percent; ≤, less than or equal to; µS/cm, microsiemens per centimeter; >, greater than; mg/L, milligrams per liter; FNU, formazin nephelometric units]

Sensor	Standard sensor stabilization criteria (Note that the actual accuracy of the sensor varies, depending on sensor model and manufacturer)
Temperature (thermistor)	± 0.2ºC
Specific electrical conductance (SC)	± 5% for SC ≤100 µS/cm, or ± 3% for SC >100 µS/cm
Dissolved oxygen (polarographic or optical)	± 0.2 mg/L to ± 0.3 mg/L
pH	± 0.1 to 0.2 pH unit; if drifting persists or if measuring low-conductivity waters (≤75 µS/cm), allow ± 0.3 pH units
Turbidity	± 0.5 FNU or 5% of the measured value, whichever is greater, for turbidity 100 FNU; or 10% of the measured value, for turbidity >100 FNU

SURFACE WATER 6.8.3.A

Field measurements commonly are monitored within a cross section of the surface-water body to (a) help determine how well mixed the stream is, and consequently the sampling method to be used (NFM 4.1), and (b) determine the field-property values of the water body at the selected site. In situ use of a multiparameter instrument is the most efficient means of obtaining such data.

- Many instruments include a pressure transducer that produces a value for water depth or level. For instruments without pressure transducers, the approximate depth of the sonde as it is lowered through a transect can be noted by placing incremental marks along the instrument cable or be connected to a pressure transducer. Depending on site conditions, the sonde might need to be weighted (consult the manufacturer).
- Wait a minimum of 60 seconds for the sensors to reach thermal equilibrium with the water temperature at each new location. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
- At each measuring point, allow the field-measurement values on the instrument display to stabilize within an established criterion before recording final field measurements (table 6.8–5).
  - Field-measurement values generally are considered stable if the variability among three or more consecutive readings, spaced some number of minutes apart, conforms to the designated criteria. See NFM 6.0 for a discussion on sensor-stabilization criteria.
  - After making multiple measurements across a stream transect, return to the original measurement location within the transect and make a second measurement at that location, to check for measurement stability. Repeat the transect measurements if the original measurement is not replicated within the stabilization criterion shown on table 6.8–5.
  - When aggregating the data from a cross section, **document the median** of the cross-sectional data for each field measurement.
- Biological growth or debris in the water can foul sensors, which will adversely affect sensor readings. If field conditions and quality-assurance protocols allow, adjust the spacing of the measurement intervals along the cross section or transect in order to avoid areas that will result in having to stop and clean algae, sediment, or debris from the sensors.

6.8.3.B GROUND WATER (revised 3/8/2012)

The stability of field-measurement values is monitored toward the end of well purging to help indicate when the water being withdrawn represents fresh formation water and when sample collection for other analytes should begin (NFM 4.2). The final field measurement typically is recorded after three or more well volumes have been purged and stability criteria have been met.

If the purpose of sampling is to obtain field measurements only, these data can be obtained in situ by deploying the sensor or multiparameter sonde downhole, followed by a submersible pump to draw water upward. If water-quality samples will be collected, pumping the water from the well to and through a flowthrough cell that contains the sonde or sensors is another efficient method for collecting field-measurement data without having to remove and redeploy sampling instruments. Flowthrough cells are supplied by the manufacturers of the multiparameter instruments.

- Connect all sampling-pump discharge-tubing fittings securely so that atmospheric oxygen does not enter the flowthrough cell of the multiparameter instrument, as this can affect the accuracy and quality of the measurements.
- Shield the flowthrough cell from direct sunlight to minimize changes in the temperature of the ground-water sample as it is withdrawn; changes in temperature also can affect the accuracy of the pH, ORP, and DO measurements, with respect to their ambient ground-water values, and incident light can affect turbidity readings.
- Wait a minimum of 60 seconds for the sensors to equilibrate to ambient ground-water conditions before monitoring field-measurement values. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
    - Allow the value(s) on the instrument display to stabilize before recording a final field-measurement value (table 6.8–5).

— Field-measurement values generally are considered stable if, while purging the last of three well volumes of water, the variability among three or more consecutive readings spaced at least 3 to 5 minutes apart conforms to the designated criteria. See NFM 6.0, section 6.0.1 for a discussion on sensor-stabilization criteria and problems. See NFM 4.2.3 for detailed information about well purging.

— Good field judgment and experience are required to make a final determination when readings keep drifting or if what the values represent is in question. Such problems should be documented and advice (if needed) should be sought from a senior technician.

Field-measurement sensors must first be allowed to equilibrate to the ambient temperature of the water body being sampled or monitored. This can take from 60 seconds to more than 30 minutes, depending on the instrument and the start and final temperature range. Ensure that all field-measurement readings have stabilized before recording the final field measurement values.

6.8.3.C MEASUREMENT TIPS

Measurement accuracy depends on the adequacy of the calibration procedures used, and many of the precautions described in section 6.8.2 on calibration also apply when measuring the field properties of environmental waters. The following tips can enhance the quality of the field measurement and address some common onsite practices or issues.

- **Equipment use:** Each instrument must be tested and the sensors calibrated before use.
  - Apply the same precautions for measurement as were recommended for calibration.
  - Avoid faulty readings by cleaning calibration residues and dirt from sensors before use.
  - Instruments may be sensitive to static electricity. Keep the instrument at least 3 ft (about 1 m) away from objects that are not electrically grounded.
- **Sensor-sample equilibration:** Allow a minimum of 60 seconds for an instrument to warm up and the sensors to reach thermal equilibrium with the water temperature before recording field measurements. Some instruments require a longer equilibration time (up to 30 minutes); check the manufacturer's recommendations.
- **Measurement accuracy:** If the water matrix or other condition triggers a concern regarding the accuracy or replication of the measurement, check the sensor calibration and document any changes in the sensor response after sampling or completing a set of field measurements. This record will help to determine deterioration or malfunction of one or more of the sensors. A calibration check of the DO sensor is recommended as a routine practice, especially if the measurement was made in a suboxic environmental water.
- **pH and ORP** (see NFM 6.4, section 6.4.3, and NFM 6.5, section 6.5.3, respectively):
  - Check the slope of the pH electrode before use to verify that the electrode is working properly (the slope is determined as part of the calibration process; see section 6.8.2.B and NFM 6.4 for pH calibration tips).

- Record changes in ambient air or water temperature while onsite, as temperature affects pH and ORP readings.
- Depending on the sensor type and manufacture, pH or ORP sensors may or may not be designed for horizontal or near horizontal placement during measurement; check manufacturer's instructions (Hach pH sensors, for example, do allow for horizontal placement).
- ORP field values that are determined with a silver/silver chloride reference electrode must be converted to standard hydrogen electrode (SHE) values. See NFM 6.5 for calculation instructions.

▶ **Turbidity** (see NFM 6.7, section 6.7.3):

- Cover the flowthrough cell with aluminum foil to avoid potential bias to the readings from ambient light.
- Inspect the sensor body to ensure that no bubbles are on the optical surface before beginning measurement.
- If using a flowthrough cell, ensure that no bubbles are entrained in the sample water. The presence of bubbles will result in a high bias to readings.
- For sensors with wipers, follow the manufacturer's instructions for how to verify that the wiper arm is operating correctly.
- **Instrument precision often decreases at turbidities less than 2 turbidity units—**consult the manufacturer's specification for the expected accuracy of the measurement. Some instruments have the capability of processing low-turbidity data to improve reproducibility. Check whether the instrument has a user-adjustable turbidity data-filter option. If working in low-turbidity water, review the guidance in NFM 6.7 for selection of the appropriate multiparameter (or single-parameter) instrument type.

▶ **Dissolved oxygen** (see NFM 6.2, section 6.2.1):

- Table 6.8–6 provides general guidelines for use of the amperometric (polarographic or Clark cell) and luminescent (optical) sensors. Use of the luminescent-sensor method may be more practical for dissolved-oxygen measurement in the field, depending on site conditions.

— For surface-water measurements, selection of the DO amperometric or luminescent sensor should be based on flow regime and stratification of the water body.

— **For an amperometric (polarographic sensor or Clark cell) measurement**, some manufacturers recommend transporting the sonde with the sensor guard (instead of the storage/calibration cup) installed, keeping the sonde wrapped in the wet light-colored towel used for calibration. To reduce evaporation in hot weather, place the entire sonde and wet towel into a perforated plastic bag (that is kept unsealed). The wrapped sonde can be transported in a bucket or cooler.

  o Allow the amperometric instrument to warm up after turning on the display. The DO output should read saturation for the barometric pressure determined for the site.

  o Allow the polarographic sensor to equilibrate to the temperature of the stream, lake, or ground water.

  o **For low-velocity water**, follow the manufacturer's instructions when using an amperometric instrument.

    – Use the stirrer for the DO sensor that is provided or recommended by the manufacturer. **Alternatively, use the luminescent-sensor method, which is not flow dependent.**

    – If the instrument has no stirrer, move the sonde up and down (or side to side in shallow water) at the rate recommended by the manufacturer. (A stirrer is preferable to manually induced flow, especially under stratified conditions at the thermocline of a surface-water body).

    – Flow dependence is diminished when using a "rapid-pulse sensor;" however, some flow over the membrane is needed. Check the manufacturer's instructions.

— To verify the accuracy of the amperometric measurement, rinse the sensors and check the DO calibration by rewrapping it in the wet white towel. The instrument display should return to its saturation set point (±2 percent) within a few minutes. Record any post-measurement calibration check in the field notes.

Table 6.8–6. General guidelines for use of amperometric and luminescent dissolved-oxygen sensors on multiparameter instruments

Amperometric sensor (polarographic or Clark cell) [1]	Luminescent sensor (optical) [1]
Inspect the sonde and sensor for damage, improper installation, or excessive buildup of biofouling matter. Follow the manufacturer's recommendations for cleaning and calibration. Inspect the membrane for damage or improper installation (the average replacement interval is 2 to 4 weeks). Inspect the membrane for biofouling. Replace the membrane if biofouling is evident. Avoid contact of the membrane and sensor with acids, bases, and organic solvents. Replace the potassium chloride (KCl) solution once a month or sooner if performance degrades, and when replacing the sensor. Inspect O-rings periodically and replace as needed or per the manufacturer's recommendation.	Inspect the sonde and sensor for damage, improper installation, or excessive buildup of biofouling matter. Follow the manufacturer's recommendations for cleaning and calibration. The maintenance and use of optical dissolved-oxygen sensors are highly dependent on the technology used by the specific manufacturer. Follow the instructions specified by the manufacturer. *Example A – YSI "ROX" optical sensor*. This sensor should not be left exposed to air for 2 hours or more or otherwise allowed to dry out. Store the sensor wet to avoid drift or having to rehydrate the sensor. *Example B – Hydrolab "LDO" optical sensor*: This sensor should not be left exposed to air and allowed to dry out. The sensor needs to be stored in liquid with its cap on. If the sensor is in a dry environment for several hours it may need to be soaked for up to 5 days before use. The sensor drifts slightly during hydration and must be fully hydrated before being calibrated. *Example C – In-Situ "RDO" optical sensor*. This sensor can be exposed to ambient air for extended periods, can be stored dry, and does not require a hydration period before deployment.
For short-term storage, keep the DO sensor immersed in a calibration cup with enough water to keep electrolyte from evaporating.	Check the manufacturer's instructions for short-term and long-term sensor storage, as requirements can differ substantially among manufacturers.
Anode and cathode maintenance: • The silver anode can be contaminated and might be the cause of poor sensor performance: clean according to the manufacturer's recommendation. • The gold cathode must be bright. Follow the manufacturer's recommendations for cleaning.	Sensors with wipers require manufacturer-specific maintenance procedures: • Use only the wiper recommended by the manufacturer for the sensor in use. • Inspect the wiper pad periodically for wear and tear, and biofouling. • Change the wiper before each long-term deployment, or as recommended by the manufacturer.

[1]Refer to Section 6.2.1 for detailed information on amperometric and luminescent-sensor methods for measuring dissolved-oxygen concentrations.

6.8.4 TROUBLESHOOTING

Multiparameter instruments that perform poorly can be tested and the cause can be identified. The complexity of the series of tests increases with the number of sensors in the sonde. The troubleshooting tests should be performed in a prescribed order that depends on the type of sensors in use and potential for sensor contamination. General troubleshooting tips are provided below in table 6.8–7. More detailed guidance is available from the manufacturer. **Consult the manufacturer's user manual for the specific instrument being used.**

- **If the display shows a warning message, do not use the sensor** until the error has been identified and corrected.
- **Sensor ports on the instrument body should be dry before replacing sensors.** Use compressed air, methanol, or isopropyl alcohol to dry the ports. When using methanol or isopropyl alcohol, gently shake off the excess liquid from the port and allow sufficient time for the liquid to evaporate.

  WARNING: Alcohol or other solvents can damage certain types of plastics and can destroy the sensing surface of the optical DO sensor.

CAUTION: Avoid skin contact with, and fume inhalation of, potentially hazardous equipment-cleaning solutions such as methanol and isopropyl alcohol. If such substances will be used, wear a face mask and protective clothing. If possible, replace sensors under a fume hood.

Table 6.8–7. Troubleshooting tips for use of multiparameter instruments

[DO, dissolved oxygen; NIST, National Institute of Standards and Technology; SC, specific electrical conductance; ORP, oxidation-reduction (redox) potential; Cl, chloride; NH_4, ammonium; NO_3, nitrate; NTU, nephelometric turbidity unit]

Symptom	Possible cause(s), corrective actions, and tips
Erratic or jumpy readings	• May be caused by loose connections or sensitivity to the electrical capacitance of your body and to static electricity**:** avoid touching the sonde housing and try to keep a distance of about 1 meter from the sonde.
Display does not turn on	• Check that the batteries are installed properly and are fully charged. • Battery performance decreases with deceasing temperature. Batteries that charge at room temperature may not perform well when the temperature approaches freezing. Carry spare batteries.
The display does not show readings; the readings seem to be wrong	• Check that the readings are displayed in the appropriate units. Inspect all connectors for moisture, dirt, damage, or a loose connection. Clean as recommended by the manufacturer. • Disconnect and reconnect and recalibrate the sensors. When replacing sensors, the waterproof and dustproof properties of the instrument must be maintained or instrument performance will degrade.
Data on the display appear scrambled	• Check for computer speed and software and hardware compatibility. • Check for a damaged cable. • Check that the correct units are displayed. • If data remain scrambled, consult the manufacturer or authorized service center.
Initial drifting of the readings	• Increase the time for sensors to equilibrate to the water temperature. • Check that the sensors are appropriately submerged and (if necessary for the instrument) that they are at the appropriate inclination from the horizontal.
Dissolved-oxygen reading is unstable or inaccurate	• Check that the sensor has been calibrated to the true onsite barometric pressure or altitude; recalibrate the sensor at the proper barometric pressure and, to the extent possible, with calibrants brought to sample temperature. • Amperometric DO method: Inspect the membrane for a puncture, bubbles, or improper installation. Verify the integrity of the membrane, electrolyte solution, and O-ring by checking the reading against a zero-DO solution. Rinse the sonde thoroughly.
Temperature reading is unstable or inaccurate	• Check for water in the connector; dry the connector and reinstall the sensor. • Check the accuracy of the reading with an NIST-traceable thermometer and have it replaced if necessary. Usually, only the manufacturer can replace a faulty thermistor.
Reading is unstable or inaccurate for SC, pH, ORP, turbidity, Cl, NH_4, or NO_3	• Examine the sensor for dirt or damage. Clean dirty sensors according to the manufacturer's instructions. Replace damaged sensors and recalibrate. • Ensure that the temperature reading is accurate by allowing sufficient time for the temperature sensor to equilibrate to the water temperature. • Check that the calibration solutions used for SC, pH, and ORP were not expired or subject to contamination. • Recalibrate the sensor(s), first bringing the calibration solutions as close to the ambient temperature of the sample as is practical, given ambient field conditions. • Check pH reference junction: if dry, follow manufacturer's instructions for soaking the sensor in tap water or buffer solution until readings stabilize. Alternatively, replace the junction. • Check the sensor connector for water; dry the connector and reinstall the sensor. • If the ZoBell check fails, was temperature dependence of the ZoBell solution accounted for? • The SC sensor must be fully immersed for proper calibration and sample measurement. There must be no bubbles in the cell. • The turbidity sensor wiper must be clean, activated, and rotating properly. Check that expired turbidity calibrants were not used, including any diluted 4000-NTU formazin standard (which must be used within 24 hours of preparation).

6.8.5 REPORTING

USGS personnel are instructed to record all field-measurement values on electronic or paper field forms, and to complete the field-measurement fields on Analytical Services Request forms of the USGS National Water Quality Laboratory or other laboratory at which samples will be analyzed. Field-measurement entries should be checked by a second party and compared for accuracy and consistency with those entered into NWIS.

Table 6.8–8. USGS guidelines for reporting field-measurement values

[±, plus or minus; °C, degrees Celsius; µS/cm, microsiemens per centimeter; >, greater than; mg/L, milligrams per liter; mV, millivolt; SHE, standard hydrogen electrode; FNU, formazin nephelometric units; ppt, parts per trillion; psu, practical salinity units calculated from specific electrical conductance at 25 degrees Celsius]

Field measurement[1]	USGS reporting convention for the National Water Information System (NWIS)[2]	Unit
Temperature	±0.1°C, depending on instrument accuracy and precision	°C
Specific conductance	Three significant figures to the nearest whole number	µS/cm at 25°C
Dissolved oxygen (DO)	Nearest 0.1 mg/L (for the amperometric or luminescent-sensor method) Nearest 0.01 mg/L (for the spectrophotometric/Rhodazine-D™ method) Report ">20 mg/L" for a DO measurement that exceeds 20 mg/L	mg/L
pH	Nearest 0.1 unit for most applications. Can be reported at 0.05 pH unit, depending on accuracy and precision of the calibrated sensor	pH, in standard units
Oxidation-reduction potential	Nearest 1 mV, calculated relative to the SHE (do not report raw data) and the temperature of the sample at the time of measurement	mV
Turbidity	Range: 0 to 10 to the nearest 0.1 FNU 10 to 100 to the nearest 1 FNU >100 to the nearest 10 FNU	FNU[3]
Salinity	<1 to 10, to the nearest 0.1 ppt or psu 10 to 100, to the nearest 1 ppt or psu	ppt or psu

[1]Information is based on manufacturers' specifications for the following multiparameter systems: Hydrolab Quanta and DataSonde 5 and 5X, DS5; YSI 6600; In-Situ Troll 9500; and Eureka Manta.

[2] It is USGS practice to enter values into NWIS that have more significant figures than are the standard for data publication. The NWIS databases produce the values that are rounded correctly, which are then reported in publications. This practice eliminates investigator mistakes when reporting rounded values. NWIS data must be input with the correct parameter and method codes, which can be found by accessing QWDATA.

[3] Most multiparameter instruments used for USGS turbidity measurement contain single-beam infrared wavelength turbidity sensors and are reported in FNU. Check the Excel spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls to determine the appropriate turbidity unit of measure and NFM 6.7 for detailed information on turbidity measurement and instrumentation.

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6.8.7 ACKNOWLEDGMENTS

The authors are indebted to the following USGS scientists who offered their individual and collective expertise in reviewing and improving this section on multiparameter instruments: Chauncey W. Anderson, Kathleen K. Fitzgerald, Sarah M. Flanagan, W. Scott McBride, Michael E. Lewis, Stanley C. Skrobialowski, and Richard J. Wagner. Special appreciation is extended to Yellow Springs Incorporated (YSI), In-Situ Inc., and Hach Environmental, who were generous with their time and expertise to provide information for, and review of, this section. Editorial and production support were provided by Iris M. Collies and Loretta J. Ulibarri.

APPENDIX 6.8–A

Example of a USGS field form for recording sensor calibrations and field measurements

NOTE: USGS personnel are advised to use the latest available version of this and other field forms.

November 2006 **METER CALIBRATIONS/FIELD MEASUREMENTS** STN NO_____

Calibrated by:_____ Location:_____
Date:_____ Time:_____

TEMPERATURE Meter MAKE/MODEL _____ S/N _____ Thermister S/N _____ Thermometer ID _____

Calibration criteria: ± 1 percent or ± 0.5 °C for liquid-filled thermometers ± 0.2 °C for thermisters

Lab Tested against NIST Thermometer/Thermister? N Y Date: _____ ±_____ °C

Measurement Location: SINGLE POINT AT _____ ft DEEP STREAMSIDE _____ FT FROM LEFT RIGHT BANK VERTICAL AVG/MEDIAN OF _____ POINTS

Field Readings #1 _____ #2 _____ #3 _____ #4 _____ #5 _____ **MEDIAN:** _____ **°C** Method code _____ Remark ___ ___ Qualifier ___ ___

pH Meter MAKE/MODEL _____ S/N _____ Electrode No. _____ Type: GEL LIQUID OTHER _____

Sample: FILTERED UNFILTERED CHURN SPLITTER SINGLE POINT AT _____ FT DEEP VERTICAL AVG. OF _____ POINTS CONE SPLITTER

pH BUFFER	BUFFER TEMP	THEO-RETICAL pH FROM TABLE	pH BEFORE ADJ.	pH AFTER ADJ.	SLOPE	MILLI-VOLTS
pH 7						
pH 7						
pH 7						
pH ___						
pH ___						
pH ___						
CHECK pH ___						

TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED? Y N

BUFFER LOT NUMBERS :
pH 7: _____
pH ____: _____
CHECK pH ____: _____

BUFFER EXPIRATION DATES:
pH 7: _____
pH ____ : _____
CHECK pH ____: _____

Calibration Criteria: ± 0.1 pH units

Field Readings #1_____ #2_____ #3_____ #4_____ #5_____ **MEDIAN:** _____ **Units** Method code _____ Remark ___ ___ Qualifier ___ ___

SPECIFIC CONDUCTANCE Meter MAKE/MODEL _____ S/N _____ Sensor Type: DIP FLOW-THRU OTHER _____

Sample: CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS CONE SPLITTER

Std Value µS/cm	Std Temp	SC Before Adj.	SC After Adj.	Std Lot No.	Std type (KCl; NaCl)	Std Exp. Date

AUTO TEMP COMPENSATED METER ___
MANUAL TEMP COMPENSATED METER ___
CORRECTION FACTOR APPLIED? Y N
CORRECTION FACTOR= _____

Calibration Criteria: ± 5 % for SC ≤100 µS/cm or 3% for SC >100 µS/cm

Field readings #1_____ #2_____ #3_____ #4_____ #5_____ **MEDIAN:** _____ **mS/cm** Method code _____ Remark ___ ___ Qualifier ___ ___

DISSOLVED OXYGEN Meter MAKE/MODEL _____ S/N _____

Sensor Type: Polarographic Luminescent Sensor ID _____

Water-Saturated Air Air-Saturated Water Air Calibration Chamber in Water Air Calibration Chamber in Air Winkler Titration Other _____

Sample: SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS BOD BOTTLE OTHER _____ Stirrer Used? Y N

WATER TEMP °C	BAROMETRIC PRESSURE mm Hg	DO TABLE READING mg/L	SALINITY CORR. FACTOR	DO BEFORE ADJ.	DO AFTER ADJ.

Calibration Criteria: ± 0.2 mg/L

Zero DO Check _____mg/L Adj. to _____ mg/L Date: _____
Zero DO Solution Date_____ Thermister Check? Y N Date_____
Membrane Changed? N Y Date: _____ Time: _____
Barometer Calibrated? N Y Date: _____ Time: _____
Battery Check: REDLINE _____ RANGE _____

Field readings #1_____ #2_____ #3_____ #4_____ #5_____ **MEDIAN:** _____ **mg/L** Method code _____ Remark ___ ___ Qualifier ___ ___

Calibration form ver. 4.0

Appendix 6.8–A. Example of a USGS field form for recording sensor calibrations and field measurements. (USGS personnel should use the latest available version of this and other field forms.)

U.S. Geological Survey
Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A7.

BIOLOGICAL INDICATORS

Franceska D. Wilde
Managing Editor

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
KEN SALAZAR, *Secretary*

U.S. GEOLOGICAL SURVEY
Suzette M. Kimball, *Acting Director*

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

This report is available only online at http://pubs.water.usgs.gov/twri9A/.

BIOLOGICAL INDICATORS

National Field Manual for the Collection of Water-Quality Data

Chapter A7.

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Chapter A7. BIOLOGICAL INDICATORS

Franceska D. Wilde, ***Managing Editor***

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) is comprised of nine chapters that provide guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter of the *National Field Manual* includes guidelines for the determination of (1) biochemical oxygen demand (using a 5-day bioassay test), (2) fecal indicator bacteria, (3) fecal indicator viruses (coliphages), (4) protozoan pathogens, (5) algal biomass, and (6) cyanobacterial taste-and-odor compounds.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters are posted on the Web on the USGS page "National Field Manual for the Collection of Water-Quality Data" (http://pubs.water.usgs.gov/twri9A/).

INTRODUCTION

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the impartial collection of quality-assured data that accurately describe the physical, chemical, and biological attributes of environmental water systems. The quality assurance of data is essential to the credibility of the water-resources appraisals carried out by the USGS. These data are available to, and used by, environmental agencies, scientific organizations, and the general public.

Documentation of the methods used by USGS personnel serves to maintain consistency and technical quality in our data-collection activities. The *National Field Manual* is Section A of Book 9 of the

USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters that are designed to be used in conjunction with each other. Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 7 refers to chapter A7 entitled *Biological Indicators,* and NFM 7.3 refers to the section in NFM 7 that pertains to the collection of samples for protozoan pathogens.

PURPOSE AND SCOPE

The *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to water-quality data collection and analysis. This manual is targeted specifically toward data collectors in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this chapter. The *National Field Manual* is meant to guide and complement such training. Chapter A7 contains standard USGS procedures, protocols, and guidelines for collecting data on biological indicators, such as biological oxygen demand; indicator bacteria, viruses, and protozoans; and algal biomass and cyanobacterial taste-and-odor compounds. A description of the determination for ultimate carbonaceous biochemical oxygen demand is beyond the scope of Section 7.0 (Five-Day Biochemical Oxygen Demand), but is provided in Stamer and others (1979, 1983). The information provided in Section 7.1 (Fecal Indicator Bacteria) and in Section 7.2 (Fecal Indicator Viruses) is to be used in conjunction with *Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples* edited by L.J. Britton and P.E. Greeson (TWRI, Book 5, Chapter A4, 1989), the 20th edition of *Standard Methods for the Examination of Water and Wastewater*, and with the other chapters of this *National Field Manual* series.

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. It is the fundamental responsibility of data collectors to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard

procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. Whenever a standard procedure is modified or is not used, a description of the procedure that is used and the supporting quality-assurance information is to be reported with the data.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual,* the terms **required** and **recommended** have the following USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected Water Science Center[1] or other professional personnel, as appropriate. Technical memorandums or other documents that define the policy pertinent to such requirements are referenced in this manual. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented in permanent and readily accessible records.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this chapter to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints can affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment. Departure from or modifications to recommended procedures must be quality assured and documented in permanent and readily accessible records.

[1]"Water Science Center" refers to an organizational unit of the USGS in any of the States or Territories of the United States.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* are reviewed, revised, and reissued periodically to correct any errors, update information, incorporate technical advances, and address additional water-quality topics. Dates of revisions appear in the footer of each chapter section. Each chapter's revision history can be found under "Comments and Errata" on the *National Field Manual's* Home Page (http://pubs.water.usgs.gov/twri9A/). Comments on the *National Field Manual*, and suggestions for updates or revisions, should be sent to nfm-owq@usgs.gov.

ACKNOWLEDGMENTS

The information included in this *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include unpublished USGS training and field manuals.

Technical critique and contributions that improved the section on *Five-Day Biochemical Oxygen Demand* were provided by C.R. Demas, D.N. Myers, G.B. Ozuna, F.A. Rinella, J.K. Stamer, W.E. Webb, and W.G. Wilber.

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The authors and managing editor thank I.M. Collies for editorial assistance and L.J. Ulibarri for production assistance that have been instrumental in maintaining the quality of this report.

Special thanks go to T.L. Miller and former Chiefs of the Office of Water Quality whose encouragement, faith, and practical support have been the force behind our ability to produce and maintain a national field manual for water-quality studies.

FIVE-DAY BIOCHEMICAL OXYGEN DEMAND 7.0

by G.C. Delzer and S.W. McKenzie

Illustrations

Tables

Notes:

References for section 7.0, Five-day biochemical oxygen demand, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 1, for information on the parameter code for biochemical oxygen demand that is used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.0) of NFM 7 is as follows:

Delzer, G.C., and McKenzie, S.W., November 2003, Five-day biochemical oxygen demand: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.0, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/.

7.0 FIVE-DAY BIOCHEMICAL OXYGEN DEMAND

The presence of a sufficient concentration of dissolved oxygen is critical to maintaining the aquatic life and aesthetic quality of streams and lakes. Determining how organic matter affects the concentration of dissolved oxygen (DO) in a stream or lake is integral to water-quality management. The decay of organic matter in water is measured as biochemical or chemical oxygen demand. Oxygen demand is a measure of the amount of oxidizable substances in a water sample that can lower DO concentrations (Nemerow, 1974; Tchobanoglous and Schroeder, 1985).

Biochemical oxygen demand represents the amount of oxygen consumed by bacteria and other microorganisms while they decompose organic matter under aerobic conditions at a specified temperature.

The test for biochemical oxygen demand (BOD) is a bioassay procedure that measures the oxygen consumed by bacteria from the decomposition of organic matter (Sawyer and McCarty, 1978). The change in DO concentration is measured over a given period of time in water samples at a specified temperature. Procedures used to determine DO concentration are described in NFM 6.2. It is important to be familiar with the correct procedures for determining DO concentrations before making BOD measurements. BOD is measured in a laboratory environment, generally at a local or USGS laboratory.

Accurate measurement of BOD requires an accurate determination of DO.

There are two stages of decomposition in the BOD test: a carbonaceous stage and a nitrogenous stage (fig. 7.0-1).

- The carbonaceous stage, or first stage, represents that portion of oxygen demand involved in the conversion of organic carbon to carbon dioxide.
- The nitrogenous stage, or second stage, represents a combined carbonaceous plus nitrogeneous demand, when organic nitrogen, ammonia, and nitrite are converted to nitrate. Nitrogenous oxygen demand generally begins after about 6 days. For some sewage, especially discharge from wastewater treatment plants utilizing biological treatment processes, nitrification can occur in less than 5 days if ammonia, nitrite, and nitrifying bacteria are present. In this case, a chemical compound that prevents nitrification should be added to the sample if the intent is to measure only the carbonaceous demand. The results are reported as carbonaceous BOD (CBOD), or as $CBOD_5$ when a nitrification inhibitor is used.

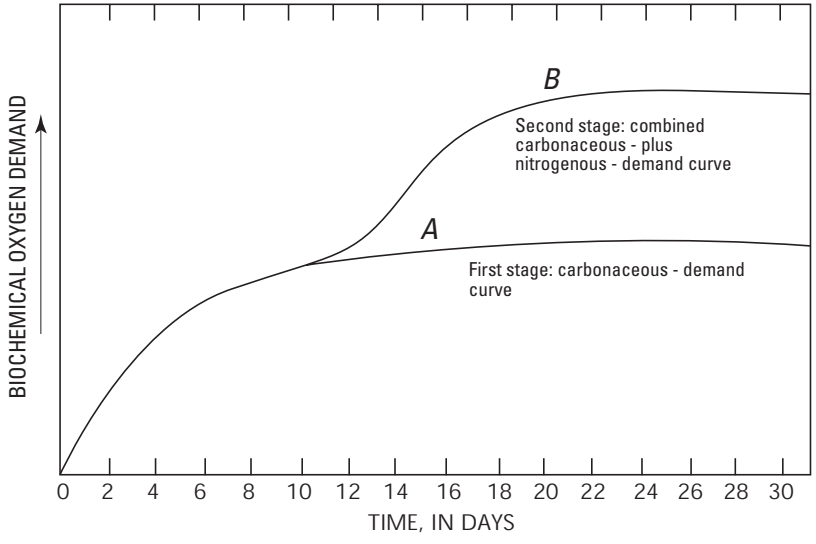

Figure 7.0-1. Biochemical oxygen demand curves: (*A*) typical carbonaceous-demand curve showing the oxidation of organic matter, and (*B*) typical carbonaceous- plus nitrogeneous-demand curve showing the oxidation of ammonia and nitrite. (Modified from Sawyer and McCarty, 1978.)

The standard oxidation (or incubation) test period for BOD is 5 days at 20 degrees Celsius (°C) (BOD_5). The BOD_5 value has been used and reported for many applications, most commonly to indicate the effects of sewage and other organic wastes on dissolved oxygen in surface waters (see TECHNICAL NOTE). The 5-day value, however, represents only a portion of the total biochemical oxygen demand. Twenty days is considered, by convention, adequate time for a complete biochemical oxidation of organic matter in a water sample, but a 20-day test often is impractical when data are needed to address an immediate concern.

- The BOD_5 and $CBOD_5$ tests have limited value by themselves in the assessment of stream pollution and do not provide all of the relevant information to satisfy every study objective (Nemerow, 1974; Stamer and others, 1983; Veltz, 1984). Additional analyses of water samples for chemical oxygen demand, fecal bacteria, and nutrients can aid in the interpretation of BOD_5.
- An ultimate carbonaceous BOD ($CBOD_u$) test is needed to obtain additional BOD information, and can be used for modeling DO regimes in rivers and estuaries (Hines and others, 1978; Stamer and others, 1983). Guidelines for the $CBOD_u$ determination are described in Stamer and others (1979, 1983).
- Note that BOD results represent approximate stream oxygen demands because the laboratory environment does not reproduce ambient stream conditions such as temperature, sunlight, biological populations, and water movement.

TECHNICAL NOTE: A 5-day duration for BOD determination has no theoretical grounding but is based on historical convention. Tchobanoglous and Schroeder (1985) provide the following background: "In a report prepared by the Royal Commission on Sewage Disposal in the United Kingdom at the beginning of the century, it was recommended that a 5-day, 18.3°C, BOD value be used as a reference in Great Britain. These values were selected because British rivers do not have a flow time to the open sea greater than 5 days and average long-term summer temperatures do not exceed 18.3°C. The temperature has been rounded upward to 20°C, but the 5-day time period has become the universal scientific and legal reference."

7.0.1 EQUIPMENT AND SUPPLIES

Table 7.0-1 lists equipment and supplies commonly used in the BOD_5 test using amperometric determination of DO. For more detailed guidance on equipment, supplies, maintenance, and calibration of the DO instrument, refer to NFM 6.2. If the iodometric (Winkler) method of DO determination is to be used, refer to table 6.2-3 in NFM 6.2 for a list of equipment and supplies. Equipment used for BOD sampling must be thoroughly cleaned with nonphosphate detergent and rinsed with tap water and deionized water, as described in NFM 3.

CAUTION: Before handling chemical reagents, refer to Material Safety Data Sheets. Wear safety glasses, gloves, and protective clothing.

Table 7.0-1. Equipment, supplies, chemical reagents, and preparation of dilution water and chemical solutions used in the procedure for determination of 5-day biochemical oxygen demand

[±, plus or minus; °C, degrees Celsius; BOD, biochemical oxygen demand; mL, milliliter; mm, millimeter; NFM, *National Field Manual for the Collection of Water-Quality Data*; L, liter; g, gram; KH_2PO_4, potassium dihydrogen phosphate; $KHPO_4$, potassium monohydrogen phosphate; Na_2HPO_4, sodium monohydrogen phosphate; NH_4Cl, ammonium chloride; *N*, normality; DO, dissolved oxygen; KCl, potassium chloride; $CoCl_3$, cobalt chloride]

Item	Description
Equipment and supplies	
Constant-temperature chamber or water bath	Thermostatically controlled to maintain 20 ± 1°C. During incubation, exclude all light to prevent the possibility of photosynthetic production of oxygen.
Aquarium pump, plastic air tubing, and air diffusion stones	Wash tubing and air diffusion stone thoroughly with a 0.2-percent nonphosphate detergent solution and rinse thoroughly 3 to 5 times with deionized or distilled water before use.
BOD bottles	300 mL, ground glass stoppered. Wash bottles thoroughly with a 0.2-percent nonphosphate detergent solution and rinse with deionized or distilled water before each test. Label bottles appropriately for sample identification.
Glass beads	Borosilicate, solid spherical; 5-mm diameter. Wash thoroughly with a 0.2-percent nonphosphate detergent solution and rinse with deionized or distilled water before use.
Graduated cylinder	Borosilicate, 50- to 250-mL capacity, depending on the volume of sample to be tested.
Overcap	Paper or plastic cup, or aluminum foil, to be placed over BOD stoppers to prevent evaporation of the water seal.
Pipet	Bacteriological, large bore, borosilicate, volume ranging from 1 to 50 mL, depending on the volume of sample to be tested.
Thermometer	Calibrated within temperature range of approximately 5 to 40°C with 0.5°C graduations (NFM 6.1).
Sample container(s)	Wide mouth, screwtop lid, polyethylene, polypropylene, or borosilicate glass. Containers of 1-L capacity are sufficient for most samples.
Waste disposal container(s)	Capped, and of appropriate material to contain specified sample and chemical wastes.
Chemical reagents[1] and preparation of dilution water	
Calcium chloride ($CaCl_2$) solution[2]	Dissolve 27.5 g of $CaCl_2$ in deionized water and dilute to 1 L.
Dilution water	Deionized water of high quality; must be free from toxic substances such as chlorine or toxic metals.
Ferric chloride ($FeCl_3$) solution[2]	Dissolve 0.25 g of $FeCl_3 \cdot 6H_2O$ in deionized water and dilute to 1 L.
Magnesium sulfate ($MgSO_4$) solution[2]	Dissolve 22.5 g of $MgSO_4 \cdot 7H_2O$ in deionized water and dilute to 1 L.
Phosphate buffer solution[2]	Dissolve 8.5 g of KH_2PO_4, 21.8 g of $KHPO_4$, 33.4 g of $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g of NH_4Cl in about 500 mL of deionized water. Dilute to 1 L.

(Table 7.0-1 continues on the next page.)

Note: Instructions for phosphate buffer solution apply to BOD only -- not to buffer for indicator bacteria.

Table 7.0-1. Equipment, supplies, chemical reagents, and preparation of dilution water and chemical solutions used in the procedure for determination of 5-day biochemical oxygen demand—*Continued*

Item	Description
Chemical reagents for sample pretreatment and preparation of chemical solutions	
Sodium hydroxide (NaOH) for caustic acidity pretreatment	Add 40 g of NaOH to about 900 mL of deionized water. Mix and dilute to 1 L (1 *N* NaOH). Store in a plastic container.
Sodium sulfite (Na_2SO_3) or sodium thiosulfate ($Na_2S_2O_3$) for residual chlorine pretreatment solution	Dissolve 1.575 g of Na_2SO_3 or NaS_2O_3 in 1 L of deionized water. This solution is not stable and should be prepared daily to weekly, as needed. Store refrigerated in a dark bottle.
Sulfuric acid (H_2SO_4) for caustic alkalinity pretreatment	Slowly and while stirring add 28 mL of concentrated H_2SO_4 to about 900 mL of deionized water. Mix and dilute acid solution to 1 L (1 *N* H_2SO_4).
DO equipment and supplies (refer to NFM 6.2)	
Calibration chamber	Follow manufacturer's recommendations.
DO instrument system	Temperature and pressure compensated.
Stirrer attachment for DO sensor	Must fit in 300-mL BOD bottle.
Pocket altimeter-barometer	Calibrated, Thommen™ model 2000 or equivalent.
DO sensor membrane replacement kit	Membranes, O-rings, KCl filling solution.
Oxygen solubility table	Refer to table 6.2-6 in NFM 6.2.
Zero DO calibration solution	Dissolve 1 g Na_2SO_3 and a few crystals of $CoCl_3$ in 1 L water. Prepare fresh zero DO solution before each use.

[1] Properly discard chemical reagents if there is any sign of biological growth or if past the expiration date.
[2] Can be purchased from the HACH™ Instrument Company in the form of nutrient buffer pillows ready for immediate use.

SAMPLE COLLECTION AND STORAGE 7.0.2

Samples can degrade significantly during extended storage. To minimize sample degradation, and thus avoid negative bias in the measurement of BOD_5, analyze samples promptly or store chilled without freezing (maintain a temperature from 1 to 4°C). Chilling the sample is not necessary if the analysis begins within 2 hours of collection (American Public Health Association and others, 1995).

- If a sample is refrigerated prior to analysis, allow the sample to warm to 20°C before starting the test. A sample may be removed from an ice chest or refrigerator during transit to allow it to warm to 20°C before analysis begins.
- It is optimum to start the BOD_5 analysis immediately after sample collection to minimize changes in bacterial concentration.
- **The maximum holding time of a sample to be analyzed for BOD is 24 hours.**

Do not freeze samples.

Bacteria are commonly associated with suspended sediment, which can vary spatially and temporally along a stream cross section (Britton and Greeson, 1989). Like suspended sediment, the oxygen-demanding compounds may not be equally distributed along a cross section. Where possible, use the equal-width-increment or equal-discharge-increment procedures described in NFM 4 to collect a BOD sample representative of the stream cross section.

When using cross-sectional, depth-integrating, or discharge-weighted methods:

1. Use a DH-81 or D-77 sampler in most situations (NFM 2). If stream depths exceed 5m (meters) (16.4 feet), use the bag version of the D-77 sampler.
2. Clean all equipment thoroughly and rinse with sample water before use (NFM 3).
3. Collect samples using appropriate procedures and pour sample water into a compositing device (NFM 4; Edwards and Glysson, 1999).
4. Withdraw a composite sample from the sample-compositing device into a clean container of sufficient capacity to perform the desired BOD tests. The volume of sample depends on the number of BOD tests to be completed and any prior knowledge of BOD for the water of interest. Generally, a 1-liter (L) sample is sufficient.
5. Cap the container securely and protect the sample from light during transport to the laboratory for analysis.
6. Store the sample on ice if not processed and analyzed within 2 hours of collection.

If depth-width-integrated or discharge-weighted methods cannot be used, collect a grab sample by the hand-dip method. A grab sample can be collected directly from the stream using a clean container of sufficient capacity (American Public Health Association and others, 1995).

When collecting a hand-dipped sample:

1. Grasp the sample container near the base on the downstream side of the bottle.
2. Plunge the bottle opening downward below the water surface. **Avoid contact with the streambed during this process.**
3. Allow the sample container to fill with the opening pointed slightly upward into the current.
4. Cap the container securely and protect the sample from light during transport to the laboratory for analysis.

FIVE-DAY TEST FOR BIOCHEMICAL OXYGEN DEMAND 7.0.3

The BOD_5 test procedure is based on DO concentration and requires an accurate DO determination. Follow procedures described in NFM 6.2 to determine DO concentration. Iodometric titration or amperometric (DO meter) methods used to measure DO are used for the BOD_5 test procedure (American Public Health Association and others, 1995). The procedures presented below incorporate the amperometric method for determining DO concentration. Refer to section 6.2.1.B in NFM 6.2 if the iodometric method will be used to determine DO.

> **TECHNICAL NOTE:** If using the iodometric titration method to measure DO concentration, double the sample volume, number of dilutions, and number of bottles to account for determining an initial DO and a final DO.

SAMPLE PREPARATION 7.0.3.A

Most relatively unpolluted streams have a BOD_5 that ranges from 1 to 8 mg/L (milligrams per liter) (Nemerow, 1974). If the BOD_5 value of a sample is less than 7 mg/L, sample dilution is not needed. A BOD_5 value greater than 7 mg/L requires sample dilution. Dilution is necessary when the amount of DO consumed by microorganisms is greater than the amount of DO available in the air-saturated BOD_5 sample (American Public Health Association and others, 1995). The BOD_5 analyst is responsible for determining the dilution(s) that will be needed. Table 7.0-2 provides general dilutions based on anticipated ranges of BOD_5 (Sawyer and McCarty, 1978).

BOD_5 values are acceptable only if the following criteria are met:

- The DO concentration after 5 days must be at least 1 mg/L and at least 2 mg/L lower in concentration than the initial DO (American Public Health Association and others, 1995).

- At least three different dilutions are set per sample to cover the anticipated range of BOD. The three sample volumes used are selected to provide an overlapping range in expected BOD concentrations. For example, if the BOD_5 is known to range from 3 to 28 mg/L for a particular stream, then the sample volumes used for the test would be 50 mL, 100 mL, and 300 mL (no dilution). If there is no prior knowledge of the BOD_5 of the stream water, use a minimum of four volumes to accommodate a range of BOD_5 from 0 to 210 mg/L.

When less than a 300-mL sample is to be analyzed, sample volumes are added to a standard solution of dilution water to bring the total sample volume to 300 mL. Because bacteria need nutrients and micronutrients to survive, these compounds are added to the dilution water. Similarly, the pH of the dilution water needs to be maintained in a range suitable for bacterial growth (6.5 to 7.5). Consequently, sulfuric acid or sodium hydroxide may need to be added to the dilution water to lower or raise the pH, respectively.

Some types of sewage, such as untreated industrial wastes, disinfected wastes, and wastes that have been heated to a high temperature contain too few bacteria to perform the test. Thus, the samples must be seeded with a population of microorganisms to produce an oxygen demand. Discussion of the seeding procedure is beyond the scope of this chapter. Most natural waters contain an adequate amount of microorganisms. For guidance on seeding procedures, including the BOD_5 equation when dilution water is seeded, refer to American Public Health Association and others (1995).

Table 7.0-2. Recommended sample volumes for the 5-day biochemical oxygen demand test

[Adapted from Sawyer and McCarty, 1978. BOD_5, 5-day biochemical oxygen demand]

Anticipated range of BOD_5 (in milligrams per liter)	Milliliters of sample	Milliliters of dilution water
0–7	300	0
6–21	100	200
12–42	50	250
30–105	20	280
60–210	10	290
120–420	5	295
300–1,050	2	298
600–2,100	1	299

INTERFERENCES 7.0.3.B

Certain constituents present in a water sample can inhibit biochemical oxidation and interfere with the BOD analysis. Interferences in the BOD analysis include caustic alkalinity or acidity; the presence of residual chlorine; or the presence of toxic elements, including trace elements such as copper, lead, chromium, mercury, and arsenic, or compounds such as cyanide. Procedures for pretreating samples for some common interferences are described in this chapter. Refer to American Public Health Association and others (1995) for further guidance on sample seeding and pretreatment.

The following preparations are needed before implementing the BOD_5 test procedure:

1. Prepare dilution water 3 to 5 days before initiating BOD_5 tests to ensure that the BOD of the dilution water is less than 0.2 mg/L. **Discard dilution water if there is any sign of biological growth.**
2. Determine sample pH. Adjust sample to a pH between 6.5 and 7.5, if necessary, using sulfuric acid (H_2SO_4) for samples with pH greater than 7.5 or sodium hydroxide (NaOH) for samples with pH less than 6.5 (American Public Health Association and others, 1995).
3. Add sodium sulfite (Na_2SO_3) to remove residual chlorine, if necessary. Samples containing toxic metals, arsenic, or cyanide often require special study and pretreatment (American Public Health Association and others, 1995). Samples must be seeded after pretreatment.

7.0.3.C BOD_5 TEST PROCEDURE

Use the following procedure for the BOD_5 test (troubleshooting suggestions are provided in section 7.0.5,* table 7.0-3*):

1. Determine the amount of sample to be analyzed; if available, use the historical results of a previous test of BOD_5 for a particular sampling site, and refer to table 7.0-2.
2. Place a clean, calibrated thermometer into the constant temperature chamber. (See NFM 6.1 for thermometer care and calibration.)
3. Turn on the constant temperature chamber to allow the controlled temperature to stabilize at 20°C ±1°C.
4. Turn on the DO instrument, but not the stirring attachment. Some DO instruments need to be turned on 30 to 60 minutes before calibration—check the manufacturer's instruction manual.
5. Aerate dilution water before adding nutrient solutions.

6. After aeration,

   a. Add to dilution water

      - 1 mL each of the potassium phosphate, magnesium sulfate, calcium chloride, and ferric chloride solutions per 1 L of dilution water, or
      - Hach Company nutrient buffer pillows to a selected volume of dilution water per the manufacturer's recommendation.

   b. Shake the container of dilution water for about 1 minute to dissolve the slurry and to saturate the water with oxygen.

   c. Place the dilution water in the constant temperature chamber to maintain a temperature of 20°C until sample dilutions and analyses begin.

   d. The initial and final (after 5 days ± 4 hours) DO tests of the dilution water is determined and recorded simultaneously with each batch of environmental samples.

7. Check the temperature of the air incubator or water bath using a laboratory thermometer to ensure that the temperature has been maintained at 20° ± 1°C. A minimum/maximum recording thermometer can be used to audit the temperature during times when checks cannot be made.

8. Place the sample container in the constant-temperature chamber or water bath to begin warming the sample to 20°C ± 1°C. While the sample is warming, insert the air diffusion stone into the container and aerate the sample for about 15 minutes. After removing the air diffusion stone, allow several minutes for excess air bubbles to dissipate. The initial DO of the BOD sample needs to be at or slightly below saturation.

9. **Prepare dilutions as required—**Measure the appropriate amounts of sample necessary for the analysis. BOD_5 dilutions should result in a DO residual of at least 1 mg/L and a DO depletion of at least 2 mg/L after a 5-day incubation to produce the most reliable results. Prepare the dilutions to obtain a DO uptake in this range using the dilution water prepared earlier.

   a. For each subsample, mix thoroughly by inverting 20 times.

      - Use a large-bore pipet for sample volumes less than 50 mL. Withdraw a subsample that is representative of all the particle sizes present.

- Use a graduated cylinder for sample volumes greater than or equal to 50 mL.

b. Dilute two additional samples to bracket the appropriate dilution by a factor of two to three. Prepare at least three samples diluted according to volumes specified in table 7.0-2.

c. Pour the sample from the pipet or graduated cylinder into a clean BOD bottle.

- Agitate the dilution water and fill the remaining portion of the BOD bottle with dilution water.
- Prepare three samples containing only dilution water. These samples serve as blanks for quality control. If two of the three samples meet the blank-water criterion, accept the data.

10. Calibrate the DO instrument in accordance with the procedures outlined in NFM 6.2.

11. After bringing the samples to saturation and preparing the dilutions (steps 8 and 9 above), measure the initial DO concentration (D_1) of each sample and each dilution blank.

    a. Carefully insert the self-stirring sensor into the BOD bottle, avoiding air entrapment.

    b. Turn on the stirrer and allow 1 to 2 minutes for the DO and temperature readings to stabilize.

12. Record the bottle number, date, time, and D_1 on a form similar to that shown in figure 7.0-2.

13. Turn off the stirrer and remove the sensor from the BOD bottle. Rinse the sensor and stirrer with deionized water from a wash bottle. Discard rinse water into a waste container.

14. Add glass beads to the BOD bottle, if necessary, to displace the sample up to the neck of the bottle so that inserting a glass stopper will displace all air, leaving no bubbles.

15. Carefully cap the BOD bottle with the ground-glass stopper. Tip the bottle to one side and check for an air bubble.

    - If an air bubble is present, add glass beads to the bottle until the bubble is removed. Cap the bottle and check again for an air bubble. Repeat if necessary.
    - If no bubble is present in the sample, create a water seal by adding distilled or deionized water to the top of the BOD bottle around the glass stopper. Then place the overcap over the stopper on the BOD bottle to minimize evaporation from the water seal.

16. Place the sealed BOD sample in the air incubator or water bath and incubate the sample at 20°C ± 1°C for 5 days.

17. At the end of 5 days ± 4 hours, remove the BOD bottles from the incubator, remove the overcap, pour off the water seal, remove the ground-glass stopper, and measure the final DO concentration (D_2).

    - The DO uptake ($DO_{0\ days}$ - $DO_{5\ days}$) in the dilution water should not be greater than 0.2 mg/L and preferably not more than 0.1 mg/L. **Exceeding the 0.2-mg/L criterion could be grounds for rejecting results of the BOD analysis of the environmental sample**.
    - Dilution water of poor quality will cause an oxygen demand and appear as sample BOD. Improve purification or get the dilution water from another source if DO uptake exceeds 0.2 mg/L (see section 7.0.5, Troubleshooting).

18. Complete the field form by recording the date, time, and D_2 for each respective sample bottle (fig. 7.0-2).

Quality control. The BOD_5 test can be quite variable. Collect sufficient field and split replicates (10 to 20 percent) to provide an estimate of method variability.

5-Day Biochemical Oxygen Demand (BOD_5) Worksheet

Site/station:_____ **Collection date and time:**_____
Project:_____ **Personnel:**_____

Dilution-water blanks

Bottle number	Initial DO reading (D_1)	Date/time of reading	Final DO reading (D_2)	Date/time of reading	BOD (D_1-D_2)	BOD average (<0.2 mg/L)

Environmental sample

Bottle number	Sample size (mL)	Initial DO reading (D_1)	Date/ time of reading	Final DO reading (D_2)	Date /time of reading	BOD $\frac{D_1 - D_2}{P}$	BOD average (mg/L)

If dilution-water demand is <0.2 milligrams per liter (mg/L), use

$$BOD_5\ (mg/L) = \frac{D_1 - D_2}{P}$$

where
D_1 = initial sample dissolved-oxygen (DO) concentration (in mg/L)
D_2 = sample DO (in mg/L) after 5 days
P = decimal volumetric fraction of sample used

Figure 7.0-2. Example of a 5-day biochemical oxygen demand worksheet.

CALCULATIONS 7.0.4

The general equation for the determination of a BOD_5 value is:

$$BOD_5\,(mg/L) = \frac{D_1 - D_2}{P}$$

where D_1 = initial DO of the sample,
D_2 = final DO of the sample after 5 days, and
P = decimal volumetric fraction of sample used.

If 100 mL of sample are diluted to 300 mL, then $P = \frac{100}{300} = 0.33$. Notice that if no dilution was necessary, $P = 1.0$ and the BOD_5 is determined by $D_1 - D_2$.

If more than one dilution of the sample results in residual DO of at least 1 mg/L and a DO depletion of at least 2 mg/L, and there is no evidence of toxicity at higher sample concentrations or the existence of an obvious anomaly, average the results that are in the acceptable range (American Public Health Association and others, 1995).

7.0.5 TROUBLESHOOTING

The troubleshooting suggestions in table 7.0-3 are not all-inclusive. Refer to the troubleshooting suggestions for DO instruments (table 6.2-4 in NFM 6.2). Remember that faulty batteries can cause erratic readings.

Table 7.0-3. Troubleshooting guide for the 5-day biochemical oxygen demand test

[DO, dissolved oxygen; BOD_5, 5-day biochemical oxygen demand; mg/L, milligrams per liter; HCl, hydrochloric acid]

Symptom	Possible cause and corrective action
DO readings drift downward	• Weak batteries for stirring unit result in inadequate flow across membrane—replace batteries.
BOD_5 demand in dilution water is greater than the acceptable 0.2 mg/L	• Deionized water contains ammonia or volatile organic compounds—increase purity of dilution water or obtain from another source. Age water for 5-10 days before use. • Deionized water contains semivolatile organic compounds leached from the resin bed—increase purity of dilution water or obtain from another source. Age water for 5-10 days before use. • Bacterial growth in reagents and poorly cleaned glassware—more vigorous cleaning of glassware, including washing followed by a 5- to 10-percent HCl rinse followed by 3-5 rinses with deionized water. Discard reagents properly.
Sample BOD values are unusually low in the diluted sample (BOD_5 dilution water is within the acceptable range)	• Dilution water contains interferences inhibiting the biochemical oxidation process—increase purity of dilution water or obtain from another source. • Use deionized water that has been passed through mixed-bed resin columns. **Never use copper-lined stills.** Distilled water may be contaminated by using copper-lined stills or copper fittings—obtain from another source.

REPORTING 7.0.6

When reporting results of a BOD_5 test, be sure to use the correct parameter code (Appendix A7-A, table 1).

- Report BOD_5 values less than 2 mg/L as <2 mg/L rather than as 2.0 mg/L.
- Report BOD_5 values less than 10 mg/L to the nearest 0.1 mg/L.
- Report BOD_5 values greater than or equal to 10 mg/L to two significant figures.
- Report the results of replicate samples and dilution blanks with the BOD_5 results.

FECAL INDICATOR BACTERIA 7.1

By **Donna N. Myers, Donald M. Stoeckel, Rebecca N. Bushon, Donna S. Francy, and Amie M.G. Brady**

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Illustrations

Tables

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FECAL INDICATOR BACTERIA 7.1

Fecal indicator bacteria are used to assess the microbiological quality of water. Although these bacteria are not typically disease causing, they are associated with fecal contamination and the possible presence of waterborne pathogens. The density of indicator bacteria[1] is a measure of water safety for body-contact recreation or for consumption.

Fecal indicator bacteria: bacteria used to measure the sanitary quality of water

Fecal material from warm-blooded animals may contain a variety of intestinal microorganisms (viruses, bacteria, and protozoa) that are pathogenic to humans. For example, bacterial pathogens of the genera *Salmonella*, *Shigella*, and *Vibrio* can result in several types of illness and diseases in humans, including gastroenteritis and bacillary dysentery, typhoid fever, and cholera.

Bacteriological tests for specific indicator bacteria are used to assess the sanitary quality of water and sediments and the potential public health risk from gastrointestinal pathogens carried by water. The suitability of indicator organisms for these purposes is ranked according to a specific set of criteria, described below.

Criteria for selecting an indicator of fecal contamination in water

The preferred fecal indicator:

- Can be tested for easily
- Is of human or other animal origin
- Survives as long as, or longer than, pathogens
- Is present at densities correlated with fecal contamination
- Can be used as a surrogate for many different pathogens
- Is appropriate for fresh and saline aqueous environments

[1]The term "indicator bacteria" is used synonymously with fecal indicator bacteria in this section.

This section describes tests that can be completed in the field for identifying and enumerating five types of fecal indicator bacteria: total coliform bacteria, fecal coliform bacteria, *Escherichia coli* (*E. coli*), fecal streptococci, and enterococci (Britton and Greeson, 1989; U.S. Environmental Protection Agency, 1985, 1991a, 1996, 2000, 2002a, b, c, d). Two methods can be used to test for indicator bacteria in the field: (1) the membrane-filtration method (section 7.1.3.C) and (2) the liquid broth method, using the presence-absence format (section 7.1.3.D) or the most-probable-number (MPN) format (section 7.1.3.E). Also included is guidance on how to collect samples to be analyzed for *Clostridium perfringens* (*C. perfringens);* these samples are shipped to a microbiological laboratory for analysis (U.S. Environmental Protection Agency, 1996).

- The presence in water of *E. coli*, and often enterococci, is direct evidence of fecal contamination from warm-blooded animals. Their presence indicates the possible presence of pathogens (Dufour, 1977; Wade and others, 2003). A few strains of *E. coli* are pathogenic, such as *E. coli* O157:H7, but most strains are not.
- Densities of other indicator bacteria (total coliforms, fecal coliforms, and fecal streptococci) can be, but are not necessarily, associated with fecal contamination. Despite this limitation, total coliforms are used to indicate ground-water susceptibility to fecal contamination. Fecal coliforms also are used to assess the sanitary quality of shellfish-growing waters and, in some States, for attainment of recreational-water-quality standards. The use of fecal streptococci generally has been discontinued by the U.S. Geological Survey for water-quality monitoring.
- The presence of *C. perfringens* in water, as spores and (or) vegetative cells, indicates contamination of water with treated or untreated sewage or similar wastes (Bisson and Cabelli, 1980; Fujioka and Shizumura, 1985). *C. perfringens* is used as an alternative indicator of fecal contamination in tropical and subtropical waters because other indicator bacteria may regrow in these environments.

The indicator bacteria used to assess fecal contamination depend on regulations associated with the type of water being tested, which is classified according to its use, as shown below.

Type of water	Description of water type and its use	Federally required indicator bacteria
Ambient water	Any water body encountered in the environment, regardless of use designation.	(Depends on use.)
Recreational water	Water bodies where people engage in, or are likely to engage in, activities that could lead to ingestion of the water or immersion in the water. Recreational water is designated as such in State and Tribal water-quality standards.	Enterococci and *E. coli* — required for ocean and Great Lakes beaches (coastal waters). Requirements for inland beaches are subject to State regulations.
Shellfish-growing water	Any site that supports or could support the propagation and harvesting of shellstock (molluscan shellfish, such as oysters, clams, mussels, and scallops) in the natural environment or at fish farms.	Total coliform and fecal coliform.
Potable (drinking) water	A water supply that meets the requirements of the Safe Drinking Water Act, as administered by the U.S. Environmental Protection Agency and any applicable State or local jurisdictions.	Total coliform. Detection requires follow-up testing for fecal coliform and *E. coli*. The U.S. Environmental Protection Agency Ground Water Rule for public supply systems includes testing for total coliform, *E. coli*, enterococci, and coliphage viruses.
Treated drinking water	Potable water from a public water supply that has been treated by physical or chemical means to improve water quality.	
Public water system	A water system that serves 25 or more people or that has 15 or more service connections and operates at least 60 days per year.	

Water-quality criteria have been developed for densities of indicator bacteria in recreational and ambient waters with designated uses (U.S. Environmental Protection Agency, 1986).

- **Recreational waters.** The U.S. Environmental Protection Agency (USEPA) criteria for indicator bacteria, used to classify the sanitary quality of recreational waters, are shown in table 7.1–1 and are used to develop State standards. ***E. coli* and enterococci are the indicators of sanitary quality most commonly used for recreational waters because both are predictors of swimming-associated gastroenteritis.** In 1986 they replaced total and fecal coliforms and fecal streptococci as the recommended indicator bacteria, as the latter have not been shown to be predictive of swimming-associated gastroenteritis (U.S. Environmental Protection Agency, 1986 and 2000; Cabelli, 1977; Dufour and Cabelli, 1984; Wade and others, 2003). The Beaches Environmental Assessment and Coastal Health Act of 2000 (Public Law 106-284) requires the use of *E. coli* and (or) enterococci to assess water quality of coastal and Great Lakes beaches in all bathing-beach monitoring programs; this became effective May 2004, based on the USEPA criteria of 1986 (table 7.1–1).
  - Enterococci are the preferred indicator bacteria in marine waters because of their salt tolerance.
  - Either *E. coli* or enterococci are recommended for monitoring fresh water (U.S. Environmental Protection Agency, 2004).

Table 7.1–1. Recreational water criteria under the Beaches Environmental Assessment and Coastal Health Act of 2000 (U.S. Environmental Protection Agency, 2004).

[mL, milliliters]

Indicator	Geometric mean: 5 samples (density per 100 mL)	Single-sample maximum: criterion may be exceeded in no more than 10 percent of samples (density per 100 mL)			
		Designated beach area[1]	Moderate use, full-body contact[2]	Light use, full-body contact[2]	Infrequent use, full-body contact[2]
	Fresh water				
Escherichia coli	126	235	298	410	576
Enterococci	33	62	78	107	151
Marine water					
Enterococci	35	104	158	276	501

[1]Designated beach areas are frequently lifeguard protected, provide parking and other public access, and are heavily used by the public (U.S. Environmental Protection Agency, 1986, p. 7).
[2]Other recreational uses, which involve various levels of full-body contact, are designated by individual State water-quality standards (U.S. Environmental Protection Agency, 1986, p. 7).

- **Shellfish-growing area.** Water-quality criteria for shellfish-growing areas have been developed by the U.S. Food and Drug Administration under the National Shellfish Sanitation Program. The 2005 guide for the control of molluscan shellfish (U.S. Food and Drug Administration, 2005) specifies criteria, based on total coliform and fecal coliform densities, to indicate the sanitary quality of water in shellfish-growing areas.

- **Potable water supplies: treated, untreated, private, and public.** Water-quality criteria for drinking water, based on total coliform density, are specified in the Safe Drinking Water Act, as amended in 1986 (U.S. Environmental Protection Agency, 1986).

  — Under the provisions of the Safe Drinking Water Act, all public water supply systems must disinfect their water unless criteria are met that ensure equivalent protection.

  — Under the Total Coliform Rule (U.S. Environmental Protection Agency, 2001), public water supply systems also must monitor distribution systems for contamination. When total coliforms are detected, follow-up tests for fecal coliforms or *E. coli* are required and a more intensive monitoring schedule may be required.

  — Water-quality criteria for ground water are specified in the Ground Water Rule, which was passed by Congress in October 2006. The Rule covers public water systems, which are defined as those that serve 25 or more people or have 15 or more service connections and operate at least 60 days per year. In addition to total coliforms and *E. coli* as indicators of sanitary quality in ground water, the Rule includes enterococci and coliphage viruses (U.S. Environmental Protection Agency, 2006). Ground water typically contains substantially lower densities of indicator bacteria compared to bodies of surface water.

The USEPA maintains a listing of approved methods for microbiological monitoring at http://www.epa.gov/safewater/methods/rules_micro.html (accessed January 21, 2007).

7.1.1 SAMPLING EQUIPMENT AND EQUIPMENT STERILIZATION PROCEDURES

Sterile technique must be followed and documented when collecting and processing samples for fecal indicator bacteria. Specific equipment and supplies are needed for collection of samples and analysis for indicator bacteria by use of sterile technique. The equipment and supplies listed in table 7.1–2 should be sufficient to begin membrane-filtration, presence-absence, or most-probable-number analysis of fecal indicator bacteria in water and sediment. Table 7.1–3 describes equipment cleaning and sterilization procedures.

- **Equipment for the collection and analysis of bacterial samples must first be cleaned and then sterilized** (table 7.1–3). Sterilize the filtration unit and sampling equipment before traveling between sites or before each sample collected at the same site at different times. There are several sterilization methods, but autoclaving is preferred.
- **Quality assurance and quality control of sterilization procedures must be documented.** Keep a logbook of autoclave operation or other sterilization procedure(s) used. In the log, include a brief description of the quality-assurance procedures used and quality-control tests run; note the date, the test results, and the name of the autoclave operator and (or) analyst.
- **If sample water contains residual chlorine or other halogens:** Add sodium thiosulfate ($Na_2S_2O_3$) to the sample bottles before the bottles are autoclaved. Residual chlorine commonly is found in samples collected from sources such as treated drinking water (withdrawn from taps), wastewater effluents, and in the mixing zones directly downstream from wastewater-treatment plants, or from the residue of sodium hypochlorite used to sterilize nonautoclavable sampling equipment (section 7.1.1.D).

Table 7.1–2. Equipment and supplies used for membrane-filtration and liquid broth analyses (presence-absence or most-probable-number format) for fecal indicator bacteria in water or sediment samples.

[TD, to deliver; NIST, National Institute of Standards and Technology; UV, ultraviolet; mENDO, total coliform medium; mTEC, *Escherichia coli* medium; mFC, fecal coliform medium; NFM, *National Field Manual for the Collection of Water-Quality Data;* MPN, most probable number; °C, degrees Celsius; mL, milliliters; nm, nanometers; mm, millimeters; µm, micrometer; psi, pounds per square inch; cm, centimeters]

✓	Item	Description
General equipment and supplies needed for microbiology		
	Autoclave	For sterilization, capable of maintaining 121°C
	Balance	For measuring weight, sensitive to 0.01 gram
	Buffered water	Sterile phosphate-buffered water with magnesium chloride
	Distilled or deionized water	Sterile distilled or deionized water, unbuffered, for use when diluting samples for defined-substrate tests
	Graduated cylinders	Borosilicate glass or plastic, 25 and 100 mL, covered and sterilized
	Incubator	Aluminum heat sink (heater block), or forced-air, or water bath incubator; capable of maintaining specified temperature ranges during incubation (temperature is test-specific)
	Pipets	Sterile, TD, bacteriological or Mohr, glass or plastic with cotton plugs; 1, 10, and 25 mL
	Pipettor or pipet bulb	For drawing liquids into pipets
	Thermometer	Range 30-110°C, glass-alcohol or digital, calibrated in 0.2°C increments, checked against a NIST-certified thermometer
	Ultraviolet lamp, long wave	For use with various tests that result in UV-fluorescent colonies or wells, 366-nm, 6-watt
	Ultraviolet view box	To help with viewing UV-fluorescent test results
	Wrapping for equipment	Kraft paper, aluminum foil, autoclavable plastic bags
Equipment and supplies needed for membrane-filtration analyses		
	Absorbent pads	For use with total coliform test on mENDO medium and with *Escherichia coli* on mTEC medium for urease test
	Alcohol burner	Glass or metal, containing ethanol, for flame sterilizing forceps
	Alcohol bottle	Wide mouth, 100 mL, containing 70 percent ethanol for forceps sterilization
	Cultivation media and amendments	Liquid or solid media and reagents specific to the test method, prepared in advance (NFM 7.1.3.A)
	Counter	Handheld, for counting bacterial colonies
	Dilution bottles	Plastic or glass, 100-mL capacity or greater, with autoclavable screwcaps, filled with 90 or 99-mL buffered water, sterilized and labeled with volume and date
	Filtration assembly	Filter funnel, filter base, and stainless steel, glass, or plastic filter holder; wrapped in aluminum foil, autoclavable bag, or kraft paper; sterile; autoclavable

Table 7.1–2. Equipment and supplies used for membrane-filtration and liquid broth analysis (presence-absence or most-probable-number format) for fecal indicator bacteria in water or sediment samples—*Continued*

✓	Item	Description
	Forceps	Stainless steel, smooth tips
	Hot plate	With magnetic stirrer or boiling water bath for media preparation
	Magnifier	Wide-field type dissecting scope with 5 to 15 magnifications, or equivalent, with fluorescent lamp
	Membrane filters	47-mm, sterile, white, gridded, mixed cellulose ester, cellulose acetate, or cellulose nitrate, 0.45-µm pore size, 0.65-µm may be used with mFC agar
	Culture plates	Sterile, plastic, disposable top and bottom plates, 50 by 12 mm in size
	Vacuum source	Hand pump with gage, electric vacuum, or peristaltic pump; vacuum not to exceed 5 psi or 25 cm mercury
Equipment and supplies needed for liquid broth analyses (presence-absence format)		
	Comparator bottle	Required to evaluate the threshold for a positive reaction when using Colilert-based tests
	Cultivation bottles	Cultivation bottles, greater than 100 mL capacity, with autoclavable screwcaps for cultivation of water samples
	Defined-substrate reagent packs	Single-use snap packs containing defined-substate broth reagents, such as Colilert and Enterolert
Equipment and supplies needed for liquid broth analyses (MPN format)		
	Comparator tray	Required to evaluate the threshold for a positive reaction when using Colilert-based tests
	Defined-substrate reagent packs	Single-use snap packs containing liquid broth reagents, such as Colilert and Enterolert
	Dilution bottles	Glass or plastic, 100-mL capacity or greater, with autoclaveable screwcaps, filled with 90 or 99-mL distilled or deionized water, sterilized
	Quanti-Trays	Quanti-Tray 200 or 2000, depending on target concentration
	Quanti-Tray sealer	Needed to seal sample into Quanti-Trays
Equipment and supplies needed for analyses of indicator bacteria eluted from sediment samples		
	Bottles	Sterile plastic, used to mix sediment with buffer water during elution of bacteria from sediment into buffered water
	Drying dish	Heat-tolerant glass or metal dish used for determination of proportion dry-weight sediment
	Drying oven	Oven capable of maintaining 105°C to measure proportion dry-weight sediment
	Jars	Wide mouth, sterile plastic; used to composite sample in laboratory (if necessary)
	Spatula	Stainless steel, sterile or flame sterilized
	Wrist-action shaker	Used to shake samples during elution of bacteria from sediment into buffered water

- **Equipment that has been decontaminated using a methanol rinse can affect the viability of the microbial population** for which analyses will be performed. Ensure the removal of methanol residue from sampling equipment before samples are collected for bacteria analysis.
  - Allow the methanol to evaporate completely from the interior and exterior surfaces of equipment. In an office setting, filtered argon or nitrogen gas under pressure can be forced through equipment to help evaporate the methanol from interior spaces that cannot be exposed adequately to the atmosphere.
  - After evaporating the methanol, rinse the equipment with pesticide grade blank water (PBW) or volatile/pesticide grade blank water (VPBW) and autoclave the equipment. For nonautoclavable equipment, rinse thoroughly with PBW or VPBW that has been autoclaved. **Methanol-tainted water must be collected and disposed of as a hazardous substance: follow local and (or) State and Federal regulations.**
  - Collection and analysis of a blank sample for volatile organic compound analysis can help document the absence (or presence) of methanol in the sample.
  - Collect bacteria samples last.
  - As an alternative to the procedures described above, use completely separate sampling equipment that is dedicated for microbial sample collection.
- **When using a pump system to collect ground-water samples for both chemical and bacteria analysis,** it is recommended that individual lengths of tubing be dedicated to, and prepared for, each well at which samples will be collected.
  - To clean the tubing, (a) follow the office cleaning procedures described in NFM 3, removing the methanol by pushing it out with at least two tubing volumes of PBW or VPBW or (and) by forcing clean gas through the tubing, as described above; and (b) autoclave the tubing. Be certain, first, that the tubing can be autoclaved. Sterilization by autoclave is the preferred method. If the tubing cannot be autoclaved, use autoclaved PBW or VPBW to push methanol from, and subsequently rinse, the tubing.

— Tubing should be dry if it will be stored and transported under warm conditions, to prevent microbial growth. Forced gas can be used to dry the tubing; however, the tubing should be autoclaved afterwards.

— Between sites, clean the pump using the field procedures described in NFM 3, taking extra care to remove methanol residue from the pump interior either by using a forced gas method or rinsing copiously with autoclaved VPBW or PBW.

Store and transport sterile equipment in a sterile container.

Table 7.1–3. Equipment cleaning and sterilization procedures

[DIW, distilled or deionized water; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; L, liter; EDTA, ethylenediaminetetraacetic acid; UV, ultraviolet light; psi, pounds per square inch; °C, degrees Celsius]

Equipment	Procedures
Cleaning	
All equipment (this includes water-level tape measure, all sample-collection and sample-processing equipment used in the field and laboratory)	Wash equipment thoroughly with a dilute, nonphosphate laboratory-grade detergent. Rinse three times with tap water. Rinse again three to five times with DIW Wipe the wetted portion of water-level tapes with disinfectant (0.005 percent bleach solution or 70-percent methyl or ethyl alcohol) and rinse thoroughly with sterile water.
Sterilization (Refer to table 7.1—4 for recommended times for autoclaving glassware, liquids, and other media and materials.)	
Magnetic plastic filtration field units, glass, plastic, and Teflon bottles and containers, volumetric flasks, pipets and pipettors, and other autoclavable materials	If sample may contain residual chlorine or other halogens, add 1 mL of 10-percent $Na_2S_2O_3$ solution per liter volume of sample. This can be added to the sample bottle before autoclaving. If sample may contain toxic trace metals, add 3 mL of a sterile 15-percent EDTA stock solution per 1 L of sample. This can be added to the sample bottle before autoclaving. Wrap equipment in kraft paper, aluminum foil, or place into autoclavable bags. Autoclave at 121°C, 15 psi, for 15 minutes. **NOTE:** If an autoclave is not available, refer to sections 7.1.1.B, 7.1.1.C, and 7.1.1.D for alternative sterilization techniques.

Table 7.1–3. Equipment cleaning and sterilization procedures—*Continued*

Equipment	Procedures
Stainless steel filtration field units	Autoclave at 121°C, 15 psi, for 15 minutes, flame sterilize with methanol (Millipore Hydrosol® units only, section 7.1.1.B), or use ultraviolet irradiation for 15 minutes (section 7.1.1.C).
Portable submersible pumps and pump tubing	**Autoclavable equipment** (preferred): Wrap components in kraft paper, aluminum foil, or place into autoclavable bags. Autoclave at 121°C, 15 psi, for 15 minutes. **Non-autoclavable equipment:** (1) Submerge sampling system in pH-neutral sodium hypochlorite solution prepared from household laundry bleach (section 7.1.1.D). (2) Circulate solution through pump and tubing for 30 minutes. (3) Follow step 2 by thoroughly rinsing, inside and out, with a working solution of 1 mL 10-percent sterile $Na_2S_2O_3$ per liter of water, and circulate solution for 5 minutes. (4) Pump $Na_2S_2O_3$ to waste, then circulate sterile DIW through pump, followed by sample water pumped from the well. Dispose of waste solutions according to regulatory requirements. **CAUTION:** Prolonged or repeated use of a hypochlorite solution on interior or exterior metallic surfaces of a pump can cause corrosion or other damage to the pump and compromise the quality of samples collected for a trace-element or organic-compound analysis.

To prepare a 10-percent stock solution of sodium thiosulfate ($Na_2S_2O_3$) for treatment of samples:

1. Dissolve 100 grams (g) of $Na_2S_2O_3$ into 500 milliliters (mL) of deionized or distilled water; stir until dissolved, and fill a flask to 1,000 mL (Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). Sterilize by autoclaving (table 7.1-3).

2. Dispense 1 milliliter (mL) of 10-percent $Na_2S_2O_3$ stock solution for every liter of sample (final concentration is 0.01 percent).

3. Store the $Na_2S_2O_3$ stock solution at room temperature in a tightly capped bottle that is labeled with its contents and expiration date. Discard after 6 months and prepare a fresh solution.

- **If sample water contains toxic trace metals:** Add ethylenediaminetetraacetic acid (EDTA) to sample bottles when water to be collected contains toxic concentrations of trace metals. EDTA can be combined with the $Na_2S_2O_3$ solution in the sample bottle before sterilization.

  Although thresholds for toxic concentrations vary somewhat in the literature, trace metals such as copper, nickel, or zinc that are present at concentrations greater than 10 to 1,000 micrograms per liter (µg/L) are generally toxic to bacteria (Britton and Greeson, 1989, p. 5; Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). Toxic concentrations may be found in urban runoff samples or industrial effluents. When in doubt, add EDTA to sterilized sample bottles before adding the water sample.

To prepare a 15-percent stock solution of EDTA or treatment of sample bottles:

1. Dissolve 100 g of EDTA in 90 mL of deionized or distilled water; stir until dissolved, and fill a flask to 100 mL. Adjust to pH 6.5 and sterilize by autoclaving (table 7.1-3).
2. Dispense 3 mL of the 15-percent EDTA stock solution per 1 liter (L) of sample (American Public Health Association and others, 1998, p. 9-19).
3. Store the EDTA stock solution at room temperature in a tightly capped bottle that is labeled with its contents and expiration date. Discard after 6 months and prepare a fresh solution.

7.1.1.A AUTOCLAVING

Autoclaves that have temperature, pressure, and dry-utensil-cycle controls are recommended. In addition, a liquid-cycle control is needed for autoclaving liquids. Steam sterilizers, vertical autoclaves, and pressure cookers without temperature controls are not recommended.

- Take care to ensure that materials to be autoclaved, such as tubing and containers, are thermally stable. Plastic polymers that can be autoclaved include polycarbonate, polypropylene, polyallomer, polymethylpentene, Teflon® and Tefzel®. Each material type has different thermal characteristics and tolerances to repeated autoclaving.

- Before autoclaving, wrap clean equipment in Kraft paper, autoclavable plastic bags, or aluminum foil. Wrap loosely to allow steam to penetrate the wrapping. Cap tubing ends with aluminum foil.
  - Sterilize and store the equipment in a clean area.
  - Resterilize equipment if the foil, bag, or Kraft paper is torn.
- Consult table 7.1–4 for recommended times for autoclave sterilization of various media and materials.
  - Liquids must be exposed to 121°C at 15 psi (pounds per square inch (lbs/in^2)) for the specified time for effective sterilization—larger volumes of liquid take longer to reach 121°C.
  - If the autoclave does not reach the specified temperature and pressure or fails a quality-control test, service the autoclave and then resterilize all materials (American Public Health Association and others, 1998, p. 9-2 to 9-14).
- In addition to the guidance listed above, it is necessary to:
  - Use sterilization indicator tape with each load.
  - Use commercially available biological indicators at least quarterly to test autoclave performance. Biological indicators are composed of endospores—living cells that are resistant to heat but are killed by effective autoclaving.
  - Drain the autoclave daily. Clean with mild soap and water once per week during periods of daily use. Record cleaning procedures in the logbook.
  - Avoid overloading the autoclave with equipment or materials; overloading will result in incomplete sterilization.

Table 7.1–4. Recommended times to autoclave media and materials.
[°C, degrees Celsius; mL, milliliters]

Media or material	Autoclave time[1]
Glassware and other dry materials	15 minutes
Liquid, 250 mL	15 minutes
Liquid, 500 to 2,000 mL	30 minutes
Liquid, 2,000 to 6,000 mL	15 minutes per 1,000 mL
Liquid, greater than 6,000 mL	90 minutes
Carbohydrate-containing media	15 minutes
Contaminated materials and discarded cultures	45 minutes

[1]Timing should begin after the autoclave reaches operating temperature (121°C).

Autoclaving is the preferred method for sterilizing equipment that is used to test for fecal indicator bacteria.

7.1.1.B FLAME STERILIZATION OF THE HYDROSOL® FIELD FILTRATION UNIT

The Millipore Hydrosol® field filtration units are designed to be flame sterilized with methanol. Formaldehyde gas, a by-product of methanol combustion, kills all bacteria in the unit. However, the use of autoclavable units is preferred over flame-sterilized units because of safety concerns. If an autoclave is not available, presterilized disposable funnels are a safe alternative.

The following sterilization procedure is acceptable for the Hydrosol unit (fig. 7.1–1) in field situations where other sterilization techniques are not practicable (Millipore, 1973, p. 48–49).**When following these procedures, work in a ventilated area and wear appropriate protective equipment such as safety glasses, face mask, and gloves. Avoid breathing noxious fumes.**

CAUTION:
When flame sterilizing, have proper safety equipment such as a fire extinguisher on hand, and implement procedures carefully.

To flame sterilize the Hydrosol unit, carefully:

1. Remove the clean, dry stainless steel flask from the base of the filter-holder assembly.
2. Saturate the asbestos ring (wick) around the base assembly with methanol dispensed from a squeeze bottle or with an eye dropper.
3. Ignite the methanol on the asbestos wick and allow the wick to burn for 30 seconds.

4. Invert the stainless steel flask over the funnel and the burning asbestos ring, and seat the flask on the base of the filter-holder assembly. Leave the flask in place for 15 minutes. Before filtering the next sample, rinse the flask and funnel thoroughly with sterile buffered water to remove all residues of formaldehyde.
5. Repeat the sterilization procedure before processing the next sample.

Figure 7.1–1. Procedure to flame sterlize the Millipore Hydrosol® field filtration unit.

7.1.1.C STERILIZATION OF EQUIPMENT BY ULTRAVIOLET IRRADIATION

Ultraviolet (UV) germicidal irradiation makes use of short-wave UV light (specifically, 254 nanometers) to disinfect equipment (table 7.1–2) and should not be confused with the long-wave UV light (366 nanometers) used to detect positive reactions in various analytical methods (see table 7.1–2, and table 7.1–9 in section 7.1.3.C). Several commercial units are specifically designed to field-sterilize stainless-steel filtration units. Manufacturers' recommendations should be followed when using these sterilization units and equipment should be tested for sterility following treatment. **Since UV light does not penetrate most materials (even most clear plastic and glass) only surfaces that are directly exposed to UV light are properly sterilized.**

7.1.1.D STERILIZATION OF EQUIPMENT WITH SODIUM HYPOCHLORITE

A solution of sodium hypochlorite (bleach) is used to sterilize equipment that is non-autoclavable or to sterilize equipment in the field when an autoclave is not readily available. Sodium thiosulfate is used to remove residual chlorine after sterilization.

1. Prepare a working solution of 50 mg/L (0.005 percent) sodium hypochlorite from household bleach by adding 1 mL of fresh household bleach per liter of distilled or deionized water. Most household bleach is 5 to 7 percent sodium hypochlorite (50,000 to 70,000 mg/L), **but household bleach that has been opened for more than 60 days before use may not be full strength.** Prepare fresh working solutions with each use, because the concentration will diminish with time. (U.S. Environmental Protection Agency, 1982, p. 253 and 1996, p. VIII-41).
2. Adjust the pH of the working solution from pH 6 to pH 7 with 1 *Normal* hydrochloric acid (1 *N* HCL). The 1 *N* HCL can be purchased from a commercial supplier of scientific products. The unadjusted pH of bleach is approximately 12, a pH at which the hypochlorite ion has limited germicidal activity (U.S. Environmental Protection Agency, 1996).

3. Clean the equipment and submerge it in the sodium hypochlorite solution, or completely fill the equipment with the sodium hypochlorite solution. Maintain contact for 30 minutes.
4. Remove or drain the equipment.
5. Thoroughly rinse the equipment, inside and out, with sterile $Na_2S_2O_3$ solution (prepared as 1 mL of 10-percent stock per liter of water) to remove residual chlorine. Maintain contact for 5 minutes.
6. Remove or drain the equipment.
7. Rinse the equipment thoroughly with sterile deionized or distilled water.
8. If adding EDTA to the sample bottle, use a sterile pipet and sterile EDTA.

CAUTION:
Prolonged or repeated use of a sodium hypochlorite solution on interior or exterior metallic surfaces of equipment can cause corrosion or other damage and compromise the quality of samples collected for a trace-element or organic-compound analysis.

7.1.2 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

Sterile conditions must be maintained during collection, preservation, storage, and analysis of indicator bacteria samples. Specific procedures have been developed that must be strictly followed; these vary with types of equipment and sample source (surface water, ground water, treated water, or wastewater) (table 7.1–5).

Methanol residue (from decontamination of equipment used for sampling organic compounds) can kill bacteria. If sampling with equipment that has been exposed to methanol, take extra care or use special procedures to ensure that the methanol has completely evaporated from all exterior and interior surfaces of the equipment (see section 7.1.1). Collect the bacteria sample after collecting samples for other analyses.

Table 7.1–5. Summaries of equipment for sample collection, procedures for sample preservation, and holding times for indicator bacteria

[EWI, equal-width increment; EDI, equal-discharge increment; L, liter; mL, milliliter; EDTA, ethylenediaminetetraacetic acid; °C, degrees Celsius; *E. coli, Escherichia coli*; *C. perfringens, Clostridium perfringens*]

Equipment for sample collection
To collect EWI or EDI surface-water samples: US D-95, US DH-95, or US DH-81 with sterile, 1-L wide-mouth bottle, with sterile caps and nozzles. US D-96 with sterile autoclavable bag.
To collect surface-water and ground-water samples using a pump, point samplers from a tap, or by the hand-dipped method: a sterile container, 125-, 250-, 500-, or 1,000-mL capacity, depending on the number of tests and samples.
All containers must be composed of sterilizable materials such as borosilicate glass, polypropylene, stainless steel, or Teflon®.
Procedures for sample preservation
If necessary, add 1 mL of a 10-percent sodium thiosulfate solution per 1 L of sample for halogen neutralization (see section 7.1.1).
If necessary, add 3 mL of a 15-percent EDTA stock solution per 1 L of sample for chelation of trace elements (see section 7.1.1).
Chill all samples at 1 to 4°C before analysis.
Maximum holding times for indicator bacteria
A 30-hour holding time after sample collection for total coliform bacteria, fecal coliform bacteria, and *E. coli* collected from **drinking-water sources** (Bordner and Winter, 1978 p. 30).
A 6-hour holding time for *E. coli*, fecal coliform bacteria, total coliform bacteria, and enterococci in **nonpotable water for compliance purposes** (American Public Health Association and others, 1998, p. 9.21).
A 24-hour holding time for *E. coli*, fecal coliform bacteria, total coliform bacteria, enterococci, and fecal streptococci in **water for noncompliance purposes** (American Public Health Association and others, 1998, p. 9.21).
A 24-hour holding time for *C. perfringens*. A 6-hour maximum holding time after sample collection for *C. perfringens* is recommended if comparisons between *C. perfringens* and other fecal-indicator bacteria collected at the same time are planned (U.S. Environmental Protection Agency, 1996, p. XI-8).
A 24-hour holding time between **bed sediment** collection and initiation of analysis of fecal-indicator bacteria. Do not exceed the recommended 24-hour holding time.

7.1.2.A SURFACE-WATER SAMPLE COLLECTION

The areal and temporal distribution of bacteria in surface water can be as variable as the distribution of suspended sediment because bacteria commonly are associated with solid particles. To obtain representative data for bacteria analysis, follow the same methods used to collect surface-water samples for suspended sediment analysis (NFM 4.1 and table 7.1–4). Sample bottles are not to be field rinsed with native water but should be autoclaved or otherwise sterilized before use.

- **Flowing water**—use depth- and width-integrating sampling methods (NFM 4.1.3.A).[2]
- **Still water** (lakes or other surface-water conditions for which depth- and width-integrating methods may not be applicable)—use the hand-dip method or a sterile point sampler (NFM 4.1.3.C). It may be necessary to collect multiple samples across the depth or area of the targeted lake volume to accomplish data-quality objectives.

Wear laboratory-type gloves and avoid sample contact with eyes, nose, mouth, and skin when working in and with contaminated waters.

[2]Sample-collection methods may be modified to ensure consistency with study objectives and as appropriate for site conditions.

Depth- and width-integrating methods

Depth- and width-integrating sampling methods (the equal-discharge increment (EDI) method or the equal-width increment (EWI) method) are the standard U.S. Geological Survey (USGS) methods used when sampling flowing waters and are required unless study objectives or site characteristics dictate otherwise (NFM 4.1.3.A and table 7.1–5).

- The EDI method is preferred to the EWI method for sites where there is some knowledge of the distribution of streamflow in the cross section; for example, at a gaging station with a long period of discharge record (Edwards and Glysson, 1999).
- Select the appropriate sampler and equipment (recommended sampling devices may change as a result of technological advances or other considerations—check for updates in NFM 2.1 and 4.1). **Sampling equipment that comes in contact with the sample water must be sterile,** including the collection bottle, nozzle, and cap (or bag for the bag sampler) (table 7.1–3).
  - For streams with depths of 5 meters (m) or less, use a US D-95, US DH-95, or a US DH-81 sampler (NFM 2.1.1).
  - For stream sections where depths exceed 5 m, use the US D-96, with either autoclavable Teflon® bags or autoclavable cooking bags. Thermotolerant polymers are described in 7.1.1, "Sampling Equipment and Equipment Sterilization Procedures."
  - For wide channels, several samples—each composed of subsamples composited into a sterile large-volume container—may be needed. A sterile 3-L or larger bottle may be used to composite subsamples.
  - For narrow channels, collect subsamples at 5 to 10 or more vertical locations in the cross section without overfilling the bottle.
  - Use the proper nozzle size and transit rate for the velocity conditions in the section to ensure isokinetic collection of the sample (NFM 2.1 and 4.1).

Point-sampling methods

If the stream depth and (or) velocity is not sufficient to use a depth- and width-integrating method to collect a sample, use the hand-dip method (table 7.1–5). Sampling at depth in lakes, reservoirs, estuaries, and oceans often requires a sterile point sampler. Niskin, ZoBell, and Wheaton point samplers, for example, hold a sterile bottle or bag.

To collect a hand-dipped sample:

1. Grasp the bottle near the base with hand and arm on the downstream side of the bottle.
2. One of two methods may be used to avoid collecting surface scum: (a) submerge the bottle with cap on and remove the cap underwater to collect the sample, or (b) plunge the open bottle mouth quickly downward below the water surface. Lower the bottle in a manner that avoids contact with or disturbance of the streambed.
3. Allow the bottle to fill with the opening pointed slightly upward into the current.
4. Remove the bottle with the opening pointed upward toward the water surface and tightly cap it, allowing about 2.5 to 5 centimeters (cm) of headspace for proper mixing (American Public Health Association and others, 1998, p. 9-19; Bordner and Winter, 1978, p. 8). Another option would be to cap the bottle underwater. When the bottle is out of the water, uncap it and pour off enough water to allow adequate headspace for mixing. Then recap the bottle.

CAUTION:
Do not sample in or near a water body without wearing a correctly fitted personal flotation device (PFD).

Special considerations for beach-water sampling. The steps below will aid in collecting samples for use in support of beach closure or posting decisions for swimming or other full-body-contact recreation. Sampling procedures for other purposes are based on project objectives.

1. Collect samples in the area used for swimming at 0.7- to 1-m water depths, maintaining consistency in water depth throughout the sampling period. The sample typically is taken 15 to 30 cm below the water surface using the hand-dip method. Position the bottle to collect the sample from any incoming current (U.S. Environmental Protection Agency, 2002e). Avoid contaminating the water sample with bottom material kicked up from the bottom while sampling.
2. At some beaches, multiple samples may be needed to adequately represent overall water-quality conditions. Producing a composite from multiple samples on an equal-volume basis may provide results that are as accurate as those obtained by averaging analyses from multiple points.
3. **A Chain-of-Custody record is recommended for beach sampling done in support of beach closures or posting of warnings to swimmers** (U.S. Environmental Protection Agency, 2002e, Appendix J).

Quality control in surface-water sampling. Depending on the data-quality requirements of the study and site conditions, quality-control samples will include field blanks, equipment and procedure blanks, field replicates, and positive and negative control samples (controls). Quality-control terms (shown below in bold type) are defined at the beginning of NFM 7, in "Conversion Factors, Selected Terms, Symbols, Chemical Formulas, and Abbreviations."

- **Field blanks—**Collect and analyze field blanks at a frequency of one blank for every 10 to 20 samples, or as required by the data-collection objectives of the study, to document that the sampling and analysis equipment have not been contaminated. If sampling for compliance with beach regulations, at a minimum collect a field blank at the beginning, middle, and end of the sampling season.
    1. Pass sterile buffered water (for membrane filtration) or sterile distilled or deionized water (for liquid broth tests) through sterile sampling equipment and into a sterile sampling container.
    2. Analyze field blanks for fecal indicator bacteria. If no growth is observed, then the sample was collected by use of sufficiently sterile procedures.

- **Analytical blanks—**Process **filter blanks** and **procedure blanks** (for membrane filtration) or **method blanks** (for liquid broth tests) during sample processing to document that equipment and rinse or dilution water were sterile.
  - — A filter blank is processed for each sample before the sample is filtered.
  - — A procedure blank is processed through the filtration unit after the sample has been filtered, at a frequency of one blank for every 10 to 20 samples.
  - — Method blanks are processed at a frequency of one blank for every 10 to 20 samples.
- **Field concurrent replicates—**Collect and analyze one field replicate for every 10 to 20 samples. A split concurrent replicate is recommended. Two samples are collected and each sample is analyzed in duplicate by membrane filtration. Replicate data are used to quantify the uncertainty in density estimates (see Francy and Darner, 1998, for an example).
- **Positive and negative controls—**These types of quality-control samples are required if media are prepared from basic ingredients by field or laboratory personnel, and are recommended if media are purchased from a commercial supplier. The frequency of analysis depends on project objectives and the type of medium. Positive controls test the medium's ability to recover target bacteria; negative controls are used to ensure that nontarget bacteria are inhibited or recognized. Refer to section 7.1.3.A for details.

7.1.2.B GROUND-WATER SAMPLE COLLECTION

As with surface water, most bacteria in ground water are associated with solid particles. Collecting a 100-mL ground-water sample for bacteria analysis is standard procedure because ambient ground water flowing through aquifers typically contains much fewer particulates, and bacteria density is expected to be low. Applying the protocols for purging wells before collecting water-quality samples (NFM 4.2) is necessary to ensure that the particulate content and bacteria density sampled represent ambient aquifer conditions.

- When using the same sampling equipment for chemical and bacteria analyses, give special consideration to the effect of equipment-preparation procedures on sample integrity (section 7.1.1).
  - Sampling equipment that has been sterilized for microbial sample collection using chlorinating and dechlorinating agents can affect the chemistry of samples collected for analyses of some inorganic analytes.
  - Equipment subjected to a methanol rinse for decontamination for organic-compound sample collection can affect the viability of the microbial population for which analyses will be performed.
  - **Recommendation:** Prepare separate tubing lengths that are designated for the sole use of sampling at a specified well. Clean the tubing at the office or office laboratory. Tubing should be autoclaved after routine cleaning, if possible (section 7.1.1).
- Collect bacteria samples last.
- If a different sampler will be used for bacteria sampling, remove at least one well volume of well water and compare the turbidity and dissolved-oxygen measurements with those recorded after purging the well with the first sampler, to ensure collection of a sample that represents ambient ground-water quality.

Supply wells

Selection of a sampling strategy for supply wells (NFM 4.2) depends, in part, on the objectives of the study. For all objectives, select a tap (spigot) that supplies water from a service pipe connected directly to the main: **do not use a tap that leaks or one that is attached to a pipe served by a cistern or storage tank** (American Public Health Association and others, 1998, p. 9-19 to 9-20; Britton and Greeson, 1989, p. 5; Bordner and Winter, 1978, p. 5-16).

- For aquifer-monitoring studies, locate the point of ground-water withdrawal upgradient of (before the water reaches) a chlorination or other treatment system (unless study objectives dictate otherwise).
- For drinking-water studies, sample the ambient water in the well regardless of the history of treatment. Dechlorination with $Na_2S_2O_3$ is required if the sample is collected after the water has passed through a chlorination unit (section 7.1.1).

To sample a supply well for indicator bacteria:

1. Before collecting the sample, remove screens, filters, or other devices from the tap.
2. Swab or spray the inside and outside rim of the tap with ethanol. If possible, flame sterilize the tap and allow it to dry and cool. Rinse the tap with sterile deionized or distilled water.
3. Supply wells commonly are equipped with permanently installed pumps.
   - If the well is pumped daily, then purge the tap water for a minimum of 5 minutes, discarding the purged water appropriately. Monitor field measurements and record stabilized values (NFM 6.0).
   - If the well is used infrequently, then purge the tap until a minimum of three well volumes are purged and stable field measurements are obtained in sequential measurements (NFM 4.2 and 6.0).
4. Collect a sample directly from the tap into a sterile bottle without splashing or allowing the sample bottle to touch the tap.

Monitoring wells

If a well used to monitor ground-water quality does not have an in-place pump, then obtain samples by using a portable sampler, such as a submersible pump or a bailer (U.S. Environmental Protection Agency, 1982). If possible, autoclave or disinfect the sampling devices and the sample line (table 7.1–3). If disinfected with a sodium hypochlorite solution, then the sampler and sample line must be dechlorinated and rinsed with sterile deionized or distilled water. In either case, finish by flushing the sampler and sample line with native ground water before samples are collected into sterile bottles.

- ▶ Use autoclavable samplers, if possible. After flushing the sterilized pump lines with sample water, collect the sample directly into the sterile sample bottles.
- ▶ Check data-quality objectives before using a disinfectant. Disinfectants are corrosive; they can damage the metal parts of a pump, and can render the pump inadequate for sampling trace-element and other constituents.

- Some sampling equipment does not require chlorine disinfection. If the water level in a well is less than 7 to 10 m (roughly 20 to 30 ft) below land surface, then a sample can be collected without contamination and without chlorine disinfection by use of a peristaltic or vacuum pump, as long as the tubing is sterile.
- If sampling equipment has been in contact with methanol, implement the methanol removal techniques described in section 7.1.1.

To disinfect a pump with a sodium hypochlorite solution:

1. Follow the instructions for cleaning equipment with a hypochlorite solution (bleach) (section 7.1.1.D and table 7.1–3)
2. Lower the pump carefully into the well. Purge the residual chlorine and $Na_2S_2O_3$ from the system by pumping three tubing volumes of well water through the system; contain or appropriately discard this waste water. Take care not to contaminate samples for chemical analysis with residual chlorine or $Na_2S_2O_3$. **The pump must have a backflow check valve (an antibacksiphon device) to prevent residual chlorine from flowing back into the well.**

To use a pump that cannot be disinfected:

1. Clean equipment as thoroughly as possible (section 7.1.1).
2. Handle the pump and tubing carefully to avoid contamination. If the pump is a downhole dedicated pump, skip to step 4.
3. Collect field blanks through the sampling equipment.
4. Lower the pump in the well to the desired intake location.
5. Purge the well with the pump to thoroughly flush the pump and tubing with aquifer water before sampling (NFM 4.2 and 6.0).
6. An alternative to sampling with the pump is to remove the pump after purging the well. Complete the collection of other samples, and then collect the bacteria sample using a sterile bailer (U.S. Environmental Protection Agency, 1982, p. 252–253). When using the bailer method, the potential for bias exists from stirring up particulates to which bacteria may adhere during pump removal and bailing that would not otherwise be included in the sample.

Sample-preparation activities, such as purging, must be carried out in such a way as to avoid contaminating the well, the equipment, or the samples. Avoid collecting surface film from the well water in the sample, and ensure that the sampler intake is within that portion of the screened interval targeted for study.

- Select a point sampler, such as a bailer with a double-check valve.
- Use only bailers that can be appropriately sterilized; preferably autoclaved.

Be aware that the type of well, its use, construction, composition, and condition can lead to alteration or contamination of the ambient aquifer water that enters the well. For example, a poor surface seal around the well opening can allow contaminants to move quickly from the land surface to the well water.

Exercise the following precautions when collecting samples from monitoring wells:

1. Avoid collecting samples from wells with casings made of galvanized materials; such casings can contain bactericidal metals. If samples must be collected from these types of wells, add 3 mL of EDTA solution per 1 L of sample to the sample bottle prior to autoclaving (section 7.1.1). Collect the sample directly into the bottle.
2. Purge the well (NFM 4.2.3) while monitoring field measurements. Measurements of turbidity and dissolved oxygen are especially relevant. For wells in which field measurements do not stabilize after increasing the total number of measurements, record the problem and the measurements and proceed with sampling.

Quality control for ground-water sample collection. Depending on the data-quality requirements of the study, quality-control samples include pump, filter, procedure, and method blanks; field replicates; and positive and negative controls. Quality-control terms (shown below in bold type) are defined at the beginning of NFM 7 in "Conversion Factors, Selected Terms, Symbols, Chemical Formulas, and Abbreviations."

- **Pump blanks—**This type of blank should be collected ahead of sampling so that results can be evaluated before field sampling. Thereafter, collect pump blanks with ground-water samples at a frequency of one blank for every 10 to 20 samples, or as required by the data-quality objectives of the study. Collect pump blanks by passing sterile buffered water (for membrane filtration) or sterile distilled or deionized water (for liquid broth tests) through the sampling equipment and into a sterile sampling container. A standpipe may be used to collect a pump blank, but it first must be cleaned and disinfected. Analyze pump blanks for fecal indicator bacteria and record results. If no growth is observed, the use of sufficiently sterile procedures is confirmed and documented.

- **Analytical blanks—**Process **filter blanks** and **procedure blanks** (for membrane filtration) or **method blanks** (for liquid broth tests) during sample processing to document that the equipment and the rinse or dilution water were sterile. A filter blank is processed for each sample before the sample is filtered. A procedure blank is processed through the filtration unit after the sample has been filtered, at a frequency of one blank for every 10 to 20 samples. Method blanks also are processed at a frequency of one blank for every 10 to 20 samples.

- **Field sequential replicates**—Because few ground-water samples test positive for indicator bacteria, it may be necessary to collect field sequential replicates for every sample. A lower frequency may be used if a large percentage of wells are positive or study objectives do not require quantification of variability.

- **Positive and negative controls—**These types of quality-control samples are required if media are prepared from basic ingredients, and is recommended if the medium is purchased from a commercial supplier. The frequency of analysis depends on project objectives and the type of medium. Positive controls test the medium's ability to recover target bacteria; negative controls are used to ensure that nontarget bacteria are inhibited or recognized. Refer to section 7.1.3.A and table 7.1–6 for details.

7.1.2.C BED-SEDIMENT SAMPLE COLLECTION

Due to the spatial heterogeneity of bacteria in sediments, three bed-sediment samples should be collected from each site at the same depth and composited (Francy and Darner, 1998). One of two sampling methods can be used, depending on the depth of the water: (1) sampling by wading, or (2) using a sampler for deep-water sites.

To sample by wading. Use three sterile, plastic, wide-mouthed, 125-mL or 250-mL jars are used for sample collection.

1. Secure the lid on a sterile jar and plunge to the bottom.
2. Upon reaching the bottom, open the jar and scoop the bed sediments into the jar.
3. To minimize contamination by overlying water, secure the lid before surfacing.
4. Repeat for the remaining two jars.
5. Immediately place the jars on ice in a cooler and keep them chilled until the samples are processed.

To use a sampler for deep-water sites. Select the grab sampler that is most appropriate for the site to be sampled (for example, Ponar, and Petite Ponar, Van Veen, and Ekman samplers). These heavy devices collect sediment samples by biting down into bottom materials and closing tightly to hold the sample. Collect and composite three grab samples into one sterile jar in the field as follows:

1. The sampler needs to be sterilized before collecting samples for bacterial analysis. Because of the dimensions of these samplers, autoclaving generally is not practical. **If more than one site is to be sampled, the sampler needs to be resterilized in the field at each of the sites.** To field-sterilize the sampler:
    a. Put on laboratory gloves.
    b. Wash and scrub the sampler in dilute nonphosphate, laboratory-grade detergent and rinse with tap water and then deionized or distilled water.
    c. Soak the sampler in a 0.005-percent sodium hypochlorite solution for 15 minutes (section 7.1.1.D)
    d. Soak in a sterile 0.01-percent $Na_2S_2O_3$ solution for 5 minutes (section 7.1.1).

2. Lower the sampler through the water column and collect the sediment sample according to the manufacturer's instructions.
3. Drain off excess water. Deposit the sediment into a clean, sterile washtub.
    a. Sterilize the washtub by (1) autoclaving, if possible, or (2) following procedures for sterilization with sodium hypochlorite (section 7.1.1.D).
    b. Once sterilized, store washtubs individually in new, clean plastic bags (such as garbage bags) until ready for use.
4. Collect two more grab samples from the same site and deposit in the same washtub. Since samples will be composited, the sampler does not need to be resterilized between collection of each of the three subsamples.
5. Use a sterile spatula to mix the three samples thoroughly and then deposit a portion into a sterile jar. For indicator-bacteria analysis, collect at least 200 g of sediment.
6. Immediately refrigerate or place the samples on ice in a cooler until the samples can be processed. See section 7.1.2.D for sample-preservation and holding-time requirements.
7. Sterilize the sampler before using it at another site (section 7.1.1.D).

Quality control for bed-sediment sample collection. Depending on the data-quality requirements of the study, quality-control samples include field blanks, filter and procedure blanks or method blanks, field replicates, and positive and negative controls. Quality-control terms (shown below in bold type) are defined at the beginning of NFM 7 in "Conversion Factors, Selected Terms, Symbols, Chemical Formulas, and Abbreviations."

- **Field blanks**—Collect and analyze field blanks when using a sampler to collect bed-sediment samples at a frequency of one blank for every 10 to 20 samples, or as required by study objectives, to document that sampling and analysis equipment have not been contaminated. Process field blanks before sample collection if the sampler does not need to be sterilized in the field. If the sampler does need to be sterilized in the field, process field blanks after collection of a sample and resterilization of the sampler. This will demonstrate that the field-sterilization procedure is working appropriately.

    1. Pass sterile buffered water (for membrane filtration) or sterile distilled or deionized water (for liquid broth tests) over the sterile sampler and into a sterile washtub. Collect the field blank into a sterile bottle or jar.
    2. Analyze field blanks for fecal indicator bacteria. If no growth is observed, then the sample was collected by use of sufficiently sterile procedures.

- **Analytical blanks—**Process **filter blanks** and **procedure blanks** (for membrane filtration) or **method blanks** (for liquid broth tests) during sample processing to document that the equipment and the rinse or dilution water were sterile. A filter blank is processed for each sample before the sample is filtered. A procedure blank is processed through the filtration unit after the sample has been filtered, at a frequency of one blank for every 10 to 20 samples, or as otherwise required. Method blanks also are processed at a frequency of one blank for every 10 to 20 samples.

- **Field replicates**—Collect and analyze one field replicate for every 10 to 20 samples, or as otherwise required by study objectives. A split sequential replicate is recommended. For samples collected from wading sites, an additional three jars of sediment are collected and treated as a separate sample. For samples collected using a sampler, the sampler is resterilized before collection of the replicate; the sediment is deposited into a new, sterile washtub, composited in the field, and treated as a separate sample. In the laboratory, each sequential replicate is analyzed twice to produce a total of four split sequential replicate samples.

- **Positive and negative control samples—**These types of quality-control samples are required if media are prepared from basic ingredients by field or laboratory personnel and recommended if media are purchased from a commercial supplier. The frequency of analysis depends on project objectives and the type of medium. Positive control samples test the medium's ability to recover target bacteria; negative control samples are used to ensure that nontarget bacteria are inhibited or recognized. Refer to section 7.1.3.A for details.

SAMPLE PRESERVATION, STORAGE, AND HOLDING TIMES 7.1.2.D

After collection, immediately chill samples in an ice chest or refrigerator at 1 to 4°C. **Do not freeze samples. Process water samples as quickly as possible; store on ice if not analyzed within 1 hour of collection** (American Public Health Association and others, 1998, p. 9-21). Adhering to holding times minimizes changes in the density of indicator bacteria; however, for non-compliance ambient monitoring a longer holding time may be used as long as it is consistently maintained and documented (Pope and others, 2003). Holding times for indicator bacteria are summarized in table 7.1–5.

- For treated drinking water, do not exceed 30 hours before initiation of analysis.
- For nonpotable water for compliance purposes, analyze samples within 6 hours of collection.
- For other types of water for noncompliance purposes, samples should be analyzed within 24 hours of collection.
- *C. perfringens* spores can survive for extended periods of time, and a 24-hour holding time is acceptable if a relation between *C. perfringens* and other fecal indicator bacteria is not part of the planned study; otherwise, observe the same holding time as for the other indicators (U.S. Environmental Protection Agency, 1996). An acceptable holding time for bed-sediment samples is 24 hours.
  - *C. perfringens* is analyzed at the laboratory, and not in the field. Information on analysis of *C. perfringens* is available at http://oh.water.usgs.gov/micro/clos.html (accessed January 16, 2007).
  - Ship samples for analysis of *C. perfringens* to the laboratory in a double-bagged sample container separate from any bagged ice in the ice chest. Include a chain-of-custody form with sample identification and relevant information for use by the laboratory.

Chill samples from 1 to 4°C and store samples in the dark until analysis.

7.1.3 IDENTIFICATION AND ENUMERATION METHODS

Membrane-filtration (MF) and liquid broth tests (presence-absence and most-probable-number (MPN) formats) are used for identification and enumeration of indicator bacteria. Procedures to analyze water samples using the MF method and a liquid broth method (enzyme substrate test in presence-absence or MPN format) are described below in sections 7.1.3.C, D, and E. Procedures to elute bacteria from sediments as a preliminary step to analysis by MF or liquid broth methods are described in section 7.1.3.B. For general enumeration of indicator bacteria, either the MF or enzyme substrate test in MPN format may be used.

Fecal indicator bacteria are operationally defined by the method employed for identification and enumeration, as shown in table 7.1–6. Enumeration is done based on observation of reactions typical of the target bacteria on the test medium. Detailed confirmation and identification of these bacteria require additional culturing and biochemical testing, the details of which are beyond the scope of this manual. Additional confirmation methods may be needed under certain circumstances, such as use of the data in support of environmental regulation and enforcement (U.S. Environmental Protection Agency, 2000). Methods should be selected that are appropriate for the sample and project objectives. For example, methods for analyzing total coliform and *E. coli* in ground water and drinking water are different from those recommended for surface water and recreational water (table 7.1–6).

Table 7.1–6. Fecal-indicator test media, typical applications, incubation times and temperatures, and types of rinse or dilution water.

[mENDO, total coliform medium; ±, plus or minus; °C, degrees Celsius; MI, total coliform and *Escherichia coli* medium; $MgCl_2$, magnesium chloride; NA-MUG, *E. coli* medium; mTEC, *E. coli* medium; mFC, fecal coliform medium; KF, fecal streptococci medium; mEI, enterococci medium; mCP, *Clostridium perfringens* medium.]

Test (medium)	Typical application	Incubation time and temperature	Type of rinse and (or) dilution water[1]
Total coliform bacteria (mENDO)	Drinking water and ground water	24 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Total coliform bacteria (MI)	Drinking water and ground water	24 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Total coliform bacteria (Colilert or Colilert-18)	Drinking water and ground water	24-28 hours at 35.0 ± 0.5°C (Colilert) 18-22 hours at 35.0 ± 0.5°C (Colilert-18)	Distilled or deionized water
Escherichia coli (NA-MUG)	Drinking water and ground water	4 hours at 35 ± 0.5°C after primary culture on mENDO medium	(See mENDO)
Escherichia coli (MI)	Drinking water and ground water	24 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Escherichia coli (modified mTEC)	Fresh waters—recreational and other surface water	Resuscitate, 2 hours, 35.0 ± 0.5°C Incubate, 22 to 24 hours, 44.5 ± 0.2°C	Phosphate-buffered water with $MgCl_2$
Escherichia coli (on urea substrate broth after primary culture on mTEC)	Fresh waters—recreational and other surface water	Resuscitate, 2 hours, 35.0 ± 0.5°C Incubate, 22 to 24 hours, 44.5 ± 0.2°C Transfer filter to urea substrate broth, 15 to 20 minutes, before counting	Phosphate-buffered water with $MgCl_2$
Escherichia coli (Colilert or Colilert-18)	Fresh waters—recreational and other surface water, drinking water and ground water	24-28 hours at 35.0 ± 0.5°C (Colilert) 18-22 hours at 35.0 ± 0.5°C (Colilert-18)	Distilled or deionized water
Fecal coliform bacteria (mFC)	Recreational water, shellfish-harvesting water	24 ± 2 hours at 44.5 ± 0.2°C	Phosphate-buffered water with $MgCl_2$
Fecal streptococci (KF)	Recreational water	48 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Enterococci (mEI)	Fresh and saline recreational waters, proposed for ground water	24 hours at 41.0°C ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Enterococci (Enterolert)	Fresh and saline recreational waters, proposed for ground water	24-28 hours at 41.0°C ± 0.5°C	Distilled or deionized water
Clostridium perfringens (mCP)	All waters	24 ± 2 hours at 44.5 ± 0.2°C	Phosphate-buffered water with $MgCl_2$

[1]Buffered water type for all tests changed as of November 2004.

Update 2005.02 to 2007.06 and year 2005 to 2007

7.1.3.A CULTURE MEDIA AND REAGENTS

Analyses for indicator bacteria require several types of culture media and reagents specific to the indicator bacteria and method being used. Detailed information about sources of media and preparation protocols are described in Office of Water Quality Technical Memorandum 2005.02 (U.S. Geological Survey, 2005) and on the Ohio Water Microbiology Laboratory Web page ~~http://oh.water.usgs.gov/micro/qcmanual/manual.html (accessed January 17, 2007~~). The necessary media and reagents include sterile buffered water, sterile distilled or deionized water, agar- or liquid broth-based selective and differential growth media, and media and reagents for additional biochemical tests (as needed). **The preparation of selective and differential culture media for indicator bacteria is an important part of analysis. Adhering to and documenting proper preparation, storage, and holding-time requirements will help ensure data quality.**

- Sterile phosphate-buffered water amended with magnesium chloride (U.S. Environmental Protection Agency, 2000) is used to dilute samples and to rinse the filtration unit and utensils.
  - Sterile buffered water can be obtained in 99-mL dilution bottles and in 500-mL volumes.
  - **Do not use sterile buffered water that exceeds the expiration date indicated on the label.**
  - Obtain buffered water from a commercial vendor that provides quality-control documentation. Buffered water also can be prepared according to the instructions found at ~~http://oh.water.usgs.gov/micro/qcmanual/appendm.pdf (accessed January 17, 2007~~). Buffered water prepared according to these instructions must be autoclaved and checked for sterility before use.
- Culture media (including dehydrated media) for enumeration of fecal indicator bacteria for USGS studies are obtained commercially. Instructions for preparation are printed on the labels of dehydrated media bottles and should be followed carefully. For studies that require small amounts of media, or that require media with complex preparation steps (such as mEI and MI agars), the use of pre-poured plates is recommended. Sources of dehydrated and pre-poured media are listed in Office of Water Quality Technical Memorandum 2005.02 (U.S. Geological Survey, 2005). Updated, detailed information about media and reagent preparation also can be found at http://oh.water.usgs.gov/micro_qaqc.htm ~~http://oh.water.usgs.gov/micro/qcmanual/manual.html~~ (accessed ~~January 16, 2007~~ July 16, 2013).

Update 2005.02 to 2007.06 and year 2005 to 2007

- Enzyme substrate tests in presence-absence or MPN format can be done in the field by use of commercially produced media that commonly come in the form of single-use dry reagent packs (such as Colilert® and Enterolert™).

To store media and reagents:

1. Refer to the manufacturer's instructions for the storage of dehydrated media. Store reagents in a dust-free laboratory cabinet (not in a field vehicle) or in a laboratory desiccator.
2. Label all media with the date received, date opened, and analyst's initials. Discard media and reagents that have an expired shelf life.
3. Refrigerate reagents when required.
4. Label all prepared plates to identify the media type, the preparation date, and the analyst.
5. Store prepared plates upside down in a sealed plastic bag in a refrigerator.

Do not use sterile buffered water beyond its expiration date discard it.

Quality control for culture media and reagents. Each batch of media that is prepared from basic ingredients or dehydrated media by the analyst must be quality-control tested. Pre-poured plates are already quality-control tested by the manufacturer; however, some testing is still required.

- If sterile buffered water is prepared by the user, it should be prepared under laboratory conditions and must be quality-control tested.
- Buffered water obtained from a commercial vendor already has been quality-control tested and does not require further testing.
- Use the quality-control procedures applicable to microbiological testing found in the 20th edition of "Standard Methods" (American Public Health Association and others, 1998, p. 9-18) and Office of Water Quality Technical Memorandum 2005.02 (U.S. Geological Survey, 2005).

For each batch of media prepared from **basic ingredients or dehydrated media**, it is recommended to analyze a filter blank, and positive and negative control samples (quality-control terms are described below). It is also recommended to analyze a filter blank and positive and negative control samples on **pre-poured plates**. These plates should be tested at least at the beginning and middle of the sampling period, and when the lot number of the plates has changed.

To test the sterility of the **buffered water**, analyze a filter blank each time the buffer is prepared in the laboratory.

- **Positive control—**Positive controls test the ability of the medium and reagents to support growth of the target microorganism. Refer to table 7.1–7 for guidance on which organism to use for specific media. Refer to the distributor's instructions for preparation and processing of positive control samples.
- **Negative control—**Negative controls are used to ensure that the medium does not support the growth of nontarget organisms. Refer to table 7.1–7 for guidance on which organism to use for specific media. Refer to the distributor's instructions for preparation and processing of negative control samples.
- **Filter blanks—**Filter blanks document that buffered water and equipment are sterile. A 50- to 100-mL sample of sterile buffered water is passed through the filtration unit onto a sterile membrane filter. Growth on the filter after incubation indicates contamination.

Table 7.1–7. Positive- and negative-control test organisms for specific media types

[TC, total coliform; NC, non-coliform; FS, fecal streptococci; KF, fecal streptococcus medium; mEI, enterococci medium; mENDO, total coliform medium; NA-MUG, *Escherichia coli* medium; mFC, fecal coliform medium; FC, fecal coliform; MI, total coliform and *Escherichia coli* medium; mTEC, *Escherichia coli* medium]

Media type	Positive control organism	Negative control organism
Colilert and Colilert-18	*Escherichia coli* and *Enterobacter cloacae* (TC)	*Pseudomonas aeruginosa* (NC)
Enterolert	*Enterococcus faecalis* (FS)	*Enterobacter cloacae* (TC)
KF	*Enterococcus faecalis* (FS)	*Enterobacter cloacae* (TC)
mEI	*Enterococcus faecalis* (FS)	*Enterobacter cloacae* (TC)
mENDO and mENDO/NA-MUG	*Escherichia coli* and *Enterobacter cloacae* (TC)	*Pseudomonas aeruginosa* (NC)
mFC	*Escherichia coli* (FC)	*Enterobacter cloacae* (TC)
MI	*Escherichia coli* and *Enterobacter cloacae* (TC)	*Pseudomonas aeruginosa* (NC)
modified mTEC	*Escherichia coli*	*Enterobacter cloacae* (TC)
mTEC	*Escherichia coli*	*Enterobacter cloacae* (TC)

PROCESSING BED SEDIMENTS 7.1.3.B

Standard methods for processing bed sediments for analysis of fecal indicator bacteria are not documented by the American Public Health Association or by the U.S. Environmental Protection Agency. The following method is recommended for general use.

Samples are processed in a laboratory environment to elute fecal indicator bacteria from bed sediments. Once eluted, the supernatant is analyzed for fecal indicator bacteria by use of membrane-filtration or enzyme substrate methods. The proportional dry weight of the bed sediment is also determined.

To process bed sediments:

1. Prepare for processing by labeling the following items with site identifiers and date and time of sample collection: sterile jar for compositing (if done in the laboratory), a 500-mL sterile bottle for eluting, a 500-mL sterile bottle for collection of supernatant, and a dish for proportional dry-weight analysis.
2. Samples collected at deep-water sites with a sampler are composited in the field. If the sample was collected from a wading site, prepare a composite in the laboratory, as follows:
    a. Measure the tare weight of a clean, sterile, wide-mouthed jar.
    b. Using a sterile spatula, remove 50 g of bed sediment from each of the three replicate sample jars and place into the wide-mouthed composite jar.
    c. Mix the 150 g of sediment thoroughly.
3. Prepare an aliquot of composite bed sediment for proportional dry weight of sediment.
    a. Weigh a clean, dry, heat-tolerant glass or metal dish and record as "tare weight."
    b. Add approximately 25 g of composited sediment and record as "weight before drying."
    c. Place in an oven at 105^{o}C. If an oven is not available, dry in a desiccator until a constant weight is obtained.

4. Elute bacteria from the sediment as soon as possible after compositing the sample.

    a. Place 20 g of the sediment composite into a bottle containing 200 mL of phosphate buffered water with magnesium chloride (U.S. Environmental Protection Agency, 2000). NOTE: If preparing a sample for split replicate analysis, increase the amount of sediment and buffered water appropriately. For example, place 30 g of the sediment composite into a bottle containing 300 mL of buffered water.

    b. Label the lid of this bottle with the time the bottle should be removed from the shaker (the bottle will be shaken for 45 minutes).

    c. Place the bottle on a wrist-action shaker.

    d. After 45 minutes, remove the bottle from the shaker and let it stand for 30 seconds undisturbed. Pour off the supernatant into a new, labeled sterile bottle.

5. Analyze the supernatant using the membrane-filtration method (section 7.1.3.C) or by the enzyme substrate MPN method (section 7.1.3.E). Autoclave the sediment and supernatant and discard.

> **TECHNICAL NOTE:** Supernatants commonly carry high concentrations of suspended sediments. In cases when the sediments in the supernatant clog membrane filters, the enzyme substrate in MPN format is recommended.

6. Remove the dish for proportional dry weight of sediment after 24 hours or until a constant weight is obtained.

    a. Record the constant weight obtained as "weight after drying."

    b. Use the following equation to calculate the proportional dry weight:

    Proportional dry weight = $(W_{dry} - W_{tare}) / (W_{wet} - W_{tare})$

    where,

    W_{tare} = Tare weight of empty dish,

    W_{wet} = Weight of dish with wet bed sediment before drying, and

    W_{dry} = Weight of dish with bed sediment after drying.

MEMBRANE FILTRATION 7.1.3.C

Before beginning to process the sample, select the appropriate sample volumes and assemble and label plates with the station number (or other site identifiers), the volume of sample filtered, and the date and time of sample collection. Select several sample volumes that are anticipated to yield one or two filters with counts in the ideal range (tables 7.1–8 and 7.1–9).

> **TECHNICAL NOTE:** It is useful to review the historical data for each site to help determine the number of sample volumes to be filtered. Where past analyses of samples from a site have shown a small variation in the number of fecal indicator bacteria, the filtration of as few as three or four sample volumes may suffice. However, where past analyses have shown the variation to be large or where the variation is not known, filtering a series of volumes in half-log-scale intervals is recommended.

Always wear laboratory gloves when processing samples for analysis of fecal indicator bacteria.

To prepare to filter samples:

1. If possible, process samples inside the field vehicle or a building, and out of direct sunlight and wind.
2. Before and after processing the samples, clean counter tops with an antibacterial cleaning solution, such as 70-percent isopropyl or ethyl alcohol, or 0.005-percent sodium hypochlorite.
3. Preheat incubators for at least 2 hours at temperatures specified for each test (table 7.1–6). Portable heater-block incubators must not be left in closed, unventilated vehicles when the outside air temperature is less than 15°C (60°F) or greater than 37°C (98°F).

To filter samples:

1. Select several sample volumes (table 7.1–8, fig. 7.1–2) that are expected to yield one or two filters with counts in the ideal range. The ideal range and number of sample volumes to filter depend on the test and the expected bacterial densities (table 7.1–9).
2. Record the site name, date, time of sample collection, and sample volume on the plate and on the record sheet or field form. Label filter and procedure blanks and other quality-control samples. Record the time of sample processing on the record sheet or field form.

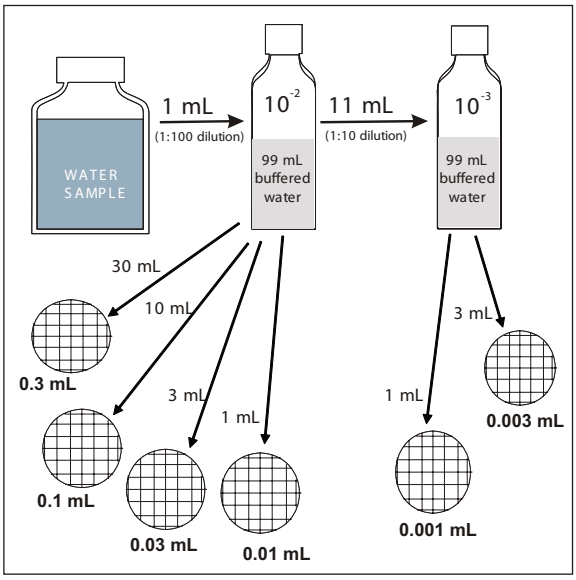


Figure 7.1–2. Preparation of sample volumes by dilution.

Table 7.1–8. Detection ranges achieved by analyzing various sample-water volumes by membrane filtration

[mL, milliliter; CFU, colony-forming units]

Detection limits for various volumes plated in membrane filtration analysis		
Sample volume (mL)[1]	**Volume of sample added (in mL)[2]**	**Detection limits (for ideal count of 20 to 80 colonies)**
100	100	<1 to 80
30	30	60 to 270
10	10	200 to 800
3.0	3.0	600 to 2,700
1.0	1.0	2,000 to 8,000
.3	3.0 of a 1:10 dilution[2] or 30 of a 1:100 dilution	6,000 to 27,000
.1	1.0 of a 1:10 dilution or 10 of a 1:100 dilution	20,000 to 80,000
.03	3.0 of a 1:100 dilution	60,000 to 270,000
.01	1.0 of a 1:100 dilution	200,000 to 800,000
.003	3.0 of a 1:1,000 dilution, prepared by diluting 11 mL of a 1:100 in 99 mL	600,000 to 27,000,000

[1]Sample volumes smaller than those indicated may be needed when bacterial concentrations are greater than those listed.

[2]All sample volumes less than 1.0 mL require dilution in sterile buffered water.

Table 7.1–9. Test (medium type), ideal colony count range, and typical colony color, size, and morphology for indicator bacteria colonies

[m-ENDO, total coliform medium; mm, millimeters; MI, total coliform and *Escherichia coli* medium; nm, nanometer; NA-MUG, *Escherichia coli* medium; mTEC, *E. coli* medium; mFC, fecal coliform medium; KF, fecal streptococcus medium; mE, enterococcus medium; EIA, enterococcus confirmation medium; mEI, enterococci medium; mCP, *Clostridium perfringens* medium]

Test (medium type)	Ideal colony count range (colonies per filter)	Typical colony color, size, and morphology
Total coliform bacteria (mENDO)	20 to 80	Colonies are round, raised, and smooth; red with a golden-green metallic sheen.
Escherichia coli After primary culture as total coliform colonies on mENDO (NA-MUG)	Not applicable[1]	Colonies are cultured on m-ENDO media as total coliform colonies. After incubation on NA-MUG, colonies have blue fluorescent halos with a dark center. Count under a long-wave ultraviolet lamp at 366 nm in a completely darkened room or viewing box.
Total coliform bacteria (MI)	20 to 80	Colonies fluoresce blue-white or blue-green or have a blue-green fluorescent halo[2] under long-wave ultraviolet light (366 nm); blue colonies that do not fluoresce are also total coliforms. Count in a completely darkened room or viewing box.
Escherichia coli (MI)	Not applicable[1]	Colonies are blue under ambient light, and blue green with or without fluorescent edges under long-wave ultraviolet light (366 nm).
Escherichia coli (mTEC)	20 to 80	Colonies are round, raised, and smooth; colonies remain yellow, yellow-green, or yellow brown after urease test; may have darker raised centers.
Escherichia coli (modified mTEC)	20 to 80	Colonies are round, raised, and smooth; deep pink to magenta.
Fecal coliform bacteria (mFC)	20 to 60	Colonies are round, raised, and smooth with even to lobate margins; light to dark blue in whole or part. Some may have brown or cream-colored centers.
Fecal streptococci (KF)	20 to 100	Colonies are small, raised, and spherical; glossy pink or red.
Enterococci (mEI)	20 to 60	Colonies have blue halos regardless of colony color. Count under a fluorescent lamp with 2 to 5 times magnification.
Clostridium perfringens (mCP)	20 to 80[3]	Colonies are round and straw yellow before exposure to ammonium hydroxide, dark pink to magenta afterward.

[1] mENDO/NA-MUG and MI media are used to detect concentration of total coliforms and presence of *Escherichia coli* in ground or drinking water.

[2]Be aware that non-target colonies grow and fluoresce paler orange or green on MI agar. It sometimes is difficult to distinguish target from non-target growth on MI agar.

[3]*C. perfringens* colonies often bubble on mCP agar, making it difficult to achieve the recommended ideal colony count upper limit of 80 colonies (U.S. Environmental Protection Agency, 1996).

3. If the sample volume to be plated is less than 1 mL, prepare dilutions with sterile buffered water in 99-mL dilution bottles (fig. 7.1–2 and table 7.1–8).

    - Transferring 11 mL of sample to a 99-mL dilution bottle creates a 1 to 10 dilution. Transferring 1 mL of sample to a 99- mL dilution bottle creates a 1 to 100 dilution.
    - These can be diluted in series, as needed. For example, transferring 1 mL of the 1 to 100 dilution to another 99-mL dilution bottle creates a 1 to 10,000 dilution.
    - When preparing a dilution series, use a sterile pipet to measure each sample volume. After each sample-volume transfer, close and shake the dilution bottle vigorously at least 25 times.
    - **Filter the diluted samples within 20 minutes after preparation.** Keep dilution bottles out of sunlight and do not transfer less-concentrated sample volumes with pipets that were used to transfer more-concentrated sample volumes.

4. Assemble the filtration unit by inserting the base of the sterile filter-holder assembly into a side-arm flask or manifold (fig. 7.1–3). Connect the filtration unit to a hand-held pump, vacuum pump, or peristaltic pump.

5. If flame sterilization is used (Hydrosol units), rinse the inside of the filtration unit with sterile buffered water to remove any residue of formaldehyde.

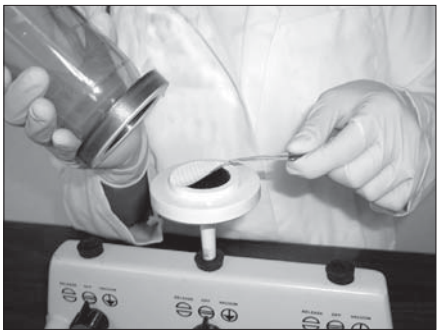
6. Sterilize stainless steel forceps:

    a. Immerse tips in a small bottle or flask containing 70- or 90-percent ethanol.

    b. Pass forceps through the open flame of an alcohol burner. Allow the alcohol to burn out and allow the forceps to cool to avoid scorching the membrane filter.

7. Remove the filter from its sleeve. Remove the sterilized funnel from the base. Always hold the funnel in one hand while placing or removing the membrane filter. Placing the funnel on anything other than the filter unit base might result in contamination of the funnel.

8. Using the sterile forceps, place a sterile, gridded membrane filter (47 mm) on top of the filter base, gridded side up (fig. 7.1–3). Carefully replace and secure the filter funnel on the filter base. Avoid tearing or creasing the membrane filter.



A

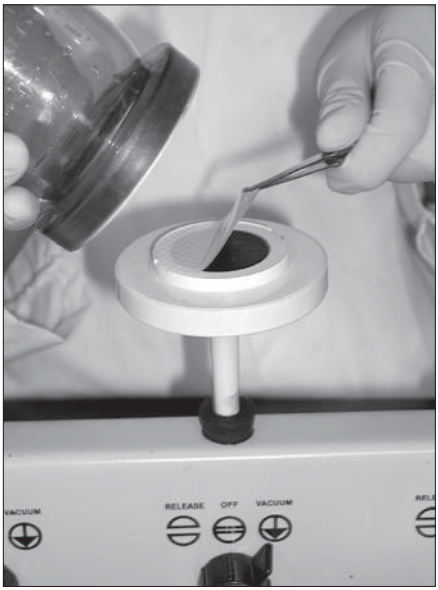
B

C

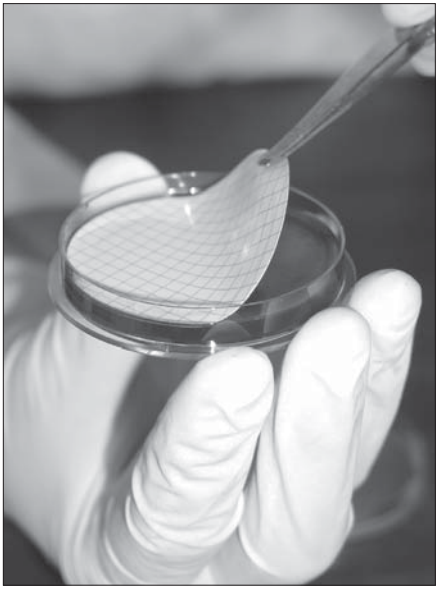
PROCEDURE

1. Preheat the incubator, prepare work areas.
2. Select sample volumes. If needed prepare dilutions for filtration of sample volumes less than 1.0 mL (tables 7.1–6 and 7.1–8; and figure 7.1–2).
3. Label plates.
4. Assemble sterile filtration apparatus.
5. Place sterile filter on filtration apparatus using sterile forceps (A).
6. Shake sample 25 times and deliver to filtration apparatus by use of graduated cylinder (B) or pipet (C). Add 20 mL sterile buffered water to filtration apparatus before filtering sample volumes less than 10 mL.
7. Apply vacuum; afterwards, rinse filtration apparatus and cylinder twice with sterile buffered water.

Figure 7.1–3. Steps in membrane-filter procedure.



D



E

PROCEDURE

8. Sterilize forceps and remove filter (D). Replace funnel on filtration apparatus.

9. Roll filter onto media in plate (E). Place inverted plate in incubator.

10. Repeat steps 4–9 for each sample volume on order of the smallest to the largest volume. A filter blank is processed before each sample. Filter a procedure blank after every 10 to 20 samples or once per day at each site, according to study objectives.

11. Filter a replicate sample after every 10 to 20 samples or at each site, according to study objectives.

Figure 7.1-3. Steps in membrane-filter procedure—*Continued*

9. Return forceps to the alcohol container between transfers. **Do not set forceps on the countertop.**

   Quality control. Rinse the funnel with about 100 mL of sterile buffered water before filtering sample volumes to obtain a filter blank. Place the filter on the plate labeled "filter blank."

10. Filter the sample in order of smallest to largest sample volume. Resterilize forceps before each use.

11. Shake the sample vigorously at least 25 times before each sample volume is withdrawn in order to break up particles and to ensure an even distribution of indicator bacteria in the sample container.

Always shake the sample before removing a volume for plating to make sure the bacteria are evenly distributed in the sample.

12. Remove the required volume by pipet or by pouring into a graduated cylinder (>10 mL) within 5 seconds of shaking the sample. If pipetting, place the pipet tip in the center of the sample volume and use a pipettor or pipet bulb with a valve for volume control. It is acceptable to use the upper and lower graduations to measure the volume (line-to-line) or simply draw up the selected volume.

13. Pour or pipet the measured volume of sample into the filter funnel (fig. 7.1-3*B* or *C*).

    a. **If the volume of sample to be filtered is from 1 to 10 mL,** pour about 20 mL of sterile buffered water into the funnel before pipetting the sample to allow even distribution of bacteria on the membrane filter.

    b. **If the volume of sample to be filtered is more than 10 mL,** transfer the sample with a sterile pipet or graduated cylinder directly into the funnel.

14. Allow the pipet to drain, touching the pipet to the inside of the funnel to remove any remaining sample (fig. 7.1–3*C*). However, if a serological pipet is used, a small amount of liquid will remain in the tip after the liquid is dispensed. Gently force out the remaining liquid using a pipettor or pipet bulb, taking care not to produce an aerosol by blowing out the pipet too forcefully.

CAUTION: Do not pipet by mouth.

15. Apply a vacuum. **To avoid damage to bacteria, do not exceed a pressure of about 5 lb/in^2 (25 cm of mercury).**
16. Rinse the inside of the funnel twice with 20 mL to 30 mL of sterile buffered water while applying a vacuum. If a graduated cylinder is used, rinse the cylinder with sterile buffered water and deliver rinse water to the filtration unit.
17. Remove the funnel and hold it in one hand—do not set the funnel on the counter top.
18. Remove the membrane filter using sterile forceps (fig. 7.1–3*D*).

Do not exceed 5 psi of pressure when filtering the sample.

19. Replace the funnel on the filter base and release the vacuum. (Releasing the vacuum after removing the filter prevents backflow of sample water onto the filter. Unnecessarily wet filters promote confluent growth of colonies and poor results.)
20. Open a labeled plate and place the membrane filter on the medium, grid side up, and starting at one edge by use of a rolling action (fig. 7.1–3*E*). Avoid trapping air bubbles under the membrane filter. If air is trapped, use sterile forceps to remove the membrane filter and roll it onto the medium again. **Do not expose prepared plates to direct sunlight.**
21. Close the plate by pressing the top firmly onto the bottom. Invert the plate. Incubate within 20 minutes to avoid growth of interfering microorganisms.
22. Continue to filter the other sample volumes in order, from smallest to largest volume. Record on field forms the volumes filtered and the time of processing. For USGS personnel, the microbiology section of the Personal Computer Field Form (PCFF) version 5.2.1 and above is a tool to help record and maintain analytical data and perform key calculations.

Quality control. After filtrations are complete, place a sterile, gridded-membrane filter onto the filtration unit base, replace the funnel, and rinse with about 100 mL of sterile buffered water to obtain a procedure blank. Procedure blanks are analyzed at a frequency of one blank for every 10 to 20 samples.

23. Place the inverted plates into a preheated aluminum heater-block or into water-tight plastic bags and then into a water-bath incubator. Incubate at the prescribed times and temperatures (table 7.1–6).

24. Wash the counter top between each sample with an antibacterial cleaning solution (see "To prepare to filter samples" at the beginning of section 7.1.3.C). Wash and sterilize the filter apparatus before the next use.

Quality control. Verify the incubator temperature on a regular schedule against a National Institute of Standards and Technology (NIST) thermometer or a thermometer certified to a NIST thermometer. Record results in a logbook with the date and analyst's name. Do not use incubators that fail to meet temperature criteria until they are repaired or the problem is corrected.

To count colonies and calculate results:

1. After the prescribed length of incubation, remove the plates from the incubator. For each sample volume filtered, count and record on the field forms the number of target colonies (table 7.1–9). **Recount the colonies until results agree within 5 percent, and record the results.** Recounting is accomplished by turning the plate 90 degrees to obtain a different view. Count by use of a preset plan (a side-to-side pattern along grid lines is suggested; fig. 7.1–4). Count the colonies with the aid of 5 to 15 magnification and a fluorescent illuminator or other light source placed directly above the filter.

   Quality control. A second analyst should recount the colonies and record the results for at least one in every 20 samples. Table 7.1–9 and figure 7.1–5 contain further information on colony identification.

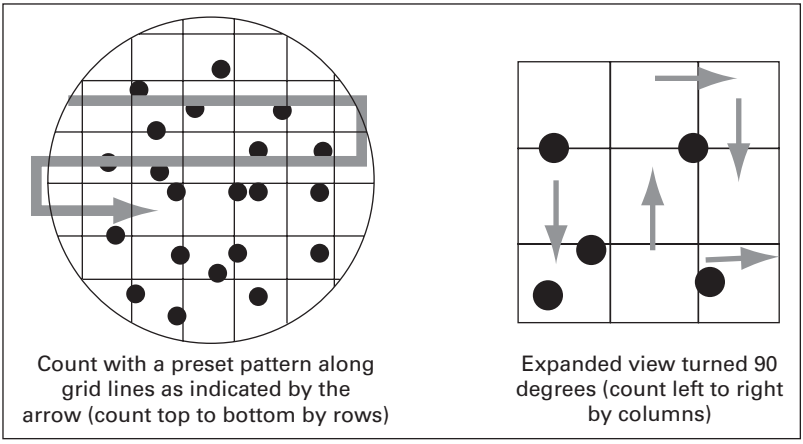


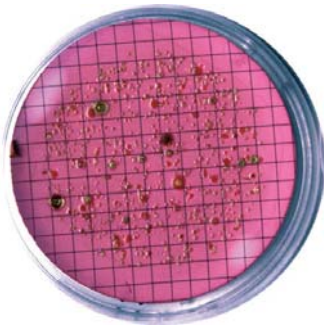
Figure 7.1–4. Method for counting colonies on gridded membrane filters.

Media-specific guidance for making colony counts:

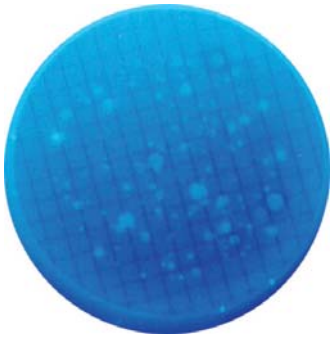
- For total coliform colonies on mENDO medium, count pink to dark red colonies with a golden-green metallic sheen. Enhance sheen production by removing filters from media and placing them on absorbent pads to dry for at least 1 minute before counting (fig. 7.1–5*A*).
- If the NA-MUG test is done for *E. coli*, transfer the mENDO total coliform filter onto NA-MUG plates and incubate for 4 hours at 35°C. Afterwards, count colonies with a dark center and bright blue fluorescent halo under a long-wave ultraviolet light in a completely darkened room (U.S. Environmental Protection Agency, 1991b) or in a viewing box (fig. 7.1–5*D*).
- For total coliforms on MI medium, count colonies that fluoresce blue-white or blue-green or have a blue-green-fluorescent halo under a long-wave ultraviolet light in a completely darkened room (U.S. Environmental Protection Agency, 2002d) or in a viewing box (fig. 7.1–5*B*). Blue colonies that do not fluoresce are also counted as total coliforms. Be aware that non-target colonies may have pale orange- or green-colored fluorescence under long-wave ultraviolet light.
- For *E. coli* on MI medium, count blue colonies under natural light (U.S. Environmental Protection Agency, 2002d; fig. 7.1–5*C*).

- For *E. coli* on mTEC medium, transfer the filter to a filter pad saturated with urea-phenol reagent; count only colonies that are yellow, yellow-green, or yellow-brown after 15 to 20 minutes at room temperature (U.S. Environmental Protection Agency, 2002a; fig. 7.1–5*E*).
- For *E. coli* on modified mTEC medium, count colonies that are red to magenta under natural light (U.S. Environmental Protection Agency, 2002c; fig. 7.1–5*F*).
- For fecal coliforms on mFC medium, count colonies that are light to dark blue, in whole or in part, under natural light (fig 7.1–5*G*).
- For fecal streptococci on KF medium, count colonies, using magnification, that are glossy pink or red under natural light (fig. 7.1–5*H*).
- For enterococci on mEI medium, count colonies of any color that have a blue halo under magnification with a small fluorescent lamp. (U.S. Environmental Protection Agency, 2002b; fig. 7.1–5*J*). Always use 2 to 5 times magnification when counting colonies on mEI agar.
- For *C. perfringens* on mCP medium, count colonies that are straw yellow, turning dark pink to magenta under natural light when exposed to ammonium hydroxide in a laboratory fume hood (U.S. Environmental Protection Agency, 1996; fig. 7.1–5*K*).

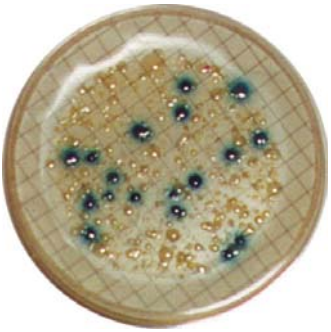
2. Check quality-control blanks for colony growth, and report results on the field forms. The presence of colonies on blanks indicates that results of the bacterial analyses are suspect and should not be reported or the results should be clearly qualified. It is not valid to subtract colony counts on blanks from results calculated for samples.
   - One or more colonies on the field or filter blank indicates inadequate sterilization of either the equipment or the buffered water, or contamination during the sampling and analysis process.
   - One or more colonies on the procedure blank indicates either inadequate rinsing or contamination of the equipment or the buffered water during sample processing.
3. Calculate the number of colonies per 100 mL of sample as described in section 7.1.4.
4. Put all plates to be discarded into an autoclavable bag and **autoclave at 121°C for 45 minutes before discarding in the trash**. If plates cannot be autoclaved immediately, they may be held in a freezer or refrigerator for up to a week before being autoclaved. Other contaminated, disposable supplies should also be placed in autoclavable bags for autoclaving. Reusable equipment that contains contaminated sample water, including sample bottles and dilution bottles, should be autoclaved before disposing of the water.



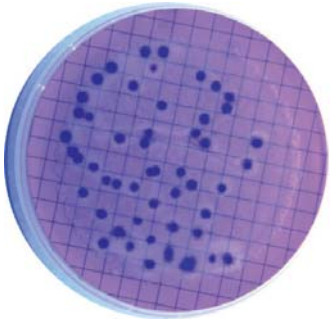
(a) Total coliform bacteria on mENDO medium



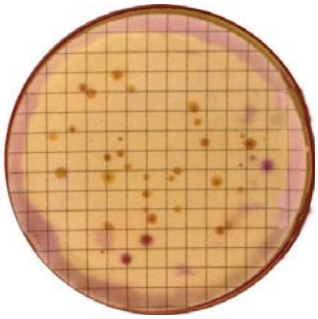
(b) Total coliform bacteria on MI medium



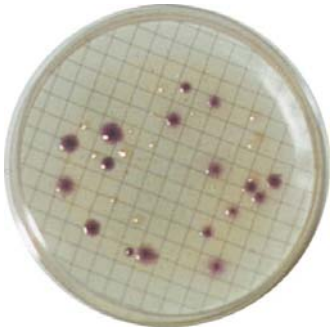
(c) *Escherichia coli* on MI medium



(d) *Escherichia coli* on NA-MUG medium

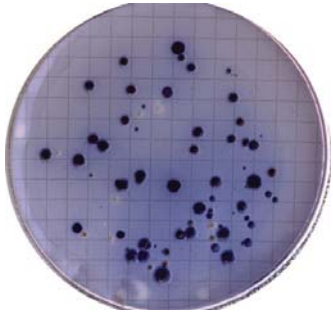


(e) *Escherichia coli* on mTEC medium

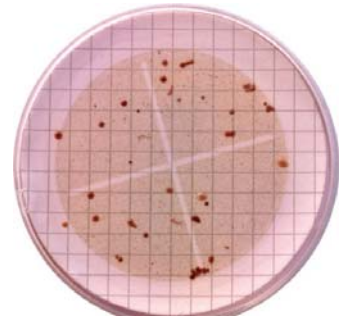


(f) *Escherichia coli* on modified mTEC medium

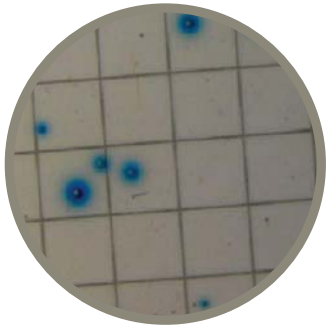
Figure 7.1–5. Photographs of typical colonies of fecal indicator bacteria on culture media.



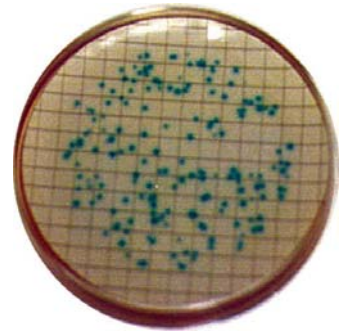
(g) Fecal coliform bacteria on mFC medium



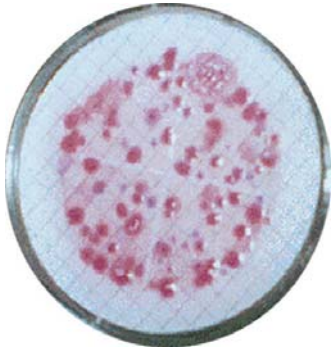
(h) Fecal streptococci bacteria on KF medium



(i) Enterocci bacteria on mEI medium under 2-5X magnification



(j) Enterocci bacteria on mEI medium



(k) *Clostridium perfringens* on mCP medium

Figure 7.1–5. Photographs of typical colonies of fecal indicator bacteria on culture media—*continued*

7.1.3.D ENZYME SUBSTRATE TESTS IN THE PRESENCE-ABSENCE FORMAT

Potable surface water or ground water used as a drinking-water source typically is tested for fecal indicator bacteria by use of enzyme substrate tests in the presence-absence format. The volume of sample tested is usually 100 mL. Commercially available, USEPA-approved enzyme substrate media include Colilert and Enterolert (IDEXX, Westbrook, Maine), Readycult® (EMD Chemicals, Gibbstown, N.J.), E*colite™ (Charm Sciences, Lawrence, Mass.), and Colitag™ (CPI International, Santa Rosa, Calif.). These media measure fecal indicator bacteria in a presence-absence format. For these tests, the manufacturers supply single-use reagent packs and culture bottles. The Colilert (for total coliforms and *E. coli*) and Enterolert (for enterococci) tests are described herein as commonly used examples.

To prepare to process samples:

1. If possible, process samples inside the field vehicle or a building, and out of direct sunlight and wind.
2. Before and after processing the samples, clean counter tops with an antibacterial cleaning solution, such as 70-percent isopropyl or ethyl alcohol, or 0.005-percent bleach. Turn on incubators or waterbaths with sufficient time to reach operating temperature.

Quality control. For each day's samples, run at least one method blank consisting of 100 mL sterile distilled or deionized water with a reagent pack added to test for equipment cleanliness and sterility.

To process samples and read results:

1. For analysis of potable water by use of Colilert-18, pre-warm the sample in a 35°C water bath for 20 minutes or in a 44.5°C water bath for 7-10 minutes.

   Quality control. Verify the incubator temperature before beginning the analysis.
2. Record the site name, date, time of sample collection, and time of sample processing on the culture bottle and on the record sheet or field form.
3. Shake the sample at least 25 times.

4. Measure 100 mL of sample by use of a sterile graduated cylinder and pour into the culture bottle.
5. Holding the reagent packet with the foil toward you, snap the packet open. There may be a puff of powdered reagents that should be directed away from yourself and other people.
6. Pour the contents of the reagent packet into the culture bottle.
7. Mix well by shaking at least 25 times.
8. Incubate for 24 to 28 hours (Colilert and Enterolert) or for the portion of 18 to 22 hours remaining after the pre-warming step (Colilert-18).
9. Read total coliform positive (yellow) or negative (colorless) and *E. coli* or enterococci positive (fluoresces under ultraviolet light) or negative (does not fluoresce).

   Quality control. Use a comparator (available from the manufacturer) to evaluate whether lightly colored or dimly fluorescing Colilert results are above the threshold of positive reactions.
10. Sterilize culture bottles by autoclaving before disposal.

ENZYME SUBSTRATE TESTS IN THE MOST-PROBABLE-NUMBER FORMAT 7.1.3.E

The enzyme substrate MPN test uses a multi-well disposable tray into which the sample is poured and mixed with medium. A sealer is used to seal the tray and distribute the sample among the wells. The incubator must be large enough to accommodate the trays; several trays may be stacked in the incubator. For these tests, the manufacturers supply single-use trays, reagent packs, and mixing bottles. The Quanti-Tray and Quanti-Tray2000 (IDEXX Laboratories, Inc., Westbrook, Maine) are commercially produced products in the enzyme substrate MPN format. Colilert (for total coliforms and *E. coli*) and Enterolert (for enterococci) are enzyme-substrate media produced by IDEXX and are described herein as commonly used examples.

The sample volume tested is typically 100 mL, as this will provide results for densities ranging from less than 1 to 200 or 2,000 MPN/100 mL for Quanti-Tray or Quanti-Tray2000, respectively. If greater densities are expected, samples may be diluted. The enzyme substrate MPN test is recommended when water is too turbid to give accurate results by membrane filtration.

TECHNICAL NOTE: Data summary for densities measured by enzyme substrate MPN tests includes both the uncertainty in the MPN estimate and analytical variability. As a result, the 95-percent confidence interval around the geometric mean tends to be broad.

To prepare to process samples:

1. If possible, process samples inside the field vehicle or a building, and out of direct sunlight and wind.
2. Before and after processing the samples, clean counter tops with an antibacterial cleaning solution, such as 70-percent isopropyl or ethyl alcohol, or 0.005-percent bleach. Turn on incubators with sufficient time to reach operating temperature.
3. Pre-warm the sealer and ensure that the sealer is level to allow even distribution of sample among the wells.

Quality control. For each day's samples, run at least one method blank consisting of 100 mL sterile distilled or deionized water with a reagent pack added to test for equipment cleanliness and sterility.

To process samples and read results:

1. Step one for reading results updated on 5/12/2014.

   Quality control. Verify the incubator temperature before beginning the analysis.
2. Label the back of a tray with the station (or other site identifier) and the date and time of sample collection, along with the dilution factor.
3. If needed, prepare a 1:10 dilution by mixing 10 mL of sample with 90 mL of sterile distilled or deionized water. Prepare a 1:100 dilution by mixing 1 mL of sample with 99 mL of sterile distilled or deionized water. Dilutions must be made with sterile distilled or deionized water because the reagent packs contain all necessary buffers.
   - All marine waters must be diluted at least 1:10 when using Colilert or Enterolert products.
   - Prepare a dilution for any water type when fecal indicator bacteria densities are expected to be high.

It is critical to mix the sample gently but thoroughly in order to distribute bacteria as evenly as possible without causing foaming.

4. Shake the sample at least 25 times.
5. Measure 100 mL of sample by use of a sterile graduated cylinder and pour into the sterile mixing bottle.
6. Holding the reagent packet with the foil toward you, snap the packet open. There may be a puff of powdered reagents that should be directed away from yourself and other people.
7. Pour the contents of the reagent packet into the mixing bottle.
8. Mix well by shaking at least 25 times.
9. Add mixture to the multi-well tray. With well-side down, hold at an angle and tap lower wells to release air bubbles.
10. Place loaded tray into rubber sealer mat and seal.
11. Incubate for 24 to 28 hours (Colilert and Enterolert) or for 18 to 22 hours (Colilert-18).
12. Count wells that are total coliform positive (yellow) and *E. coli* or enterococci positive (fluoresces under ultraviolet light).
    - Use a comparator tray provided by the manufacturer to determine positive wells, if available.
    - The IDEXX Quanti-Tray has 51 wells and the IDEXX Quanti-Tray2000 has 49 large wells and 48 small wells; results for large and small wells must be recorded separately for the Quanti-Tray2000.
13. Record results and obtain MPN density by use of the tables provided by the manufacturer (IDEXX), or an electronic database such as the one written into PCFF versions 5.2.1 and later.
14. Before being disposed of, the tray(s) must be autoclaved or otherwise sterilized.

7.1.4 CALCULATING AND REPORTING FECAL INDICATOR BACTERIA DENSITIES

The range of ideal colony counts depends on the fecal indicator group to be enumerated (table 7.1–9). Crowding and competition for nutrients to support full development of colonies can result if the bacterial density on the filter exceeds the upper limit of the ideal range. As the number of colonies fall below the lower limit of the ideal range, statistical validity becomes questionable (Britton and Greeson, 1989, p. 14). For potable waters, results are routinely less than 20 colonies per filter. Consult table 7.1–9 and figure 7.1–5 for information on typical colony color, size, and shape. Density per 100 mL is calculated by dividing the colony count for the sample by the volume filtered, then multiplying by 100.

The MPN result is based on the number of wells in the well tray that test positive, the sample volume analyzed, and the total number of wells tested. The MPN can be determined by calculation or, more simply, by using a table provided by the manufacturer. If more than one dilution for a sample is analyzed, the most reliable estimate should be reported; this can be determined as the result having the smallest 95-percent confidence interval. Analyses with many or only a few positive wells have wide confidence intervals compared with analyses with an intermediate number of positive wells.[3] The MPN statistics require that each well has an equal probability of holding each indicator bacteria cell, so insufficient mixing is an important potential source of error and variability in this method.

For bed-sediment analyses, the ideal count and 95-percent confidence rules for membrane filtration and enzyme substrate MPN tests, respectively, should be used.

- Enumeration results for membrane-filtration methods in water are expressed as a density in units of colony-forming units per 100 mL (CFU/100 mL).

[3]For USGS personnel, use version 5.2.1 and later of the personal computer field form (PCFF). USGS personnel can find the correct parameter codes to report fecal indicator bacteria data in the USGS National Water Information System by accessing the QWDATA component of NWIS.

- Results for the presence-absence methods in water are expressed as presence or absence per 100 mL.
- Enumeration results for MPN methods in water are expressed as most probable number per 100 mL (MPN/100 mL).
- Enumeration results for density in bed sediment are expressed as CFU or MPN per gram dry-weight sediment (CFU/g_{DW} or MPN/g_{DW}), depending on the analytical method used.
- Whole numbers are reported for results less than 10, and two significant figures are reported for results greater than or equal to 10.

For calculations based on colony count for water samples: Scenarios that are commonly experienced when counting colonies are presented in the following six cases.[4]

Case 1. Colony counts in the ideal range.

Case 2. Colony counts outside the ideal range but not zero or too numerous to count.

Case 3. No typical colonies on any of the filters.

Case 4. Less than the ideal range, including some zero counts but no filters with colonies that are too numerous to count.

Case 5. Colony counts on all filters exceed the ideal count but a credible count is possible (fewer than approximately 200 colonies).

Case 6. Colony counts on all filters exceed the ideal count and a credible count is not possible (confluent growth) (too numerous to count).

[4]For USGS personnel, the appropriate calculations have been coded into the PCFF version 5.2.1 and later software to assist in data reporting.

Case 1: Colony counts in the ideal range.

Example 1: Ideal colony count on one filter

Sample volume	Colony count
3	7 (do not use)
10	21
30	101 (do not use)
Sum 10	21

Density = (21 x 100)/10 = 210 CFU/100 mL

Example 2: Ideal colony counts on two or more filters

Sample volume	Colony count
3	7 (do not use)
10	21
30	58
Sum 40	79

Density = (79 x 100)/40 = 200 CFU/100 mL

Example 3: Ideal colony count on one filter with a sample volume less than 1 mL:

Sample volume	Colony count
0.1*	50
0.3	TNTC (do not use)
1.0	TNTC (do not use)
Sum 0.1	50

Density = (50 x 100)/0.1 = 50,000 CFU/100 mL

*0.1 mL is obtained by filtering 10 mL of a 1:100 dilution.

CFU, colony-forming unit
TNTC, too numerous to count

Case 2: Colony counts outside the ideal range but not zero or too numerous to count

Example 1: Less than ideal range on all filters

Sample volume	Colony count
3	2
10	6
30	18
Sum 43	26

Density = (26 x 100)/43 = 60 CFU/100 mL

Qualify the reported density as an estimate because of non-ideal colony count.

Example 2: Both less than and greater than the ideal range

Sample volume	Colony count
3	18
10	82
30	TNTC (do not use)
Sum 13	100

Density = (100 x 100)/13 = 770 CFU/100 mL

Qualify the reported density as an estimate because of non-ideal colony count.

CFU, colony-forming unit
TNTC, too numerous to count

Case 3: No typical colonies on any of the filters

Sample volume	Colony count
10	0 (do not use)
30	0 (do not use)
100	0 assume 1
Sum 100	1

Density = (1 x 100)/100 < 1 CFU/100 mL

Qualify the reported density as less than 1 CFU/100 mL.

CFU, colony-forming unit

Case 4: Less than the ideal range, including some zero counts* but no filters with colonies that are too numerous to count

Example 1: Only one filter has colonies

Sample volume	Colony count
3	0 (do not use)
10*	0 (do not use)
30	5
Sum 30	5

Density = (5 x 100)/30 = 17 CFU/100 mL

Qualify the reported density as an estimate because of non-ideal colony count.

Example 2: More than one filter has colonies

Sample volume	Colony count
3	1
10*	0
30	5
Sum 43	6

Density = (6 x 100)/43 = 14 CFU/100 mL

Qualify the reported density as an estimate because of non-ideal colony count.

*Zero values are used in the calculation if bracketed by plates with colony growth.

CFU, colony-forming unit

Case 5: Colony counts on all filters exceed the ideal count but a credible count is possible

Sample volume	Colony count
10	112
30	TNTC (do not use)
100	TNTC (do not use)
Sum 10	112

Density = (112 x 100)/10 = 1,100 CFU/100 mL

Qualify the reported density as an estimate because of non-ideal colony count.

TNTC, too numerous to count
CFU, colony-forming unit

Case 6: Colony counts on all filters are too numerous to count

Sample volume	Colony count
10	TNTC (assume 80*)
30	TNTC (do not use)
100	TNTC (do not use)
Sum 10	80

Density = (80 x 100)/10 > 800 CFU/100 mL

Qualify the reported density as greater than 800 CFU/100 mL.

*Assume upper ideal count on the filter with the smallest volume filtered.

TNTC, too numerous to count
CFU, colony-forming unit

For MPN estimation based on enzyme substrate media reactions for water samples: Enzyme substrate results are obtained by consulting an MPN table or by entering the results in an MPN calculator (available from IDEXX Laboratories or, for USGS personnel, the Microbiology Field Form within PCFF versions 5.2.1 and later). Enumeration results for enzyme substrate MPN methods in water are expressed as most probable number per 100 mL (MPN/100 mL).

For calculations based on colony count or enzyme substrate MPN tests for sediment samples: Densities of bacteria in sediment are reported as colony-forming units per gram of dry-weight sediment (CFU/g_{DW}) or most-probable number per gram of dry-weight sediment (MPN/g_{DW}).

- ▶ Measure and calculate the sediment dilution factor.
  - Sediment dilution factors are site specific and are determined by performing several displacement experiments of representative sediments.
  - Example: based on beach sediments from Lake Erie (Francy and Darner, 1998), 20 g of dry or wet sediment displaced approximately 10 mL of water, so the total volume of the sediment/buffer mixture was 210 mL. The dilution factor for the sediment samples in this study was, therefore, 10.5 mL/g (210 mL/20 g).
- ▶ To calculate CFU/g_{DW} for membrane filtration results:

  CFU/g_{DW} = (density x dilution factor) / (proportional DW),

  where density is the result in CFU/100 mL, dilution factor is the site specific dilution factor in mL/g, and DW is proportional dry weight of sediment (see section 7.1.3.B).

- ▶ To calculate MPN/g_{DW} for enzyme substrate MPN results:

  MPN/g_{DW} = (density x dilution factor) / (proportional DW),

  where density is the result in MPN/100 mL, dilution factor is the site specific dilution factor in mL/g, and DW is the proportional dry weight of sediment.

Two scenarios are provided to illustrate these calculations:

Case 7. Calculation of results in terms of CFU per gram of dry-weight sediment.

Case 8. Calculation of results in terms of MPN per gram of dry-weight sediment.

Case 7: Calculation of results in terms of CFU per gram dry weight

Calculate proportional dry weight

Tare weight of empty dish (W_{tare})	1.86 g
Weight of dish with wet bed sediment before drying (W_{wet})	27.4 g
Weight of dish with bed sediment before drying (Wdry)	13.6 g

Proportional dry weight 0.46

(13.6 g - 1.86 g) / (27.4 g - 1.86 g)

Calculate density in supernatant

Sample volume	Colony count
3	7 (do not use)
10	21
30	101 (do not use)
Sum 10	21

Density in supernatant = (21 CFU / 10 mL) X 100 = 210 CFU/100 mL

Calculate densitiy in sediment

Sediment dilution factor (calculated from site specific displacement experiments)	10.5 mL/g
Density in supernatant	210 CFU/100 mL
Proportional dry weight	0.46

Density in sediment ***48 CFU/g $_{DW}$***

(210 CFU/100 mL x 10.5 mL/g) / 0.46

CFU, colony-forming unit

Case 8: Calculation of results in terms of MPN per gram dry weight

Calculate proportional dry weight

Tare weight of empty dish (W_{tare})	1.86 g
Weight of dish with wet bed sediment before drying (W_{wet})	27.4 g
Weight of dish with bed sediment after drying (W_{dry})	13.6 g

Proportional dry weight 0.46
(13.6 g - 1.86 g) / (27.4 g - 1.86 g)

Calculate density in supernatant

Positive large wells	46
Positive small wells	10

Density in supernatant 150 MPN/100 mL
from MPN table

Calculate density in sediment

Sediment dilution factor (calculated from site specific displacement experiments)	10.5 mL/g_{DW}
Density in supernatant	150 MPN/100 mL
Proportional dry weight	0.46

Density in sediment ***34 MPN/g_{DW}***
(150 MPN/100 mL x 10.5 mL/g) / (0.46)

MPN, most probable number

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7.1.6 Acknowledgments

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OWQ Technical Memo 2005.02 has been superseded by OWQ Tech Memo 2007.06

FECAL INDICATOR VIRUSES 7.2

By R.N. Bushon

Tables

Notes:

References for section 7.2, Fecal indicator viruses, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 3, for parameter codes for somatic and F-specific coliphages that are used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.2) of NFM 7 is as follows:

Bushon, R.N., November 2003, Fecal indicator viruses: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.2, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/

7.2 FECAL INDICATOR VIRUSES

More than 100 types of human pathogenic viruses may be present in fecal-contaminated waters, but only a small number of them can be detected by currently available methods (Havelaar and others, 1993). Coliphages are used as indicators of fecal contamination and of the microbiological quality of the water.[5] Coliphages are viruses that infect and replicate in coliform bacteria and are not pathogenic to humans; coliphages have been suggested as potential indicators of enteric viruses because of their similar structure, transport, and persistence in the environment (Gerba, 1987).

Two main groups of coliphages are used as viral indicators:

Coliphages: Viruses that infect and replicate in coliform bacteria. Coliphages are used as indicators of fecal contamination in water.

- **Somatic coliphages** infect coliform bacteria by attaching to the outer cell membrane or cell wall. They are widely distributed in both fecal-contaminated and uncontaminated waters.
- **F-specific coliphages** attach only to hairlike projections (called F pili) of coliform bacteria that carry an extrachromosomal genetic element called the F plasmid; F pili are produced only by bacteria grown at higher temperatures. F-specific coliphages presumably come from warm-blooded animals or sewage (Handzel and others, 1993).

[5]The term "fecal indicator viruses" is used synonymously with coliphages in this report, as coliphage analysis currently is the only standard viral method used by the U.S. Geological Survey for indicating fecal contamination.

Somatic and F-specific coliphages are found in high numbers in sewage and are thought to be reliable indicators of sewage contamination of waters (International Association of Water Pollution Research and Control Study Group on Health Related Microbiology, 1991). Raw sewage typically contains somatic and F-specific coliphage concentrations of about 1,000 plaque-forming units per milliliter (Sobsey and others, 1995).

Two methods are commonly used to analyze samples for somatic and F-specific coliphages:

- The single-agar layer (SAL) method is recommended for use with surface-water samples. It is a quantitative, plaque assay method that can analyze sample volumes of 100 mL (milliliters).
- The two-step enrichment method is recommended for use with ground-water samples. It is a presence/absence method that can analyze sample volumes of either 100 mL, 1 L (liter), or 4 L.

Coliphage methods of analysis must be performed in the laboratory by a trained microbiologist.

The type of coliphage detected by these methods depends on the bacterial host strain used. Two host strains commonly used for the detection of somatic coliphages are *Escherichia coli* (*E. coli)* C and *E. coli* CN-13. Both hosts are equivalent in coliphage detection; however, *E. coli* CN-13 is resistant to nalidixic acid and is preferable for analyzing samples with a high background or unknown level of indigenous bacteria (Sobsey and others, 1995). Antibiotics such as nalidixic acid are used to minimize overgrowth of indigenous bacteria in environmental samples; this overgrowth may mask the detection of coliphage. Three host strains commonly used for the detection of F-specific coliphages are *E. coli* F-amp, *E. coli* C3000, and *Salmonella typhimurium* WG49. The *E. coli* F-amp strain appears to be the most reliable host for detecting only F-specific coliphages; the F-amp strain is resistant to ampicillin and streptomycin, so it is less susceptible to bacterial contamination in water samples (Sobsey and others, 1995).

SAMPLING EQUIPMENT AND EQUIPMENT STERILIZATION PROCEDURES 7.2.1

Sterile techniques must be followed and documented when collecting and processing samples for fecal indicator viruses. **The specific equipment and supplies that are needed to collect and analyze samples for fecal indicator viruses must be kept clean and sterile** (tables 7.2-1, 7.2-2). The equipment and procedures described in the following paragraphs are applicable to fecal indicator viruses and to fecal indicator bacteria (NFM 7.1). Equipment to be autoclaved must first be wrapped in aluminum foil, autoclavable bags, or kraft paper. Non-autoclavable equipment must be cleaned and, if possible, sterilized and then similarly wrapped for storage and transport.

- Sterilize and store the equipment in a clean area.
- Resterilize equipment if foil, bag, or kraft paper is torn.

Add sodium thiosulfate ($Na_2S_2O_3$) to sample bottles before sterilization if the water to be collected is suspected to contain residual chlorine or other halogens. $Na_2S_2O_3$ also may be added to the sample bottle immediately after sample collection. Residual chlorine commonly is found in treated (disinfected) potable water (for example, public water systems), and in sources such as wastewater effluents or mixing zones directly downstream from wastewater-treatment plants. Most taps or wells (for example, small private water systems) do not contain residual chlorine.

Autoclaving is the preferred method for sterilizing equipment.

Table 7.2-1. Equipment cleaning and sterilization procedures

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DIW, distilled or deionized water; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; °C, degrees Celsius; mg/L, milligrams per liter]

Equipment	Cleaning and sterilization procedures
All equipment (this includes water-level tape measure, all sample-collection and sample-processing equipment used in the field and laboratory)	Wash equipment thoroughly with a dilute nonphosphate, laboratory-grade detergent (NFM3). Rinse three times with hot tap water. Rinse again three to five times with DIW. Wipe down the wetted portion of water-level tapes with disinfectant (0.005-percent bleach solution or methyl or ethyl alcohol) and rinse thoroughly with DIW.
Autoclavable glass, plastic, and Teflon bottles	If sample will contain residual chlorine or other halogens, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per liter of sample to the sample bottles. Wrap all autoclavable equipment in aluminum foil, kraft paper, or place into autoclavable bags.[1] Autoclave at 121°C for 15 minutes.
Portable submersible pumps and pump tubing	**Autoclavable equipment** (preferred): Wrap components in aluminum foil, kraft paper, or place into autoclavable bags. Autoclave at 121°C for 15 minutes. **Non-autoclavable equipment: (1)** Submerge sampling system into a 50-mg/L (0.005 percent) sodium hypochlorite solution prepared from household laundry bleach. **(2)** Circulate solution through pump and tubing for 30 minutes. **(3)** Follow step (2) by thoroughly rinsing, inside and out, with 0.5 mL of a 10-percent sterile $Na_2S_2O_3$ solution per liter of water and circulate solution for 5 minutes; **(4)** pump $Na_2S_2O_3$, discarding this waste appropriately; pump sterile DIW through the pump, followed by pumping three tubing volumes of well water to waste (discard appropriately) before collecting the sample. **CAUTION:** Prolonged or repeated use of a hypochlorite solution on interior or exterior surfaces of a pump can cause corrosion or other damage to the pump and compromise the quality of samples collected for trace-element or organic-compound analysis.

[1]Equipment to be wrapped in aluminum foil, kraft paper, or placed into autoclavable bags includes, for example, bottles, tubing, flasks, bailers, pump components. The $Na_2S_2O_3$ solution also is autoclaved.

To prepare for collecting a halogenated sample:

1. Prepare a 10-percent solution of $Na_2S_2O_3$ as follows:
   a. In a volumetric flask, dissolve 100 g of $Na_2S_2O_3$ into 500 mL of deionized or distilled water (DIW).
   b. Stir until dissolved.
   c. Fill the flask to 1,000 mL (Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). Autoclave at 121°C for 30 minutes (U.S. Environmental Protection Agency, 1996, p. VIII–II).
   d. Store the $Na_2S_2O_3$ solution at room temperature or under refrigeration. After 6 months prepare a fresh solution.
2. Before collecting the sample, pipet into the sample bottle 0.5 mL of 10-percent $Na_2S_2O_3$ solution for every 1 L of sample. If the sterile $Na_2S_2O_3$ is used, be sure to use only sterile pipets and sterile sample bottles. If the $Na_2S_2O_3$ is not sterile, dispense the required volume of $Na_2S_2O_3$ into the sample bottle and autoclave at 121°C for 15 minutes.

$Na_2S_2O_3$ solution has a 6-month shelf life. Discard unused solution that has expired, prepare fresh solution, and label bottle with date of preparation.

Clean and sterilize sampling equipment (table 7.2-1). All equipment, including tubing and containers, must be cleaned and sterilized between sites or for each sample collected at the same site at different times. Autoclaving is the preferred method of sterilization.

- Use only autoclaves that have temperature, pressure, and liquid- and dry-utensil-cycle controls. Steam sterilizers, vertical autoclaves, and pressure cookers without temperature controls are not recommended.
- Take care to ensure that materials to be autoclaved are thermally stable. Plastics (such as polycarbonate, polypropylene, polyallomer, and polymethylpentene) and Teflons and Tefzel® (such as perfluoroalkyoxypolymers or PFA, ethylenetetrafluoroethylene or ETFE, fluorinated ethylene propylene or FEP, and polytetrafluoroethylene polymers or PTFE) can be autoclaved. **Note that each of these materials has different thermal characteristics and tolerances to repeated autoclaving.**
- When autoclaving, be sure to:
  - Use sterilization indicator tape with each load.
  - Use commercially available biological indicators at least quarterly to test autoclave performance. Biological indicators are composed of endospores—living cells that are resistant to heat, but are destroyed by autoclaving.
  - Drain the autoclave at the end of each period of use. Clean with mild soap and water once per week during periods of daily use. Record cleaning dates in the logbook.
  - Autoclave cultures of microorganisms and all media plates for at least 30 minutes before disposal.
  - Wrap silicone tubing in kraft paper or aluminum foil before autoclaving.
  - Avoid overloading the autoclave with equipment or materials; overloading will result in incomplete sterilization.

- The 20th edition of "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1998, p. 9-2 to 9-14) contains specifications for the length of time, temperature, and pressure for autoclave sterilization of various media and materials.

Quality control in sterilization procedures is mandatory. Keep a logbook of autoclave operation. Enter into the logbook the quality-assurance and quality-control procedures used, noting the date, the test results, and the name of the autoclave operator and (or) analyst. Record the autoclave temperature, pressure, date, and time of each autoclave run. If the autoclave does not reach the specified temperature and pressure or fails a quality-control test, then the autoclave should be serviced and all materials resterilized (American Public Health Association and others, 1998, p. 9-2 to 9-14).

SAMPLE COLLECTION, PRESERVATION, TRANSPORT, AND HOLDING TIMES 7.2.2

Sterile conditions must be maintained during collection, preservation, transport, and analysis of fecal indicator virus samples. Specific procedures have been developed that must be strictly followed. These procedures vary with types of sampling equipment and sources of sample (surface water, ground water, treated water, or wastewater).

A summary of requirements for sample-collection containers and procedures for sample preservation is given in table 7.2-2.

Table 7.2-2. Summary of equipment for sample collection and procedures for sample preservation of fecal indicator viruses

[EWI, equal-width-increment; EDI, equal-discharge increment; L, liter; NFM, *National Field Manual for the Collection of Water-Quality Data*; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; °C, degrees Celsius]

Equipment for sample collection (All containers must be composed of sterilizable materials such as borosilicate glass, polypropylene, stainless steel, or Teflon®)
To collect EWI or EDI surface-water samples: US D-95, US DH-95, or US DH-81 with sterile 1-L wide-mouth bottle, caps, and nozzles. US D-96 with sterile autoclavable bag (NFM 2.1.1).
To collect surface-water and ground-water samples using point samplers from a tap, or hand-dipped method: a sterile, narrow-mouth container, 500 mL to 1 L capacity, or a sterile 3-L container if both types of coliphages are to be analyzed.
To collect pumped samples: Use sterile tubing, clean and sterile pump components (autoclaved, if possible; see text).
Procedures for sample preservation
Before sample collection, if halogen neutralization is necessary, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per 1 L of sample. – If sterile $Na_2S_2O_3$ is used, dispense with sterile pipet into sterile bottle. – If $Na_2S_2O_3$ is not sterile, dispense with pipet into sample bottle and autoclave (table 7.2-1). **Chill all samples at 1-4°C before analysis.**

7.2.2.A SURFACE-WATER SAMPLE COLLECTION

The areal and temporal distribution of fecal indicator viruses in surface water can be as variable as the distribution of suspended sediment because viruses commonly are associated with solid particles. To obtain representative data for fecal indicator virus analysis, follow the same methods used to collect surface-water samples for suspended sediment analysis (Edwards and Glysson, 1999; NFM 4.1 and table 7.2-2).

- **Flowing water**—use depth-and-width-integrating sampling methods[6] (NFM 4.1.1.A).
- **Still water** (lakes or reservoirs, or other surface-water conditions for which depth-and-width-integrating methods are not applicable)—use the hand-dip method or a sterile point sampler (NFM 4.1.1.B).

[6]Sample-collection methods may be modified to ensure consistency with study objectives and as appropriate for site conditions. It is necessary to describe any methods modifications in a report of the results of the study.

- **Beach water**—use a hand-dip method in shallow wadable water and a sterile point sampler for deeper water. Collect samples by the hand-dip method at knee depth, a depth of approximately 15 to 30 cm (6 to 12 in.) below the water surface.
  - — Collect samples near known or suspected pollution sources, in areas of concentrated activity (for example, near lifeguard chairs), or for approximately every 500 m (every quarter mile) of beach length (U.S. Environmental Protection Agency, 2002).
  - — Position the sampler downstream from any water currents to collect the sample from the incoming flow (U.S. Environmental Protection Agency, 2002) and record sampling location. Avoid contaminating the water sample with bottom material dislodged by disturbing the bottom while sampling.
  - — A Chain of Custody record is recommended for beach sampling done in support of beach closures or posting of warnings to swimmers (U.S. Environmental Protection Agency, 2002, Appendix J).

Always wear laboratory gloves when handling sampling equipment and samples. Take care to prevent contaminated water from contacting skin, mouth, nose, or eye areas (NFM 9.7).

Depth-and-width-integrating methods

Depth-and-width-integrating sampling methods (the equal-discharge-increment (EDI) method or the equal-width-increment (EWI) method) are the standard USGS methods used when sampling flowing waters, and are recommended unless study objectives or site characteristics dictate otherwise (NFM 4.1.1.A and table 7.1-4).

Select the EDI or EWI method:

1. The EDI method is preferred to the EWI method for sites where the velocity distribution across a stream section is well established or at a section where the depth varies; for example, at a gaging station (Edwards and Glysson, 1999).

2. Select the appropriate sampler and equipment. **Sampling equipment must be sterile,** including the collection bottle, nozzle, and cap (or bags for the bag sampler) (table 7.2-1).

   - For streams with depths of 5 m (16.4 ft) or less, use a US D-95, US DH-95, or a US DH-81 sampler (NFM 2.1.1).
   - For stream sections where depths exceed 5 m (16.4 ft), use the US D-96, with either autoclavable Teflon® bags or autoclavable cooking bags. Thermotolerant polymers are described in more detail in section 7.2.1 under "Sampling Equipment and Equipment Sterilization Procedures."
   - For compositing subsamples, use a sterile 3-L or larger bottle.
     — For wide channels, several samples, each composed of subsamples composited into a sterile large-volume container, may be needed.
     — For narrow channels, collect subsamples at 5 to 10 or more vertical locations in the cross section without overfilling the bottle.
   - Use the proper nozzle size and transit rate for the velocity conditions in the section to ensure isokinetic collection of the sample.

Hand-dip method

If the stream depth and (or) velocity is not sufficient to use a depth-and-width-integrating method, collect a sample using a hand-dip method (table 7.1-4). Sampling still water or sampling at depth in lakes, reservoirs, estuaries, and oceans requires a sterile point sampler. Niskin, ZoBell, and Wheaton point samplers hold a sterilizable bottle or bag.

Wearing laboratory gloves, collect a hand-dipped sample as follows:

1. Open a sterile, narrow-mouth borosilicate glass or plastic bottle; grasp the bottle near the base, with hand and arm on the downstream side of the bottle.
2. Without rinsing, plunge the bottle opening downward, below the water surface. Allow the bottle to fill with the opening pointed slightly upward into the current.

3. Remove the bottle with the opening pointed upward from the water surface and tightly cap it, allowing about 2.5 to 5 cm of headspace (American Public Health Association and others, 1998, p. 9-19; Bordner and Winter, 1978, p. 8). This procedure minimizes collection of surface film and prevents contact with the streambed.

Do not sample in or near an open water body without wearing a correctly fitted personal flotation device (PFD).

Quality control in surface-water sampling. Depending on the data-quality requirements of the study and site conditions, quality-control (QC) samples (field blanks, field replicates, and matrix spikes) generally constitute from 5 to 20 percent or more of the total number of samples collected over a given period of time. See "Selected Terms and Symbols" in the Conversion Factors section at the end of this chapter, which contains definitions of the quality-control terms shown below in bold type.

- **Field blanks**—Collect field blanks at a frequency of 1 in every 10 to 20 samples to document that sampling equipment has not been contaminated.

  Process field blanks before collecting the water sample as follows:

  1. Pass sterile DIW through sterile sampling equipment and into a sterile sample container.
  2. Analyze sterile DIW for fecal indicator viruses. If no viruses are observed, then the sample was collected by use of sterile procedures.

- **Field replicates**—Collect one field replicate for every 10 to 20 samples.

- **Matrix spikes**—Collect a set of matrix spike samples for each coliphage type when samples are first received from a water source. Once received from a water source, collect a set of matrix spike samples after every 20th sample from that source. The matrix spike samples are spiked with known amounts of coliphage by the analyzing laboratory.

7.2.2.B GROUND-WATER SAMPLE COLLECTION

As with surface water, most viruses in ground water are associated with solid particles. Stable values of field measurements (turbidity, temperature, dissolved-oxygen concentration, pH, and specific conductance), especially turbidity and dissolved oxygen, are important criteria for judging whether a well has been sufficiently purged for the collection of a representative ground-water sample for fecal indicator virus analysis (NFM 4.2 and 6.0.3.A). Sampling equipment that has been subjected to chlorinating and dechlorinating agents can affect the chemistry of samples collected for non-microbial analysis; therefore, collect blank samples to be analyzed for chloride, sulfate, and other constituents, as appropriate, to document that chemical sample quality has not been compromised.

- If using the same equipment for chemical-analysis and virus-analysis samples, clean the equipment by first using standard procedures (NFM 3), followed by disinfecting and rinsing procedures described in section 7.2.1. Purge the well as described in NFM 4.2 before collecting samples.
- If different equipment will be deployed in a well for virus sampling, first check for stable turbidity and dissolved-oxygen readings to ensure collection of a representative sample.

Supply wells

If samples are to be collected from a water-supply well (see definition in NFM 4.2), select a tap (spigot) that supplies water from a service pipe connected directly to the main; do not use a tap on a pipe served by a cistern or storage tank (American Public Health Association and others, 1998, p. 9-19 to 9-20; Britton and Greeson, 1989, p. 5; Bordner and Winter, 1978, p. 5-16). Avoid sampling after downhole chlorination. Dechlorination with $Na_2S_2O_3$ is required if you cannot avoid collecting the sample before the water has passed through the treatment unit.

Do not sample from leaking taps.

To sample a supply well for fecal indicator viruses:

1. Before collecting the sample, remove screens, filters, or other devices from the tap.
2. Before sampling, swab the inside and outside rim of the tap with ethanol. Flame sterilize the tap and allow it to dry and cool. Rinse the tap with sterile DIW.
3. Collect a sample directly from the tap into a sterile bottle without splashing or allowing the sample bottle to touch the tap.
    - Supply wells commonly are equipped with permanently installed pumps. If the well is pumped daily, then (a) purge the tap water for a minimum of 5 minutes, discarding the purged water appropriately; (b) monitor field measurements and record stabilized values (NFM 6); and (c) collect the sample directly from the tap into a sterile container (described in table 7.2-2).
    - If the well is used infrequently, then purge the tap or well of water until a minimum of three borehole volumes are purged and stable field measurements are obtained in sequential measurements (NFM 4.2 and 6.0.3.A).

Monitoring wells

If a monitoring well does not have an in-place pump, then obtain samples by using a portable sampler, such as a submersible pump or a bailer (U.S. Environmental Protection Agency, 1982). Samplers and sample lines must be sterilized or disinfected (table 7.2-1). If disinfected, then the sampler and sample line must be dechlorinated and rinsed with sterile DIW. In either case, finish by flushing the sampler and sample line with native ground water before samples are collected into sterile bottles.

- ▶ Use autoclavable samplers, if possible. After flushing the sterilized pump lines with sample, collect the sample directly into the sterile sample bottles.
- ▶ Check data-collection objectives before using a disinfectant. Disinfectants are corrosive; repeated use can result in damage to the metal and plastic parts of a pump, thus rendering the pump inadequate for sampling trace elements and other constituents.

To disinfect a pump:

1. Submerge the pump and pump tubing in a 0.005 percent (50 mg/L) sodium hypochlorite solution prepared from household laundry bleach.

   - Most bleach is about 5 to 7 percent sodium hypochlorite (50,000 to 70,000 mg/L), but bleach in a container left open for more than 60 days may not be full strength.
   - Prepare solutions fresh with each use, because they will diminish in concentration with time. Add 1 mL of household laundry bleach to 900 mL of water and bring to a volume of 1,000 mL for a 0.005 percent disinfectant solution (U.S. Environmental Agency, 1982, p. 253 and 1996, p. VIII–41). This concentration is sufficient for waters with pH between 6 and 8 and temperatures greater than 20°C. Outside these ranges, a more concentrated disinfectant solution, up to 0.02 percent (200 mg/L), should be used (U.S. Environmental Protection Agency, 1982, p. 253).

2. Circulate the disinfectant through the pump and tubing for 30 minutes.

3. Next, rinse the pump thoroughly with a sterile $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ solution is prepared by adding 0.5 mL of a 10-percent sterile solution to every 1 L of sterile DIW. Recirculate for 5 minutes and rinse with sterile DIW.

4. Lower the pump carefully into the well. Pump some well water to waste to remove any residual chlorine and $Na_2S_2O_3$. Take care not to contaminate samples for chemical analysis with residual disinfectant or $Na_2S_2O_3$. **The pump must have a backflow check valve (an antibacksiphon device) to prevent residual disinfectant from flowing back into the well.**

If the pump cannot be disinfected:

1. Handle the pump and tubing carefully to avoid contamination. If the pump is a downhole dedicated pump, proceed to step 3.
2. Collect field blanks through the sampling equipment. Lower the pump in the well to the desired intake location.
3. Purge the well with the pump used for sampling to allow the pump and tubing to be thoroughly flushed with aquifer water before sampling (NFM 4.2 and 6.0.3.A).
4. An alternative to sampling with the pump is to remove the pump after completion of purging and collection of other samples, and then to collect the coliphage sample using a sterile bailer (U.S. Environmental Protection Agency, 1982, p. 252–253). Evaluate the potential for bias from stirring up particulates during pump removal and bailing that otherwise would not be included in the sample.

Sample-preparation activities, such as purging, must be carried out in such a way as to avoid contaminating the well, the equipment, or the samples. Avoid collecting surface film from the well water in the sample and ensure that the sampler intake is within the screened interval targeted for study. Select a point-source sampler, such as a bailer with a double-check valve. Do not use a bailer unless the bailer can be sterilized.

The type of well, its use, construction, composition, and condition could lead to alteration or contamination of samples. For example, a poor surface seal around the well opening can allow contaminants to move quickly from the land surface into the well water.

- If the water level is less than 7 to 10 m (roughly 20 to 30 ft) below land surface, a sample can be collected without contamination and without chlorine disinfection by use of a surface peristaltic or vacuum pump, a sterile vacuum flask, and two lengths of sterile tubing (U.S. Environmental Protection Agency, 1982).

- Purge the well (see NFM 4.2 and 6.0.3.A) while monitoring field measurements, especially measures of turbidity and dissolved oxygen. For wells in which field measurements do not stabilize after increasing the total number of measurements, record the final measurements and proceed with sampling.

Be vigilant in avoiding contamination. The detection of even one coliphage in ground water is cause for concern because it indicates the possible presence of pathogens.

Quality control for ground-water sample collection. Depending on the data-quality requirements of the study, quality-control samples (field blanks and matrix spikes) generally constitute from 5 to 20 percent or more of the total number of samples collected over a given time period. See "Selected Terms and Symbols" in the Conversion Factors section at the end of this chapter, which contains definitions of the quality-control terms shown below in bold type.

- **Field blanks—**Collect field blanks at a frequency of 1 in every 10 to 20 samples if required by data-quality objectives. **Process field blanks before collecting the water sample.** Pass sterile DIW through the sampling equipment and into a sterile sample container. Analyze the field blank for fecal indicator viruses and record the results. If no viruses are observed, the use of sterile procedures is confirmed and documented.

  TECHNICAL NOTE: The field blank discussed herein is equivalent to the "pump blank" described in NFM 4.3.1. Refer to NFM 4.3.1 for more information on collecting a field blank for ground-water sampling. A standpipe may be used to collect a field blank, but first must be cleaned and then disinfected. **This type of blank should be collected a week or more ahead of time so that results can be evaluated before field sampling.**

- **Field replicates** (sequentially collected samples)—Field replicates for ground-water samples are optional and their use depends on study objectives and site conditions. Ground-water samples typically are negative for coliphage.
- **Matrix spikes—**Collect a set of matrix spike samples for each coliphage type when samples are first received from a water source or aquifer type. Once received from a water source or aquifer type, collect a set of matrix spike samples after every 20th sample from that source or type. The matrix spike samples are spiked with known amounts of coliphage by the analyzing laboratory.

SAMPLE PRESERVATION, TRANSPORT, AND HOLDING TIMES 7.2.2.C

After collection, immediately chill samples in an ice chest or refrigerator at 1 to 4°C. **Do not freeze samples.** To ship samples to the laboratory, double bag the sample containers before placing them into the bagged ice in the ice chest. Seal the analytical services request form and chain-of-custody form in double plastic bags and tape this to the inside lid of the ice chest being shipped to the laboratory. Check that the sample identification and relevant information for use by the laboratory have been recorded correctly. **The laboratory must begin the analysis of samples within 48 hours of sample collection.**

The holding time for fecal indicator virus samples is 48 hours from the time of sample collection.

7.2.3 LABORATORY METHODS

Two methods described in this manual for the detection of fecal indicator viruses are the single-agar layer (SAL) method and the two-step enrichment method. The host bacteria recommended for use by these methods are *E. coli* CN-13 for the detection of somatic coliphage and *E. coli* F-amp for the detection of F-specific coliphage. Analytical protocols are available in more detail from the USGS Ohio District Microbiology Laboratory (U.S. Geological Survey, website: http://oh.water.usgs.gov/micro/lab.html#am) (accessed November 25, 2003).

7.2.3.A SINGLE-AGAR LAYER METHOD

The SAL method detects and enumerates somatic and F-specific coliphages in water. It is a plaque assay method that is recommended for use with surface-water samples.

USEPA Method 1602 (U.S. Environmental Protection Agency, 2001b) is a SAL method that requires the addition of host bacteria, magnesium chloride, appropriate antibiotics, and double-strength molten agar to the sample, followed by pouring the total volume of the mixture into plates. After an overnight incubation, the plates from a sample are examined for plaque formation (zones of bacterial host lawn clearing). The plaques are counted and summed for all plates from a single sample. The quantity of coliphage in a sample is expressed as plaques per 100 milliliters. This method requires one overnight incubation; therefore, results are available 24 hours after the beginning of the analysis.

Quality Control. Each laboratory and analyst that uses USEPA Method 1602 must fulfill the following general quality-control requirements, as described in the method:

- **Initial Precision and Recovery (IPR)**—The laboratory and analyst must demonstrate the ability to generate acceptable results by performing an IPR test before analyzing any environmental samples.
- **Method Blanks**—The laboratory must analyze reagent water samples containing no coliphage to demonstrate freedom from contamination. Method blanks should be run with each batch of samples. A batch is defined as all samples analyzed during a single day, up to a maximum of 20 samples per coliphage type.
- **Ongoing Precision and Recovery (OPR)**—The laboratory must demonstrate that the method is in control on an ongoing basis through analysis of OPR samples. OPR samples are reagent-water samples spiked with known amounts of coliphage and analyzed exactly like environmental samples. The laboratory must analyze one OPR sample for each batch of samples. A batch is defined as all samples analyzed during a single day, up to a maximum of 20 samples per coliphage type. The OPR serves as the positive control for Method 1602.

TWO-STEP ENRICHMENT METHOD 7.2.3.B

The two-step enrichment method determines the presence or absence of somatic and F-specific coliphages in water. **This method is recommended for use with ground-water samples.**

USEPA Method 1601 (U.S. Environmental Protection Agency, 2001a) is a two-step enrichment method that requires the enrichment of coliphage in tryptic soy broth supplemented with magnesium chloride, appropriate antibiotics, and host bacteria. After an overnight incubation, samples are spotted onto a lawn of host bacteria specific for each type of coliphage. The spot plates are incubated and examined for lysis zone formation in the lawn. Lysis zone formation indicates the presence of coliphages in the sample. This method requires two overnight incubations; therefore, results are available 48 hours after the beginning of the analysis.

Quality control. Each laboratory and analyst that uses Method 1601 must fulfill the following general quality-control requirements as described in the method.

- **Initial Demonstration of Capability (IDC)**—The laboratory and analyst must demonstrate the ability to generate acceptable results by performing an IDC test before analyzing any environmental samples.
- **Method Blanks**—The laboratory must analyze reagent-water samples containing no coliphage to demonstrate freedom from contamination. The laboratory must analyze one method blank per spot plate.
- **Positive Controls**—The laboratory must analyze positive control samples (reagent water spiked with a known amount of coliphage) to demonstrate that method reagents are performing properly. The laboratory must analyze one positive control per spot plate.
- **Ongoing Demonstration of Capability (ODC)**—The laboratory must demonstrate that the method is in control on an ongoing basis through analysis of ODC samples. The laboratory must analyze one set of ODC samples after every 20 field and matrix spike samples. For each coliphage type, at a minimum, one out of three reagent-water samples spiked with a known amount of coliphage must be positive.

CALCULATION AND REPORTING OF FECAL INDICATOR VIRUSES 7.2.4

The calculation and reporting protocols differ, depending on the laboratory method used. A list of parameter codes for reporting coliphages in the USGS National Water Information System (NWIS) are given in Appendix A7-A, table 3.

- **SAL method**—Count the total number of plaques from all plates for a sample. If the plaques are not discrete, results should be recorded as "too numerous to count" (TNTC), and the remaining sample should be diluted and reanalyzed if possible within 48 hours of collection. Record the result as the total number of plaques per 100 milliliters (plaques/100 mL).
- **Two-step enrichment method**—Record results as presence (1) or absence (2) of coliphage.

For each sample analyzed, document:

- **the type of coliphage analyzed,**
- **the bacterial host strain used,**
- **the sample volume analyzed, and**
- **the corresponding QC results from the laboratory.**

PROTOZOAN PATHOGENS 7.3

By R.N. Bushon and D.S. Francy

Illustrations

Tables

Notes:

References for section 7.3, Protozoan pathogens, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 4, for parameter codes for protozoan pathogens that are used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.3) of NFM 7 is as follows:

Bushon, R.N., and Francy, D.S., November 2003, Protozoan pathogens: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.3, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/.

PROTOZOAN PATHOGENS 7.3

Protozoan pathogens are widely distributed in the aquatic environment and have been implicated in several outbreaks of waterborne diseases (Lee and others, 2002; Rose and others, 1997). *Cryptosporidium* and *Giardia* are the principal protozoan pathogens that are known to affect the acceptability of water supplies for public use within the United States (U.S.). *Cryptosporidium* and *Giardia* produce environmentally resistant forms (oocysts for *Cryptosporidium* and cysts for *Giardia*) that allow for the extended survival of the organisms in natural and treated waters.

PROTOZOAN PATHOGENS, such as *Cryptosporidium* and *Giardia,* are unicellular microorganisms that cause disease in humans and other animals.

In comparison with fecal indicator bacteria, oocysts and cysts are more resistant to disinfection, survive longer in the environment, and are much larger and more complex. Fecal indicator bacteria are, therefore, inadequate as indicators for *Cryptosporidium* and *Giardia* in source waters. The presence of protozoan pathogens in water must be verified by identification of the pathogens themselves.

Fecal indicator bacteria cannot be used to indicate the presence of *Cryptosporidium* or *Giardia* in source water.

A sampling program for *Cryptosporidium* oocysts and *Giardia* cysts should be conducted over an extended period of time because of cyclical and seasonal variations in their environmental concentrations (LeChevallier and Norton, 1995). For example, seasonal differences in the volume and intensity of precipitation or in the shedding of parasites by animals can account for elevated occurrences of oocysts and cysts in water (Atherholt and others, 1998). The average percentages of *Cryptosporidium* and *Giardia* occurrence in U.S. waters vary considerably among published studies, ranging from 10 to 60 percent for *Cryptosporidium* and 16 to 90 percent for *Giardia* (Atherholt and others, 1998; LeChevallier and Norton, 1995; LeChevallier and others, 2003; Rose and others, 1988; Rose and others, 1991). In these studies, concentrations of protozoan pathogens in environmental waters were considerably lower than concentrations of fecal indicator bacteria; average concentrations of *Cryptosporidium* ranged from 0.7 to 10 oocysts per 10 liters (L) of water and of *Giardia* from 0.8 to 7 cysts per 10 L. Higher concentrations of *Cryptosporidium* and *Giardia* were found in waters receiving industrial and sewage effluents than were found in waters not receiving these wastes and (or) having more extensive watershed-protection practices (LeChevallier and others, 1991).

The U.S. Environmental Protection Agency (USEPA) Method 1623 (Method 1623—filtration/immunomagnetic separation (IMS)/fluorescent antibody (FA)) currently is the method of choice for detecting *Cryptosporidium* oocysts and *Giardia* cysts in water. This method does not identify the species of *Cryptosporidium* and *Giardia*, nor does it determine the viability or infectivity of the detected organisms. Method 1623 is a performance-based method, which means that alternative components not listed in the method may be used, provided that the results meet or exceed the acceptance criteria described in the method. Aspects of the method that may be modified can include, but are not limited to, the type of filter used, the manufacturer of the magnetic beads, and the protocol used to separate the oocysts and cysts from the magnetic beads. Because the method is complex, only experienced analysts should use it (U.S. Environmental Protection Agency, 2001a).

Recoveries of *Cryptosporidium* and *Giardia* are determined in the same manner as are recoveries of chemical constituents, such as pesticides. A suspension is prepared of *Cryptosporidium* oocysts and *Giardia* cysts and quantified by use of an accurate method, such as flow-cytometry, which uses a particle-sorting instrument capable of counting protozoa. The suspension with known concentrations of organisms then is used to spike an environmental water sample in the laboratory. Recoveries of oocysts and cysts from environmental water samples using Method 1623 can vary greatly, which is an important consideration for data interpretation.

TECHNICAL NOTE: Recoveries of *Cryptosporidium* ranged from 2 to 63 percent in 11 stream-water samples (Simmons and others, 2001), 20 to 60 percent in 430 samples from 87 source waters (U.S. Environmental Protection Agency, 2001b), and 9 to 88 percent in samples from 19 surface-water sites (Kuhn and Oshima, 2002). In one large study, average recoveries of *Giardia* were 47 percent, with a relative standard deviation of 32 percent (U.S. Environmental Protection Agency, 2001b).

7.3.1 STERILIZATION PROCEDURES FOR SAMPLING EQUIPMENT

Sterile technique must be implemented and documented when collecting and processing samples for protozoan pathogens. **In addition, the specific equipment and supplies that are needed to collect and analyze samples for protozoan pathogens must be kept clean and sterile** before sampling at each site and for each sample collected at the same site at different times (table 7.3-1, and table 7.3-2 in section 7.3.2).

- All equipment should be cleaned with nonphosphate, laboratory-grade detergent and rinsed thoroughly with deionized/distilled water (DIW) before being sterilized.
- Procedures to sterilize equipment involve either: (1) cleaning selected equipment with a 12-percent sodium hyplochlorite (bleach) solution (section 7.3.1.A), or (2) rigorous washing followed by autoclaving ("Alternative Sterilization Method," section 7.3.1.B).
- Equipment must be wrapped.
  - — Wrap equipment that has been sterilized using the sodium hypochlorite method in sterile aluminum foil, sterile autoclavable bags, or sterile kraft paper. The equipment is then ready for storage or for transport.
  - — If the sodium hypochlorite method is not used, then equipment first must be wrapped in aluminum foil, autoclavable bags, or kraft paper, and then autoclaved. After autoclaving, equipment must remain wrapped for storage or transport.
- Resterilize equipment if foil, bag, or kraft paper is torn.

Autoclaving kills oocysts and cysts and eliminates infectivity; however, epitopes (proteins on the surface of cells) are not inactivated by autoclaving. Epitopes attach to the fluorescent stain used in Method 1623 and are detected microscopically. To avoid false positives that are caused by residual epitopes from a previous sample, use a strong (12-percent) sodium hypochlorite solution (full-strength swimming-pool bleach) to sterilize the equipment (section 7.3.1.A).

Table 7.3-1. Summary of equipment cleaning and sterilization procedures

[L, liter; DIW, distilled or deionized water; g/L, grams per liter; °C, degrees Celsius]

Equipment and supplies
• Autoclavable 1-L bottle or 3-L bag, nozzle, and cap. • Collapsible low-density polyethylene cubitainer for collection of a 10-L bulk sample. • Regular and sterile DIW. • Nonphosphate, laboratory-grade detergent. • 12-percent sodium hypochlorite solution. • Aluminum foil, autoclavable bag, or kraft paper.
Cleaning and sterilization procedures
Sodium hypochlorite sterilization method: • Scrub equipment with a dilute (1-percent) nonphosphate, laboratory-grade detergent solution. • Rinse three to five times with tap water. • Submerge equipment in a 12-percent (120 g/L) sodium hypochlorite solution for 30 minutes. • Using sterile DIW, rinse thoroughly, inside and out, at least three times. • Wrap equipment in sterile aluminum foil or sterile kraft paper, or place into a sterile bag. **Do not use this method to disinfect equipment used to collect samples for subsequent determination of trace elements and organic substances – metallic and plastic equipment components can be damaged and subject to early deterioration after repeated sterilization with a strong sodium hypochlorite solution.**
Alternative sterilization method: (Use if equipment contact with sodium hypochlorite should be avoided). • Soak equipment in a dilute (1-percent) nonphosphate, laboratory-grade detergent solution for 30 minutes. • Scrub well and rinse three to five times with tap water. • Rinse again three to five times with DIW. • Wrap equipment in aluminum foil or kraft paper, or place into autoclavable bags. • Autoclave at 121°C for 20 minutes.

7.3.1.A SODIUM HYPOCHLORITE STERILIZATION METHOD

As noted previously, to avoid false positives that are caused by residual epitopes from a previous sample, it is necessary to immerse the equipment in a strong sodium hypochorite solution.

To sterilize sampling equipment using the bleach sterilization method:

1. Set up a clean area and assemble the needed equipment and supplies.
2. Scrub equipment with a dilute (1-percent) nonphosphate, laboratory-grade detergent (if equipment is being cleaned in the field, use a 0.1-percent detergent solution and rinse thoroughly with DIW).
3. Rinse three to five times with tap water.
4. Soak equipment for 30 minutes in a 12-percent (120 grams per liter) sodium hypochlorite (full-strength pool bleach) solution.
5. Rinse the equipment a minimum of three times with sterile DIW. Use only sterile DIW to rinse the equipment—**do not use a sodium thiosulfate solution to neutralize the sodium hypochlorite when rinsing the equipment.**
6. Wrap equipment in sterile aluminum foil or sterile kraft paper, or place into a sterile autoclavable bag.

The 12-percent sodium hypochlorite solution is very caustic and, over time, can damage sampling equipment.

ALTERNATIVE STERILIZATION METHOD 7.3.1.B

To avoid deterioration of equipment that also is used to collect samples for trace-element or organic-compound analyses, an alternative sterilization method should be used. As a result of repeated exposure to a strong sodium hypochlorite solution, metallic surfaces can corrode and plastic equipment components can become brittle, shortening the life of the equipment. The alternative sterilization method described below consists of two major steps: (1) rigorous equipment washing, and (2) autoclaving.

Equipment Washing

Rigorous washing of sample-collection and sample-processing equipment is essential before equipment is autoclaved.

To sterilize sampling equipment using the alternative sterilization method:

1. Soak equipment in 1-percent nonphosphate, laboratory-grade detergent for 30 minutes. Scrub the equipment well, using a soft brush.
2. Rinse all parts of the equipment thoroughly three to five times with tap water, followed by three to five rinses with DIW.
3. Wrap equipment in aluminum foil or kraft paper, or place into autoclavable bags.
4. Autoclave equipment, following the guidelines described below.
5. **Collect additional quality-control samples** (for example, equipment and field blanks) to determine whether the alternative sterilization method was effective. **Use sterile DIW as the blank solution.**

The alternative sterilization method avoids use of the strong sodium hypochlorite solution, but requires collection of an equipment blank for quality control of the method's efficacy.

Autoclaving

Sampling equipment must be autoclaved for 20 minutes at 121°C before use. (If the sodium hypochlorite sterilization method is used, autoclaving is not necessary.)

- Use only autoclaves that have temperature, pressure, and liquid- and dry-utensil-cycle controls. **Do not use** steam sterilizers, vertical autoclaves, and pressure cookers without temperature controls.
- Ensure that the materials to be autoclaved are thermally stable. Autoclavable materials include plastics (such as polycarbonate, polypropylene, polyallomer, and polymethylpentene) and Teflon® and Tefzel® (such as perfluoroalkyoxy-polymers (PFA), ethylenetetrafluoroethylene (ETFE), fluorinated ethylene propylene (FEP), and polytetrafluoroethylene polymers (PTFE)). **Note that each of these materials has different thermal characteristics and tolerances to repeated autoclaving.**
- Consult the 20th edition of "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1998, Section 9020 B, table 9020:III) for specifications regarding the length of time, temperature, and pressure for autoclave sterilization of various materials.

- When using the autoclave, it is necessary to:
  - Use sterilization indicator tape with each load.
  - Test the autoclave performance at least quarterly, using commercially available biological indicators. Biological indicators are composed of endospores—living cells that are resistant to heat but that can be destroyed by autoclaving.
  - Drain the autoclave at the end of each period of use.
  - Clean the autoclave with mild soap and water once a week during periods of daily use.
  - Avoid overloading the autoclave with equipment or materials; overloading will result in incomplete sterilization.
- Keep a logbook of the autoclave operation.
  - Record the temperature, pressure, date, and time of each autoclave run.
  - Record the date of each cleaning and the procedures used.
  - Enter into the logbook the results from the regularly scheduled quality-control (biological-indicator) checks, noting the date, the test results, and the name of the autoclave operator and (or) analyst.

Quality-control tests for autoclave operation are mandatory.

If the autoclave does not reach the specified temperature and pressure or fails the quality-control test, then service the autoclave, retest the autoclave, and resterilize all materials (American Public Health Association and others, 1998, p. 9-2 to 9-13).

7.3.2 SAMPLE COLLECTION, PRESERVATION, TRANSPORT, AND HOLDING TIMES

The specific procedures that have been developed for the collection, preservation, transport, and holding times of water samples before the samples are analyzed for protozoan pathogens must be followed strictly. These procedures can vary with types of sampling equipment and source of sample (surface water, ground water, treated water, or wastewater).

Maintain sterile conditions throughout sample collection, preservation, transport, and analysis.

Currently, samples for analysis of protozoan pathogens are collected primarily from surface water. Protozoan pathogens are not commonly found in ground water, although they have been known to occur in ground water that is in direct hydraulic connection with ("under the influence of") surface water. A summary of requirements for sample-collection equipment, procedures for sample preservation, and holding-time requirements is given in table 7.3-2.

Table 7.3-2. Summary of equipment and sample-preservation procedures used for surface-water sample collection for protozoan pathogen analysis

[EWI, equal-width increment; EDI, equal-discharge increment; L, liter; *NFM, National Field Manual for the Collection of Water-Quality Data*; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; EDTA, ethylenediaminetetraacetic acid; °C, degrees Celsius]

Equipment for sample collection
For EWI or EDI surface-water samples: use US D-95, US DH-95, or US DH-81 samplers with a sterile 1-L wide-mouth bottle, and sterile caps and nozzles, or the US D-96 with a sterile 3-L autoclavable bag (NFM 2.1.1).
For surface-water samples using point samplers or the hand-dip method: use a sterile, narrow-mouth container, 1-L or 3-L capacity.
For preparing sample composites: use a collapsible, low-density polyethylene cubitainer for collection of the 10-L bulk sample (fig. 7.3-1)
Procedures for sample preservation
Before sample collection: if halogen neutralization is needed to preserve the sample, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per 1 L of sample (NFM 7.3.2.B). -If sterile $Na_2S_2O_3$ is used, then dispense with sterile pipet into sterile bottle. -If $Na_2S_2O_3$ is not sterile, then dispense with pipet into sample bottle and autoclave.
Before sample collection: if chelation of trace elements is needed to preserve the sample, then add 0.3 mL of a 15-percent EDTA solution per 100 mL of sample (NFM 7.3.2.B).
After sample collection: Chill all samples at 0 to 8°C to preserve the sample until analysis.
Maximum holding time
Do not hold the sample for longer than 96 hours after sample collection and before sample analysis for protozoan pathogens.

7.3.2.A SAMPLE COLLECTION

The spatial and temporal distribution of microorganisms can be as variable as the distribution of suspended sediment in water because microorganisms generally associate with solid particles. **Collection of quality-control (QC) samples is an essential component of the sampling process.**

CAUTION: Always wear gloves when handling sampling equipment and samples. Take care to prevent contaminated water from contacting skin, mouth, nose, or eyes (NFM 9.7).

- **Ground Water:** Follow the guidelines described in NFM 7.1.1.B for the collection of fecal indicator bacteria in ground water, but collect a 10-L bulk sample. The use of the alternative sterilization method is recommended when using a pump with metallic components (see section 7.3.1).
- **Surface Water:** To obtain data that accurately represent the site at the time of sampling, use the same methods for collecting surface-water samples for protozoans as for suspended sediment (Edwards and Glysson, 1999; NFM 4.1).
  - For the isokinetic or hand-dip sample-collection methods described below, collect the water using 1-L bottles or 3-L bags and prepare a 10-L bulk composite sample by pouring the bottle or bag contents into a collapsible, low-density polyethylene cubitainer (fig. 7.3-1).
    - **Flowing water:** use isokinetic depth-and-width-integrating sampling methods[7] (NFM 4.1.1.A).

[7]Sample-collection methods may be modified to ensure consistency with study objectives and as appropriate for site conditions. It is necessary to describe any modifications to methods in a report of the results of the study.

- **Still water** (lakes or reservoirs, or other surface-water conditions for which depth-and-width-integrating methods are not applicable): use the hand-dip method or a sterile point sampler (NFM 4.1.1.B).

— Be sure to fill the cubitainer completely, to ensure collection of a full 10-L sample.

Figure 7.3-1. Samples for protozoan pathogens are collected in a sterile 1-liter or 3-liter bottle and composited into a 10-liter sterile cubitainer. (Photograph by Richard P. Frehs.)

Quality Control

Plan to collect quality-control samples. Although subject to the specific data-quality requirements and site conditions of the study, quality-control samples typically constitute at least 5 to 20 percent of the total number of samples collected over a given period of time at a given location. General requirements and recommendations for the common types of quality-control samples are described below ("Selected Terms" in the Conversion Factors section at the end of NFM 7 contains definitions of these quality-control terms as they apply to protozoan pathogens).

- **Equipment blanks**—An equipment blank is required when equipment is sterilized using the alternative sterilization method, or when study objectives require additional quality-control samples. Equipment blanks are optional for the sodium hypochlorite sterilization method.
- **Field blanks—**Field blanks generally are not required because of the low potential for contamination. Their use depends on study objectives and site conditions.
- **Field replicates—**Field replicates generally are optional because of the low numbers of protozoans in most waters. The use of replicate samples depends largely on site conditions and study objectives.
- **Matrix spikes—**Samples for matrix spikes are collected routinely for studies involving protozoan analyses. **A second 10-L sample must be collected for the matrix spike.** Matrix-spike samples are fortified (spiked) with known amounts of oocysts and cysts by the analyzing laboratory. As previously noted, the recovery of oocysts and cysts from environmental samples using Method 1623 has been found to be highly variable and affected by water chemistry, as well as by streamflow and other characteristics of the water body.

— Collection of a 10-L matrix-spike sample along with the first 10-L sample that is collected from a water source is required (U.S. Environmental Protection Agency, 2001a, Section 9.5).

— Although USEPA guidelines stipulate the collection of additional matrix-spike samples from the same source water after at least every 20th sample, **the USGS recommends collecting matrix-spike samples more frequently, as is appropriate for specific study objectives, streamflow conditions, and chemical characteristics.**

Isokinetic Sampling Methods

Isokinetic sampling methods, including the equal-discharge-increment (EDI) method, equal-width-increment (EWI) method, and single vertical at centroid-of-flow (VCF) method, are the standard USGS methods used for sampling flowing waters and are recommended unless study objectives or site characteristics dictate otherwise (NFM 4.1.1.A).

1. Select the appropriate isokinetic method (NFM 4.1). The EDI method is preferred at sites where the velocity distribution across a stream section is well established or at a section where the depth varies (for example, at a gaging station) (Edwards and Glysson, 1999).

2. Select the appropriate sampler and equipment and prepare the equipment for use (section 7.3.1). **Sampling equipment must be sterile,** including the collection bottle (or bags for the bag sampler), nozzle, and cap (table 7.3-1).

   - For streams with depths of 5 meters (m) (approximately 16.4 feet) or less, use a US D-95, US DH-95, or US DH-81 sampler (NFM 2.1.1).
   - For stream sections where depths exceed 5 m (16.4 feet), use the US D-96, with either autoclavable Teflon® bags or autoclavable cooking bags. Thermotolerant polymers are described in section 7.3.1.B under "Autoclaving."
   - Use the proper nozzle size and transit rate for the velocity conditions in the section to ensure isokinetic collection of the sample (NFM 4.1.1.A).

Hand-Dip Sampling Method

If the stream depth and (or) velocity are not sufficient to use an isokinetic sampling method, collect a sample using a hand-dip method. Sampling still water or sampling at depth in lakes, reservoirs, estuaries, and oceans requires a sterile point sampler. For example, Niskin, ZoBell, and Wheaton point samplers hold a sterilizable bottle or bag. Wearing nonpowdered nitrile or latex gloves (NFM 2), collect a hand-dip sample as follows:

1. Open a sterile, plastic bottle; grasp the bottle near the base, keeping hand and arm on the downstream side of the bottle.
2. Without rinsing it, plunge the bottle opening downward, below the water surface, with the opening pointed slightly upward into the current. Allow the bottle to fill.
3. Remove the bottle with the opening pointed upward from the water and tightly cap it. Composite several bottles into a 10-L cubitainer until it is full.

CAUTION:
Do not sample in or near an open water body without wearing a correctly fitted personal flotation device (PFD).

SAMPLE PRESERVATION, TRANSPORT, AND HOLDING TIMES 7.3.2.B

Halogens and trace metals that are present in the source water can compromise an accurate analysis of the sample for protozoan pathogens. Residual chlorine commonly is found in treated (disinfected) potable water (for example, public water systems), and in sources such as wastewater effluents or mixing zones directly downstream from wastewater-treatment plants. Most taps or wells (for example, small private water systems) do not contain residual chlorine. Trace metals such as copper, nickel, and zinc that are present at concentrations from 10 to greater than 1,000 micrograms per liter (µg/L) can be toxic to microorganisms; the concentration at which toxicity occurs varies in the literature (Britton and Greeson, 1989, p. 56; Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). The sample must be treated at the time of collection to prevent halogen and trace-metal interferences.

- **Add sodium thiosulfate ($Na_2S_2O_3$)** to sample bottles, either before sterilization or immediately after sample collection, if the water to be collected is suspected to contain residual chlorine or other halogens.
- **Add ethylenediaminetetraacetic acid (EDTA)** to sample bottles before filling the bottles with sample, if trace-metal concentration is suspected at levels that could be toxic to protozoan pathogens.

To prepare for collecting a halogenated sample:

1. Prepare a 10-percent solution of $Na_2S_2O_3$ as follows:

   a. In a volumetric flask, dissolve 100 grams (g) $Na_2S_2O_3$ into 500 milliliters (mL) of DIW. Stir until dissolved. Fill flask to 1,000 mL with DIW (Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19).

   b. Autoclave at 121°C for 30 minutes (U.S. Environmental Protection Agency, 1996, p. VIII–11).

   c. Store the $Na_2S_2O_3$ solution at room temperature or under refrigeration. **After 6 months, prepare a fresh solution** and label the bottle with the contents and date of preparation. **Discard unused solution that has expired, either through a certified laboratory or according to existing regulations for your locale.**

2. Before collecting the sample in the sample bottle, pipet into the sample bottle 0.5 mL of 10-percent $Na_2S_2O_3$ solution for every 1 L of sample. If the sterile $Na_2S_2O_3$ is used, then be sure to use only sterile pipets and sterile sample bottles. If the $Na_2S_2O_3$ is not sterile, then dispense the required volume of $Na_2S_2O_3$ into a sample bottle and autoclave at 121°C for 15 minutes.

To prepare for collecting samples with potential trace-metal toxicity:

1. Prepare the EDTA stock solution as follows:

   a. Dissolve 372 milligrams (mg) of EDTA in 1,000 mL of DIW (American Public Health Association and others, 1998, p. 9-19).

   b. Store the EDTA stock solution at room temperature.

   c. Keep the bottles tightly capped between uses. **After 6 months, prepare a fresh solution** and label the bottle with the contents and date of preparation. **Discard unused solution that has expired, either through a certified laboratory or according to existing regulations for your locale.**

2. Before sterilization, add 0.3 mL of the EDTA stock solution per 100 mL of sample to sample bottles. EDTA can be combined with the $Na_2S_2O_3$ solution in the sample bottle.
3. Autoclave the sample bottle containing EDTA stock solution at 121°C for 15 minutes.

$Na_2S_2O_3$ and EDTA solutions have a 6-month shelf life.

To prepare the samples for transport:

1. **Chill—do not freeze—**the 10-L sample cubitainer in an ice chest or refrigerator at 0 to 8°C **immediately after the samples have been collected and treated.**
2. Check that the sample identification and relevant information for use by the laboratory have been recorded correctly on the sample container and on the analytical services request (ASR) form and, if being used, on a chain-of-custody form.
   - Seal the ASR form and chain-of-custody form in plastic bags and tape the bags to the inside lid of the ice chest to be shipped to the laboratory.
   - Upon receipt, the laboratory should record the temperature of the samples and store them at 0 to 8°C until processed.
   - It is best for the laboratory to process the samples as soon as possible, but **sample analysis must be within 96 hours of sample collection.**

The holding time for samples to be analyzed using USEPA Method 1623 is 96 hours from sample collection.

7.3.3 LABORATORY METHOD: USEPA METHOD 1623

Project personnel should be aware of the analytical method to be used by a laboratory on samples to be analyzed for protozoan pathogens, and the requirements for quality control for the method. The field and laboratory procedures for protozoan samples that are described in this chapter are specific to analysis by USEPA Method 1623: *Cryptosporidium* and *Giardia* in water by filtration/IMS/FA (U.S. Environmental Protection Agency, 2001a). Method 1623 must be performed in a certified laboratory by a qualified analyst, and involves the following steps:

1. **Filtration**—*Cryptosporidium* oocysts and *Giardia* cysts from the water sample are concentrated on a filter, eluted from the filter with an elution buffer, and reconcentrated by centrifugation.
2. **Immunomagnetic separation (IMS)**—The oocysts and cysts are magnetized by attachment of magnetic beads conjugated to antibodies and then separated from extraneous materials in the sample with a magnet.
3. **Immunofluorescence assay (FA)**—Fluorescently labeled antibodies and vital dye are used to make the final microscopic identification of the oocysts and cysts. The organisms are identified when the size, shape, color, and morphology agree with specified criteria.

Quality Control. Laboratory performance is compared to established performance criteria to determine whether the results of the analyses meet the performance characteristics of the method, as described in U.S. Environmental Protection Agency, 2001a, Section 9.0. Any laboratory that uses USEPA Method 1623 must fulfill the following minimum quality-control requirements: Initial Precision and Recovery (IPR) tests, Ongoing Precision and Recovery (OPR) tests, and the use of method blanks.

- **Initial Precision and Recovery (IPR)**—Each analyst in the laboratory must establish the ability to demonstrate control over the analytical system and to generate acceptable precision and recovery. IPR tests consist of reagent-water samples that are spiked with known amounts of *Cryptosporidium* and *Giardia* and that are analyzed exactly like environmental samples. The IPR test must be completed before the analysis of any environmental samples (U.S. Environmental Protection Agency, 2001a, Section 9.4).

- **Ongoing Precision and Recovery (OPR)**—The laboratory must demonstrate that the method is under control by analyzing OPR samples. OPR samples consist of reagent-water samples that are spiked with known amounts of *Cryptosporidium* and *Giardia* and that are analyzed exactly like environmental samples. The laboratory must analyze one OPR sample for each week in which environmental samples are analyzed, or after every 20th environmental sample, whichever comes first (U.S. Environmental Protection Agency, 2001a, Section 9.7).

- **Method Blank**—The laboratory must analyze reagent-water samples containing no protozoans to demonstrate freedom from contamination. Method blanks should be analyzed immediately before conducting the IPR and OPR tests. The laboratory should analyze one method blank for each week in which environmental samples are analyzed, or after every 20th environmental sample, whichever comes first (U.S. Environmental Protection Agency, 2001a, Section 9.6).

7.3.4 CALCULATION AND REPORTING OF PROTOZOAN PATHOGENS

As prescribed by USEPA Method 1623, report the total number of *Cryptosporidium* oocysts and (or) *Giardia* cysts counted.

- Record the result as the total number of oocysts or cysts per 10 L.
- Record the percent recovery for matrix spikes analyzed.

Use the list of parameter codes shown in Appendix A7-A, table 4, when reporting protozoans in the USGS National Water Information System (NWIS).

ALGAL BIOMASS INDICATORS 7.4

By **Julie A. Hambrook Berkman and Michael G. Canova**

Illustrations

Tables

The citation for this section (7.4) of NFM 7 is as follows:

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ALGAL BIOMASS INDICATORS 7.4

By **Julie A. Hambrook Berkman and Michael G. Canova**

Indicators of algal biomass are used to assess water quality in both moving (lotic) and stillwater (lentic) ecosystems. Algal biomass in a water body can be estimated in three ways: (1) by quantifying chlorophyll *a* (CHL *a*), (2) by measuring carbon biomass as ash-free dry mass (AFDM), or (3) by measuring the particulate organic carbon (POC) in a sample. The CHL *a* procedure measures photosynthetic pigment common to all types of algae, while AFDM and POC procedures measure the carbon in a filtered water sample.

Algae: Chlorophyll-bearing, nonvascular aquatic plants. Examples of algae include diatoms, green and red algae, and primitive photosynthetic bacteria such as Cyanobacteria (also called blue-green algae).

Note the star-shaped chloroplasts in the filament on the left and their relative size in the cell.

Figure 7.4 –1. Chlorophyll pigments in the filaments of the green alga *Zygnema*. (Photo provided by Morgan L. Vis, Ohio University, 2007.)

Chlorophyll is the green molecule in plant cells essential for energy fixation in the process of photosynthesis. Besides its importance in photosynthesis, chlorophyll is probably the most-often used estimator in North America of algal biomass in lakes and streams. Chlorophyll is used to measure algal biomass that is relatively unaffected by non-algal substances. Chlorophyll provides an estimate for measuring algal weight and volume, and acts as an empirical link between nutrient concentration and other biological phenomena in aquatic ecosystems. Nutrients and other chemicals in a watershed, together with factors such as temperature and light, affect the biomass production of algae in streams and lakes. Algal production, in turn, affects the entire biological structure of an ecosystem.

Measurement of algal biomass is common in many river and lake studies and may be especially important in studies that address nutrient enrichment or toxicity. High nutrient concentrations can affect recreational water users when the nutrients produce dense growths of algae and (or) aquatic vegetation, which are aesthetically undesirable. Use of waters for a public water supply can be affected if algal blooms result in an unpleasant taste and odor in the treated water. Fisheries, up to a point, are positively affected by increased primary algal production resulting from increased nutrient loads. However, when eutrophication begins to reduce dissolved oxygen concentrations substantially, fisheries can be adversely affected. CHL *a*, AFDM, and POC are measured because they form the direct link between the excessive nutrients and the degradation of recreational waters and ecosystem health.

The relations among algal indicators can provide additional information regarding the condition of an algal community. The amount of CHL *a* per cell changes based on the health and growth status of the cell. This means that carbon-to-CHL *a* ratios change dramatically based on the physiological status of the algal populations. The carbon-to-CHL *a* ratio can be used as a diagnostic tool, as can other elemental ratios. The AFDM/CHL *a* ratio, known as the autotrophic index, has been used to indicate organic inputs (for example, from wastewater) where the higher the ratio, the greater the amount of bacteria, and the lower the quality of water. Consistent field-sampling techniques are necessary to allow for comparisons among studies.

Currently, the United States has some regulations or guidelines for protecting human health and ecosystem viability from nuisance levels of algal biomass or from cyanobacteria algal blooms, which can be detrimental to water quality when they occur in fresh, estuarine, and marine water environments. For example, North Carolina has a 40 µg/L standard for CHL *a* in lakes, and Texas uses narrative water-quality standards to prevent nuisance levels of algae (Texas Water Conservation Association, 2005). The U.S. Environmental Protection Agency (USEPA) requires States to establish nutrient criteria levels in order to control excessive algal growth and to provide protection for the aquatic ecosystems in each State. Some States are considering use of standards for CHL *a* instead of nutrient standards. Green algae (Chlorophyta) and blue-green algae (Cyanophyta/cyanobacteria) commonly are associated with the nuisance algal blooms, but they are just 2 of 10 algal divisions (Bold and Wynne, 1985), each of which contains CHL *a* and a distinct combination of additional pigments that can be used to assess community composition and algal biomass.

Procedures for determining algal biomass include CHL *a* quantification, measurement of organic biomass as AFDM, and determination of POC.

- **Quantifying the amount of CHL *a*.** CHL *a* provides a measure of the amount of active algal biomass (as periphyton) present per area of stream bottom, or a measure of phytoplankton from a volume of water. CHL *a* is a photosynthetic pigment present in all green plants and occurs in the chloroplast of most plant cells. Figure 7.4–1 illustrates the filamentous green alga *Zygnema*, where the chlorophyll in the star-shaped chloroplast can be seen as part of the cell contents.
  - Pigments that occur in varying concentrations along with CHL *a* include CHL *b*, CHL *c*, phycocyanin, allophycocyanin, and phycoerythrin, depending on the evolutionary line of the algal division. Algae also have secondary or assessory pigments and degradation products. Phaeophytin *a* is the most common degradation product resulting from the loss of a magnesium atom.
  - Depending on the objective of a water-quality study, CHL *a* may need to be distinguished from the other primary and secondary pigments. Select the laboratory method to be used for analysis accordingly.

- **Measuring the carbon biomass associated with an algal sample as AFDM.** The AFDM analysis measures the difference in mass of a dried (dewatered) sample after organic matter in the sample has been incinerated (American Public Health Association, 1999).
  - AFDM is recommended for analysis of periphyton biomass instead of a dry mass analysis because silt can account for a substantial portion of dry mass in some samples. Ash mass in samples can be used to infer the amount of silt or other inorganic matter in samples (Stevenson and Bahls, 1999).
  - AFDM concentrations are near the detection level in phytoplankton samples unless the sample is collected from a highly eutrophic stream or lake. However, periphyton samples can be concentrated through filtration or centrifugation for AFDM.
- **Analysis of POC.** An alternative approach to measuring AFDM for phytoplankton samples is to obtain a measure of carbon by laboratory analysis of a subsample for POC.
  - The POC fraction is derived by subtracting the particulate inorganic carbon (PIC) from the total particulate carbon (TPC): POC = TPC - PIC (see NFM 5).[1]
  - The presence of macroalgae or aquatic plants in large amounts may necessitate accounting for this biomass. As a general rule, if aquatic plants are more than 5 centimeters (cm) long or if they cover areas of a square meter or more, use the methods described in section 7.4.4.B, "Macroalgae and macrophyte ash-free dry mass sampling methods."

[1]U.S. Geological Survey (USGS) personnel can find the correct method and parameter codes for entry into the USGS National Water Information System (NWIS) by accessing the QWDATA component of NWIS or by accessing the Office of Water Quality spreadsheet available at http://water.usgs.gov/owq/FieldManual/Chapter7/7.4.html.

PRESAMPLING CONSIDERATIONS AND PLANS 7.4.1

The purpose and objectives of a study will determine whether samples are to be collected from natural and (or) artificial substrates, and whether the sampling methods used are to yield quantitative and (or) qualitative results. For the purpose of measuring algal chlorophyll, this section (7.4) of the *National Field Manual* of the U.S. Geological Survey *(USGS)* covers sampling methods for the quantitative collection of algal samples from natural substrates and the water column. Procedures are described for the collection of periphyton from river and stream habitats; also, considerations for collecting phytoplankton from lakes, reservoirs, and rivers are discussed. Although the procedures have general applicability to other habitats such as estuaries and wetlands,[2] the specific adaptations required for sampling in such environments are beyond the scope of this section. Also not included in this section are qualitative sample-collection methods used to identify the taxonomic composition of the algal community, and collecting samples from artificial substrates such as concrete channels.[3]

The two primary habitats for sampling algal chlorophyll are (1) the water column (phytoplankton/seston), as described in sections 7.4.2 and 7.4.3, and (2) benthic substrates (periphyton), as described in section 7.4.4. Within each of these macrohabitats are numerous microhabitats to consider. For example, differences between natural lakes and manmade reservoirs, with respect to the hydrology and relative contributions from the perimeter of the basin, will influence the location for collecting phytoplankton samples. Reservoirs may receive only a small portion of their total inflow as direct runoff from the adjacent watershed, with the majority of the water, nutrient, and sediment load entering from one or two tributaries located a considerable distance upstream from the dam. Selection of sampling locations should be based on study objectives; for example, managing

[2]Methods for using algae to assess environmental conditions in wetlands can be found in U.S. Environmental Protection Agency (2002), and Danielson (2006).

[3]Qualitative sample-collection methods can be found in Moulton and others (2002). Refer to Porter and others (1993) and Stevenson and Bahls (1999) for literature references for collecting algal samples from artificial substrates.

reservoir water quality may include sampling at the headwater inflow(s) as well as at the dam or outflow. Lakes are more variable in the relative contribution of runoff from the surrounding area and sampling should take that into consideration. The depth and condition of the water column are important considerations for collecting water-column samples from streams. Upstream from riffle areas provides deeper locations for evaluating light penetration, whereas downstream from riffle areas provides well-mixed stream water for collecting an integrated water-quality sample. Larger rivers typically are sampled from a bridge.

In addition to selecting the sampling location within the water body, one must determine the appropriate depth(s) within the water column from which to collect the sample. Depending on the sampling objectives of the study, either discrete or integrated samples of the whole water column, or euphotic zone sampling, may be warranted. A measure of water transparency typically is used to estimate the euphotic depth, and the sampling depth is adjusted to collect the sample from the area where plankton will receive sufficient light to grow. Although a Secchi disk commonly is used for a depth estimate, a light meter is preferred because it can accurately measure the euphotic depth. Recent advancements in technology provide equipment that can record *in vivo* measurements of chlorophyll so that sampling can be targeted to collect from specific zones of production that would be of interest for documenting the biomass of toxic algal blooms. For example, depending on study objectives, peak algal biomass can occur in or below the thermocline at depths in lakes and reservoirs where 1 to 3 percent of photosynthetically available surface irradiance penetrates (Fee, 1976).

Euphotic depth: The depth at which 1 percent of subsurface irradiance remains (also known as the **light extinction depth).**

Before field work can begin, project personnel need to:

1. Identify the type of water body to be sampled.
2. Determine what the data collected are to represent and the intended use of the data (for example, for status, trends, or regulatory purposes).
   - Decide on the number and type of environmental and quality-control samples to be collected.
   - Decide if an in situ sensor will be used.
   - Determine the ancillary data needed, the frequency of collection, and the methods to be used.
3. Determine sampling methodology.
   - Select the laboratory method to be used or, if using an in situ sensor, follow proper calibration procedures.
   - Consider whether a benthic sample (periphyton), or water-column sample (phytoplankton, seston) or both are to be collected.

Field work requires close attention to safety practices and regulations. Field personnel should comply with U.S. Geological Survey (2005) safety guidelines. All members of sampling teams are advised to wear properly fitted personal safety devices when working in or near water and review field-safety guidance presented in this *National Field Manual*, chapter 9 (NFM 9) (Lane and Fay, 1997).

10/23/2007 UPDATE
TAKE NOTE OF THE FOLLOWING INFORMATION

After sample collection and processing:

-- Chlorophyll samples must be kept frozen until analysis and should be shipped within 1 week of sampling.

-- The holding time for the frozen chlorophyll samples is 24 days from the date of sample collection. Although the NWQL will analyze chlorophyll/pheophyton samples that arrive in excess of this holding time, the data will be qualified appropriately if samples are analyzed after 25 days from sample collection.

****

7.4.1.A SELECTING A CHLOROPHYLL EXTRACTION METHOD

Three common laboratory extraction methods can be used to measure the concentration of chlorophyll pigments and degradation compounds. Each method has advantages and disadvantages that depend on the method sensitivity and the ability of the method to distinguish between the various pigments and degradation products (table 7.4–1 and table 7.4–2). The method to use will depend on project objectives and the type of water body being sampled. If the objective includes comparing values with historical records or with other studies, then the same methodology and laboratory should be used. Common similarities and differences between analytical methods used in chlorophyll extraction are shown in table 7.4–3 and figure 7.4–2. Split samples can be analyzed between methods and between laboratories; however, a correction factor may not be possible to develop, especially with historic records, and an evaluation of laboratory quality and precision is an important consideration in these method comparisons.

- **Fluorometry** is recommended for low-concentration freshwater that predominately consists of CHL *a* greater than 1 microgram per liter (µg/L) or where pigment differentiation is not a concern.
- **Spectrometry** is recommended for freshwater that has a moderate to high concentration of CHL *a* (greater than 1 milligram per liter (mg/L)) or where precise pigment differentiation is not a concern.
- **High performance liquid chromatography** (HPLC) is the most precise (greater than 1 nanogram per liter (ng/L)) of the three methods and is recommended for marine waters, where a higher concentration of CHL *b* may bias results from other methods.

Table 7.4–1. Advantages and disadvantages of three U.S. Environmental Protection Agency laboratory extraction methods commonly used to measure the concentration of photosynthetic pigments.

[EPA, U.S. Environmental Protection Agency; HPLC, high performance liquid chromatography; CHL, chlorophyll; DMSO, dimethyl sulfoxide; USGS, U.S. Geological Survey]

Method	Advantages	Disadvantages
Fluorometric EPA 445.0[1]	• Better precision than the HPLC method • Lower associated cost than the HPLC method • Requires less sample than spectrometry • Uses fewer hazardous chemicals [2]	Cannot distinguish between the various photosynthetic pigments and may overestimate or underestimate CHL *a* concentration.
Spectrophotometric EPA 446.0	• Simple method, somewhat capable of distinguishing between CHL *a*, *b*, and *c*	The least sensitive of the three methods.
HPLC EPA 447.0[1]	• Able to distinguish between the various photosynthetic pigments • Potentially useful for determining the type of algae in blooms	Most expensive of the three methods; values are generally lower than other methods; difficult to use compared to other methods. Uses DMSO, a hazardous material.

[1]The specific method codes and parameter codes used in the USGS National Water Information System (NWIS) are available from http://water.usgs.gov/owq/FieldManual/Chapter7/7.4.html.
[2]As documented in EPA method 445.0, the fluorometric method uses fewer hazardous chemicals (acetone and hydrochloric acid) than the HPLC method (dimethyl sulfoxide, methyl alcohol, and diethyl ether). Although DMSO has been used as an extraction solvent in combination with the fluorometric method, it is not specifically mentioned as a primary or alternative solvent for method 445.0. DMSO poses a potential health hazard, so use of 90 percent acetone is recommended instead of DMSO.

Table 7.4–2. Comparison of instrumental detection limits for chlorophyll *a*, phaeophytin, and chlorophyll *b*

[EPA, U.S. Environmental Protection Agency; CHL *a*, chlorophyll pigment common to all photosynthetic organisms; Pheo *a*, phaeophytin pigment; CHL *b*, a chlorophyll pigment; µg/L, micrograms per liter; HPLC, high performance liquid chromatography; N/A, not applicable]

Method and Instrument		Instrumental Detection Limits (in µg/L)		
EPA Method[1]	Instrument Type	CHL *a*	Pheo *a*	CHL *b*
445.0	Fluorometer	0.05	0.06	N/A
446.0	Spectrophotometer	80	85	93
447.0	HPLC chromatograph	0.0007	N/A	0.0004

[1]The upper concentration limit for use of EPA method 445.0 is 250 µg/L. There is no upper concentration limit for use of EPA methods 446.0 or 447.0; however, if the concentration is greater than 250 µg/L, the chlorophyll extract must be diluted and reanalyzed.

Table 7.4–3. Similarities and differences between chlorophyll extraction analytical methods (Edward T. Furlong, U.S. Geological Survey, written commun., 2006)

[HPLC, high-performance liquid chromatography; DMSO, dimethyl sulfoxide]

Sample Preparation and Analysis	Analytical method					
	Spectro-photometric	Trichromatic	Fluorometric, acidified	Fluorometric, non-acidified	Gradient HPLC	Isocratic HPLC
Extraction with 90 percent aqueous acetone	X	X	X	X	X	
Extraction with DMSO, diethyl ether, methanol						X
HPLC separation using gradient elution profile					X	
HPLC separation using isocratic elution profile						X
Analysis by fluorescence spectroscopy			X	X	X	X
Analysis by absorbance spectroscopy	X	X				

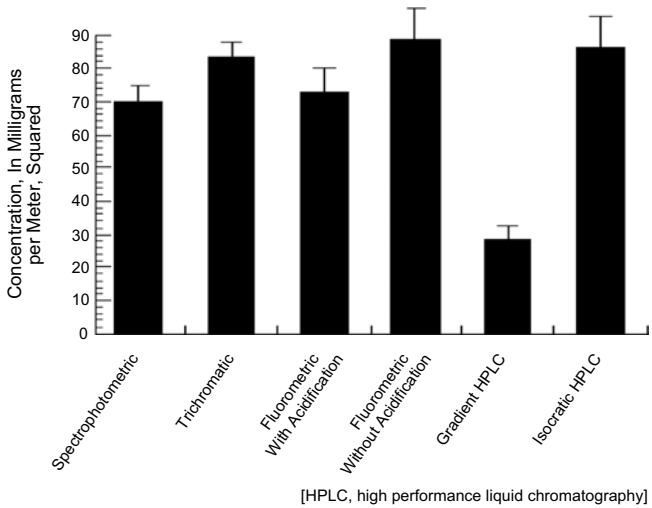

Figure 7.4–2. Example of midrange concentration results for six methods of chlorophyll *a* analysis (from Edward T. Furlong, U.S. Geological Survey, written commun., 2006).

The bar graph in figure 7.4–2 shows mean CHL *a* concentrations for several split samples analyzed by the different methods. At midrange concentrations, the gradient HPLC method determined lower values than the whole-extract spectrophotometric methods. But concentrations determined by the isocratic HPLC method determine equivalent if not higher values than whole-extract-spectrophotometric methods. A similar analysis was done for phytoplankton from seawater (U.S. Environmental Protection Agency, 1997a, table 9). The results show less variance for phytoplankton than the results for the periphyton samples illustrated in figure 7.4–2. Jeffrey and others (1997) provides a more detailed discussion of algal pigments and analysis.

COLLECTING ANCILLARY DATA 7.4.1.B

Seasonal differences in primary physicochemical factors (light, temperature, current velocity, and nutrients) influence the development, structure, and growth rates of algal communities. Collecting ancillary data therefore is recommended, as well as sampling during normal, low-flow, or stable-flow periods. Sampling should be delayed at least 2 weeks after stormwater runoff has disturbed and scoured the periphyton from the substrate in streams or increased turbidity in lakes and reservoirs.

Selecting the specific ancillary data to be collected at each site depends on study objectives and site conditions; however, basic water-quality field measurements (see NFM 6), recording of visual observations, physical habitat measurements, nutrient concentrations, and measurement of light availability are recommended and are routine within the USGS (table 7.4–4). These data can be important for the interpretation of the chlorophyll and biomass sample analysis. In general, such ancillary data take only a short time to collect in the field; however, they require prior planning, training, and preparation of appropriate field forms, as well as acquiring and maintaining field instruments.

Table 7.4–4. Suggested ancillary data for chlorophyll and biomass sampling.

[NFM, *National Field Manual for the Collection of Water-Quality Data*; USEPA, U.S. Environmental Protection Agency; CHL, chlorophyll; PAR, photosynthetically active radiation; *in vivo*, measured in the water column from living cells]

Ancillary data	Description	Reference(s)
Basic field measurements	Measure and record: • discharge • temperature, water and air • dissolved oxygen in water • specific electrical conductance • pH • alkalinity, acid neutralizing capacity • turbidity	• Rantz and others, 1982 • NFM 6.0, 6.1 • NFM 6.0, 6.2 • NFM 6.0, 6.3 • NFM 6.0, 6.4 • NFM 6.6 • NFM 6.7
Site information and visual observations	Record site information and observations on field forms: describe • algae • water color and clarity • presence of surface scum • severity of streamflow • number of days since rainfall • extent of periphyton coverage Take at least three photographs at each site from vantage points that provide the best overall view of the site and document the sampling location. Record on the field form the photo or image number and brief description; print the photos and file them with the field forms.	• NFM 4 • Barbour and others, 1999, Chapter 5
Physical habitat conditions	Describe weather and bank conditions and the type of riparian area(s). Measure and record: • wind speed and water body width and depth • percent vegetation cover; percent bank erosion • width and type of riparian areas	• Fitzpatrick and others, 1998 (for rivers and streams) • USEPA, 1998 (for lakes and reservoirs)
Nutrient concentrations	Collect samples for analysis of total and dissolved forms of nutrients, including phosphorus and nitrogen[1]. Carbon is determined by analysis of particulate organic carbon.	• NFM 4.0, 4.1 • NFM 5
Light availability	Select the appropriate measuring method: • Secchi disk measures transparency; widely used in lakes and reservoirs • Turbidimeter - portable instruments, including a turbidity sensor in multi-parameter instruments, are used routinely for USGS water-quality studies[2]. • Light meter with underwater quantum sensor - provides quantitative measurements of PAR available to algae. Use of a light meter is recommended, as it provides a direct measure of the energy available for algal growth.	• Procedures described in 7.4.1.B and at http://dipin.kent.edu/secchi.htm • NFM 6.7 • Procedures described in section 7.4.1.B, and in Moulton and others, 2002.
In vivo CHL	Fluorescence and other sensors used in situ to measure relative CHL concentration; these measurements must be supported with extractive *in vitro* laboratory analysis.	• Procedures and pros and cons are described in table 7.4–7, and USEPA (1996)

[1]Growth of algae is dependent on availability of nutrient concentrations to the plants; total nitrogen and phosphorus include the phytoplankton itself, resulting in strong correlations between phytoplankton and total phosphorus. The amount of dissolved nutrients represents what is available to the plants for growth.

[2]Turbidity tubes are an alternative method for turbidity measurement, but require care in reading and interpretation because of the tendency for particulates to fall out of suspension; the reading is subjective and its accuracy relies heavily on the experience of the analyst.

Continuous monitoring

Instruments are available for continuous monitoring of all basic field properties (Wagner and others, 2006) and for some chemical constituents and measures of physical habitat. Continuous measurements can be useful in modeling, particularly in studies of climate variability where the interaction of temperature and water are important. Continuous monitoring over several days is recommended for measuring properties such as dissolved-oxygen (DO) concentration and pH, which can be controlled by biological activity. Monitoring DO concentration over 24 hours is especially important, since the diurnal variation of DO in water bodies with high algal concentrations can be extreme. Thus, minimum, maximum, and mean daily values can be helpful in water-body assessment and data interpretation. Measures of DO over time can be used to calculate rates of oxygen production and respiration. The minimum DO concentration usually occurs in the early morning and the maximum occurs in the late afternoon or early evening, depending on the available sunlight and water temperature.

Measures of light availability: Secchi disks and light meters

Measurement of light availability through the water column is an important factor for algal studies. Once light reaches the water surface, particulate matter within the water column (sediment, plankton, and other organic matter) absorb, reflect, and scatter the wavelengths of light. The amount of light available to periphyton and phytoplankton will influence the type of taxa and the amount of chlorophyll and biomass. Another consideration for sampling in lakes is the importance of light profiles to help locate layers of algae in the lake. These layers are referred to as subsurface or deep chlorophyll maxima layers. When present, these subsurface layers of algal concentrations can represent 80 percent of the algal biomass in the water column.

Transparency: A measure of water clarity.

Water clarity can be measured using Secchi disks, turbidimeters, light meters, and sensors. Procedures for the use of Secchi disks and light meters and sensors to measure light availability are described below. Procedures for use of turbidimeters and discussion of the capabilities of various types of turbidimeters are detailed in NFM 6.7.

TECHNICAL NOTES AND TIPS–1. Transparency:

- Transparency can be affected by the color of the water, as well as by algae and suspended sediments in the water.
- Transparency decreases as color, suspended sediments, or algal abundance increases.
- Water often is stained yellow or brown by decaying plant matter. In bogs and some lakes, the brown stain can make the water the color of strong tea.
- Transparency can be affected by the amount of nutrients and suspended sediment coming into the water body from natural and anthropogenic sources; wind speed can be responsible for the resuspension of bottom sediments.

Secchi disks (fig. 7.4–3). Secchi disks are widely used in lakes and reservoirs to measure transparency, but the method, although inexpensive and easy to use, usually is not practical in streams. The water might be too clear and pools might not be deep enough to take a reading, or the maximum wadeable depth might be less than the Secchi depth. The Secchi disk is typically an 8-inch-diameter (20 cm) disk with alternating black and white quadrants. The disk is lowered into the water until the observer can no longer see it. The average of the depth of disappearance and reappearance is called the Secchi depth and is a measure of the transparency of the water (see **Technical Notes and Tips-1**).

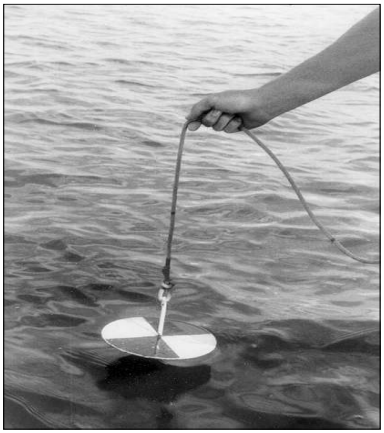

Figure 7.4–3. Lowering a Secchi disk into water. (Photo provided by Kent State University, Ohio.)

- Many State agencies routinely obtain Secchi depth measurements in lakes from the shaded side of a boat. Investigators should be aware, however, that minor differences, such as whether observations are made in full, partial, or shaded sunlight, can affect the measurements (Kent State University, 2007).
- Establish a uniform procedure for measuring Secchi depth in individual studies and water-quality monitoring programs to ensure data comparability and interpretability.
  - — If transparency is measured at regular intervals throughout the year, trends in transparency may be observed.
  - — If light profiles are taken at the same time as Secchi-depth transparency, a general relation can be developed between Secchi-depth transparency and percentage of incident light energy.

To make a transparency measurement using a Secchi disk:

1. Attach a measuring tape (recommended) or rope to the Secchi disk.
2. Lower the disk straight down into the water until the disk just disappears from sight.
   - The sun should be behind you whenever a Secchi depth measurement is made. An exception to the rule would be when the sun is directly overhead.
   - Sunglasses should be removed unless conditions warrant otherwise.
   - If an anchor is used to prevent drifting from a sampling site, be careful not to disturb the sediments on the bottom as this could cloud the water and interfere with the reading, especially in shallow lakes. The same is true if a Secchi depth measurement is made in a stream, especially in slow moving streams.
3. If the disk is suspended with a measuring tape, note this on the field form and record the depth. If a rope suspends the disk, mark the rope at the depth at which the disk disappears.
4. Slowly raise the disk through the water column until it becomes visible. Record the depth at which the disk reappears (or mark the rope at this depth).

5. The Secchi depth is the midpoint between the disappearance and reappearance measurements. In other words, this point is one-half the distance between the point of disappearance of the disk and the point of reappearance.
6. Measure the distance from the Secchi disk to the midpoint determined in step 5.
7. Record the Secchi depth on the field form to the nearest centimeter or tenth of a foot, and repeat the measurement a second time for quality control.

Light meters and submersible sensors. Light meters and underwater sensors, such as the LI-CORTM 250 meter with LI-CORTM 192SA (illustrated here, for estimates of light penetration in streams) or the LI-193SA (spherical quantum sensor that measures light from all directions-better for deeper water bodies) underwater quantum sensor, can be used to obtain quantitative measurements of the **photosynthetically active radiation** available to the algal community (fig. 7.4–4).

- Use of a light meter is the recommended approach because it provides a direct measure of the energy available for algal growth.
- Light profiles may be used to estimate the light attenuation coefficient as well as the compensation point.

Photosynthetically active radiation: Radiation in the 400 to 700 nanometer waveband.

Light meter and sensor disk with sensor cord running through a graduated PVC pipe. The light-sensor disk is taped so it is facing upward on the measuring rod.

Measuring light penetration using a light meter and light-sensor disk.

Figure 7.4–4. Examples of (*A*) light meter and sensor disk, and (*B*) a light-penetration measurement using a light meter and light-sensor disk. (Photographs by S. Mark Nelson, Bureau of Reclamation.)

To measure photosynthetically active radiation:

1. Assemble the light meter and underwater light sensor to read and record the measurement, in units of photon flux density (micromoles of photons per square meter per second).
   a. Attach the light sensor to a 1.5-m-long 1.3-cm-diameter PVC pipe by feeding the sensor cord through the pipe for streams (fig. 7.4–4a), or using a standard hanging frame for the sensor when used in lakes or reservoirs.
   b. Secure the sensor to the bottom of the pipe with duct tape and a plastic tie, or use a hanger frame and clamp the sensor to the PVC pipe.
   c. Mark the pipe at 10-cm intervals from where the sensor is attached.
   d. If necessary, modify the PVC pipe to ensure that it remains plumb and steady while light readings are taken. Helpful modifications include adding weight to the bottom of the pipe or a bubble level to the top of the pipe.
2. Locate a pool in the reach (or an area in a lake with steady sun or shade) from which light readings can be taken. Ideally, the pools should be shaded if complete cloud cover is not available on the day of sampling. If pools are not present in the reach, locate a pool outside the reach (for example, at a bridge scour) that can be representative.
3. When taking light readings, be aware that the amount of available light at the surface is sensitive to changes in the wind, cloud cover, and disturbance at the water surface.
4. Lower the sensor into the water and take a light reading about 1 cm below the air/water interface (fig. 7.4–4b).
5. Continue lowering the sensor and take a reading at 5- to 10-cm intervals (in streams; take readings at feet or meter intervals for lakes) until the sensor reaches the stream bottom or the instrument reads 1 percent of the first (subsurface) light reading, whichever comes first. The objective is to maximize the number of light readings at each location. During stable flow, wadeable streams rarely have sufficient depth and material to fulfill the condition of 1 percent of the surface reading.

6. Record on the field form the beginning time of the light readings, the depth (in centimeters as indicated by the depth interval on the PVC pipe), and the light readings for all measurements taken at each location. Repeat two or three times and record the measurements each time (replicate measurements). See examples of field forms in Appendix 7.4–A.

7. For data from deep pools or lakes: plot the data using a log-linear plot of readings and depths. The slope of this line approximates the light attenuation coefficient for the water body being sampled. (Section 7.4.2 below on sample collection provides more detail on light profiles.)

TECHNICAL NOTES AND TIPS–2. Calculating the portion of the water body in which light is sufficient for photosynthesis (the euphotic depth):

The light intensity or irradiance (I), at depth z, is a function of intensity at the surface (I_0) to the log base (e) of the negative extinction coefficient (n) at the depth distance, z in meters (Wetzel, 1975, p. 53):

$$I_z = I_0 e^{-nz}$$

where, I = Photosynthetically Active Radiation, in micromoles of photons per square meter per second, or other consistent measurement of irradiance or light,

z = depth, in meters,

n = extinction coefficient, in per meter

Taking the natural logarithms of both sides:

$$Ln(I_z) = Ln(I_0) - nz$$

Using a statistical package, data pairs of light intensity and depth can be used to estimate regression coefficients that correspond to $Ln(I_0)$ and n. Let $Ln(I_z)$ be the light readings (dependent variable) and z be the depths at which they were taken (independent variable), so that the statistics generated are **n** (the extinction coefficient) and $Ln\ I_0$ (Y-intercept). In a statistical package, simply set the depth as the independent variable and LOG_LIGHT as the dependent variable. The CONSTANT (the Y-intercept) and the COEFFICIENT (the slope, the extinction coefficient) are determined from X and Y (data) values. Also, the antilog of the CONSTANT (the Y-intercept) should be very close to the light reading recorded at the surface (I_0) (James F. Coles and Stephen D. Porter, U.S. Geological Survey, written commun., 2001).

The euphotic depth is defined as the depth at which $I_z/I_0 = 0.01$, and Ln (0.01) = -4.6. By rearranging terms in the previous equation:

$$Euphotic\_Depth = 4.6 / n$$

7.4.1.C EQUIPMENT AND SUPPLIES

Equipment and supplies should be ordered and checked in advance of a field trip (tables 7.4–5 and 7.4–6). All equipment and field instruments must be in good operating condition and cleaned according to USGS recommendations and requirements. Instrument calibration or calibration checks should be executed onsite on the day of sampling.

To prevent sample contamination, sample-collection equipment (table 7.4–5) and sample-processing equipment (table 7.4–6) must be cleaned properly. This is especially important in eutrophic systems where it is best to sample from sites of lowest concentration (cleanest sites) to higher concentration sites.

- Follow the USGS cleaning procedures for inorganic-constituent equipment that are detailed in NFM 3, for pre-field and onsite equipment rinsing and cleaning.
- Thoroughly rinse the equipment for sample collection or sample processing with tap water or deionized water (DIW) between each sample collected and before the equipment has time to dry. **Do not let sample-wetted equipment dry before this preliminary rinse is done and before the actual equipment cleaning.**
- **Multiple samples at the same site.** Thoroughly rinse the processing equipment immediately after processing each sample, and before the equipment has time to dry. Rinse all surfaces of the equipment three times with tap water and three times with DIW, or six times with DIW if tap water is not available, before processing another sample.
- **Between sites.** Apply the following procedures to in-field cleaning:

  1. Rinse the equipment with tap water (or DIW) immediately after use.
  2. Soak equipment for 30 minutes in a 0.1- to 0.2-percent non-phosphate detergent solution.
  3. Scrub equipment with a brush to remove residues from the previous sample.
  4. Rinse the equipment three times with tap water, followed by three or more rinses with DIW.

- **Sites with high algal concentrations** — the equipment may require a 30-minute soak in acid solution to assist in the removal of residues (see NFM 3).

Table 7.4–5. Example checklist of basic and ancillary field supplies and sampling equipment used in the collection of algal samples

[L, liter; mL, milliliter; mm, millimeter]

Items for sample collection	✓
Phytoplankton Collection	
Secchi disk and a measuring tape	
Water sampler (Kemmerer, a weighted bottle sampler, DH 81, or other sampler)	
1-L amber high-density polyethylene sample bottles	
Periphyton Collection	
Wide-mouth sample bottles (for example, Nalgene™) (size depends on sampling method, typically between a 100 mL and 1 L bottle)	
SG-92 with brushes (see section 4.3.1 in Moulton and others, 2002)	
Ruler and tape measure	
Wax pencil (for top-rock scrape)	
Aluminum foil	
Hand brush	
Plastic petri dishes (47-mm diameter)	
Spatula (without holes)	
Gravel sampler with masonry trowel	
General	
PFD (personal flotation device)	
Forceps	
Graduated cylinder	
Squirt bottles for washing algae off sampling forceps, pipettes, and pans	
Sample labels and tape	
Field forms, printed on waterproof paper, for recording date, time, conditions, area samples and volumes filtered	
Camera	
Global positioning system unit, to document site and sample location	
100-meter tape	
Depth measuring stick	
Gravelometer or ruler to measure substrate size	
Angular densiometer to measure channel shading	
Clinometer to measure stream slope	
Light meter and quantum sensor, or Secchi disk for lakes	
Instrument(s) for measuring water pH, conductance, temperature, and dissolved-oxygen concentration	
In vivo chlorophyll or phaeophytin sensor	

Table 7.4-6. Example checklist of equipment and supplies used in the processing of algal samples

[L, liter; mm, millimeter; TNPC-POC, total nitrogen and particulate carbon and particulate organic carbon; lbs, pounds]

Items for sample processing	✓
Hand-held electric stirrer (periphyton homogenizer) or blender	
Graduated cylinders	
Pipettor and disposable pipette tips (for example, Oxford™ or Eppendorf™)	
Plastic Erlenmeyer flask (1 or 2 L) with appropriately sized one-hole stopper	
Filter funnel and base (for 47-mm-diameter filters). Note: adapt to 25 mm for TNPC-POC	
Vacuum pump with pressure gage	
Glass fiber filters, 47-mm diameter (for example, WhatmanTM). Note: 25 mm for TNPC-POC	
Plastic gloves	
Forceps	
Aluminum foil	
Dry ice, 10 lbs. per day of transit	
Cooler to hold dry ice and filtered samples	
Plastic petri dishes (47-mm diameter)	
Electrical tape to seal petri dishes	
Squirt bottles for washing algae off sampling forceps, pipettes, and pans	

7.4.1.D QUALITY CONTROL

Algal concentration may vary substantially from sample to sample. The variability can be attributed to spatiotemporal variability of the collection, as well as variability in the processing, storage, and analysis of the sample. Quality-control samples, such as blanks and replicates, should be used to determine the cause of the variability or to assess precision. One quality-control sample is typically collected for every 10 to 15 samples; however, the frequency, types, and distribution of quality-control samples must be based on the data-quality objectives of the study. Note that analyses using fewer than four blanks or replicates carry little statistical power.

- In water bodies with high algal concentrations, collect blanks to help determine the effect of carryover or positive bias.
  - Blanks should be targeted for field and laboratory methods. Field blanks are best collected at the end of the day, after the last sample.
  - Blanks intended to determine laboratory carryover should be collected and processed under the controlled conditions of the office laboratory.

- Collect replicate and split samples to determine the variance in laboratory or field procedures.
  - Consider split and replicate samples to partition the variance associated with laboratory analysis of the sample and the variance associated with collecting the sample. Chlorophyll concentrations can vary with light (riparian shading and (or) water turbidity), velocity, algal community composition (particularly when filamentous green algae are predominant in periphyton samples), community age and patchiness, and other factors. Develop a quality-control design that takes into account the results of preliminary measuring and recording of these ancillary data.
  - Special considerations for lake plankton include water column structure, euphotic depth, wind speed, and wind direction. Consider how the algae are distributed with depth, especially for stratified lakes or deep pools in streams. If the mixed layer of the lake or pool is very deep, or if light penetrates deep into the lake, consider collecting samples at multiple depths. Samplers also are available to collect depth-integrated samples over the mixed layer. In general, lake algae are not uniformly distributed with depth, and so the sampling plan should take this into account. For lakes and reservoirs, sampling at multiple depths is more important than collecting replicate samples at the same depth, because the major source of variability at any one site is the change in concentration of algae with depth. See section 7.4.3 on sample collection for more detail on integrated sampling.
  - If chlorophyll extraction from the sample will be performed at multiple laboratories or by multiple laboratories or personnel within a laboratory, use of split samples for inter- and intra-laboratory comparisons is recommended.
  - **Post sample-collection handling.** Algae samples are susceptible to degradation. Heat and light are the primary sources of sample degradation. Remember that algae are living microorganisms with relatively fast growth rates. **Samples cannot be held for more than 24 hours before significant changes begin to occur.** Sample filtration followed by freezing is the best protection from degradation; however, freezing and thawing can also cause sample degradation.

7.4.2 *IN VIVO* MEASUREMENT OF CHLOROPHYLL AND PHYCOCYANIN

Field measurements taken *in vivo* (within a living organism or a natural setting) are performed on whole living algal cells and are adequate to provide a realistic estimate of CHL *a*. Fluorescence-based sensors (*in vivo* fluorescence[4]) can be used in situ to provide a continuous record of CHL *a* concentration. These chlorophyll sensors output a relative measure of the total chlorophyll concentration; to adjust the readings to CHL *a*, the total concentration must be related to the analysis of extracted CHL *a* samples collected from the site. The fluorometer emits an excitation light at a particular wavelength (approximately 430 to 470 nanometers (nm)) that causes the CHL *a* contained within the algal cells to fluoresce at another wavelength (approximately 650 to 700 nm). The concentration of CHL *a* is proportional to the amount of CHL *a* fluorescence emitted. All algae contain CHL *a*, but there are many kinds of algae and each division has distinctly different accessory pigments that fluoresce at different wavelengths. Some accessory pigments such as CHL *b* and CHL *c* fluoresce within the same wavelength and may influence the CHL *a* determination.

Cyanobactera: A group of phytoplankton and periphyton organisms containing the photosynthetic pigments chlorophyll *a* and accessory pigments that give cyanobacteria their blue-green color.

Cyanobacteria or cyanophyta are blue-green algae found in all aquatic environments throughout the year. In addition to CHL *a*, these phytoplankton and periphyton organisms contain phycocyanin, allophycocyanin, and phycoerythrin, collectively referred to as phycobilin pigments. The abundance of cyanobacteria in phytoplankton samples is expressed as the number of cells or trichomes (filaments) per milliliter (cells/mL or trichomes/mL) or as a biovolume in cubic micrometers per milliliter (μm^3/mL). Excessive growth of cyanobacteria can cause the nuisance water-quality conditions referred to as Cyanobacterial Harmful Algal Blooms, or CyanoHABs.

[4]Throughout this section, *in vivo* fluorescence refers to the measurement of any of the photosynthetic pigments.

An estimated concentration of cyanobacteria in the plankton community can be measured *in vivo* by measuring phycocyanin fluorescence in much the same way as CHL *a* fluorescence. The primary differences are the wavelength of light used by the sensor, and the units of measure; the measured fluorescence is correlated to a cell count (cells/mL). Phycocyanin is an accessory pigment in cyanobacteria that is measured in freshwater environments (using an excitation wavelength of approximately 595 nm and an emission wavelength of approximately 670 nm). Phycoerythrin is another pigment that occurs in cyanobacteria and typically is measured in marine waters using an excitation wavelength of approximately 528 nm and an emission wavelength of approximately 573 nm. Advantages and disadvantages of using *in vivo* measurements are included in table 7.4–7.

Table 7.4–7. *In vivo* chlorophyll and phycocyanin measurement: advantages and disadvantages

Advantages	Disadvantages
The measurement is simple and laboratory equipment is not required.	The measured fluorescence is affected by cell structure, particle size, organism type, physiological state of the cell, and environmental conditions.
In vivo spot sampling can determine points of interest in real time and can indicate where to collect samples for extractive analysis.	Different phytoplankton species may show differing fluorescence intensities even with similar chlorophyll contents. It is not usually possible to differentiate between different forms of chlorophyll.
Measurements from the sensor can provide useful information in either vertical or horizontal profiling studies. Instantaneous, short-term, and long-term measurements can be made.	Interferences may occur from other fluorescent species and sunlight. Depending on the sensor type, anything that fluoresces may be detected. The time of day and the turbidity of the water may affect fluorescence intensity due to the impact of available light, resulting in fluorescence variation even though chlorophyll (phytoplankton) remains constant.
In vivo fluorescence measurements allow for the continuous monitoring of chlorophyll and the observation of trends in phytoplankton concentration.	Many environmental factors can affect fluorescence, about which little is known (including diurnal variations). For example, *in vivo* fluorescence responses exhibit photoinhibition over the daily irradiance cycle, making time of day and light intensity important sampling variables. Drifting and fouling of the sensors on continuous monitors require periodic (in some cases frequent) servicing and recalibration.
In vivo sampling can complement extractive analysis by limiting labor, expense, and (or) number of samples.	The calibration of chlorophyll sensors may present a challenge. True chlorophyll standards are an extract dissolved in acetone. This mixture is not recommended for sondes. The use of a secondary standard to check sensor performance is typical among the available sonde chlorophyll sensors.

7.4.2.A SENSOR RANGE

In vivo fluorescence must be measured and calibrated within the linear range of the sensor. Most commercially available sensors operate at ranges up to 200-400 *in vivo* fluorescence units (or 200-400 µg/L). Measures that are greater than the sensor's range will increasingly become negatively biased. Refer to the sensor user's manual to determine the maximum range of the sensor and select a sensor that meets the range requirements for the study. If environmental conditions are greater than approximately 10 times the maximum range of the sensor, sample quenching may occur. The observed effect of quenching is readings that decrease even though concentrations are increasing. Quenching is due to light-absorption losses in the sample (Turner Designs, Inc., 2004). Quenching can be a problem because high concentrations of chlorophyll will produce low fluorescence measurements that may appear to be within the linear range of the sensor.

7.4.2.B CALIBRATION

The majority of *in vivo* fluorescence sensors are not calibrated using a certified primary standard but are checked using a secondary standard in order to monitor sensor performance. A primary standard contains a known concentration of chlorophyll, usually dissolved in an organic solvent such as acetone. A secondary standard contains some other fluorescent material in place of chlorophyll. As a result, the measured values are not directly related to CHL *a* concentration in micrograms per liter, such as can be obtained when calibrating with a primary standard. Rather, readings are a relative change in measured fluorescence over time and are reported in *In Vivo* Fluorescence Units (IVFU). Even if a primary standard is used, the fluorescence produced from an extracted chlorophyll standard is unlikely to be the same as the fluorescence produced by the same concentration of chlorophyll present in a whole living cell (YSI Incorporated, 2001). Since most sensors report measurements in extrapolated units—either as microgram per liter or cells per milliliter—the user must be aware of the units being reported relative to the calibration method so that data are represented appropriately.

Calibration typically is performed using a secondary standard such as rhodamine dye or a solid block standard. Consult the equipment user's manual for the type of standard, the standard preparation instructions, and the sensor's verification procedure recommended by the manufacturer.

- Due to the temperature dependency of fluormetric measurements, the temperature of the standard should be as close as possible to that of the environmental conditions.
- Always verify sensor performance before use.

Basic Calibration Procedure

Record the results of each of the following steps and the sample temperature on the field form, as appropriate, and in the instrument logbook.

1. Rinse the sensor with DIW three times and fill with DIW to obtain an initial blank reading. This step ensures no contamination is present.
2. Use at least one secondary standard to verify sensor performance. The sensor should be checked at a minimum of two points, bracketing the expected environmental concentration. Use as many points as possible.
3. Rinse the sensor with DIW to obtain a second blank reading. This step is critical if rhodamine dye is used as a secondary standard because the dye has a tendency to persist and remain detectable at low concentrations. A minimum of six DIW rinses typically is needed to obtain a reading equivalent to the initial blank reading.
4. If the data are to be quantified, obtain a measurement and collect and process a representative sample of the native water. Depending on the environmental conditions, this may be a concurrent sample or a split sample.

7.4.2.C INTERFERENCES

The distribution and concentration of various algal species can affect the variability of the measurement.

- The **physiological state and morphology of the cell** affects the correlation between the amount of fluorescence and the actual concentration of CHL *a*, because excitation and emission occur through the algal cell wall. Unhealthy cells fluoresce more than healthy cells due to the decreased ability of the unhealthy cells to use available light for photosynthesis (Turner Designs, Inc., 2004).
- **Temperature** has an inverse relation with fluorescence: as temperature increases, fluorescence decreases. Temperature coefficients vary from instrument to instrument. Check the instrument specifications or user's manual to determine the effect of temperature on the measurement. Some sensors may automatically compensate for temperature.
- **Photoinhibition** is the inhibition of chlorophyll to fluoresce in the presence of ambient light (YSI Incorporated, 2006). This would result in an apparent diurnal cycle showing less fluorescence during the day and more at night. Photoinhibition must be taken into account to avoid introducing significant error. Some sensors are capable of ambient light rejection. Thus, the impact of photoinhibition will vary depending on the sensor being used. The use of a flowthrough cell also can help to reduce the effect of photoinhibition by providing the cells with more of a constant light history before measuring fluorescence (Turner Designs, Inc., 2004).
- **Turbidity** can introduce significant error when turbidity levels are high or variable, by increasing light scatter and reducing fluorescence measurements by absorbing light. Some sensor arrays are capable of compensating for the effects of turbidity. The effects of turbidity on *in vivo* chlorophyll fluorescence can be corrected by developing a multiple regression equation using data on *in vivo* fluorescence, turbidity, and CHL *a* concentration from extracted samples (Turner Designs, Inc., 2006).

- ***In vivo* fluorometers cannot distinguish between different algal species or any other compounds that fluoresce at the measured emission wavelengths.** The optical filter bandwidth of the sensor is an important consideration because it defines the range of the excitation and emission wavelengths. The amount of interference from fluorescing compounds, other than CHL *a*, depends on the bandwidth of the optical filters (Turner Designs Inc., 2004, p. 32). A narrow bandwidth is more specific and minimizes interference.
- **Bubbles on the optical sensor** can interfere with readings. Many instruments are equipped with a mechanical wiper to remove bubbles that may have formed on the sensor surface between readings.

DATA QUANTIFICATION 7.4.2.D

The relative measured fluorescence for total CHL *a* and phycocyanin is proportional to the actual concentrations of CHL *a* and the density of cyanobacteria (respectively) in the sample and may be correlated to an extractive analysis. If fluorescence measurements are to be quantified, they must be supported with extractive laboratory analysis. To relate measured fluorescence to CHL *a* concentration, collect multiple CHL *a* samples over the range of fluorescence measurements taken in the field. A correlation rating can then be developed between fluorescence and CHL *a*. The type of extractive analysis must be taken into consideration and should be consistent throughout a study.

Extraction is the primary difference between the *in vivo* field measurement and the in vitro (an artificial environment outside of a living organism) laboratory measurement. The purpose of the extraction step used in laboratory analysis is to disrupt the cell wall and dissolve the photosynthetic pigments into an organic solvent, resulting in a filtered homogeneous sample that effectively removes many of the interferences mentioned above for the *in vivo* measurement. Although the physiological interferences have been removed, other interferences, such as from CHL *b* and *c*, may still be present.

***In vivo* chlorophyll:** Active "live" chlorophyll.
Extracted chlorophyll: "Dead" chlorophyll that is no longer part of an active cell function.

To correlate the relative measured fluorescence to an actual concentration, wholewater samples for laboratory analysis are collected and processed as described in section 7.4.3. For estimates of cyanobacteria, cell counts are used rather than an extract, because of difficulty in extracting the phycobilin pigments. The correlation is calculated the same way as chlorophyll. The number of samples to be collected will depend on the length of deployment, the variability of environmental conditions, and data-quality objectives. Since chlorophyll samples degrade rapidly once they are filtered, samples should be processed, frozen, and shipped to the laboratory by overnight express delivery before Friday. The samples for laboratory analysis should be collected throughout the range of fluorescence measured in the field.

- For long-term deployments, collect a sample for laboratory analysis during each site visit, typically 26 samples per year.
- Samples should be collected throughout the entire range of fluorescence measured in the field.
- The sample collected must be representative of the *in vivo* measurement. The greatest accuracy is achieved if the collection method:
  - Uses split or concurrent samples to compare a fluorescence reading to a laboratory analysis, or
  - Collects a point sample as close to the deployed sensor as possible and compares the in situ reading to the laboratory analysis.

Quantified data can be misinterpreted and must be presented with caution.

DATA INTERPRETATION 7.4.2.E

Several methods are used to calculate a concentration from a relative measured value. The methods range from a simple ratio, or scatter plot, to multiple-regression equations. The appropriate calculation method will depend on the environmental conditions and the number of interferences present. The number and type of interferences that may be present in various environmental settings may cause the data to be highly variable. Depending on the amount of variability and the types of interferences affecting the raw measured values, the development of a useful relation between *in vivo* fluorescence and extractive analysis may be unfeasible.

Understanding the raw fluorescence values may be more beneficial than applying an extrapolated concentration.

- Diurnal fluctuations in fluorescence are indicative of a healthy algal population.
- Increasing fluorescence values over a period of weeks may be indicative of increased algal abundance.
- An increase in the ratio of phycocyanin fluorescence to chlorophyll fluorescence may indicate increased dominance by cyanobacteria.

QUALITY CONTROL 7.4.2.F

The measurement of *in vivo* fluorescence can be highly variable. This method currently is in development. Documenting the methods used in the field and maintaining a continuous record of adaptations for specific sites is crucial to the development of a method. Use of the following steps is recommended to minimize the uncertainty of the measurement and improve the quality of the data.

- Periodically analyze a "true blank" using filtered native water and a glass fiber filter or capsule filter. The purpose is to remove algal cells from the water being measured in order to check for background interferences of dissolved constituents.

- If there is an issue with possible quenching (a decreasing instrument reading for a sample with increasing and extreme algal biomass), consider using diluted replicates to test for linearity and quenching. That is, in addition to an environmental sample and a true blank, consider analyzing a 1:1 or 1:2 mixture of environmental sample and filtered (blank) environmental water.
- If standards are prepared inhouse, then careful quality control of laboratory practices is essential. The field measurements are only as good as the standards being used. Use clean, Class A glassware to prepare standards.
- If samples are being collected to quantify data, all of the quality-control procedures described in 7.4.1.D apply.
- Sensor performance must be verified at the beginning and at the end of deployment and periodically during extended sampling.

7.4.3 PHYTOPLANKTON SAMPLING PROCEDURES FOR CHLOROPHYLL *a* AND PARTICULATE ORGANIC CARBON

The procedures for collecting phytoplankton/seston samples are described below for wadeable streams (section 7.4.3.A) and from lakes, reservoirs, and large rivers (section 7.4.3.B). Collection procedures for POC are similar to those for CHL *a*. Refer to POC methods in NFM 5.2.2.C and compare when to use each set. For POC, take an additional aliquot of sample with the same volume as the CHL *a*, and process the sample through a 25-mm glass fiber filter. Similar samples may be useful for other photopigments in some studies.

Phytoplankton (PHY): Floating or weakly swimming microalgae. Algae floating in streams **(algal seston)** include periphyton that have been lifted or scoured off the stream bottom.

COLLECTING SAMPLES FROM WADEABLE STREAMS 7.4.3.A

Quantitative phytoplankton samples are typically collected along with water-chemistry samples at streamgage locations or at ecological sites of interest. The water sample is poured into a churn splitter and the phytoplankton sample and chemical-quality samples are taken directly from the churn splitter (NFM 4.1 and NFM 5; Ward and Harr, 1990).

To collect phytoplankton samples from wadeable streams:

1. Select a sampling site/location to sample upstream from turbulent areas; for example, in a run or pool above the riffle.
2. Obtain a representative wholewater sample of sufficient volume to ensure adequate phytoplankton biomass for analysis. Use a depth-integrating sampler, such as a DH-81 sampler, or use grab samples at shallow ecological sites. Refer to NFM 4 for isokinetic and nonisokinetic sampling methods. Advantages and disadvantages of sampler types are described in table 7.4–8.
   - A 1-L sample is sufficient for productive, nutrient-enriched rivers, as indicated by a noticeable color to the water.
   - In contrast, a large sample volume, such as 5 L, may be required for phytoplankton samples collected from clear, ground-water fed streams or unproductive, low-nutrient rivers (indicated by water transparency).
3. Withdraw unpreserved subsamples from the churn splitter into an amber high-density polyethylene (HDPE) bottle. Adequate subsample volumes range from 50 mL to more than 5 L for clear, ground-water fed streams. When withdrawing a churn sample for CHL *a* analysis, filter and freeze the samples as soon as possible.
4. Label the sample bottle and store it on ice in the dark until the sample is processed.
5. Record the total sample volume and subsample volume on the field form and sample labels. The water depth at which samples are collected, along with a measure of light availability, water transparency, or the light extinction depth also should be recorded at the sample location.
6. The recommended amount of time from the time of collection until when the live samples are processed by filtering and freezing (section 7.4.5) varies, depending on study or program requirements. **Once samples are filtered, they must be frozen immediately and kept frozen until extraction in the laboratory.**

Table 7.4–8. Phytoplankton sampler types: advantages and disadvantages

[ft, feet; ft/sec, feet per second; L, liter; <, less than; lbs/in^2, pounds per square inch]

Sampler Type	Advantages	Disadvantages
Isokinetic samplers	• Common sampler and already in use. • Ideal for flowing water. • Capable of collecting a representative sample from stratified or poorly mixed streams. • Other constituents can be collected at the same time.	• Algal cells can be stressed by the swirling of the sample and the use of a churn splitter. • A minimum stream velocity is required, otherwise the sampling method is equivalent to a multiple vertical grab using an open-mouth bottle. • Maximum depth limit for 3/16-inch nozzle intake: – DH 81, 15 ft – U-DH-2, 35 ft (2 to 6 ft/sec) – D-96, 110 ft (Refer to NFM 4 and Davis (2005) for sampler selection.)
Kemmerer or Van Dorn samplers	• Ideal for slow-moving to still water. • Capable of collecting an undisturbed point sample at a specific depth; not limited in the depth capability. • Most widely accepted method to collect an algal sample.	• Can be difficult to clean between sites. • Cannot collect integrated samples. • Moving parts in the trigger mechanism may increase the likelihood of equipment failure. • May drift in flowing water.
Open-top bailer	• Can be used to collect an integrated water-column sample. • Sample volume depends on the length and diameter of the bailer selected.	• Can only collect a mixed sample. • Starts at the surface and is limited in depth by the length of the bailer and the rate of filling.
Weighted bottle or open-mouth bottle grab samplers	• Works well for surface or near-surface samples. • Sampler is easy to use and equipment is inexpensive. • The sample is collected in the actual sample container, or in a collapsible 3- to 6-L bag. • May be the only method possible in shallow, narrow streams.	• Sampling begins as soon as the sampler is submersed. • Unacceptable for deep samples in stratified waters. • Limited in the maximum depth that can be sampled. • The sampler will cause some mixing as it is lowered to the appropriate depth and as it fills.
Pump samplers	• The sampling pump may already be in use, such as on a boat. • Sample can be pumped through a glass fiber filter if the pressure is controlled to < 5 lbs/in^2. • Also capable of sampling at a specific location and depth.	• Depending on the ability to regulate pumping rate and flow, certain pumps may deform or destroy the algal cells. • May bias results, depending on the analysis to be performed. • **This sampling method is not acceptable for algal speciation.**

COLLECTING SAMPLES FROM LAKES, RESERVOIRS, AND LARGE RIVERS 7.4.3.B

Quantitative phytoplankton samples collected from lakes, reservoirs, and large rivers are typically collected in the euphotic zone (Britton and Greeson, 1987).

Euphotic zone: The part of the aquatic environment in which the light is sufficient for photosynthesis; commonly considered to be that part of a water body in which the intensity of underwater light equals or exceeds 1 percent of the intensity of surface light.

To collect samples from the euphotic zone:

1. Determine the euphotic zone using secchi depth and (or) a light meter, and the location to be sampled. (Note: The calculated euphotic depth is comparable to a Secchi-disk depth in lakes).
2. Collect samples in the euphotic zone. This depth commonly is approximated by measuring the Secchi depth and collecting the sample at half of the Secchi depth.
   - If the water body being sampled is too shallow to collect at half of the Secchi depth, then collect the sample at half the depth of the water column.
   - These methods may vary depending on study objectives.
3. Samples should be collected in a manner that does not rupture the cells. The common sampler types for lakes and reservoirs include the Kemmerer sampler, Van Dorn sampler, weighted-bottle sampler, and peristaltic pump, listed from most preferred to least. For illustrations and guidance regarding sampler types, see Britton and Greeson (1987).
4. Collect enough sample to fill a 1-L amber HDPE bottle. A 1-L sample is sufficient for productive, nutrient-enriched rivers and reservoirs, as indicated by a noticeable color to the water. A large sample volume (for example 5 L) may be required for phytoplankton samples at some locations.

5. **Store the sample bottle on ice in a dark cooler immediately after collection and until the sample is processed.** Do not exceed the holding time from sample collection to sample processing, as required by the study or program.

6. Record total sample volume and subsample volume on the field form and on the sample labels. The water depth during sample collection, along with a measure of light availability, water transparency, or the light extinction depth also should be recorded for the sample location.

TECHNICAL NOTES AND TIPS–3. Calibrating a sampling pump for accurate representation samples:

When collecting chlorophyll samples using a pump, the time required to completely fill the pump tubing must be determined before sampling. The pump should run for three times the determined length of time before sample collection begins, to allow for three volume rinses of the tubing. If field properties are being monitored, they must stabilize according to stability criteria (NFM 6).

- It is important that the same equipment is used to determine the pump time and to collect the sample. Variations in pumps, tubing, power supplies, and head can affect the pump time.

- If possible perform the following steps in the field immediately before sampling. It is assumed a peristaltic pump is being used.

To determine pump time:

1. Load the tubing into the pump head.
2. Place the end of the pump tubing in deionized water.
3. Note the speed the pump is set at. All samples must be collected at that speed or higher.
4. Turn on the pump and measure the amount of time it takes the deionized water to travel the length of the tubing.
5. Multiply the amount of time by three. This is how long the pump must run before a sample can be collected.

PERIPHYTON SAMPLING PROCEDURES FOR CHLOROPHYLL AND ASH-FREE DRY MASS IN STREAMS, LAKES, RESERVOIRS, AND LARGE RIVERS 7.4.4

The sampling procedures for periphyton vary by the substrate to be sampled. Operationally, periphyton growth forms are classified as either microalgae or macroalgae. Microalgae are microscopic, typically single-celled, and appear as pigmented accumulations or films attached to submerged surfaces. Macroalgae are visible without magnification and typically are filamentous. Macrophytes are vascular plants that typically have roots and are not periphyton. Macrophytes may account for important nutrient uptake and photosynthetic biomass in aquatic ecosystems, and for those reasons they are included with macroalgae in section 7.4.4.B.

Periphyton can be collected from a variety of locations in the sampling reach, representing the range of current velocity, water depth, and riparian shading at the time of sampling. Sampling reaches in rivers and streams typically will have all of the microhabitats listed in table 7.4–9, while the littoral zones of lakes and reservoirs more often are dominated by soft substrates. Depending on the focus of the study and the need to be able to compare results between sites over a range of physiographic regions, it may be important to choose the most representative substrate to sample among the sites.

Periphyton (benthic algae):
Algae attached to an aquatic substrate.

Recommended methods for collecting quantitative periphyton samples from the different in-stream microhabitats (table 7.4–9) and from lakes and reservoirs are described with the intention of reducing the variance in algal collection techniques and increasing data comparability. Where possible, a single habitat is selected for all sites within each study area. Seasonal differences in primary physicochemical factors (light, temperature, current velocity, and nutrients) influence the development, structure, and growth rates of algal communities; therefore, **sampling is recommended during normal, low- or stable-flow periods and delayed at least 2 weeks after spates that have disturbed and removed the periphyton.**

Table 7.4-9. Recommended quantitative periphyton sampling devices or methods for common microhabitat and substrate types

Periphyton Habitat Types		Recommended Sampling Device or Method
Microhabitat	**Substrate**	
Epilithic	Cobble	SG-92 sampler (for smooth surfaces) Top-rock scrape (for irregular surfaces)
	Gravel	Gravel sampler
	Bedrock, boulders, concrete	SG-92 sampler (or a larger adaptation using PVC pipe) Artificial substrate methods (fig. 7.4–5e; Porter and others, 1993; Britton and Greeson, 1987)
Epidendric	Woody snags	Cylinder scrape
Episammic	Sand	Inverted petri dish with spatula
Epipelic	Silt, fine-particle organic matter	Inverted petri dish with spatula

Typical examples of riverine habitats with hard substrates include a riffle in a shallow, coarse-grained, high-gradient stream (epilithic periphyton microhabitat) and a woody snag in a sandy-bottom, coastal plain stream (epidendric periphyton microhabitat). Soft substrate habitats include organically rich depositional areas, such as backwater areas or pools (epipelic or episammic microhabitats). Although these usually are not sampled for chlorophyll, soft substrates that are present in the main channel may be considered representative of the reach for those streams that lack a hard substrate.

To minimize disturbing the stream bottom, stream sampling begins at the downstream boundary of the sampling reach and progresses upstream. Stream depth, velocity, and light should be measured at locations where quantitative periphyton samples are collected, and these site characteristics are recorded on the field form. The area sampled, total sample volume, and subsample volume should also be recorded on the field data form and **on the sample labels.**

Lake edges may have abundant growth of periphyton (as well as macroalgae and macrophytes), and therefore may require a quantitative measure of chlorophyll for documenting near-shore plant biomass. Macroalgal growth such as *Cladophora* spp. can be problematic in lakes that are relatively clear but have cold, nutrient-rich inflows. Collection methods presented here may be used in lakes and reservoirs in wadeable areas near shore (especially the soft substrate), using macroalgal sampling methods. Ancillary data and photographs documenting the coverage of *Cladophora* and the macrophyte Stargrass by distance from shore, depth, and breadth along the shoreline, as well as knowledge of bathymetry and euphotic depth, will help determine the extent to which to apply the sample results (see section 7.4.4.B).

MICROALGAE CHLOROPHYLL AND ASH-FREE DRY MASS SAMPLING METHODS 7.4.4.A

Microalgal sampling procedures for periphyton should be used up to the point at which visible macroalgae become either too long or too dense for practical use of these procedures; at that point use the macrophyte methods described in section 7.4.4.B. It is important to recognize that periphyton represent a dynamic community made of microscopic forms that can accumulate into films, mats, and filaments that become visible macroalgae.

Selection of a hard substrate versus a soft substrate depends on study objectives. In general, hard substrates are preferred because, as erosional areas, they represent conditions at the time of sample collection. Soft substrates, on the other hand, often consist of a mixture of local community biomass as well as deposition from upstream; however, study objectives might dictate selection of soft substrates for this reason. Of the hard substrates, epilithic is the preferred sampling substrate (when it is available throughout the study area) instead of sampling epidendric substrates; this is because the woody branches often are suspended in the water column and located near the edge of the water, and thus are not as representative of the main stream reach.

Epilithic habitat sampling methods

Epilithic sampling locations are randomly selected from five areas in the reach. At each of the areas, a specified minimum number of cobble-sized rocks (5 to 25 cm (~2 to 10 inches)) or gravel samples are carefully lifted from the water and placed in a white plastic dishpan to minimize the loss of periphyton (fig. 7.4–5a). The rocks or gravel are transported in the tub to a convenient onsite sample-processing area. An ideal processing location is shady and flat enough to accommodate a seat (such as an upside-down bucket) for the processor to remove periphyton from the substrate. A composite sample is prepared by combining the algae scraped from the rocks collected in the five areas of the reach.

Epilithic: Benthic habitat consisting of natural, coarse-grained substrates (for example, gravels, cobble-sized rocks, or boulders) or bedrocks, or artificial hard substrates such as submerged concrete on which organisms are attached or loosely associated.

Epilithic microhabitats are sampled using one of three methods, depending on the substrate being sampled (table 7.4–9). When the algae are present in mats or as long filaments, extra effort will be needed to reduce the clumps though mechanical blending to improve reproducibility of results. Long filaments and clumps will need to be reduced to 2 millimeters (mm) or less to improve subsample reproducibility.

- The SG-92 sampler is a modified-syringe sampling device (fig. 7.4–5b) described in Moulton and others (2002) and works best on relatively smooth rock surfaces with moderate to dense assemblages of diatoms or blue-green microalgae. Large filamentous algae can be a problem when trying to prevent leakage between the SG-92 and the sampling area.
- A "top-rock scrape" sampling method is recommended for irregular rock surfaces or when rock surfaces have either sparse periphyton coverage or substantial growths of filamentous algae (fig. 7.4–5c).
- The gravel sampler (fig. 7.4–5d) is recommended for sampling periphyton attached to gravel substrates.

a. Collecting cobble-sized rocks from a stream into a dishpan for processing on the stream bank.

b. Preparing to scrape a rock using the SG-92 sampler (showing o-ring) and periphyton brush.

c. Foil covering the scraped area of a rock following the top-rock scrape method.

d. The gravel sampler. Note beveled edge on bottom of sampler to improve coring.

e. Example of an artificial substrate sampler using clay tiles placed on concrete pavers.

f. A soft substrate, epipelic sample being collected with the inverted petri dish method. Note how a spatula is placed beneath the petri dish to keep the sample intact.

Figure 7.4–5. Photographs of sampling methods for collecting periphyton. (Photographs are by U.S. Geological Survey employees: *a*–*c* and *f* by Richard Frehs, *d* by Stephen Porter, *e* by Carmen Burton.)

To use the SG-92 sampling method:

1. Assemble the SG-92 sampler and periphyton brushes, following the instructions in Moulton and others (2002).
2. Collect five cobble-sized rocks at a time from each of five sampling locations (a total of 25 cobbles per site) into a white plastic dishpan (fig. 7.4–5a) and transport the rocks to an onsite processing station to remove the periphyton.
3. Place the SG-92 barrel with the O-ring on a smooth part of the rock where the algal density is typical. Press down and rotate slightly to create a good seal.
4. Using a pipettor, dispense 5 mL of water into the SG-92 barrel on the cobble. If the water leaks out the side, select another place on the cobble and try again. If the water does not leak, insert the brush into the barrel and scrub to remove the periphyton from the enclosed area on the cobble.
5. Remove periphyton and water mixture with the pipette and dispense the sample into a 100-mL graduated cylinder.
   - Use additional volumes of water as needed.
   - Repeat the process several times until all of the visible periphyton is removed.
   - Pour the contents of the graduated cylinder into a 500-mL sample bottle.

   Note: Dispensing into a graduated cylinder instead of a 500-mL sample bottle is recommended in case the SG-92 seal fails while collecting the sample, thereby causing the collector to start over. If the seal fails, then only the contents of the graduated cylinder are discarded.
6. Repeat the sampling procedures for a single area on each of the rocks selected (the composite sample is composed of 25 discrete collections taken from 25 rocks). Place the sample bottle on ice in a cooler and keep dark until the sample is processed.
7. Measure the diameter of the area scraped by the SG-92 at the beginning and end of sampling. Record these diameters on the Periphyton Field Form (Appendix 7.4–A, fig. 2) to establish an average scrape diameter from which the sampling area can be calculated.

8. Calculate the total area of the composite sample using the average scrape diameter.

$$\text{Total area sampled } (cm^2) = n\pi\,(d/2)^2$$

where, n = number of sample replicates

$\pi = 3.1416$

d = average scrape diameter in centimeters (cm)

Note: If using the inside diameter of a 30-mL syringe, then the total surface area sampled for 25 rocks will be about 75 cm^2.

TECHNICAL NOTES AND TIPS–4. Helpful suggestions for improving the performance of the SG-92 sampler:

- To improve the seal of the SG-92: Replace the rubber O-ring with a neoprene O-ring. The added thickness provides more flexibility to seal the SG-92 against rough rock surfaces.
- If the SG-92 seal fails: Using a pen point, scribe the inside circumference of the SG-92. Set the SG-92 aside. Use a knife, brush, or single-side razor blade to remove the algae from inside the scribed area. Rinse the sample from the brush or blade into the sample bottle.
- Reverse the procedure by scraping away all the algae on the rock around the SG-92; then remove the SG-92 and measure the diameter of your sample and scrape it off into the collection bottle.

To use the top-rock scrape sampling method:

1. Select one to five representative rocks (5 to 25 cm in size) from each of five representative locations in the reach and place them in a white plastic dishpan. Avoid nearshore and shaded areas by selecting rocks from the main part of the riffle or run, partly because edge areas fluctuate with regard to water covering the substrate. The number of rocks to sample depends on periphyton density.

   - Where periphyton density is low (bare rocks), scraping up to 25 rocks may be necessary.
   - If the rocks have a thick biofilm or filamentous growth, scraping five representative rocks should be sufficient.
   - If the coverage of periphyton is variable, scraping 10 rocks is recommended.

2. Identify the area on the top of the rock where periphyton are growing and use a red wax pencil to draw a line around the middle (side) of the rock, outlining the area of periphyton growth on the upper-side of the rock (exposed to some level of light) to be sampled. In some cases, where the steambed is unstable or when excessive scouring has occurred, it can be difficult to assess the area to sample; often the bottom of the rock that has been in contact with the surrounding substrate is darker, especially in streams embedded with silt and organic matter. If it is impossible to determine the top of the rock then pick another rock, or consider sampling the whole rock and determining the area of the entire rock.

3. Using a small brush (nailbrush or toothbrush) or a pocketknife, scrape the periphyton from the sampling area on each rock (typically the top and sides) down to the red line.

4. Rinse the periphyton from each rock into the dishpan using a poultry baster and filtered stream water. If filaments are present, measure the longest one and record the length on a Periphyton Field Form, then cut all filaments into smaller pieces (approximately 2 mm) and include them in the sample to improve homogenizing and splitting the sample.

5. Pour the contents of the dishpan through a funnel into a labeled 500-mL sample bottle. **Place the bottle on ice in a cooler and keep in the dark until the sample is processed** (see "Sample Processing and Preservation," section 7.4.5).

6. The total volume of the composite periphyton sample (including dishpan rinse water) should be less than 475 mL (if mixing in a 500-mL bottle).

7. Trace the outline of each rock on waterproof paper. More than one rock can be outlined per page; number each rock outline sequentially. Label each page with site name, date, number of rocks collected from each site, and initials of the person making the outline.

8. Wrap aluminum foil around the surface of each rock, covering the area that was scraped to remove periphyton (down to the red line on the side). Mold the foil tightly (fig. 7.4–5c) and trim the excess from the bottom edge of the scraped area.

9. Remove the foil from the rock. Make radial cuts in the foil to allow it to be flattened. Place the foil templates into a labeled resealable plastic bag for later determination of the area of each template.

10. In the laboratory, determine the area of each scrape as soon as practical, using a clear plastic grid, digitizer, or mass-area relations.
    - Note that determining a mass area requires an analytical balance; any excess foil not accounting for sample area must be removed.
    - For the digitized foil areas use the hand-drawn outlines of the rocks as a reference.
    - Sum the area for all the rocks sampled in the reach and record the total area on sample labels and on the Periphyton Field Form (Appendix 7.4–A, fig. 2) (modify the section for measured areas sampled by device and microalgal cover).

To use the gravel-sampler sampling method:

1. Assemble the gravel sampler from a plumbing "clean-out" pipe (7.6 cm diameter) (fig. 7.4–5d). Attach the threaded cap; bevel the bottom edge of the clean-out by using a grinding wheel to improve the coring capability of the sampler. Obtain a large masonry trowel wide enough to enclose completely the bottom of the samples.
2. Select 5 to 10 sampling areas throughout the reach.
3. Press the beveled end of the sampler into the gravel substrate to a depth that will exceed the height of the sampler cap. After the sampler is in place, carefully remove the gravel surrounding the outside of the sampler and insert the masonry trowel.
4. Slide the sampler onto the trowel and carefully lift it out of the water.
5. Quickly invert the sampler to contain the gravel and water in the sampler cap.
6. Unscrew the cap and let the excess gravel fall back into the stream, retaining all the surficial gravel that supports periphyton and discarding excess water and granules that have no periphyton.
7. Pour each discrete collection into a dishpan and rinse the sampler before collecting another discrete sample.
8. Repeat these steps to complete 5 to 10 discrete sample collections, which form the composite sample.
9. Extract macroalgal filaments (if present) from the gravel with forceps and then cut them into fine pieces about 2 mm long or less.

10. Brush and rinse the gravel with dishpan water to remove the algae. Recycle the processing water to limit the total sample volume.
11. Rinse the gravel with clear stream water or tap water and pour the rinsate into the sample bottle until there is no sign of periphyton on the gravel in the pan.
12. Pour the sample from the dishpan through a funnel into a 500-mL sampling bottle. **Place the bottle on ice in a cooler and keep in the dark until the sample is processed. Do not exceed holding times** (see "Sample Processing and Preservation," section 7.4.5).
13. Calculate the total sampling area by using the formula presented for the SG-92 sampling method, and record the total area on the field form and sample label.

Epidendric habitat sampling: Cylinder scrape (snag) method

Collecting quantitative epidendric samples (woody snags) from natural substrates presents a challenge because they have an irregular surface and are difficult to remove from the water without loss of algal biomass.

Epidendric: Benthic habitat consisting of woody substrates on which organisms are attached or loosely associated.

Since roots and branches tend to be near the water's edge where streamflow and light often are reduced, selection of epidendric microhabitats with streamflow and exposure to sunlight should be considered before sampling. In cases where the only epidendric surface is too large to be removed, an artificial sampling substrate made from wood can be used. If the woody snag has a smooth surface, it can be sampled in a similar manner to epilithic habitats by using the SG-92 sampler. Otherwise, periphyton is collected from woody snags by using the cylinder scrape method.

To use the cylinder scrape (snag) sampling method:

1. Look for woody snags, roots, and branches that are cylindrical in shape, and select one woody snag in each of five locations throughout the reach.
2. Record the current velocity, water depth, and light-extinction measurements for each sampling site on the Periphyton Field Form.
3. Identify the part of the branch that will be sampled for periphyton. Carefully cut off a 10- to 20-cm-long piece with pruning shears so the attached algal community is not disturbed, and place the snag in a white plastic dishpan.
4. Scrub the entire surface of each woody snag section in the dishpan with a stiff brush. Rinse the brush and each section into the dishpan. Recycle rinse water to minimize the sample volume.
5. Pour the sample from the dishpan through a funnel into a plastic graduated cylinder to measure the volume, and then pour the sample into the 500-mL sampling bottle.
6. **Place the bottle on ice in a cooler and keep in the dark until the sample is processed. Do not exceed the sample holding times** (see sections 7.4.5.A and 7.4.6).
7. Measure the length and diameter of each cleaned woody snag section and calculate the total sampling area by using the following formula (assumes a cylinder):

$$\text{Total sampling area } (cm^2) = \Sigma_{i}^{n} \pi \, d_i \, l_i$$

where,

$\pi = 3.1416$

d_i = diameter of a snag, in centimeters

h_i = height (length) of a snag, in centimeters

Alternatively, a foil template can be used (see the top-rock scrape method) for irregularly shaped woody snag sections.

Episammic and epipelic habitat sampling: inverted petri dish method

Soft substrates such as silt, clay, and sand are frequently sampled to represent depositional habitats. Quantitative periphyton samples are collected from the upper 5- to 7-mm layer of sand (episammic) or fine silt (epipelic) microhabitats in depositional areas of the sampling reach. Depositional habitats where sediment and algae accumulate are: on the downstream side of an object that protrudes into the flow, such as a log or large boulder; at the water's edge in slow-flow areas; and on the bottom of pools.

Episammic: Benthic habitat consisting of sand-sized (>0.064 to 2 mm) particles on which organisms are attached or loosely associated.

Epipelic: Benthic habitat consisting of silt-sized (<0.064 mm) streambed sediments on which organisms are loosely associated. This habitat is commonly found in areas of low velocities, such as pools and side-channel areas, where silt can deposit.

To compare the data from different sites, it is best to target one type of habitat. There are some difficulties collecting samples from the bottom of pools: the sample collector often must swim to get to the bottom of the pool; deep pools often have low visibility; and soft substrates are easily disturbed, so any movement in the pool can disrupt the sample area. For these reasons, collecting from the first two areas mentioned above are recommended. Soft substrates are sampled with the inverted petri dish method.

TECHNICAL NOTES AND TIPS–5. Use only the lid of the petri dish and keep only the lid with sampling equipment and supplies to prevent use of the petri dish bottom, which has a different area.

To use the inverted petri dish method:

1. Select five locations in the reach that have a depositional zone consisting of either sand or silt substrates. All five locations must be either sand or silt.
2. At each location, hold the lid of a small plastic petri dish (about 47 mm, or approximately 17 cm^2) upside down in the water; rub the inside of the lid to remove air bubbles.
3. Turn the inside of the lid toward the substrate that will be sampled without disturbing the sediments.
4. Carefully and slowly press (in cookie-cutter fashion) the petri dish lid into the streambed sediment.
5. Slide the lid onto a spatula (fig.7.4–5f) or trowel to enclose the discrete collection. Holding the petri dish tight against the spatula, carefully wash extraneous sediment from the spatula and then lift out of the water.
6. Invert the lid and remove the spatula.
7. Rinse the sediment from the lid with filtered stream water into a 500-mL sample bottle.
8. Repeat this collection procedure at each additional sampling location in the reach.
9. Combine the five discrete collections in a 500-mL sample bottle (the total area will be about 85 cm^2).
10. Rinse the silt and sand from the threads of the sample bottle, tighten the lid, and **keep the bottle on ice in the cooler until the sample is processed.**
11. Measure and record the depth, current velocity, and light conditions at each location. Include these records along with the total sampling area on the sample label and Periphyton Field Form.

7.4.4.B MACROALGAE AND MACROPHYTE ASH-FREE DRY MASS SAMPLING METHODS

To adequately characterize biomass from quantitative periphyton samples of macroalgae, for example, *Cladophora* (fig. 7.4–6a), or of macrophyte/vascular plants such as stargrass (fig. 7.4–6b), requires sampling from relatively larger areas than suggested for microalgae. Estimates of macroalgal biomass based on analysis of AFDM can be valuable for water-quality modeling and eutrophication-process studies, such as the effect of benthic macroalgae on diel cycles of dissolved-oxygen concentrations, pH, and alkalinity in the water of nutrient-enriched streams.

Macrophytes: Aquatic plants growing in or near water that are either emergent, submergent, or floating. **Aquatic plants** are also called **hydrophytic plants** or **hydrophytes.** Aquatic vascular plants can be ferns or angiosperms (from both monocot and dicot families).

Quantitative samples of macroalgae and macrophytes can be collected with invertebrate sampling equipment such as a Slack sampler (Cuffney and others, 1993; Moulton and others, 2002; Peterson and Porter, 2002), or with other devices that define a measured area of stream bottom (Britton and Greeson, 1987). **The recommended sampling method for lotic (flowing water) habitats (described here) uses the Slack sampler with a sampling area template (Moulton and others, 2002, pages 38, 39, and 75) that is placed over a representative macroalgal assemblage.** A separate Quantitative Macroalgae Field Form should be used to record the wet and dry weights along with the supporting information regarding the locations where they were collected. See example in Appendix 7.4–A, figure 3.

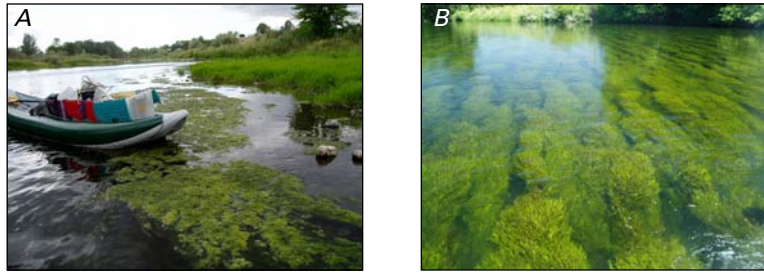

Figure 7.4–6. Examples of (*A*) filamentous green algae (*Cladophora*), and (*B*) Water Stargrass (*Heteranthera dubia*) a rooted macrophyte in the Yakima River, Washington. (Photographs by Kurt Carpenter, U.S. Geological Survey.)

To use the slack-sampler sampling method:

1. Place the Slack sampler and frame on the stream bottom, facing upstream into the flow.

2. Remove the large filaments by hand or by using a pocketknife, scissors, or wire brush, and allow filaments to flow into the net. If filaments extend beyond the sampling frame, scissors can be used to cut and remove the extended filaments so that only the algae covering the designated area of the sampling frame are included in the collection.

3. After collecting the macroalgae from within the frame, remove the sample from the net and rinse it in a dishpan with stream water to remove most of the invertebrate biomass.

4. Place the macroalgae in a labeled, resealable plastic bag. Keep the bag on ice in a cooler and do not expose to light until it is time to measure wet and dry weights.

5. Repeat these steps at four other locations for a total of five separate samples.

6. Record the depth and current velocity at each sample location on the Quantitative Macroalgae Field Form (Appendix 7.4A, fig. 3).

To use the top-rock scrape sampling method:

Quantitative macroalgal samples also can be collected with the top-rock scrape method previously described for sampling epilithic microhabitats, as follows.

1. Instead of using a frame, select and arrange representative rocks to cover the bottom of a dishpan, and measure the area of the dishpan bottom. (Measuring the area of the dishpan bottom using a foil template is not necessary if the tops of the rocks are flat.)

2. To harvest the biomass of macroalgae such as *Cladophora*: remove extraneous invertebrates and silt, pat the macroalgal/macrophyte biomass to remove excess water, and obtain a wet weight.

3. Take subsamples of the wet weight that can be processed for CHL *a*, ADFM and/or POC from the fresh (wet) subsamples of the clipped material.

4. Dry the subsamples of the clipped biomass and weigh the dried sample to obtain the dry mass of macroalgae per square meter. The subsample analysis, of CHL *a* for example, can then be estimated per meter square of biomass.

To use the clip-plot sampling method:

1. In lentic (stillwater) habitats, select representative sample points, use a frame/template to define the area, and remove all biomass above the sediment.

2. If there is sufficient velocity in the water, collect the clippings in a Slack sampler; otherwise, collect the clippings in a dishpan, rinse them with native water to remove most invertebrates, drain through a fine mesh to reduce water volume, and store in a ziplock bag.

3. Record on field forms: depth, velocity, and area. Repeat as needed to represent the habitat unit.

To use the habitat survey method:

In order to estimate macroalgal percent cover in wadeable streams, a visual survey of the stream can be made using a viewbox approach, as described by Stevenson and Bahls (1999) or a modification using a Periphyton Abundance Survey Field Form (Appendix 7.4–A, fig. 4) that incorporates the Wolman pebble count (Wolman, 1954). For example, the results from the form can be summarized based on 100 particles for each geomorphic unit (riffle, pool, or run); or based on 100 particles throughout the targeted sampling area, where

n = Total number of locations assessed,

Microalgal percent cover = (number of checks in columns 0 to 5/n) × 100, and

Macroalgae percent cover = (number of checks in macroalgae column/n) × 100.

Using the Periphyton Abundance Survey to account for macroalgae abundance in the reach, it is also possible to summarize the particle size in the reach and relate the abundance of periphyton to particle size.

SAMPLE PROCESSING AND PRESERVATION 7.4.5

Sampling and processing methods are similar, whether algal biomass will be determined from CHL *a*, AFDM, or POC. There are many items to consider between the field collection and processing of samples.

- Laboratory analyses for CHL *a*, AFDM, and POC each utilize the entire portion of sample that is submitted. Therefore,
  - — Process and submit a separate filter or subsample for each analysis being requested.
  - — Check laboratory requirements in case more than one filter is needed for a given analytical method.
- For POC follow the procedures described in NFM 5.2.2.C "Procedures for Processing Samples for Carbon Analysis."
  - — The maximum pressure of the filtering apparatus must not exceed 15 pounds per square inch (lb/in^2) for POC samples. Greater pressure may cause loss of material through the filter and will rupture algal cells, transferring carbon and (or) chlorophyll pigment from the suspended to the dissolved portion of the sample.
  - — The amount of water to be filtered to obtain a sufficient quantity of material for the analysis depends on the suspended-sediment concentration and (or) on the concentration of humic and other substances (such as organic and inorganic colloids).
  - — A graph of the historical stream stage plotted against suspended materials concentration can aid in estimating loads of suspended materials. Suspended-material concentrations can be used to help select the volume of sample to be filtered for a POC determination.
  - — Particulate analytes (TPC, PIC, POC, SOC) are reported in units of mass per volume (milligrams per liter), and therefore the volume of sample passed through each filter must be measured accurately and recorded on the field form and on the Analytical Services Request form. Record the filtrate volume passed through each filter used for particulate analysis. This is critical for calculation of POC concentrations.
- If samples must be filtered in the field, care should be taken to avoid sample exposure to direct sunlight and to be as consistent as possible with subsampling techniques.

7.4.5.A FILTERING SAMPLES FOR CHLOROPHYLL *a*, ASH-FREE DRY MASS, AND PARTICULATE ORGANIC CARBON

Use this procedure to isolate a representative fraction of any algal sample on a filter for later analysis of CHL *a*, AFDM, or POC. A similar procedure for POC is described in NFM 5.2.2.C. This procedure may also be useful for other photopigments or algal chemicals. Filter enough of the sample to retain a mass within the laboratory calibration limits.

- When filtering, apply a pressure of about 10 lbs/in^2. The maximum pressure of the filtering apparatus must not exceed 15 lb/in^2 for POC and dissolved organic carbon (DOC) samples. Greater pressure may cause loss of material through the filter and will rupture algal cells, transferring carbon and (or) chlorophyll pigment, from the suspended to the dissolved portion of the sample.
- Filter large samples to obtain a more representative sample. The volume filtered will depend on the amount of suspended material in the water, the amount of sample being collected, and the filtration time. A moderate amount of sediment or color is more than enough.
- **Do not overload the filter.** More than a 1-mm thickness of matter accumulation on the filter is too much material. If the sample is too dense to filter at 15 lb/in^2, discard it and begin with a smaller volume of water.
- The maximum/minimum calibration range ratio for chlorophyll is greater than for many other analytical methods. For example, the calibration range of the chlorophyll is 5 to 800 µg/L with reference to the 20-mL final solution extracted from the filter(s) provided by the field personnel (Bruce Anderson, U.S. Geological Survey, written commun., 2007). This calibration range corresponds to 0.1 to 16 µg CHL a on the filter.
- Visible green or brown coloration on a single filter usually indicates sufficient CHL *a* for the analysis (fig. 7.4–7f). Nondetects of CHL *a* are rare when determined using EPA Method 445.0 (U.S. Environmental Protection Agency, 1997a).

When filtering the sample:

1. Record the original water volume or habitat area from which the sample was collected, the volume or mass of the entire sample, and the volume or mass of the filtered subsample. Record these values in sampling notes, on sample containers sent to the laboratory, and in the remarks section of the Analytical Services Request form.

2. Assemble the filtration unit and vacuum flask, and connect to the vacuum pump (fig 7.4–7a).

3. Using clean forceps to place a 47-mm glass fiber filter (Whatman™ GF/F or equivalent) on the base of the filter unit (fig 7.4–7b), clamp the funnel onto the filter unit, wet the filter with DIW (fig 7.4–7c), and use the hand pump to draw a vacuum of 3 lb/in^2. **If the vacuum does not hold, check for leaks, re-wet the filter, and try again.**

4. Homogenize the full sample to create a uniform suspension of algae from which CHL *a*, AFDM, or POC subsamples are taken. Repeat the homogenization before further processing each subsample.

   - For phytoplankton, invert the sample bottle 10 times, mix in a churn splitter, or shake vigorously for 30 seconds.
   - For periphyton, invert the sample bottle 10 times and use a battery powered stirrer to break up the clumps.
   - For macroalgae or macrophytes, remove excess moisture, as in measuring wet weight as part of the dry mass procedure (section 7.4.4.B). Repeat the homogenization before further processing of each subsample.

5. Withdraw a measured subsample volume or mass, record the amount, and pour or wash the subsamples through the filter using additional DIW as necessary (fig 7.4–7d). The volumes indicated in the bullets that follow pertain to chlorophyll and AFDM; a greater volume is recommended for POC, unless a large amount of suspended material in the water causes clogging of the filter.

   - **Phytoplankton** — Pour the subsample into a graduated cylinder, working in 50- to 100-mL increments. Record the volume increment and pour into the filter funnel. Depending on plankton density, filter a total of 50 to 200 mL, although as much as 500 mL may be needed for clear oligotrophic habitats.

- **Periphyton** — Withdraw 5.0-mL aliquots using a pipette and dispense onto the glass-fiber filter. A total of 10 mL is typically sufficient for the analysis.
- **Macroalgae and macrophytes** — Cut or tear 0.5 to 2 g wet weight of representative material from the full sample and transfer it to the filter (not to exceed 1 mm height of biomass on the filter), using a small amount of DIW if needed.

6. Apply the vacuum. Do not exceed 15 lbs/in^2, depending on the units printed on the vacuum gage. Pressures above 15 lbs/in^2 will physically break algal cell walls and carbon will transfer from the suspended phase to the dissolved phase (James Kammer, U.S. Geological Survey, written commun., 2007).
7. Do not filter a particular sample for more than 10 minutes.
8. Do not allow the filter to be sucked dry. Slowly decrease the vacuum as the water level in the filter funnel gets close to the filter.
9. Rinse any subsample containers into the filter funnel and rinse the sides of the funnel with DIW. Allow water to be vacuumed completely from the sample, then release the vacuum from the system.
10. Examine the filter (fig. 7.4–7f). Sample volumes should be withdrawn to ensure that adequate algal biomass, **indicated by a green or brown color,** is retained on the surface of the glass-fiber filter after the filtration process. If algal coverage is sparse, repeat the previous steps 4 through 10 to add an additional subsample aliquot.
11. Using clean forceps, remove the filter from the filter unit, fold it in quarters (pie shape), wrap the folded filter in aluminum foil to protect from light, and place it in a clean petri dish (fig. 7.4–7g).
12. Seal the petri dish and label the sample (figs. 7.4–7h and 7.4–7i).
13. Immediately store the filtered sample in a freezer or on dry ice. **Filter replicate samples and keep them frozen so that they can be sent to the laboratory later in case of loss, damage, or unusual results.**

a. Assemble the filtration unit and vacuum flask, and connect to the vacuum pump.

b. Use clean forceps to place a 47-millimeter glass fiber filter (Whatman™ GF/F or equivalent) on the base of the filter unit.

c. Clamp the funnel onto the filter unit, wet the filter with deionized water, and use the hand pump to draw a vacuum of 10 pounds per square inch.

Figure 7.4–7. Steps for processing algal samples.

d. Withdraw a measured volume, making sure the solution is well-mixed.

e. Pour measured amounts through the filter and record the volume.

f. Examine the filter. Sample volumes should be withdrawn to ensure that adequate algal biomass, indicated by a green or brown color, is retained on the surface of the glass-fiber filter after the filtration process. If algal coverage is sparse, repeat the previous step. This filter shows an ideal amount of algal biomass from a water source with little suspended mineral sediment.

Figure 7.4–7. Steps for processing algal samples — *continued.*

g. Using clean forceps, remove the filter from the filter unit, fold it in quarters (pie shape), wrap the folded filter in aluminum foil to protect from light, and place it in a clean petri dish.

h. Seal the petri dish with waterproof tape.

i. Label the sample, put it in a sealed plastic bag, and store in a freezer or on dry ice.

Figure 7.4–7. Steps for processing algal samples — *continued.*

TECHNICAL NOTES AND TIPS–6. Pipetting accurate volumes:

Measure and adjust, if necessary, the volume delivered by the pipettor—generally 5.0 mL—into a 10-mL graduated cylinder. The precise amount delivered by the pipettor may or may not be indicated by the graduations on the unit. Loosen the knob on the pipettor to adjust the volume up or down, depending on whether more or less volume delivery is indicated by the measurement in the graduated cylinder. Once adjusted, the volume delivered remains constant (± 0.1 mL), at least for that day.

7.4.5.B MEASURING MACROALGAL AND MACROPHYTE DRY MASS

Subsamples are processed for dry mass using Standard Methods (American Public Health Association, 1999, section 10400.D.3).

Use the following procedure when preparing a subsample for macroalgal and macrophyte dry-mass determination:

1. Measure the sample wet (fresh) weight
   a. Wash the sample to remove invertebrates, sediment, and organic debris.
   b. Remove excess moisture from the sample to obtain good consistency among samples and subsamples.
   c. Blot moisture from the sample using absorbent material such as paper towels.
   d. Supporting the sample on a nonabsorbent screen, centrifuge the sample by hand, or low-speed mechanism, or use another consistent method.
   e. Weigh the sample to the nearest 0.1 g.
2. Extract a representative subsample (at least 10 percent) from the wet-weight sample. Weigh the subsample and the record wet weight of the full sample and the subsample on field forms and the Analytical Services Request form.
3. Seal the subsample in aluminum foil, then label, freeze, and send to the laboratory.

SAMPLE HOLDING TIMES 7.4.5.C

The recommended length of time from the point of collection to the point in time when live samples are processed by filtering and freezing varies, depending on study or program requirements. The amount of time that a sample can be kept in the dark on ice without significant degradation of chlorophyll concentration ranges from hours for the most sensitive phytoplankton (oligotrophic lakes to less sensitive massive blooms of cyanobacteria), to days for periphyton (often with clumps and filaments) and larger, tougher macroalgal/macrophyte plants. Holding time is an important consideration because time-sensitive samples may need to be filtered in the field and placed on dry ice.

- The more biomass that needs to be processed, the greater the importance of doing the work under controlled conditions in the laboratory. Biggs (1987) found that mechanical blending to break up clumps of periphyton improved subsampling reproducibility. Studies by USEPA using methods 445.0 and 446.0 on phytoplankton processing from seawater suggest that the sample should be filtered as soon as possible after sampling since algal populations (thus, CHL *a* concentrations) can change in relatively short periods of time.
  - Strickland and Parsons (1972) state that phytoplankton may be stored in a cool dark place for up to 8 hours or for more prolonged periods at -20^{o}C after being filtered.
  - Storage experiments on periphyton samples (Biggs, 1987) found that it is possible to obtain reliable estimates of periphyton CHL *a* concentrations from 2 to 3 days after sample collection, as long as the samples are on ice and in the dark.
- **Once samples are filtered they must be frozen immediately and kept frozen until extraction in the laboratory.** The filters can be held in a freezer at the Water Science Center over the weekend. Holding time of filters for analysis is 24 days from the date of sample collection, so it is best to ship within a week of sampling.

7.4.6 FIELD-DATA DOCUMENTATION, LABELING, AND SAMPLE PACKAGING AND SHIPPING

Following the correct procedures for documentation, labeling, packaging, and shipping of samples is as neccessary for preserving sample integrity as is using the correct sampling and sample-processing methods and technique.

7.4.6.A Review of field forms and sample labels

The following guidance pertains to USGS protocols and procedures.

- Before departing from the sampling site, the field team should review all of the information recorded on the field forms, sample bottles, and petri dish labels for accuracy and completeness. Sample labels must include the station name and station number, date, time, type of sample, area or substrates sampled, total sample volume, subsample volume, and collector's name.
- Check the calculations of total volume and other sample information that were recorded on the field forms. Place clear tape over the completed sample label to protect it against deterioration in ice-filled or dry-ice filled shipping coolers. Place all field forms (blank and completed) in separate resealable bags for additional protection.

To complete field data documentation:

- To complete field data documentation:

  1. Record the following parameter codes on the field form and enter them into NWIS-QWDATA.
     - 00078 Secchi Depth
     - 00003 Sampling Depth
     - 84164 Sampler Type
     - 82398 Sampling Method
  2. Use the Data Qualifier Codes and the Field Result Comment to record any deviations from the sampling protocols, such as holding times, filtration times, and storage temperatures.

When labeling samples:

1. Label the petri dish with the following information:
   - Site identifier (ID)
   - Date
   - Time
   - Volume processed for CHL *a*, AFDM, or POC:
     – Record volume filtered in milliliters for phytoplankton.
     – Record total area (in square centimeters sampled, total sample volume (in milliliters), and subsample volume (in milliliters) filtered for periphyton.
   - Container type (for analysis of CHL *a*, AFDM, or POC)
2. Recommendation: On the foil surrounding the filter, write the date and a shortened form of the site and sample identifiers, in the event that the filter gets separated from its petri dish in the laboratory.

Packaging and shipping microalgal samples 7.4.6.B

Special procedures must be followed when packaging samples for microalgal analysis in order to prevent sample degradation. In addition, Federal regulations apply to all samples that are shipped on dry ice, including how to fill out the shipping label and airbill.

Sample packaging

▶ Package each filter separately by folding the filter twice with the sample folded inside, wrapping it in a small piece of foil, and placing it in a plastic petri dish (47 mm).

— Each sample that is sent to the USGS National Water Quality Laboratory (NWQL) will require a separate petri dish and label. However, if sample splits are being analyzed at a local laboratory, several filters of the same filtered volume may be placed in a single labeled petri dish.

— Although some laboratory schedules may include analysis for both CHL *a* and AFDM, these analytes have different holding times and the filters need to be packaged separately.

- The filter for POC analysis should be placed in aluminum foil envelope(s), then into two Whirl-Pak® bags (6-ounce and then a larger 18-ounce bag), and then maintained in an ice-filled cooler at or below 4°C during storage and shipment to the laboratory.
  - — **Samples can be shipped on ice or on dry ice.** Samples are frozen once they reach the NWQL.
  - — Ship POC samples and CHL *a* samples in two separate coolers.
- Seal the edge of the petri dish with plastic tape. Ensure that the necessary information is recorded on the sample label on the petri dish (site, date, total sample area, total volume, subsample volume, and sample identifier) and on the appropriate field form.
- Place the labeled petri dishes in resealable plastic bags in a cooler containing dry ice.
- Attach the necessary Analytical Services Request (ASR) form and data information to the inside lid of the cooler that contains the sample(s) and dry ice. These **ASR forms must be in the same cooler as the samples** so they do not become separated, especially if a cooler is placed within a cooler.

Shipping samples on dry ice by Priority Overnight

The U.S. Department of Transportation regulates the shipment of dry ice because it is a hazardous material. Atmospheric concentrations of carbon dioxide greater than 5 percent (60 g/m^3) are immediately dangerous to life or health. Dry ice is classified as a class 9 miscellaneous hazard and there are fines and penalties that the shipper may be subject to if improper procedures are followed. **The improper packaging of dry ice may result in explosion, suffocation, and (or) severe burns.**

- Use a minimum of 10 lbs of dry ice per day to keep samples frozen.
- The packaging must be able to withstand the extremely cold temperature of the dry ice without becoming brittle in order to prevent exposure to humans. Usually a small cooler or ice chest is used.

- The packaging must allow for the escape of carbon dioxide gas in order to prevent explosion. Punch a small hole in any plastic bags that may contain the dry ice. When taping the cooler lid shut leave a little slack in the packing tape so that the lid can move slightly.
- Samples must be secured so that they will remain in contact with the dry ice during shipping, taking into account that the dry ice will shrink as it sublimates.
- All free space must be occupied with packing material to minimize the volume of air. Good examples of packing materials are cardboard, newspaper, and styrofoam. **Do not use bubble wrap,** as the extreme cold of the dry ice causes the air to contract, turning the bubble wrap into a sheet of plastic.
- Do not ship samples unless they can be received by the laboratory the next day. Ship Monday through Thursday overnight if possible. Notify the analytical laboratory that samples are on the way.

Shipping label and airbill

- Dry ice labels can be obtained directly from the selected transportation carrier. Fill out the label completely. A dry ice sticker selection can be found at: http://images.google.com/images?svnum=10&hl=en&lr=&q=dry+ice+label (Accessed August 28, 2007.)
- On the an airbill, section 6 Special Handling, under the question "Does this shipment contain dangerous goods?" you must check "Yes Shipper's Declaration not required." Just to the right of that box is another checkbox, number 6, for Dry Ice. Check the box and enter the number of packages and their weight in kilograms.
- Note for USGS personnel when submitting frozen samples to NWQL:
  - **Call the NWQL** and make arrangements to ship CHL *a*/AFDM filters to NWQL with a shipper that can handle the dry-ice component of the samples. Prepare the NWQL ASR forms and shipping labels in advance.
  - **Do not ship samples on Fridays.** The filters can be held in a freezer at the Water Science Center over the weekend. The holding time of filters for analysis is 24 days; **ship samples within 1 week of sampling.**

— **Samples that must be submitted frozen, such as chlorophyll, will be qualified as "Sample warm when received" if they arrive at the laboratory (NWQL) at a temperature greater than 2°C.** The collector and project chief listed on the ASR will receive an e-mail indicating that an exception was created due to samples arriving at the improper temperature.

— Retain duplicate CHL *a* filters frozen, as backup samples, for analysis in case of shipping problems.

TECHNICAL NOTES AND TIPS–7. Maintaining dry ice:

To prevent dry ice from sublimating, keep the dry ice well insulated. Use a small cooler in the field for freezing the filtered samples. Package the cooler with newspaper or brown paper bags, and layer the top with a plastic bag to create an air-tight seal. Place samples at the bottom of the cooler, because warm air rises. Only open the cooler for brief periods when necessary to add or remove samples. Following these tips will decrease the amount of dry ice required (10 lbs for small 'pony' coolers) and extend the viability of the dry ice. For shipping to the NWQL, 10 lbs of dry ice per day of travel is recommended (a minimum of 20 lbs to ensure that samples arrive safely).

— Example of log-in codes for CHL *a*, AFDM, and POC, for submitting samples to the NWQL are provided in table 7.4–10. Use a consistent scheme for recording times based on the kind of sample. For example, the blank is recorded 1 minute before the environmental sample. The environmental sample is set for the nearest 10 minutes (such as 0900, 0910, 0920). The first replicate recorded as 1 minute after the environmental sample and the second replicate is recorded as 2 minutes after the environmental sample. **Note that medium codes are different for chlorophyll samples collected from phytoplankton/seston in the water column where the medium code is '9' for surface water, or from periphyton where the medium code is 'D' for plant tissue.**

Table 7.4–10. Example of log-in codes for submitting samples of chlorophyll *a,* ash-free dry mass, and particulate organic carbon to the USGS National Water Quality Laboratory.

[POC, particulate organic carbon; AFDM, ash-free dry mass; lab, laboratory; IND, Indiana Water Science Center laboratory; Q, quality-assurance sample-artificial; 2, blank sample; NWQL, National Water Quality Laboratory; 9, surface water; 7, replicate; D, plant tissue; R, quality-assurance sample-surface water; Y, quality-assurance sample-plant tissue; OEPA, Ohio Environmental Protection Agency; NA, not collected; envi, environmental; rep, replicate; --, not applicable]

	Phytoplankton and POC					Periphyton and AFDM				
Time	**Kind**	**Lab**	**Medium Code**	**Sample type**	**POC lab**	**Kind**	**Lab**	**Medium Code**	**Sample type**	**AFDM lab**
0959	blank	IND	Q	2	NA	blank	IND	Q	2	NA
1000	envi	IND	9	7	NWQL	envi	IND	D	7	IND
1001	rep	IND	R	7	NA	rep	IND	Y	7	IND
1002	rep	IND	R	7	NA	rep	IND	Y	7	IND
1003	rep	NWQL	R	7	NA	rep	NWQL	Y	7	NWQL
1004	rep	OEPA	R	7	NA	rep	OEPA	Y	7	OEPA
Total filters per site	6	--	--	--	3	6	--	--	--	5

NOTE: Only one sample is collected per site for POC (total particulate carbon and nitrogen, NWQL schedule 2631), but the sample requires three filters per sample. For the phytoplankton samples, only one filter is needed (NWQL schedule 1637:CHL *a)* because POC is collected, but for the periphyton sample the schedule calls for two filters per sample (NWQL schedule 1632: 1 for CHL *a* and one for AFDM).

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7.4.8 ACKNOWLEDGMENTS

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APPENDIX 7.4–A.
Examples of Field Forms

(Modified from Moulton and others, 2002)

Page

STATION INFORMATION

Station name:		Date: (MM/DD/YY) _____/_____/_____
Station identification number:	Reach ID:	Time:_____ h
Collectors (leader):		

RELATED SAMPLING ACTIVITIES (check)

Water chemistry	Discharge	Habitat Survey	Tissues
Invertebrate survey	Fish Survey	Bed Sediment	Other:
Sample and Photographic Notes:			
Remarks:			

PHYSICAL SITE CONDITIONS

Clouds: %	Wind (circle): Calm	Light	Moderate	Gusty			Precipitation (circle): None	Rain Sleet Snow
Other:								
Stream stage: ft @ time h	Discharge:						ft^3/s Velocity (range)	cm/s
Start time:____ h ; Water Temp. ___ C ; Dissolved oxygen (DO) _____ mg/L; ___pH; Specific cond.: ___uS/cm								
Finish time: h; Temp. C; DO mg/L; pH; Specific conductance: uS/cm								
Water clarity (circle):	Very turbid	Turbid	Slightly turbid	Clear			Turbidity:	NTUs
Water color (circle):	Clear	Black	Brown	Silty-tan	Stained	Golden	Reddish	Light green Dark green
Riparian shading (circle):	Exposed	Partially shaded	Shaded					

SAMPLING INFORMATION — Phytoplankton

Sampling method or device (check or specify):	DH 81 sampler _____	Kemmerer _____	Van Dorn _____
	Grab sample_____	Other (specify):	
	Subsurface depth where sample is collected: _____cm		
Location where sample is collected in the reach:			

Phytoplankton subsample type: (check)	Subsample volume:	Preservative volume in mL:	Sample identification numbers:
ID/enumeration:	_____mL	mL	
Chlorophyll:	___filters x ____mL=____mL	Dry ice	
Ash-free dry mass:	___filters x ____mL=____mL	Dry ice	
Residual volume:	___mL	NA	Spilled or decanted volume, no ID
Total volume of sample before subsampling: mL			
Type of preservative for ID sample, if included (circle one): Conc. Formalin Formalin (10%) Lugol's other_____			

Figure 1. Quantitative Phytoplankton Field Form

PHYTOPLANKTON SAMPLING INFORMATION (continued)			
Quality assurance sample? Y N	Type and number of QA samples: Split _____		Replicate _____
Subsample type: (check)	Subsample volume:	Preservative	Subsample ID no.:
ID/enumeration:	mL	mL	
Chlorophyll:	mL	Dry ice	
Ash-free dry mass:	mL	Dry ice	
Residual volume:	mL	NA	NA
Total	mL	NA	NA
Type of preservative (circle one): Conc. Formalin Formalin (10%); Lugol's; other _____			
Remarks:			

SUPPORTING INFORMATION					
Sample location number	Water depth (cm)	Velocity (cm/s)	Secchi depth (cm) or Turbidity NTUs	Light intensity	Other
1					
2					
3					
4					
5					

LIGHT MEASUREMENTS					
Distance from water surface	Water depth (cm)	Light intensity Reading Location #1	Light intensity Reading Location #2	Light intensity Reading Location #3	Average Light intensity Reading
Reference above water surface	-10				
1.Below water surface	1		0		
2.At equal depth intervals down to the euphotic depth, where possible					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					

Figure 1. Quantitative Phytoplankton Field Form — *continued*

STATION INFORMATION

Station name:		Date: (MM/DD/YY) _____/_____/_____
Site identification number:	Reach ID:	Time:_____ h
Collectors (leader):		

RELATED SAMPLING ACTIVITIES (check)

Water chemistry	Discharge	Habitat Survey	Tissues
Invertebrate survey	Fish Survey	Bed Sediment	Data sonde_____ Hobo Temp. ___Other:
Sample and Photographic Notes:			
Remarks:			

PHYSICAL SITE CONDITIONS

Clouds: %	Wind (circle): Calm Light Moderate Gusty	Precipitation (circle): None Rain Sleet Snow
Other:		
Stream stage: ft @ time h Discharge ft^3/s Velocity (range) cm/s		
Start time: h; Water temp. ____ C; Dissolved oxygen (DO) ___ mg/L; ___ pH; Specific cond.: ___uS/cm		
Finish time: h; Water Temp. C; DO mg/L; pH; Specific cond.: uS/cm		
Water clarity (circle): Very turbid Turbid Slightly turbid Clear : Turbidity _____NTU		
Water color (circle): Clear Black Brown Silty-tan Stained Golden Reddish Light green Dark green		
Riparian shading (circle): Exposed Partially shaded Shaded		

SAMPLING INFORMATION — MICROALGAE

Periphyton microhabitat sampled (check):	Epipelic	Epidendric	Epiphytic
	Episammic	Epilithic	Other
Sampling method or device (check or specify):	SG-92	Top-rock scrape	Cylinder scrape
	Slack sampler	Gravel sampler	Petri dish
	Other (specify)		
Measured areas sampled by device and microalgal cover (0-5) see scale below:	Beginning diameter: cm/	Ending diameter: cm/	

cm/	cm/	cm/	cm/	cm/	cm/	cm/	cm/
cm/	cm/	cm/	cm/	cm/	cm/	cm/	cm/
cm/	cm/	cm/	cm/	cm/	cm/	cm/	cm/

Average area sampled by device (SA): cm^2	
Number of areas sampled:	Total area of microalgal periphyton sample: cm^2
	Total volume of sample before subsampling: mL

Microalgal cover	Definition of periphyton abundance survey form categories
0	Substrate rough with no visual evidence of microalgae
0.5	Substrate slimy, but no visual accumulation of microalgae is evident
1	A thin layer of microalgae is visually evident
2	Accumulation of microalgae layer from 0.5 mm to 1 mm thick is evident
3	Accumulation of microalgae layer from 1 mm to 5 mm thick is evident
4	Accumulation of microalgae layer from 5 mm to 2 cm thick is evident
5	Accumulation of microalgae layer greater than 2 cm thick is evident

Figure 2. Quantitative Targeted-Habitat Periphyton Field Form

SAMPLING INFORMATION – MICROALGAE (continued)			
Subsample type:(check)	Subsample volume amounts:	Preservative volume:	Sample identification numbers:
ID/enumeration:	____mL	mL	
Chlorophyll:	___filters x____mL=____mL	Dry ice	
Ash-free dry mass:	___filters x____mL=____mL	Dry ice	
Residual volume:	_____mL	NA	Spilled or decanted volume, no ID #
Total volume of sample before subsampling: mL			
Type of preservative (circle one): Formaldehyde; Formalin (10%); Lugol's; other_____			

Quality assurance sample? Y N		Type: Split Replicate	
Subsample type: (check)	Subsample volume:	Preservative:	Sample identification numbers:
Chlorophyll:	#___filters x____mL=____mL	Dry ice	
Ash-free dry mass:	#___filters x____mL=____mL	Dry ice	
Total volume of sample before subsampling: mL			

SUPPORTING INFORMATION					
Sample location number	Water depth (cm)	Velocity (cm/s)	Secchi depth (cm) or Turbidity NTUs	Riparian shading (shaded, partial or full sun)	Macroalgae present:Y N Type of algae or color; Other:
1					
2					
3					
4					
5					

LIGHT MEASUREMENTS							
Distance from water surface	Water depth (cm)	Light intensity reading location 1	Light intensity reading location 2	Light intensity reading location 3	Average light intensity (units)	Difference between subsurface reading and available light	Percent reduction of available light with depth
Reference above water surface	-10						
1.Below water surface	1					0	0
2.At 5 to10 cm below water surface, and equal depth intervals down to streambed							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
11.							

Figure 2. Quantitative Targeted-Habitat Periphyton Field Form — *continued.*

STATION INFORMATION

Station name:		Date: (MM/DD/YY) _____/_____/_____
Site identification number:	Reach ID:	Time:_____ h
Collectors (leader):		

RELATED SAMPLING ACTIVITIES (check)

Water chemistry	Discharge	Habitat Survey	Tissues
Invertebrate survey	Fish Survey	Bed Sediment	Data sonde_____ Hobo Temp. ___Other:
Sample and Photographic Notes:			
Remarks:			

PHYSICAL SITE CONDITIONS

Clouds: %	Wind (circle): Calm Light Moderate Gusty	Precipitation (circle): None Rain Sleet Snow
Other:		
Stream stage: ft @ time h Discharge ft^3/s Velocity (range) cm/s		
Start time:_____h; Water temp. ____ C; Dissolved oxygen (DO)____ mg/L; ____pH; Specific cond.: ____uS/cm		
Finish time: h; Water Temp. C; DO mg/L; pH; Specific cond.: uS/cm		
Water clarity (circle): Very turbid Turbid Slightly turbid Clear : Turbidity _____NTU		
Water color (circle): Clear Black Brown Silty-tan Stained Golden Reddish Light green Dark green		
Riparian shading (circle): Exposed Partially shaded Shaded		

SAMPLING INFORMATION — MACROALGAE (RTH component A)

Periphyton microhabitat sampled (check):		Epipelic	Epidendric		Epiphytic	
		Episammic	Epilithic		Other	
Sampling method or device (check or specify):		Slack sampler	Top-rock scrape		Gravel core	
Other (specify)		Square frame				
Measured areas sampled by device:	Beginning area:		cm^2	Ending area:		cm^2
Average area sampled by device (SA):						
Number of areas sampled:	Total area of macroalgal periphyton sample:					m^2

Wet weight per sampling area:	g	g	g	g	g	Total g/m2
Dry weight per sampling area:	g	g	g	g	g	Total g/m2

Sample identification number:			
Subsample type (check):	Subsample volume:	Preservative voulme:	Sample identification number:
ID/enumeration:	____mL	mL	
Chlorophyll:	filters x mL= mL	Dry ice	
Ash-free dry mass:	filters x mL= mL	Dry ice	
Residual volume:	____mL		NA
Total sample volume:	____mL		NA
Type of preservative for ID sample, if included (circle one):	Conc. Formalin	Formalin (10%)	Lugol's other_____

Figure 3. Quantitative Macroalgae Field Form

Page No. [ ]

STATION INFORMATION		
Station name:		**Date: (MM/DD/YY)** _____/_____/_____ **Time:**_____ **h**
Site identification number:	Reach ID:	
Collectors (leader):		

RELATED SAMPLING ACTIVITIES (check)			
Water chemistry	Discharge	Habitat Survey	Tissues
Invertebrate survey	Fish Survey	Bed Sediment	Other:
Sampling conditions and Photographic Notes:			

Particle size diameter mm or Si = silt, Sa = sand, O = organic matter	Periphyton abundance									Comments: Periphyton color; name of dominant algae; maximum length of macroalgae
	Microalgae (check)							Macroalgae (Check)		
	0	0.5	1	2	3	4	5	Macroalgae (M or check)	Macroalgal cover: nearest 10 percent (0 to 100 percent)	
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
Subtotal										

Figure 4. Periphyton Abundance Survey Field Form

Page No. [ ]

Particle size diameter mm or Si = silt, Sa = sand, O = organic matter	Periphyton abundance: Site name and date.									Comments: Periphyton color; name of dominant algae; maximum length of macroalgae
	Microalgae (check)							Macroalgae (Check)		
	0	0.5	1	2	3	4	5	Macroalgae	Macroalgal cover: nearest 10 percent (0 to 100 percent)	
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
10										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										
42										
43										
44										
45										
46										
47										
48										
49										
50										
Subtotal										

Figure 4. Periphyton Abundance Survey Field Form — *continued*

Page No. [ ]

Particle size diameter mm or Si = silt, Sa = sand, O = organic matter	Periphyton abundance, Site name and Date.									Comments: Periphyton color; name of dominant algae; maximum length of macroalgae
	Microalgae (check)							Macroalgae (Check)		
	0	0.5	1	2	3	4	5	Macroalgae	Macroalgal cover: nearest 10 percent (0 to 100 percent)	
51										
52										
53										
54										
55										
56										
57										
58										
59										
60										
61										
62										
63										
64										
65										
66										
67										
68										
69										
70										
71										
72										
73										
74										
75										
76										
77										
78										
79										
80										
81										
82										
83										
84										
85										
Subtotal										

Figure 4. Periphyton Abundance Survey Field Form — *continued*

Page No. [ ]

Particle size diameter mm or Si = silt, Sa = sand, O = organic matter	Periphyton abundance: Site name and date									Comments: Periphyton color; name of dominant algae; maximum length of macroalgae
	Microalgae (check)							Macroalgae (Check)		
	0	0.5	1	2	3	4	5	Macroalgae (M or check)	Macroalgal cover: nearest 10 percent (0 to 100 percent)	
86										
87										
88										
89										
90										
91										
92										
93										
94										
95										
96										
97										
98										
99										
100										
Totals										

Microalgal cover	1. Definition of periphyton abundance survey form categories
0	Substrate rough with no visual evidence of microalgae
0.5	Substrate slimy, but no visual accumulation of microalgae is evident
1	A thin layer of microalgae is visually evident
2	Accumulation of microalgae layer from 0.5 mm to 1 mm thick is evident
3	Accumulation of microalgae layer from 1 mm to 5 mm thick is evident
4	Accumulation of microalgae layer from 5 mm to 2 cm thick is evident
5	Accumulation of microalgae layer greater than 2 cm thick is evident
Macroalgae percent cover	Record M if macroalgae are present and estimate the percent to the nearest 10 percent

Figure 4. Periphyton Abundance Survey Field Form — *continued*

CYANOBACTERIA IN LAKES AND RESERVOIRS: TOXIN AND TASTE-AND-ODOR SAMPLING GUIDELINES 7.5

By Jennifer L. Graham, Keith A. Loftin, Andrew C. Ziegler, and Michael T. Meyer

Illustrations

Tables

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CYANOBACTERIA IN LAKES AND RESERVOIRS: TOXIN AND TASTE-AND-ODOR SAMPLING GUIDELINES 7.5

By **Jennifer L. Graham, Keith A. Loftin, Andrew C. Ziegler, and Michael T. Meyer**

Cyanobacteria (also referred to as blue-green algae) cause a multitude of water-quality concerns, including the potential to produce toxins and taste-and-odor compounds. Toxins and taste-and-odor compounds may cause significant economic and public health concerns, and are of particular interest in lakes, reservoirs, and rivers that are used for drinking-water supply, recreation, or aquaculture. The purpose of NFM 7.5 is to provide guidelines for collecting, processing, and handling samples to be analyzed for cyanobacterial community composition (enumeration and identification) and total, particulate, and dissolved cyanobacterial toxins and taste-and-odor compounds in lakes and reservoirs (sections 7.5.5 through 7.5.9). Sections 7.5.1 through 7.5.4, however, are designed to provide some background information about cyanobacteria, including typical study designs and objectives related to the spatial and temporal occurrence of cyanobacteria (modified from Graham and others, 2008), in order to provide a useful context for sampling activities. The information presented here pertains to the occurrence of planktonic (free-floating) cyanobacteria in lakes and reservoirs.[1]

Cyanobacteria: True bacteria with a prokaryotic cell structure and containing chlorophyll-*a* (a photopigment characteristic of eukaryotic algae and higher plants).[2]

Algal groups other than cyanobacteria may cause taste-and-odor problems in drinking-water supplies, but the most frequent and severe events are associated with cyanobacteria (Wnorowski, 1992; Rashash and others, 1996; Taylor and others, 2005). One other freshwater/brackish water alga (the haptophyte *Prymnesium parvum*) is known to produce icthyotoxins under certain conditions; these icthyotoxins have been associated with fish kills only and not with human illness (Sager and others, 2007). All sampling guidelines presented in NFM 7.5 focus on planktonic cyanobacteria, but these guidelines also may apply to water-quality studies of other planktonic algal groups, depending on study objectives.

[1]Benthic cyanobacteria in lakes, reservoirs, streams, and rivers also may produce toxins and taste-and-odor compounds (Graham and others, 2008). Topics that address the sampling of benthic cyanobacteria in aquatic ecosystems are beyond the scope of this section of the *National Field Manual*.

[2]Terms related to cyanobacteria and algae are defined in the glossary, section 7.5.12.

Cyanobacterial toxins (also referred to as cyanotoxins) have been implicated in human and animal illness and death in more than 50 countries worldwide, and in at least 27 States in the United States (Graham, 2006). Human toxicoses associated with cyanobacterial toxins most commonly have occurred after exposure to the toxins through drinking water or through recreational activities (Yoo and others, 1995; Chorus and Bartram, 1999; Falconer, 2005; Huisman and others, 2005; Graham, 2006). Taste-and-odor compounds cause malodorous or unpalatable drinking water and fish flesh, resulting in increased treatment costs for drinking water and loss of recreational or aquacultural revenue. Federal and State agencies, resource managers, drinking-water treatment-facility operators, lake associations, and local officials increasingly are faced with decisions about managing cyanobacterial blooms that affect local economies and public health. Therefore, representative scientific data are needed to guide water management and public health decisions about cyanobacterial toxins and taste-and-odor compounds.

The study of cyanobacterial toxins and taste-and-odor compounds is an area of developing research. Although many approaches have been used in the design, sample collection, and analysis of studies addressing these cyanobacterial by-products, consistent guidelines for the development of such studies are necessary for making cross-comparisons among the data collected for these studies (Graham and Jones, 2007; Tillmanns and others, 2007). Collecting data that are comparable among a broad spectrum of studies is of particular importance in meeting the needs of the Nation and the mission of the U.S. Geological Survey (USGS).

7.5.1 LIGHT INTENSITY AND THERMAL STRATIFICATION IN LAKES AND RESERVOIRS

Lakes and reservoirs are characterized by vertical gradients caused by light and thermal stratification. An understanding of these gradients is required when designing water-quality studies and sampling guidelines for lakes and reservoirs.[3] More detail on light and thermal stratification in lakes and reservoirs can be found in Horne and Goldman (1994), Lampert and Sommer (2007), Wetzel and Likens (2000), and Wetzel (2001).

Light intensity decreases exponentially with depth, and a light gradient is present in all lakes and reservoirs (fig. 7.5–1). The terms photic (or euphotic) and aphotic zone are used to describe the major light gradients.

- **Photic (euphotic) zone –** The region where there is enough light to support photosynthesis; extends from the surface to the depth where light is approximately one percent of that at the surface.
- **Aphotic zone –** The region where there is not enough light to support photosynthesis; extends from below the photic zone to the bottom of the water body.

[3]The information and sampling approaches described herein are appropriate for lakes and reservoirs (the term "lakes", as used in this NFM section, applies also to reservoirs); however, lakes and reservoirs have distinct morphological and hydrological differences that influence water chemistry and biological communities. Topics that address the differences between lakes and reservoirs are beyond the scope of this report. For more information on the differences between lakes and reservoirs see Thornton and others (1990), Horne and Goldman (1994), and Wetzel (2001).

Thermal stratification creates isolated layers that result in thermal and chemical (such as nutrient) gradients; stratification is the result of differences in density associated with temperature (fig. 7.5–1). Stratification in deep lakes and reservoirs (referred to below as lakes) tends to be stable, whereas daily or continual mixing may occur in shallow lakes. Thermal stratification is a summer phenomenon in temperate lakes, but may occur year-round in subtropical and tropical lakes. Spatial variability of stratification within lakes and reservoirs is common because of changes in depth and other morphological features. Common terms that will be used throughout this guidance that relate to lake and reservoir stratification include:

- **Epilimnion –** The warm, buoyant upper layer of a stratified lake.
- **Metalimnion –** The middle layer of a stratified lake; the metalimnion is characterized by substantial decreases in temperature with depth.
- **Thermocline –** The region where temperature change is greater than or equal to 1°C per meter; the terms thermocline and metalimnion often are used synonymously.
- **Hypolimnion –** The cold, dense bottom layer of a stratified lake; the hypolimnion often becomes anoxic (little or no dissolved oxygen) in productive systems.
- **Turnover –** Complete isothermal mixing of a previously stratified lake.
- **Mixed Depth –** The depth of turbulent mixing; may include all or only a part of the water column, depending on stratification, solar irradiance, and wind.

During calm periods, temporary mixed layers (lasting hours to weeks) may form in shallow lakes, deeper lakes that do not typically stratify, or in the epilimnion of stratified lakes, creating greater complexity in vertical structure. Mixing in shallow and stratified lakes will vary daily and seasonally depending on solar irradiance and wind. Thermal stratification is most common, but gradients in water chemistry (often caused by submerged springs), such as salinity, also may cause stratification (Horne and Goldman, 1994; Lampert and Sommer, 2007; Wetzel and Likens, 2000; Wetzel, 2001).

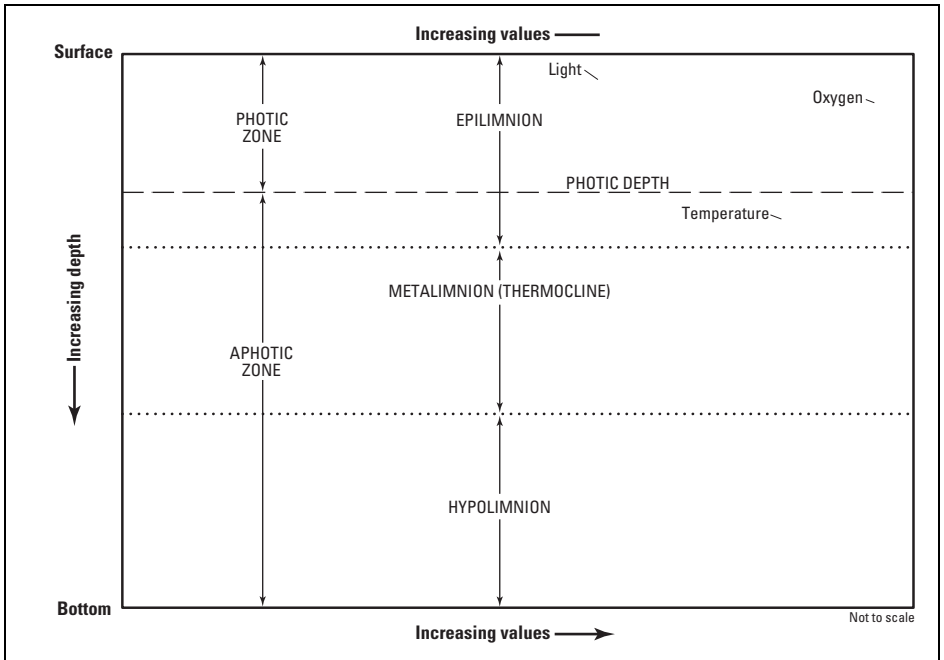


Figure 7.5–1. Stratification and light, temperature, and oxygen gradients that may develop in lakes and reservoirs. From Graham and others (2008).

7.5.2 CYANOBACTERIA, TOXINS, AND TASTE-AND-ODOR COMPOUNDS

Cyanobacteria (fig. 7.5–2) are true bacteria with a prokaryotic cell structure; however, cyanobacteria also have chlorophyll-*a*, a photopigment characteristic of eukaryotic algae and higher plants. Structurally the cyanobacteria are bacteria-like, but functionally the cyanobacteria are algae-like. Because of this photosynthetic functionality, cyanobacteria typically are sampled and analyzed as part of phytoplankton (algal) assemblages rather than bacterial assemblages in aquatic ecosystems (Wetzel, 2001; see NFM 7.4).

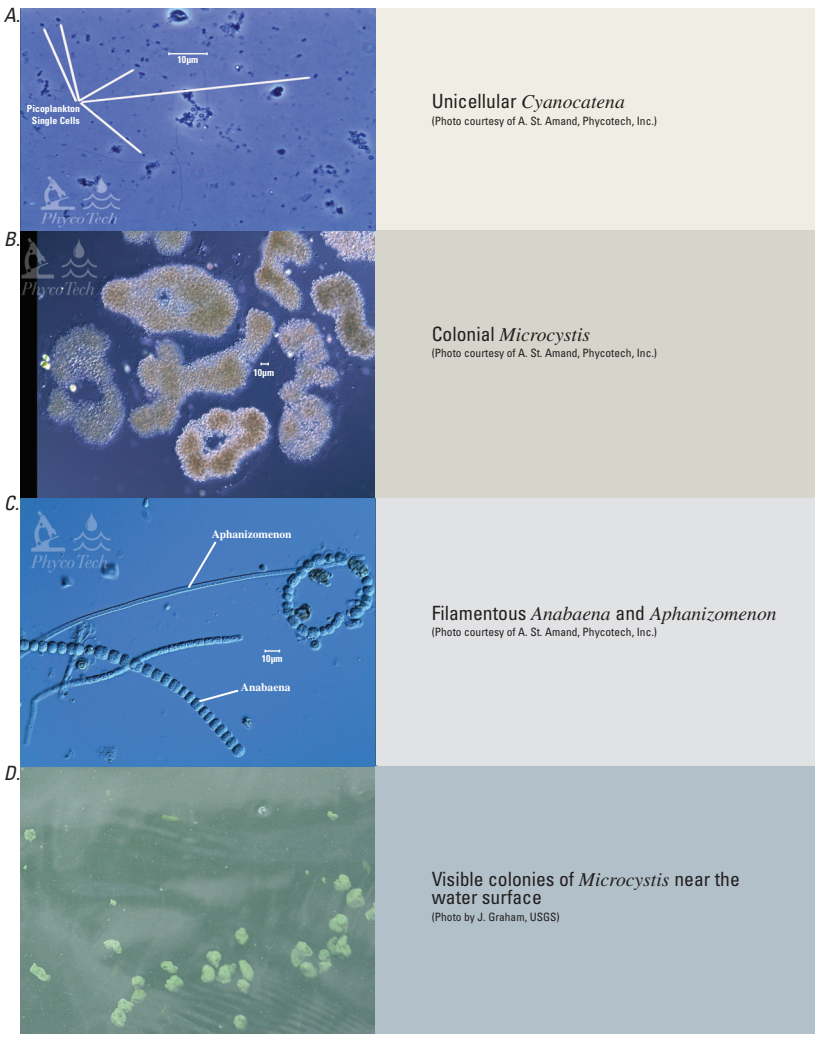


Figure 7.5–2. Examples of cyanobacteria. Cyanobacteria may be unicellular (***A***), colonial, (***B***), or filamentous (***C***) and range in size from 0.2 micrometers to greater than 1,600 micrometers. Larger filaments and colonies are often visible to the naked eye (***D***). From Graham and others (2008).

Cyanobacterial toxins and taste-and-odor compounds are naturally produced algal by-products; however, the function of these compounds currently (2008) is unknown. Hypothesized functions include primary roles in cellular processes, secondary metabolites, allelopathy, or defense mechanisms. Production of toxins and taste-and-odor compounds is strain, rather than species, dependent. Any one cyanobacterial species may have multiple strains, and toxic and non-toxic strains may occur simultaneously in an individual lake or reservoir (Vézie and others, 1998).

Most cyanobacterial taxa do not produce toxins or taste-and-odor compounds, but many of the common planktonic genera contain one or more toxin or (and) taste-and-odor producing strains (table 7.5–1). Whereas some strains may produce toxin and taste-and-odor compounds simultaneously, these compounds do not necessarily co-occur and the presence and concentration of one may not be used reliably to predict the presence and concentration of another (Chorus and Bartram, 1999).

Because toxin and taste-and-odor production is strain dependent, algal identification alone cannot be used to determine whether or not these by-products will be present, although genera that contain strains producing these compounds can be identified. Likewise, co-occurrence of potential producers and toxin and (or) taste-and-odor compounds does not positively identify the actual producer.

- Strain isolation and culture are required to conclusively determine the producer(s) of measured toxin and (or) taste-and-odor compounds.
- Genetic techniques that isolate specific gene clusters also are promising in identifying toxin producers in complex environmental samples.

Cyanobacteria typically are sampled and analyzed as part of phytoplankton (algal) assemblages rather than bacterial assemblages in aquatic ecosystems (NFM 7.4).

Table 7.5–1. Common genera of planktonic cyanobacteria that contain toxin and taste-and-odor producing strains.

[All data included in this table are based on documented production in laboratory cultures; data based on circumstantial evidence, such as co-occurrence of genera and toxin or taste-and-odor compounds in environmental samples, were not included. LYN, lyngbyatoxin-a; APL, aplysiatoxins; LPS, lipopolysaccharides; CYL, cylindrospermopsins; MC, microcystins; NOD, nodularins; ATX, anatoxins; BMAA, β-N-methylamino-L-alanine; NEO, neosaxitoxins; SAX, saxitoxins; GEOS, geosmin; MIB, 2-methylisoborneol]

	Dermatoxins				Hepatotoxins				Neurotoxins					Tastes and odors	
Cyanobacterial Genera	**LYN**	**APL**	**LPS**		**CYL**	**MC**	**NOD**		**ATX**	**BMAA**	**NEO**	**SAX**		**GEOS**	**MIB**
Colonial/Filamentous															
Anabaena			X		X	X			X	X	X	X		X	
Anabaenopsis			X			X									
Aphanizomenon			X		X				X	X	X	X		X	
Aphanocapsa			X			X									
Cylindrospermopsis			X		X					X		X			
Microcystis			X			X				X					
Nodularia			X				X			X					
Oscillatoria (Planktothrix)	X	X	X			X			X	X		X		X	X
Pseudanabaena			X			X			X					X	X
Raphidiopsis			X		X				X						
Unicellular															
Synechococcus			X			X				X				X	X
Synechocystis			X			X				X					

Sources: Wu and others (1991), Wnorowski (1992), Blevins and others (1995), Carmichael (1997), Bláha and Maršálek (1999), Chorus and Bartram (1999), Domingos and others (1999), Saadoun and others (2001), Oudra and others (2002), Watson (2003), Huisman and others (2005), and Taylor and others (2005). A comprehensive list of known cyanobacterial toxin and taste-and-odor producers is not currently (2008) available in the literature. Combined, the references used to create this table may be used to create a fairly complete list of planktonic and benthic producers.

7.5.2.A CYANOBACTERIAL ABUNDANCE, OCCURRENCE, AND DISTRIBUTION

Cyanobacteria are a natural part of phytoplankton assemblages in lakes and reservoirs and commonly are present in at least low abundances (Reynolds, 1984; Jones and Korth, 1995). Cyanobacterial abundance and community composition vary seasonally as a result of changes in water temperature, solar irradiance, meteorological conditions, hydrology, and nutrient supply. In temperate climates, cyanobacteria typically dominate the phytoplankton during midsummer to early fall, but may become dominant any time throughout the year, even under ice during winter. In subtropical and tropical climates, cyanobacteria may dominate at any time, and dominance may persist year-round (Chorus and Bartram, 1999; Wetzel, 2001; Falconer, 2005; Huisman and others, 2005).

Eutrophication results in conditions that are favorable for cyanobacterial growth (elevated nutrients, reduced light penetration), and cyanobacterial blooms frequently occur in eutrophic (nutrient rich, high productivity) lakes and reservoirs. Cyanobacterial blooms also may occur in oligotrophic (nutrient poor, low productivity) systems, although not as frequently as in eutrophic systems. Blooms in oligotrophic systems often are associated with benthic cyanobacteria or favorable nutrient and light conditions at depth in a stably stratified water column (Reynolds, 1984; Chorus and Bartram, 1999; Wetzel, 2001; Falconer, 2005; Huisman and others, 2005).

Many, although not all, cyanobacteria have gas vacuoles that allow them to maintain a favorable position in the water column by regulating buoyancy. Light (the photic depth), nutrients, carbon availability, stratification, and mixed depth (depth of turbulent mixing in the water column) all affect cyanobacterial position in the water column. Optimal water-column position is species specific. Three distinct patterns in distribution may develop (Reynolds and Walsby, 1975; Reynolds, 1987; Humphries and Lyne, 1998):

1. Cyanobacteria may maintain a position in the photic zone, regardless of mixed depth. Populations typically are distributed uniformly throughout the photic zone. This distribution may develop in well-mixed lakes or reservoirs (referred to in this list as lakes) or in the epilimnion of stably stratified lakes. Many cyanobacterial genera, including *Anabaena*, *Aphanizomenon*, *Microcystis* (fig. 7.5–2) and *Cylindrospermopsis* display this type of buoyancy regulation.
2. Cyanobacteria may migrate to different locations in the photic zone throughout the day. Populations generally move toward the surface at night or in the early morning and downward later in the day. This diel movement of cyanobacterial populations typically is linked with the development of diel mixed layers in shallow lakes or in the epilimnion of stably stratified lakes. Regardless of movement or location, cyanobacteria typically maintain a position in the photic zone. In shallow lakes, where light penetrates to the bottom, cyanobacteria may spend part of the day on the sediment surface. Diel movement most commonly is associated with species of *Microcystis*, although *Anabaena* and other gas-vacuolate taxa also may migrate on a diel basis.
3. Cyanobacteria may maintain a position at a particular depth, typically at the interface between the epilimnion and metalimnion. This phenomenon is referred to as a metalimnetic bloom, and most commonly is associated with species of *Planktothrix* (*Oscillatoria*). Metalimnetic cyanobacterial blooms occur most frequently in mesotrophic lakes. For metalimnetic blooms to develop, the water column must be stably stratified and photic depth must penetrate into the metalimnion; metalimnetic cyanobacterial blooms can exist at light levels at or below one percent of incident light.

When referring to cyanobacteria, the term "bloom" commonly is associated with the accumulation of cyanobacteria at the water surface; however, cyanobacterial blooms are more typically mixed throughout the photic zone, epilimnion, or water column. Surface accumulations, or scums, may develop when cyanobacteria float to the surface during unusually calm conditions that cause a sudden change in turbulent mixing (sudden calm will not affect metalimnetic populations) or when cyanobacteria begin to senesce (age) and are no longer able to regulate buoyancy effectively. Surface accumulations occur most frequently after periods of calm, sunny weather and may develop and dissipate within a matter of hours as conditions change. Because the entire cyanobacterial population may accumulate within 1 to 2 centimeters (cm) of the water surface, cell densities may be extremely large (more than a million cells per milliliter), even if water-column densities were relatively small (less than 20,000 cells per milliliter). Surface accumulations of cyanobacteria may concentrate even further when wind blows to leeward areas (for example, near-shore areas, bays, and inlets), often resulting in the development of dense accumulations that may extend from the surface to depths of more than 1 meter (m) (Graham and others, 2008).

7.5.2.B TOXINS

Cyanobacterial toxins are chemically and bioactively diverse (Sivonen, 1996; Carmichael, 1997; Chorus and Bartram, 1999), all targeting fundamental cellular processes and thereby affecting a wide range of organisms (Falconer, 1993; Christofferson, 1996). **The cyanobacteria are the only member of freshwater phytoplankton communities known to produce toxins that also may affect terrestrial organisms.**

The most common cyanobacterial toxin groups are described in figure 7.5–3 and table 7.5–2. The three main classes of cyanobacterial toxins, defined by their effects on human health, are neurotoxins, hepatotoxins, and dermatoxins (Graham and others, 2008). Many of the cyanobacterial toxins have multiple variants, with some variants being more toxic than others. For example, the microcystins, currently believed to be the most common group of cyanobacterial toxins, have more than 80 known variants with LD_{50}'s (lethal dose required to kill 50 percent of the test population; determined by intraperitoneal mouse assays) ranging from 25 to greater than 1,000 micrograms per kilogram (µg/kg) (most variants fall within the 50 to 300 µg/kg range). The adverse health effects caused by contact with, or ingestion or inhalation of, large concentrations of cyanobacterial toxins (acute exposure) are well documented (table 7.5–2). The effects of exposure to low levels of cyanobacterial toxins for an extended period of time (chronic exposure), however, are not well understood (Chorus and Bartram, 1999; Graham and others, 2008).

- The greatest risk of exposure to elevated concentrations of cyanobacterial toxins probably is through accidental ingestion and inhalation during recreational activities. The World Health Organization (WHO) has defined the following low, moderate, high, and very high risk categories for adverse health effects that occur through recreational exposure to microcystins (Chorus and Bartram, 1999):
  - **Low risk**: less than 10 micrograms per liter (µg/L)
  - **Moderate risk**: 10–20 µg/L
  - **High risk**: 20–2,000 µg/L
  - **Very high risk**: greater than 2,000 µg/L
- The WHO has developed a provisional guideline of 1 µg/L for microcystin-LR in treated drinking water (Chorus and Bartram, 1999) and currently (2008) is developing a guideline for cylindrospermopsin. Falconer (2005) has proposed a guideline of 1 µg/L for cylindrospermopsins in finished drinking water.
- Several countries have set national standards or guidelines for microcystins in drinking water based on the WHO guideline, including Australia, Brazil, Canada, the Czech Republic, France, Poland, and Spain (Huisman and others, 2005). In the United States the cyanobacterial toxins microcystin, cylindrospermopsin, and anatoxin currently are on the U.S. Environmental Protection Agency (2005) drinking-water contaminant candidate list.

CAUTION: **Inhalation or ingestion of large concentrations of cyanobacterial toxins can result in adverse health effects.**

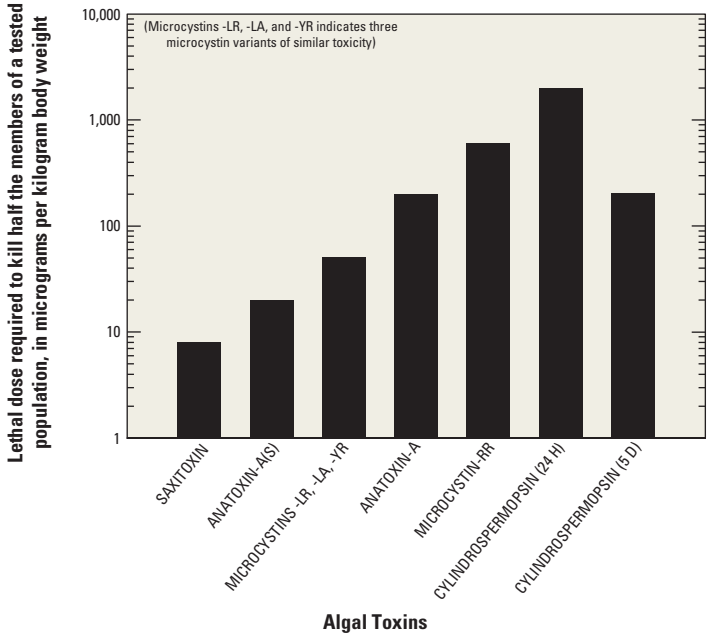


Figure 7.5–3. Toxicity of several cyanobacterial toxins (based on intraperitoneal mouse assays). From Graham and others (2008); figure based on data from Chorus and Bartram (1999).

Table 7.5–2. Common cyanobacterial toxins, toxicity (based on intraperitoneal mouse assays), and common effects of exposure.

[Most toxin groups have several variants with a range of toxicities. Although known chronic effects are listed, the chronic effects of exposure to cyanotoxins currently (2008) are not well understood. LD_{50}, lethal dose required to kill half of the members of a tested population; µg/kg, micrograms per kilogram of body weight; --, no data available; >, greater than]

Class	Toxin	Toxicity (LD_{50})	Acute effects	Chronic effects
Neurotoxins	Anatoxins	20–250 µg/kg	Seizure, paralysis, respiratory failure, death	Unknown
	Saxitoxins[1]	10 µg/kg	Tingling or numbness in extremities, paralysis, respiratory failure, death	Unknown
	β-N-methylamino-L-alanine (BMAA)	--	--	Neurodegenerative disease
Hepatotoxins	Microcystins	25 to > 1,000 µg/kg	Acute hepatoenteritis, shortness of breath, interhepatic hemorrhage, hemorrhagic shock, heart failure, death	Chronic liver injury, tumor promoter
	Cylindrospermopsins	200–2,100 µg/kg	Acute hepatoenteritis; renal, lung, heart, spleen, thymus, and adrenal damage; death	Potential carcinogen, mutagen
	Nodularins[2]	50 µg/kg	Similar to microcystins	Tumor promoter
Dermatoxins	Lyngbyatoxins	300 µg/kg	Severe dermatitis, gastroenteritis	Tumor promoter
	Aplysiatoxins	300 µg/kg	Severe dermatitis, gastroenteritis	Tumor promoter
	Lipopolysaccharides	--	Dermatitis, gastroenteritis	Unknown

[1]Also known as paralytic shellfish poisons (PSPs).
[2]To date, nodularins have been detected only in brackish waters.
Sources: Chorus and Bartram (1999), Falconer and Humpage (2006), and Stewart and others (2006).

7.5.2.C TASTE-AND-ODOR COMPOUNDS

There are many potential sources of taste and odor in finished drinking water, including biological activity in the source water, chemical contamination (natural and anthropogenic) of the source water, chemicals used in the treatment processes, and biological activity or materials present in the distribution system. Biological activity associated with naturally occurring algae in source water is among the most common causes of tastes and odors in finished drinking water. Many groups of algae produce taste-and-odor compounds, with approximately 200 compounds identified to date; however, most taste-and-odor problems in drinking water are associated with cyanobacterial production of geosmin and 2-methylisoborneol (MIB) (Wnorowski, 1992; Rashash and others, 1996; Watson, 2003; American Water Works Association, 2004; Taylor and others, 2005).

- The taste-and-odor compounds geosmin and MIB cause earthy and musty tastes and odors and are detectable by humans at concentrations between 5 and 10 nanograms per liter; therefore, these compounds may be detectable in the environment before potential cyanobacterial producers are detected. In addition, the producer may be a relatively small component of the phytoplankton community.
- Taste-and-odor episodes caused by cyanobacteria have occurred even when cyanobacteria are not at detectable levels in the water column (Wnorowski, 1992; Jones and Korth, 1995; Rashash and others, 1996; Watson, 2003; Taylor and others, 2005).
- Most taste-and-odor problems associated with geosmin and (or) MIB are caused by cyanobacteria, but bacteria in the actinomycetes group also may produce geosmin and MIB (Wnorowski, 1992; Rashash and others, 1996; Watson, 2003; Taylor and others, 2005).

Actinomycetes bacteria are not photosynthetic and are not part of the phytoplankton community in lakes and reservoirs. The actinomycetes bacteria largely are terrestrial organisms associated with soils; taste-and-odor compounds typically are produced terrestrially and washed into lakes or reservoirs with or without the bacteria that produced them. Inflow events with high suspended-sediment loads may result in taste-and-odor episodes caused by geosmin and (or) MIB produced by actinomycetes bacteria (Zaitlin and others, 2003; Zaitlin and Watson, 2006). When washed in, actinomycetes bacteria generally are associated with the sediment. However, taste-and-odor compounds produced by actinomycetes bacteria can be located in the water column and throughout the lake or reservoir, depending on whether the compounds are dissolved or associated with the bacteria, hydrology of inflows and mixing with surrounding water, and sediment settling rates. Because of settling, actinomycetes may accumulate in the hypolimnion or near the bottom of lakes or reservoirs. It currently (2008) is unknown if or for how long terrestrial actinomycetes bacteria remain metabolically active in aquatic environments (Wnorowski, 1992; Rashash and others, 1996; Watson, 2003; Zaitlin and others, 2003; Taylor and others, 2005; Zaitlin and Watson, 2006).

Bacteria in the actinomycetes group, in addition to cyanobacteria, may produce geosmin and MIB.

The actinomycetes bacteria are difficult to adequately sample, identify, and measure. Like cyanobacteria, the actinomycetes may produce geosmin and MIB simultaneously, but production is strain specific (Wnorowski, 1992; Watson, 2003; Zaitlin and others, 2003; Zaitlin and Watson, 2006). Total actinomycetes typically are measured, rather than being identified at the genera or strain level. Strain isolation and culture are required to conclusively determine actinomycetes production of geosmin and (or) MIB.

TEMPORAL AND SPATIAL VARIABILITY OF CYANOBACTERIA 7.5.3

The temporal and spatial variability of cyanobacterial populations depend on lake or reservoir hydrology, morphology, geography, water chemistry, and biological interactions. Spatiotemporal occurrence patterns are unique to individual lakes, and generalizations are difficult because of the large degree of variability among lakes. Likewise, a diverse range of physical, chemical, and biological factors may potentially limit algal growth, and no one variable is an unequivocal link to cyanobacterial bloom formation. Long-term patterns may emerge in lakes that have been studied for several years for when, where, and under what conditions cyanobacterial blooms typically develop; or cyanobacterial blooms may occur only sporadically (Reynolds, 1984, 1998; Chorus and Bartram, 1999; Wetzel, 2001; Falconer, 2005).

- Local knowledge of general lake limnology and cyanobacterial bloom occurrence will enhance the ability to select appropriate sampling times and locations to meet study objectives.
- If historical data are unavailable, initial sampling schedules may be more intensive until general patterns in occurrence begin to emerge.

Cyanobacterial toxins and taste-and-odor compounds occur in a particulate phase and in a dissolved phase. Combined, the particulate (intracellular) and dissolved (extracellular) phases comprise total toxin or taste-and-odor concentrations. Particulate, dissolved, and total toxin and taste-and-odor compound concentrations may all be measured; however, measured total and particulate concentrations are dependent on the efficacy of extraction methods (Graham and others, 2008).

- The **particulate phase** comprises compounds that are maintained intracellularly by the cyanobacteria. Intracellular toxin and taste-and-odor concentrations are strain dependent and may vary by several orders of magnitude between strains. Laboratory studies with individual strains indicate that spatial and temporal variability in toxin and taste-and-odor concentrations are likely due to changes in cyanobacterial abundance and strain composition rather than changes in intracellular content (Rashash and others, 1996; Orr and Jones, 1998; Chorus, 2001; Long and others, 2001; Oudra and others, 2002). Because production of toxins and taste-and-odor compounds is strain specific, cyanobacterial abundance in mixed field populations typically is not a good indicator of toxin and (or) taste-and-odor occurrence and concentration.
- The **dissolved phase** comprises extracellular compounds that have been released into the water column either actively by healthy cells or passively upon cell lysis and death. Cyanobacterial toxins generally are maintained intracellularly until cell lysis and death. Thus, dissolved toxin concentrations typically remain low until populations either begin to senesce naturally or are lysed by management practices, such as application of algaecides.

Because cyanobacterial toxins typically are maintained intracellularly, toxins generally have a similar spatial distribution as the cyanobacteria (Chorus and Bartram, 1999; Falconer, 2005). Theoretically, the partitioning of cyanobacterial toxins between the particulate and dissolved phases will change with time as population density increases and declines; particulate concentrations will track overall changes in cyanobacterial population density, whereas dissolved concentrations will remain relatively low until population density begins to decline.

The general pattern in the temporal distribution of total, particulate, and dissolved cyanobacterial toxin concentrations, with respect to cyanobacterial population density, is illustrated in figure 7.5–4. Field observations indicate that this pattern occurs in lakes and reservoirs (Jones and Orr, 1994; Heresztyn and Nicholson, 1997; Chiswell and others, 1999; Chorus and Bartram, 1999); however, many other patterns also may occur because toxic and non-toxic strains of cyanobacteria can co-occur and will not necessarily have the same population dynamics.

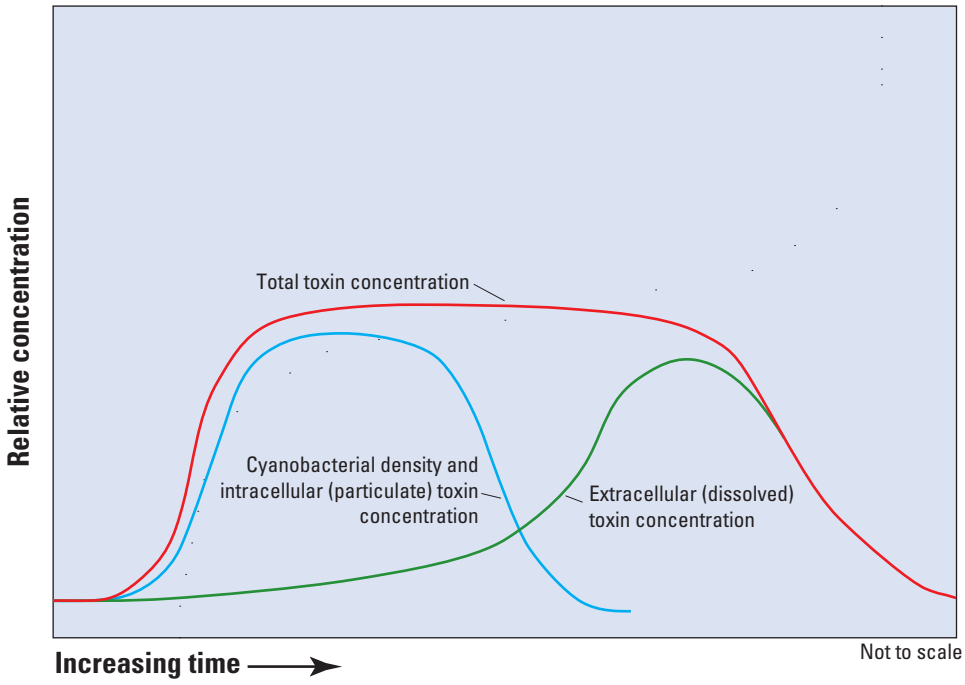


Figure 7.5–4. Theoretical temporal distribution of total, particulate, and dissolved cyanobacterial toxin concentrations with respect to cyanobacterial population density. From Graham and others (2008).

The partitioning of taste-and-odor compounds between the particulate and dissolved phases is more complex because healthy cyanobacterial cells either can maintain these compounds intracellularly or release them into the environment; therefore, taste-and-odor compounds are not necessarily associated with the cyanobacteria and may or may not have similar spatial distributions (Rashash and others, 1996; Watson, 2003; Taylor and others, 2005).

The environmental fate and transport of cyanobacterial toxins and taste-and-odor compounds under natural lake or reservoir conditions have not been well studied. Available laboratory data indicate that photolysis and biodegradation are the most likely mechanisms for the degradation of cyanobacterial by-products in lakes and reservoirs (Graham and others, 2008). Based on field observations, dissolved-phase toxins and taste-and-odor compounds may persist for several days to weeks after the decline of a cyanobacterial population (Jones and Orr, 1994; Heresztyn and Nicholson, 1997; Chorus and Bartram, 1999). The persistence of toxins and taste-and-odor compounds, coupled with the potential for transport, may lead to spatial or temporal uncoupling of cyanobacteria and their by-products.

TEMPORAL VARIABILITY 7.5.3.A

Seasonal patterns in cyanobacterial abundance and community composition are affected substantially by temperature, solar irradiance, and nutrient supply (Wetzel, 2001). Cyanobacterial populations tend to peak between midsummer and early fall when water temperatures are at seasonal maxima and nutrient concentrations are at seasonal minima; however, cyanobacteria may remain abundant year-round, even in temperate lakes or reservoirs, or peak under ice during winter. Cyanobacterial populations also may vary on much shorter time scales (hours or days). Whereas cyanobacterial abundance may increase fairly rapidly (days), vertical migration, entrainment in temporary circulation cells, or wind movement of surface accumulations may rapidly change the areal distribution or water-column location of cyanobacteria within the lake or reservoir, but not its overall abundance. Knowledge of local conditions, including patterns in circulation, mixing, and prevailing winds, will enhance the overall design of a cyanobacteria study and aid in the interpretation of observed changes in cyanobacterial abundance and community structure (Graham and others, 2008).

SPATIAL VARIABILITY 7.5.3.B

Some knowledge of the distribution of cyanobacteria, as affected by hydrology, morphology, and typical conditions throughout a lake or reservoir is required before sites are selected for toxin and taste-and-odor studies. Cyanobacterial movement affects distribution in the water column, and wind movement of surface accumulations may have a substantial effect on where cyanobacteria are located within a lake or reservoir; however, the general location of cyanobacteria largely is affected by lake or reservoir hydrology and morphology and their effects on circulation patterns. Cyanobacterial populations may be distributed evenly throughout a lake or reservoir or have an irregular distribution because of currents and prevailing winds (fig. 7.5–5). Statistically significant differences in toxin concentrations have been detected within sampling distances of 10 m (Carmichael and Gorham, 1981; Lanaras and others, 1989; Kotak and others, 2000), although extreme spatial variation is not necessarily typical (Jungmann and others, 1996; Graham and others, 2006).

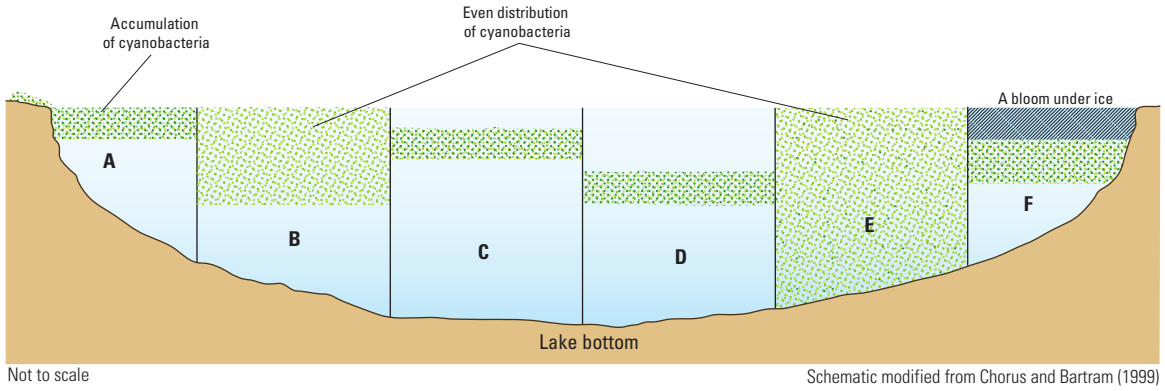
The spatial distribution of cyanobacteria may change rapidly because of changing hydrologic conditions, such as new circulation patterns or inflow events. After heavy rains, cyanobacteria in the reservoir shown in figure 7.5–5 were washed from up-reservoir areas into the main body of the reservoir. The cyanobacterial population in this case was restricted to the old river channel (near the tree line). In larger lakes or reservoirs, certain areas (shallow bays and coves, sites directly affected by nutrient-rich inflows, or structures that affect flow such as dikes, piers, or intake towers) may be more prone to the development of cyanobacterial blooms and surface accumulations. These isolated blooms may remain localized or become spread throughout the lake or reservoir because of inflow events or circulation patterns (Reynolds, 1984; Chorus and Bartram, 1999; Wetzel, 2001; Falconer, 2005).

Figure 7.5–5. Example of the spatial variability of cyanobacteria within a reservoir. From Graham and others (2008).

The ability of many toxin and taste-and-odor producing cyanobacteria to control their position in the water column needs special consideration when sampling for these compounds. The vertical distribution of cyanobacteria may vary widely over relatively short (hours or days) periods of time (Reynolds, 1984; Chorus and Bartram, 1999; Falconer, 2005). Sample location in the water column relative to cyanobacterial distribution may substantially affect cyanobacterial community composition, toxin, and (or) taste-and-odor results. For example, if cyanobacteria are maintaining a position at depth in the water column and surface samples are collected, toxins or taste-and-odor compounds may not be detected even when present. There are six general water-column distributions of cyanobacteria; detailed descriptions and occurrence information are given in figures 7.5–6 and 7.5–7:

1. Shoreline, near-shore, or open-water surface accumulations and scums (fig. 7.5–6*A* and fig. 7.5–7*A*). Surface accumulations and scums are of greatest concern for exposure to high concentrations of cyanobacterial toxins during recreational activities.
2. Even distribution throughout the photic zone or epilimnion (fig. 7.5–6*B* and fig. 7.5–7*B*).
3. Specific depth in the photic zone (fig. 7.5–6*C* and fig 7.5–7*C*). In shallow lakes or reservoirs where light penetrates to the bottom (photic depth equals maximum depth), cyanobacteria may be located on or near the bottom.

4. Metalimnetic bloom (fig. 7.5–6*D*, fig. 7.5–7*D*, fig. 7.5–8). This is a special case of a population maintaining a specific depth in the photic zone. Metalimnetic blooms are evident by sharp increases in oxygen at depth, typically near the interface of the epilimnion and metalimnion (figs. 7.5–1 and 7.5–8). Metalimnetic blooms are of particular concern in drinking-water supplies because the populations are not visibly evident and may be located at the same depth as the drinking-water intake.
5. Even distribution throughout the water column (fig. 7.5–6*E*; fig. 7.5–7*E*).
6. Under ice (fig. 7.5–6*F*; fig. 7.5–7*F*).

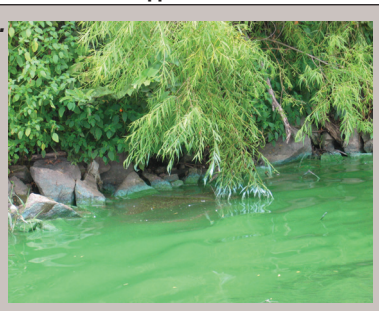


EXPLANATION

Potential water column distributions of cyanobacteria

- **A** Shoreline, near-shore, and open water accumulations and scums
- **B** Even distribution throughout the photic zone or epilimnion
- **C** Specific depth in the photic zone
- **D** Metalimnetic bloom (special case of **C**)
- **E** Even distribution throughout the water column
- **F** Under ice bloom

Figure 7.5–6. Potential water-column distributions of cyanobacteria. From Graham and others (2008).

Appearance	Location	Description	Occurrence
A.  	Shoreline, near-shore and open-water surface accumulations and scums.	Discoloration of the water surface; typically blue-green or bright green but may also be brown or red[1]. May be a thin layer near the surface or be thick or paint-like. Accumulations may extend from the surface to depths of one meter or more. Dissolved oxygen may be supersaturated near the surface.	Develop when existing cyanobacterial population accumulates near the water surface. May occur in open-water or near-shore areas. May rapidly move or dissipate with changes in wind speed and direction. May occur during calm periods or during the decline of a cyanobacterial population. May be widespread or have a patchy distribution depending on wind and circulation patterns.
B. 	Dispersed in photic zone.	Water likely has an obvious color; typically blue-green or bright green but may also be brown or red. Large colonies and filaments may be visible.	Relatively calm conditions. May occur in well-mixed or stably stratified water column.
	Dispersed in epilimnion. Appearance will vary depending on the type and abundance of cyanobacteria.	Water may or may not have obvious color; typically blue-green or bright green but may also be brown or red. Large colonies or filaments may or may not be visible.	Stably stratified water column. Breezy, windy conditions.

[1]From a distance, duckweed *(Lemna)* may be confused with a cyanobacterial bloom; duckweed has a bright green color and may cover large areas. Duckweed is a plant with visible leaves, and up close, duckweed is easily distinguished from cyanobacteria. Duckweed typically proliferates in shallow, nutrient rich ponds, bays, and small lakes/reservoirs. Examples of duckweed appearance are available on the internet at http://www.mobot.org/jwcross/duckweed/duckpix.htm and http://aquaplant.tamu.edu/database/floating_plants/common_duckweed_pics.htm.

All photographs by J.L. Graham, U.S. Geological Survey, with the exception of (***E***), courtesy of Kansas Department of Health and Environment, and (***F***), courtesy of an anonymous photographer.

Figure 7.5–7. The appearance, location, description, and occurrence of cyanobacteria in lake and reservoir water: (***A***) shoreline, near-shore, and open-water surface accumulations or scums, (***B***) dispersed in photic zone and the epilimnion, (***C***) specific depth in photic zone, (***D***) metalimnetic bloom, (***E***) even distribution throughout the water column, and (***F***) under ice. From Graham and others (2008).

Appearance	Location	Description	Occurrence
C. 	Specific depth in photic zone. Appearance will vary. Here the cyanobacteria were near the water surface during early morning.	Water may or may not have obvious color. Large colonies and filaments may or may not be visible. Specific location in the photic zone may be difficult to determine without discrete samples.	Relatively calm conditions. May occur in well-mixed or stably stratified water column.
		Caution: In shallow lakes where light penetrates to the bottom (photic depth is greater than maximum depth) cyanobacteria may be located on or near the bottom.	
D. 	Metalimnetic bloom (special case of a population maintaining a specific depth in the photic zone). Metalimnetic blooms are not visible at the water surface; they can be detected by a sharp increase in dissolved oxygen at depth.	Not visible from the surface. Evident by a sharp increase in dissolved oxygen at depth, typically near the interface of the epilimnion and the metalimnion.	Stably stratified water column. Intermediate trophic status (mesotrophic). Photic zone penetrates into the metalimnion.
E. 	Even distribution throughout the water column. Appearance will vary depending on the type and abundance of cyanobacteria.	Water may or may not have obvious color; typically blue-green or bright green but may also be brown or red. Large colonies or filaments may or may not be visible.	Well-mixed conditions in: Shallow lakes/reservoirs; Deeper lakes/reservoirs that do not typically stratify; Autumn, winter, and spring conditions in temperate lakes/reservoirs that stratify.
F. 	Under ice.	May be visible under ice depending on ice thickness; color is typically blue-green or red. Typically visible when ice plug is removed.	Ice clarity and thickness allows adequate light penetration.

All photographs by J.L. Graham, U.S. Geological Survey, with the exception of (***E***), courtesy of Kansas Department of Health and Environment, and (***F***), courtesy of an anonymous photographer.

Figure 7.5–7. The appearance, location, description, and occurrence of cyanobacteria in lake and reservoir water: (***A***) shoreline, near-shore, and open-water surface accumulations or scums, (***B***) dispersed in photic zone and the epilimnion, (***C***) specific depth in photic zone, (***D***) metalimnetic bloom, (***E***) even distribution throughout the water column, and (***F***) under ice. From Graham and others (2008).—Continued

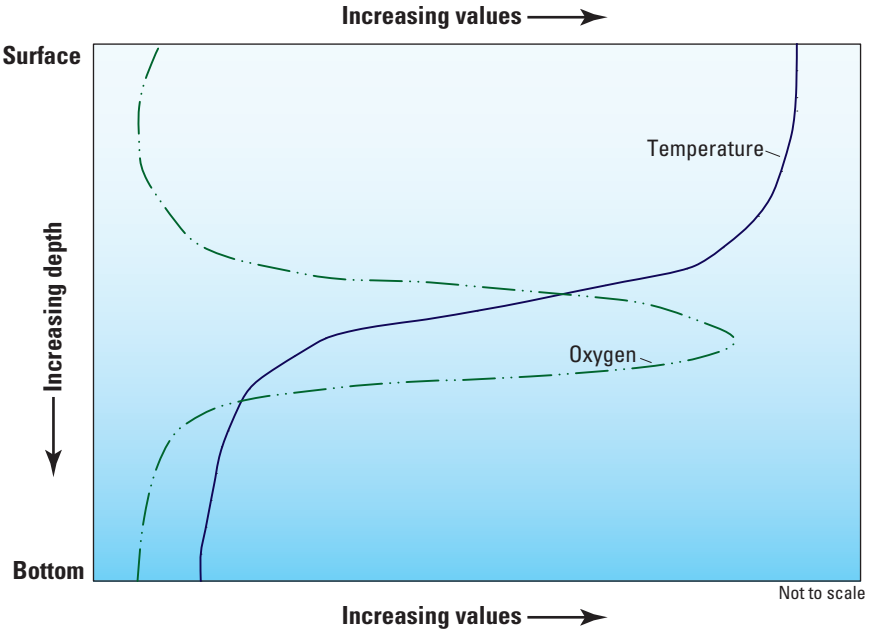


Figure 7.5–8. Graphical representation of the temperature and oxygen gradients that will develop in the water column when a metalimnetic cyanobacterial bloom is present. From Graham and others (2008).

Once toxins and taste-and-odor compounds are released by cyanobacteria into the dissolved phase, they will become uniformly distributed throughout the mixed layer in which they are released; this typically is a rapid process, but large localized concentrations may develop in hydraulically isolated areas such as coves (Jones and Orr, 1994). Generally, the distribution of dissolved compounds in the water column will depend on the layer in which the cyanobacteria were located when the compounds were released. In stratified lakes or reservoirs, cyanobacteria most likely are in the epilimnion or, less frequently, the metalimnion. Dissolved toxin and taste-and-odor samples usually can be collected from the same water column location as samples for intracellular (particulate) analysis (Chorus and Bartram, 1999; Falconer, 2005); however, high taste-and-odor concentrations may occasionally occur in the hypolimnion of stably stratified lakes or reservoirs (Carpenter, 2002; Mau and others, 2004).

7.5.4 STUDY OBJECTIVES AND DESIGNS

Averett and Schroder (1994) describe three general types of surface-water-quality studies: reconnaissance studies, monitoring studies, and interpretive studies. Cyanobacterial toxin and taste-and-odor studies are discussed with respect to these three study types. The keys to a well-designed study include using the scientific method, a well-defined problem, clear objectives, and an appropriate approach.[4] Study objectives will dictate what variables need to be measured; the ancillary data to be collected (7.5.5.F), and when, where, and how samples will be collected.

[4]A comprehensive treatment of the fundamentals of how to design water-quality studies is beyond the scope of NFM 7.5 but can be found in reports such as Friedman and Erdmann, 1982; Shampine and others, 1992; and Averett and Schroder, 1994. The information provided in NFM 7.5 is intended to be used in conjunction with these and other reports that specifically address the design of surface-water-quality studies.

The study of cyanobacterial toxins and taste-and-odor compounds is an active area of developing research, but many fundamental questions remain about the occurrence, environmental causes, and ecological consequences of these compounds (Chorus, 2001). General study objectives and guidelines on when, where, and how to sample are described below for reconnaissance, monitoring, and interpretive studies.[5] The information given is intended to illustrate how the information presented on the spatial and temporal variability of cyanobacteria and cyanobacterial blooms can be used to guide and enhance the design of field studies.

- **Reconnaissance studies**. Reconnaissance studies often assess the occurrence, distribution, and concentration of cyanobacteria and associated toxins and taste-and-odor compounds. Such studies may focus on spatial and (or) temporal variability at a range of scales, from single systems to States or regions. Studies of lakes or reservoirs used for recreation typically emphasize cyanobacterial toxins, whereas studies of lakes or reservoirs used for drinking-water supply may emphasize taste-and-odor compounds and toxins. General study objectives and guidelines describing when, where, and how samples typically are collected for reconnaissance studies are presented in table 7.5–3. An example of a study design, approach, and field form for a reconnaissance study is given in Appendix 7.5–A.

Table 7.5–3. Objectives and guidelines describing when, where, and how samples typically are collected for reconnaissance studies.

General objective	Site location	Sampling frequency	Sample type
Regional Studies			
Spatial Variability • Emphasis on presence/absence	• Single representative site, typically an open, deep-water site • Site will be determined based on the location of surface accumulations and scums	• Single point in time when most cyanobacterial-related issues occur • During known surface bloom events	• Integrated photic zone • Integrated epilimnion • Surface sample • Surface sample
Spatial and Temporal Variability • Emphasis on presence/absence and changes in concentration with time	• Single representative site, typically an open, deep-water site	• Multiple times during the period when most cyanobacterial-related issues occur – Weekly – Bi-weekly – Monthly – Annually	• Integrated photic zone • Integrated epilimnion • Surface sample
Single-System Studies			
Spatial Variability • Emphasis on presence/absence	• Multiple sites	• Single point in time when a cyanobacterial bloom is occurring	• Integrated photic zone • Integrated epilimnion • Integrated water column • Surface sample
Spatial and Temporal Variability • Emphasis on presence/absence and changes in concentration over time	• Multiple sites	• Multiple times during the period when most cyanobacterial-related issues occur – Weekly – Bi-weekly – Monthly	• Integrated photic zone • Integrated epilimnion • Integrated water column • Surface sample
• Emphasis on spatial changes within the water body or water column over relatively short periods of time	• Single representative site • Multiple sites	• Multiple points in time when a cyanobacterial bloom is occurring – Hourly – Daily	• Integrated photic zone • Integrated epilimnion • Integrated water column • Surface sample • Discrete depth

Sources: Chorus and Bartram (1999), Falconer (2005), and Wetzel and Likens (2000).

[5]A comprehensive list of all possible types, sampling approaches and methods, or site-selection criteria for studies of toxins and taste-and-odor compounds in lakes and reservoirs is beyond the scope of NFM 7.5.

- **Monitoring studies**. Monitoring studies often are conducted to evaluate the potential for human health risks and taste-and-odor events associated with cyanobacterial toxins and taste-and-odor compounds. Monitoring studies typically determine the concentration of cyanobacterial toxins and taste-and-odor compounds in areas where exposure is most likely to occur, such as popular swimming areas or drinking-water intakes. Recreational areas are monitored for cyanobacterial toxins to assess human health risks; results often are used to make decisions about posting warnings and closing recreational areas. Drinking-water intakes are monitored for taste-and-odor compounds and (or) toxins to assess the potential for taste-and-odor events and human health risks; results often are used to guide drinking-water treatment processes, such as use of activated carbon. Guidelines describing when, where, and how samples typically are collected for monitoring studies are presented in table 7.5–4. An example of a study design, approach, and field form for a monitoring study is given in Appendix 7.5–B.

Table 7.5–4. Objectives and guidelines describing when, where, and how samples typically are collected for monitoring studies.

General objective	Site location	Sampling frequency	Sample type
Recreational Areas	• Beaches • Open water areas used for full-body contact recreation • Bay or cove areas used for full-body contact recreation • Public access sites	• Routine basis during periods of peak recreational use – Daily – Weekly	• Surface sample • Integrated photic zone
Drinking-Water Supplies	• Location relevant to the drinking-water intake(s)	• Routine basis – Daily – Weekly • During periods when events have historically occurred • During events	• Discrete depth • Integrated photic zone • Integrated epilimnion • Integrated water column

Sources: Chorus and Bartram (1999), Falconer (2005), and Wetzel and Likens (2000).

- **Interpretive studies**. Interpretive studies often are conducted to assess the processes that affect the spatial and temporal distribution and abundance of cyanobacterial toxins and taste-and-odor compounds. Interpretive studies of toxins and (or) taste-and-odor compounds may include, but are not limited to, the assessment of the physical, chemical, and biological factors affecting occurrence and concentration, environmental fate and transport studies, and toxicological studies.

  — **Occurrence and concentration studies** assess the environmental factors affecting cyanobacteria and often are focused on developing empirical models (Mau and others, 2004; Christensen and others, 2006). Several years of study, with data collection over a range of hydrologic and meteorologic conditions, often are required before true patterns begin to emerge. Long-term studies are required to develop real-time water-quality and other predictive models to provide early warning of the potential occurrence and (or) concentration of cyanobacterial toxins and taste-and-odor compounds. Reliable real-time water-quality models and other predictive tools will allow resource managers to respond more effectively to cyanobacterial blooms. Table 7.5–5 presents general study objectives and guidelines describing when, where, and how samples typically are collected for studies that assess the environmental factors affecting the occurrence and concentration of cyanobacterial by-products. An example of a study design, approach, and field form for an interpretive study is given in Appendix 7.5–C.

— **Fate-and-transport and toxicological studies** are crucial to the overall understanding of environmental and public health risks associated with cyanobacterial toxins. Determination of the environmental fate and transport of cyanobacterial toxins and taste-and-odor compounds generally involves examining development, movement, persistence, and degradation of cyanobacterial populations, toxins, taste-and-odor compounds, and associated degradates within the lake or reservoir environment (for example, movement to downstream drinking-water intakes) and among its ecosystem compartments. Fate-and-transport and toxicological studies frequently require collection of water-column samples from lakes and reservoirs. In addition, these studies often involve the sampling of sediments, benthic organisms, and tissues from fish and other aquatic and terrestrial organisms; however, few data are available regarding the partitioning of cyanobacterial toxins and taste-and-odor compounds in these ecosystem compartments and sampling protocols and analytical methods have not been, or currently (2008) are being, developed. Discussion or examples of how to collect the samples needed from these media is beyond the scope of NFM 7.5.

Table 7.5–5. Objectives and guidelines describing when, where, and how samples typically are collected for interpretive studies assessing the physical, chemical, and biological factors affecting the occurrence and concentration of cyanobacteria and associated toxins and taste-and-odor compounds.

General objective	Site location	Sampling frequency	Sample type
• Environmental factors influencing spatial and (or) temporal occurrence • Real-time estimation of occurrence/concentration • Predictive models	• Single representative site, typically an open, deep-water site – Sites for drinking-water studies are typically located near intakes • Multiple sites – Sites where cyanobacterial blooms are known to initiate – Sites where cyanobacteria are typically abundant – Inflow sites[1]	• Routine basis – Weekly – Bi-weekly – Monthly	• Integrated photic zone • Integrated epilimnion • Integrated water column • Discrete depth
	• Sites where surface accumulations/scums are located	• Event samples – Sampling plans need to be flexible enough to respond to events	• Surface sample

[1]Monitoring of major inflows is essential in the development of predictive models and beneficial in the development of models for real-time estimation of occurrence/concentration. Standard U.S. Geological Survey protocols for sampling streams and rivers should be used when sampling inflows (NFM 4). Cyanobacterial samples and samples for toxin and taste-and-odor analysis may or may not be analyzed at inflow sites, depending on conditions; however, actinomycetes samples (NFM 7.1) must be collected.

Sources: Chorus and Bartram (1999), Christensen and others (2006), Falconer (2005), and Wetzel and Likens (2000).

7.5.5 SAMPLE COLLECTION

The sample collection approaches described below are appropriate for samples to be analyzed for cyanobacterial community composition (enumeration and identification) and total, dissolved, and particulate cyanobacterial toxins and taste-and-odor compounds. Site selection and sampling approach (sampling frequency, location, time of day samples are collected, sample types, samplers used, and sample holding times) need to be carefully considered with respect to the specific objectives of the study. In this regard, special consideration needs to be given to the areal and water-column distribution of the cyanobacteria in the lake or reservoir when deciding where and how to collect samples; the sampling location needs to be relevant to where the cyanobacterial community is located.

In general, **toxin and taste-and-odor samples must be shipped within 24 to 48 hours**, and sample collection should be planned accordingly. Additional considerations to be incorporated in the study sampling plan include the maintenance of sample quality under adverse conditions of site logistics, climate, or weather. When planning the project, project staff should be aware, for example, of sample holding times when shipping to or from areas of the country where adverse weather conditions, such as severe thunderstorms, flooding, or blizzards, may delay shipping or receipt of samples. Facilities may need to be modified to hold samples for cyanobacterial analysis under controlled conditions to avoid sample exposure to extreme temperatures in the event of shipment delays. If shipping delays are anticipated, contact the analyzing laboratory for information on how to hold samples. Data storage and management also are an essential component for which appropriate plans need to be made, as well as arranging for an adequate level of database development and management.

Three general types of water-quality samples are typically collected from lakes and reservoirs: surface samples, discrete-depth samples, and depth-integrated samples. For each sample type, a single grab sample may be collected or multiple grab samples may be composited. The types of sampling devices (samplers) commonly used to collect each type of sample are listed in table 7.5–6. Detailed descriptions of the samplers and proper uses are presented in NFM 2.1.1.B, NFM 4.1.3.B, NFM 4.1.3.C, Britton and Greeson (1987), and U.S. Environmental Protection Agency Standard Methods Sections 1060 and 10200 (American Public Health Association, 2005) and the advantages and disadvantages of each sampler type are presented in NFM 7.4, table 7.4–8. It is important that samples be collected in a manner that does not rupture or deform cyanobacterial cells, particularly when analyzing for species composition and particulate and dissolved toxin and taste-and-odor concentrations. In general, sampling devices and churns have a minimal impact on cyanobacterial cell integrity; exceptions are discussed in more detail below and in NFM 7.4, table 7.4–8. **Because toxins and taste-and-odor compounds are organic compounds, the samplers and churns used to collect and composite samples must be made of fluorocarbon polymers, such as Teflon®; metals, such as stainless steel; or glass (NFM 2.0.1).**

Table 7.5–6. Samplers commonly used to collect surface, discrete-depth, and depth integrated samples in lakes and reservoirs.

Sample type	Sampler
Surface	• Hand-held open mouth bottle sampler • Weighted bottle sampler (US WBH-96)
Discrete depth	• Kemmerer bottle • Van Dorn bottle – horizontal or vertical • Pump – diaphragm or peristaltic[1]
Depth integrated	• Kemmerer bottle • Van Dorn bottle – vertical • Teflon stop-cock bailer • Pump – diaphragm or peristaltic[1]

[1]This sampling method may rupture or deform cyanobacterial cells and the advantages and disadvantages of this method (discussed in NFM 7.4, table 7.4–8) must be carefully considered when collecting samples for the analysis of species composition or particulate and (or) dissolved toxin and taste-and-odor concentrations.

General field procedures are the same, regardless of whether surface, discrete-depth, or depth-integrated grab or composite samples are collected. Sample location and the method used to collect samples may be dependent on water-column stratification and the location of cyanobacteria. Where and how to collect samples often are decided in the field after an initial assessment of the presence of phytoplankton (including cyanobacteria) in the water column.

- The distribution of phytoplankton (and cyanobacteria) in the water column often can be determined by a combination of visual assessment, light profiles to determine photic depth, and temperature, dissolved oxygen, pH, and *in vivo* fluorescence (chlorophyll and (or) phycocyanin, a light-gathering pigment unique to cyanobacteria, NFM 7.4.2) profiles to determine stratification, mixed depth, and photosynthetic activity (figs. 7.5–6, 7.5–7, and 7.5–8).
- Signs of photosynthetic activity and phytoplankton (including cyanobacteria) location in the water column include:
  - Sharp increases in pH and dissolved-oxygen (DO) concentration (for example, see fig. 7.5–8).
  - Increased fluorescence of chlorophyll and (or) phycocyanin.

Because pH and DO may increase as a result of photosynthesis, these measurements will give more distinct signals under bright, sunny conditions. Conversely, fluorescence is inhibited by light (NFM 7.4.2.C) and signals will be more distinct during overcast or dark conditions (such as apparent increases in fluorescence in the aphotic zone or at night). **Profile results must be carefully interpreted with respect to weather conditions and time of sampling.** Cyanobacteria often will maintain a position in the photic zone, regardless of mixed depth; therefore, if cyanobacterial distribution in the water column cannot be conclusively determined, an integrated photic-zone sample will likely be fairly representative (Graham and others, 2008).

Signs of phytoplankton activity often are used to select sampling depths. The location of decomposing phytoplankton also may be discernable, particularly after a substantial bloom.

- Increased pH and DO during daylight hours or *in vivo* fluorescence (an estimate of chlorophyll or phycocyanin) are signs of phytoplankton activity.
- Sharp declines in pH or DO, particularly after a substantial bloom, are signs of phytoplankton decomposition.
- Intracellular compounds, including toxins and taste-and-odor compounds, may be released to the water during periods of senescence.

To collect samples for analysis of cyanobacterial community composition (enumeration and identification), toxins, and (or) taste-and-odor compounds follow these guidelines:

1. Before departing for field work, ensure that the field team is familiar with the USGS parts-per-billion protocol (for example, equipment-selection guidelines (NFM 2), equipment decontamination (NFM 3), clean hands/dirty hands (CH/DH) techniques and quality control (NFM 4 and NFM 5), safety requirements (NFM 9), and all other relevant guidance described in the study's sampling, quality-assurance, and work plans). Check that field personnel are prepared to implement such required and recommended procedures.
2. Document in field notes the water color and the presence of any visible cyanobacteria or cyanobacterial accumulations near the surface (fig. 7.5–7), the location and extent of surface accumulations, and any odors that may be associated with cyanobacterial accumulations (commonly earthy/musty, sulfurous, or septic odors).
3. Take photographs of the site, particularly areas with obvious cyanobacterial accumulations.
4. Measure and record a vertical light profile throughout the photic zone (NFM 7.4.1.B). Ideally, photic depth is measured with a light sensor; however, photic depth can be estimated as approximately 2 ½ times the Secchi disc depth (Horne and Goldman, 1994; Wetzel and Likens, 2000).
5. Measure and record vertical profiles of field properties in situ—water temperature, dissolved oxygen, pH, specific conductance, turbidity, and (or) in situ fluorescence (an estimate of chlorophyll or phycocyanin). To measure a vertical profile in a lake or reservoir, lower the sensor into the water and take readings about 1 cm below the water surface. Continue lowering the sensor and take readings every 0.5 to 1 m until the sensor reaches the bottom. More detail on measuring profiles in lakes and reservoirs is given in NFM 7.4.1.B and Wetzel and Likens (2000).
6. Use photic depth and profile data to assess the location of cyanobacteria in the water column (figs. 7.5–6, 7.5–7, and 7.5–8) and select sampling locations. Remember that if the distribution of cyanobacteria in the water column cannot be determined, a depth-integrated photic-zone sample will generally be representative. Record sampling depths and locations on the field sheet.
7. Field rinse all sampling equipment with native water immediately before the equipment is used (NFM 4.1.3).
8. Collect samples while wearing clean gloves; use parts-per-billion CH/DH techniques (NFM 4.0.2). More detail on collecting grab, composite, surface, discrete-depth, and depth-integrated samples is provided in sections 7.5.5.A–7.5.5.D. **Because cyanobacteria may be toxic, always wear gloves and avoid having sample water contact the face**. Other sample collection safety considerations are discussed in section 7.5.8.

9. Process samples (section 7.5.6 and NFM 5). Place samples on ice in the dark immediately after sample collection. As long as samples remain chilled and in the dark, they may be held for several hours before processing. Sample processing procedures typically will depend on instructions from the laboratory at which the samples will be analyzed.
10. Clean equipment. If the sampler will not be reused during a field trip, rinse the sampler components thoroughly with deionized water before they dry and place the sampler in a plastic bag for transport to the office laboratory for cleaning. If the sampler will be reused during the field trip, rinse the sampler components with deionized water before they dry. Field-clean the sampler at the next sampling site (NFM 3) and rinse with native water before use.

If the distribution of cyanobacteria in the water column cannot be determined, collect a depth-integrated photic-zone sample and record this in the field notes.

SINGLE-GRAB AND COMPOSITE SAMPLES 7.5.5.A

Whether a single grab or composite sample is collected will depend on study objectives and the volume of water needed. Compared with grab samples, composite samples are more representative of overall lake or reservoir conditions; however, because of the generally irregular distribution of cyanobacterial communities, concentrations of toxins and taste-and-odor compounds may be diluted when using a sample-composite method (American Public Health Association, 2005). Thus it is important to understand that data interpretation can be biased by the sample-collection and -processing methods used.

Grab Samples

Grab samples are collected from a specific location in the water column. Single grab samples typically are collected when:

- Spatial variability is not a concern, or multiple grab samples are being collected and analyzed separately to describe spatial variability, and the volume of water required for analyses does not exceed the volume of the sampling device.

  Example—When collecting a sample from a single representative location in a lake or reservoir.

- Temporal variability is not a concern, or multiple grab samples are being collected and analyzed separately to describe temporal variability, and the volume of water required for analyses does not exceed the volume of the sampling device.

  Example—When collecting samples on a weekly basis.

Composite samples

Composite samples are collected by combining multiple grab samples. Composite samples typically are collected when:

- The volume of water required for analyses exceeds the volume of the sampling device. In this case, multiple grab samples typically are collected from the same location.

  Example—A composite sample composed of five integrated photic zone samples collected from a single open-water location in a lake or reservoir.

- Spatial variability is a concern. Spatial composites are comprised of multiple grab samples collected from different locations either within the water column or throughout a given area of a lake or reservoir.

  Example—A composite sample composed of single grab samples, collected every meter from the lake or reservoir surface to the bottom; or single grab samples collected from 20 locations within a recreational area.

- Temporal variability is a concern. Temporal composites are composed of multiple grab samples collected during different times.

  Example—A composite sample composed of single grab samples collected every 15 minutes over a period of 2 hours. Temporal composites typically are not collected for cyanobacterial toxin and taste-and-odor studies.

7.5.5.B SURFACE SAMPLES

Open-mouth samplers typically are used to collect surface samples (NFM 2.1.1.B, 4.1.1.B, table 7.5–6). Wide-mouthed Teflon or glass bottles are used to collect samples for analysis of toxins and (or) taste-and-odor compounds.[6] Samples for cyanobacterial (phytoplankton) community composition (enumeration and identification) can be collected into polyethylene bottles, but the bottle must be triple-rinsed with native water before use (table 7.5–7). If surface samples are collected in open-water areas, samples need to be collected 0.5 to 1.0 m below the lake or reservoir surface to avoid substances in the surface film that may interfere with analyses (American Public Health Association, 2005). An exception to this would be if surface accumulations or scums are being sampled; then collection at the water surface is appropriate. Samples are collected with an open-mouth sampler and composited into a Teflon churn (see NFM 2) if the volume of water required for analyses exceeds the volume of the sampling bottle.

Study objectives must be considered when determining how to sample surface accumulations and scums, since cyanobacterial density can vary widely across the area of accumulation.

- If a general idea of maximum toxin and (or) taste-and-odor compound concentration is desired, collect a sample from the thickest part of the accumulation or scum.

[6]Some laboratories may recommend using polyethylene bottles for toxin samples, especially when samples are being frozen. Small amounts of toxins, particularly the microcystins, are known to sorb to polyethylene bottles; nevertheless, use of polyethylene still is common.

- If an average concentration in the accumulation or scum is desired, composite multiple surface samples from throughout the area into a churn. A grid or transect approach often is used for this type of collection (American Public Health Association, 2005). The number of samples used for a composite will depend on study objectives and the size of the accumulation or scum.
- If information on spatial heterogeneity is desired, collect surface grab samples throughout the accumulation or scum area, keeping them separate. Do not composite these samples.

Table 7.5–7. Bottle types and volumes commonly used for toxin, taste-and-odor, and cyanobacterial (phytoplankton) community composition (enumeration and identification) samples.

[The bottle types and volumes described here are for general information; bottle type and volume will ultimately depend on instructions from the laboratory at which the samples will be analyzed. The specific instructions from the analyzing laboratory on sample bottles and volumes should be followed carefully.]

Analysis	Bottle type(s)	Bottle volume(s), in milliliters
Toxin	• Baked amber glass • Teflon • Polyethylene[1]	500–1,000
Taste and odor	• Baked amber glass • Amber glass septum vials	125–250 10–50
Cyanobacterial community composition	• Amber glass[2] • Polyethylene[1]	125–1,000

[1]Small amounts of toxins, particularly the microcystins, are known to sorb to polyethylene bottles, but polyethylene is still commonly used. **If a polyethylene bottle is used for toxin sample collection it should be triple rinsed with native water prior to use.**
[2]Amber bottles are preferred but clear bottles may be used as long as the samples are immediately preserved and kept in the dark.

DISCRETE-DEPTH SAMPLES 7.5.5.C

Discrete-depth samples typically are collected when the location of the cyanobacterial community is known, when there is a structure of interest at depth (such as a drinking water intake), or when the vertical water-column distribution of the cyanobacterial community and associated toxins and taste-and-odor compounds is being studied in detail. Thief samplers, such as Kemmerer or Van Dorn bottles, are commonly used to collect discrete-depth samples, although pumps also may be used (table 7.5–6; NFM 2.1.1.B, Thief samplers; NFM 4.1.3).

Kemmerer and Van Dorn bottles are cylindrical tubes that have stoppers at each end and a mechanism that closes the sampler at depth (Britton and Greeson, 1987); these samplers come in a range of sizes from approximately 0.5 L to 10 L, and are made from a variety of materials including Teflon and stainless steel. The key difference between Kemmerer and Van Dorn bottles is the location of the closure mechanism: the closure mechanism of a Kemmerer bottle is inside the bottle (NFM 2.1.1.B, fig. 2–2*A*) and the closure mechanism of a Van Dorn bottle is outside the bottle (NFM 2.1.1.B, fig. 2–2*B*). Because the closure mechanism of the Van Dorn bottle is on the outside, these bottles may be used in either the vertical or horizontal position (operation in the horizontal position captures a narrower depth range than operation in the vertical position).

To operate a Kemmerer or Van Dorn bottle:

1. Check to ensure the closure mechanism is working.
2. Open the sampler and slowly lower (do not drop) the bottle to the desired depth.
3. Trip the closure mechanism and bring the sample to the surface.
4. Draw off water into a Teflon churn by means of the nozzle in the lower stopper.
5. Repeat the above steps until the volume of water required for analyses has been collected.

Pumps (NFM 2.1.1.B and 4.1.1.B) allow greater speed of collection and are particularly useful when large quantities of water are required; however, pumps may damage cyanobacteria and other organisms and are not the best option when analyzing for species composition and particulate and dissolved toxin and taste-and-odor concentrations. The advantages and disadvantages of pumps (NFM 7.4, table 7.4–8) need to be considered carefully before use. Select a diaphragmatic or peristaltic pump in order to minimize damage to cyanobacteria during sample collection (American Public Health Association, 2005). Sample tubing used with pumps needs to be made of Teflon.

To use a pump to collect a discrete water sample:

1. Lower the pump intake to the desired depth.
2. Allow three sample-tubing volumes to rinse the sample tubing with native water before collecting the sample (NFM 4.1.1.B).
3. Pump the sample directly into a Teflon churn until the volume of water required for analyses has been collected. The use of a churn may not be necessary for a discrete sample if a relatively small volume of water is required for analyses; in this case, pump water directly into a Teflon or glass bottle.

7.5.5.D DEPTH-INTEGRATED SAMPLES

Depth-integrated samples may encompass the photic zone, epilimnion, metalimnion, hypolimnion, entire water column, or other layers of interest, depending on study objectives. Depth-integrated samples typically are collected when the cyanobacterial community is evenly distributed throughout a layer of interest, or the interest is primarily in dissolved concentrations. An exception may be when the distribution of cyanobacteria in the water column cannot be determined; in this case an integrated photic-zone sample generally is considered representative. There are two types of depth-integrated samples: continuous and discontinuous.

Continuous Depth-Integrated Samples

Continuous samples incorporate the entire depth of interest and are collected using bailers or pumps (pumps may not be the best option for sampling—see discussion of pumps in 7.5.5.C above and in NFM 7.4, table 7.4–8). Several continuous samples may be composited to obtain the necessary sample volume.

Bailers are cylindrical tubes with a check valve at the bottom that allows water inflow, but prevents outflow when raised. Bailers can be open or have check valves also at the top. Bailers are available in a variety of lengths and in a variety of materials. Teflon should be used when collecting samples for cyanobacterial toxin and taste-and-odor analyses.

To collect a continuous sample using a bailer:

1. Select a Teflon bailer that is long enough to incorporate the entire portion of the water column that is of interest. For example, if the photic zone extends to a depth of 2 m and an integrated photic-zone sample is being collected, then the bailer needs to be at least 2 m in length.
2. Lower the bailer slowly, until the bottom (the check-valve intake) is at the bottom of the desired depth interval.
3. Bring the bailer to the surface.
4. Draw off the water into a Teflon churn by means of a bottom-emptying device that releases the check valve.
5. Repeat the above steps until the volume of water required for analyses has been collected.

To collect a continuous sample using a pump (NFM 4.1.1.B):

1. Lower the pump intake to the bottom of the desired depth interval.
2. Allow three sample-tubing volumes to rinse the sample tubing with native water before collecting the sample (NFM 4.1.1.B).
3. Slowly raise the sampler through the vertical while pumping continuously at a constant rate.
4. Pump the sample directly into a Teflon churn until the volume of water required for analyses has been collected. This may require raising and lowering the sampler several times; turn off the pump either at the fully raised or fully lowered position, not in the middle of the range of sampling depths.

Discontinuous Depth-Integrated Samples

Discontinuous samples do not incorporate the entire depth of interest, and typically are collected using Kemmerer or Van Dorn bottles. The percent of the water column represented can be increased by using a vertical sampler rather than a horizontal sampler (table 7.5–6; NFM 2.1.1.B, Thief samplers; NFM 4.1.3). Pumps also may be used to collect discontinuous samples. Kemmerer and Van Dorn bottles and pumps are used in the same manner as described in section 7.5.5.C, except the composite is composed of samples collected from different depths, rather than the same depth.

- A depth-integrated sample may be obtained by collecting and compositing several discontinuous samples from multiple depths within the layer of interest.
- The sampling intervals must be equal (for example, every meter within the photic zone) when collecting discontinuous depth-integrated samples (Chorus and Bartram, 1999; American Public Health Association, 2005).

7.5.5.E QUALITY CONTROL

Quality-control samples such as blanks, replicates, and splits are an integral component of well-designed water-quality studies (NFM 4.3). Replicate samples (independent or 'true' replicate samples, and split replicates) are used to assess total variability in sample collection, processing, shipping, handling, and analysis of toxins, taste-and-odor compounds, and cyanobacterial (phytoplankton) community composition. The types, number, and distribution of quality-control samples to be collected are specified in the quality-assurance plan for the study and depend on study design and objectives. General information on different types of quality-control samples are discussed elsewhere (Friedman and Erdmann, 1982; U.S. Environmental Protection Agency, 2008; NFM 4.3).

- Equipment and field blanks are collected to verify the adequacy of cleaning procedures and the influence of equipment cleaning and sample handling on analyte concentrations (NFM 4.3.1). Field blanks are particularly important when sampling equipment is being cleaned in the field after collecting samples from surface accumulations of cyanobacteria (fig. 7.5–7*A*). To ensure there is no carry-over contamination, field blanks are best collected at the end of the day after the last sample (NFM 7.4.1.D). Organic-grade blank water (that is, pesticide-grade blank water (PBW)) is used for collecting equipment and field blanks. USGS equipment and field-blank data are stored in the National Water Information System (NWIS) QWDATA database 2.
- Cyanobacterial communities tend to have an irregular distribution within the water column and throughout a lake or reservoir; therefore, field replicates (NFM 4.3.2) to assess variability among samples are particularly important in studies of cyanobacterial toxins and taste-and-odor compounds. Concurrent field replicates may be used to assess the variability introduced from sample collection as well as inherent system variability at a single location within a lake or reservoir. Because of the patchy nature of cyanobacterial communities, particularly surface accumulations, concurrent field replicates cannot be used to evaluate laboratory variability. Concurrent replicates in lakes/reservoirs are collected as described in NFM 4.3.2.A with the appropriate modifications, depending on whether surface, discrete-depth, or depth-integrated samples are being collected.

Example—To collect concurrent replicates of a composite discontinuous integrated photic-zone sample with samples collected every 1 m from the surface to a depth of 5 m, using a horizontal Van Dorn bottle:

1. Using clean equipment, complete equipment field-rinsing procedures.
2. At 0.5 m, collect a sample and draw off the sample into a field-rinsed Teflon churn splitter.
3. Resample at 0.5 m and draw off the sample into a second field-rinsed Teflon churn splitter.
4. At 1.0 m collect a sample and draw off the sample into the second churn splitter.
5. Resample at 1.0 m and draw off the sample into the first churn splitter.
6. Collect and draw off the sample into each churn splitter in this manner for each of the remaining depths (2.0 m, 3.0 m, 4.0 m, and 5.0 m), alternating churn splitters as described in steps 2 through 5 listed above.
7. Process and preserve a sample (a) from the first churn, and (b) from the second churn (see section 7.5.6).

▶ Sequential field replicates may be used to assess inherent system variability and can be designed to assess spatial variability by collecting samples from two or more locations within a given sampling area; for example, two discontinuous integrated photic-zone samples collected 10 m apart. Sequential replicates also may be used to assess temporal variability (NFM 4.3.2.B); however, because cyanobacteria may change location in the water column, use caution when interpreting data from temporal replicates that are collected hours or more apart.

▶ Split samples (NFM 4.3.2.C) may be used to evaluate intra- and inter-laboratory variability. Evaluating inter-laboratory variability is particularly important when using multiple laboratories for toxin and taste-and-odor analyses because methods for the extraction and analysis of toxins and taste-and-odor compounds are evolving rapidly and are not consistent among laboratories. Likewise, there are several accepted methods for cyanobacterial (and phytoplankton) enumeration and identification.

Use of a single laboratory throughout the study is recommended. Methods for the extraction and analysis of toxins and taste-and-odor compounds and cyanobacterial identification and enumeration often are inconsistent among laboratories.

7.5.5.F ANCILLARY DATA

Ancillary data collected during cyanobacterial toxin and taste-and-odor studies will depend on the study objectives. Chlorophyll samples commonly are collected as part of cyanobacterial toxin and taste-and-odor studies; chlorophyll is an indicator of algal biomass (NFM 7.4) and frequently is included in general water-quality monitoring programs. Other commonly measured variables are listed in table 7.5–8. Generally, all subsamples for laboratory analyses, including cyanobacterial community composition and toxin and taste-and-odor analyses, are collected from the same grab or composite sample. The volume of the grab or composite sample must be sufficient for all planned analyses.

Table 7.5–8. Commonly collected ancillary data for studies of cyanobacterial toxins and taste-and-odor compounds.

[NFM, National Field Manual for the Collection of Water-Quality Data; GPS, global positioning system]

Ancillary data	Description	References for additional information
Observational data	• General field observations such as water color and clarity, current meteorological conditions, presence of visible algae, presence of surface accumulations or scums of cyanobacteria • Meteorological conditions several days before sampling • Occurrence of recent inflow events • Water residence time • Lake level	NFM 4 Wetzel and Likens, 2000
Field measurements	• Photographs of current conditions • GPS coordinates • Vertical profiles of light, temperature, dissolved oxygen, specific conductance, pH, turbidity, and in situ fluorescence • Secchi disc depth	NFM 4 NFM 6 NFM 7.4.1B Wetzel and Likens, 2000
Laboratory analyses	• Phytoplankton community composition, abundance, and biovolume	Procedures described in this NFM section 7.5 Britton and Greeson, 1987 Standard Methods for the Examination of Water and Wastewater, Sections 1060 and 10200
	• Chlorophyll	NFM 7.4
	• Nutrients - total nitrogen and phosphorus, total Kjeldahl nitrogen (ammonia plus organic nitrogen), nitrate, nitrite, ammonia, and orthophosphorus	NFM 4.0, 4.1 NFM 5
	• Suspended sediment	NFM 4.0, 4.1 NFM 5
	• Actinomycetes bacteria (taste-and-odor studies)	NFM 7.1
	• Alkalinity	NFM 4. 0, 4.1 NFM 5 NFM 6.6
	• Cations and anions	NFM 4.0, 4.1 NFM 5
	• Carbon: total, dissolved, and particulate	NFM 4.0, 4.1 NFM 5

SAMPLE HOLDING TIME, PROCESSING, AND SHIPPING 7.5.6

Several cyanobacterial toxins and taste-and-odor compounds commonly are measured, including the toxins microcystin, cylindrospermopsin, anatoxin, and saxitoxin, and the taste-and-odor compounds geosmin and MIB.

A key decision when designing toxin and taste-and-odor studies is whether total, particulate, or dissolved concentrations will be analyzed, as this affects the procedures to be used for sample preparation, processing, and preservation. Some laboratories may request whole-water samples and do all processing in-house; others will provide specific instructions on sample bottle type and preferred preservation, whereas others may provide sample bottles and preservatives. There also may be restrictions on delivery days that can affect analyses of unpreserved samples. Clear communication with the laboratories performing the analyses is required to ensure that sample analyses will provide relevant results. Although sample preparation, processing, and shipping largely may be determined by the analyzing laboratory, general guidelines are provided below. **The guidelines below provide common processing procedures; however, if the analyzing laboratory provides contradictory or alternative instructions, those should be followed instead.**

The specific instructions from the analyzing laboratory on sample processing, preservation, and shipping should be followed carefully. Contact the laboratory with any questions.

SAMPLE HOLDING TIME 7.5.6.A

Ideally, all samples are processed on-site. If samples must be transported to the office laboratory before being processed, place the samples on ice and keep in the dark, because heat and light can degrade cyanobacterial cell integrity, toxins, and taste-and-odor compounds. **If shipping is delayed, contact the analyzing laboratory for guidance.**

- If the analyzing laboratory is processing the samples, then samples must be shipped on the same day they are collected.
- For samples being processed on-site:
  - **Phytoplankton samples** must be processed and preserved as soon as possible after collection. Once preserved, they may be stored for extended periods of time (weeks to months), although it is preferable to ship the samples to the laboratory on the day of collection or as soon as possible thereafter.

— **Toxin samples** should be processed and shipped to the laboratory on the day of collection. (Although current understanding does allow toxin samples to be held for up to 24 hours before being processed if the samples are kept cold and stored in the dark, shipping them to the laboratory on the same day as collection is preferable.)

— **Taste-and-odor samples** must be shipped on the same day they are collected, regardless of whether the samples are processed on-site or by the laboratory.

Samples should not be frozen without guidance from the analyzing laboratory. Many cyanobacterial toxins do not degrade when frozen, and samples may be stored in a freezer for several months or years (Chorus and Bartram, 1999). Keep in mind that if whole-water samples are frozen, cyanobacterial cells will lyse and release intracellular toxins. Freezing and thawing whole-water samples frequently is used to determine total toxin concentration (Graham and others, 2008). Taste-and-odor samples generally are not frozen.

Once whole-water samples are frozen, only total toxin concentrations can be measured.

7.5.6.B SAMPLE PROCESSING

How samples are processed depends on the targeted analytes and study objectives. Processing samples for cyanobacteria, toxins, and taste-and-odor compounds consists primarily of preparing composite samples, withdrawing subsamples from the composite, filtering those samples to be analyzed for dissolved-phase concentrations, and preserving the samples as dictated by the analyzing laboratory. In general, sample processing will have a minimal impact on cyanobacterial cells when implemented properly.

- The rate for churning a composite sample should not exceed the recommended 9 inches per second (NFM 5.1.1.A) and the disk should not break the surface of the water; as long as these recommendations are followed, churning should not lyse cyanobacterial cells.
- Sample bottle type and volume will usually be determined by the analyzing laboratory. Common bottle types for each analysis are listed in table 7.5–7.

Procedures are described below for processing toxin and taste-and-odor samples, and for cyanobacterial (phytoplankton) samples.

Toxin and Taste-and-Odor Samples

The procedures used for processing toxin and taste-and-odor samples depend on whether the samples are to be analyzed for total, particulate, or dissolved concentration. **Analysis of taste-and-odor compounds most commonly is performed on dissolved samples, but total and particulate concentrations also are determined regularly** (van der Ploeg and others, 1992; Wnorowski and Scott, 1992; Jones and Korth, 1995; Yen and others, 2007). Taste-and-odor compounds are semi-volatile; however, the traditional volatile organic carbon sampler does not need to be used when processing samples unless specified by the analyzing laboratory. The procedures for each are described as follows.

- **Total-Concentration Samples**. Total concentration samples measure both particulate (intracellular) and dissolved (extracellular) phases of cyanobacterial toxins and (or) taste-and-odor compounds. Total concentrations are measured in whole-water samples (fig. 7.5–9). Alternatively, total concentrations also may be calculated by summing particulate and dissolved concentrations (fig. 7.5–9).

  To process total-concentration samples:

  1. Follow the general USGS procedures for processing raw (unfiltered) samples (NFM 5.1), using CH/DH protocols (NFM 4.0.2 and NFM 5.0.1).
  2. Wear disposable, powderless gloves throughout sample collection and processing.
  3. Prelabel the sample bottle. The label must include the station name and number, date, time, type of sample (for example, integrated photic zone), sample depth (for example, 0 to 5 m), and type of analysis (for example, total toxin).
  4. Homogenize the water sample by churning as described above, and withdraw (subsample) enough water to fill the sample bottle.
     - If samples will be frozen, bottles should be filled only to two-thirds full to allow for expansion.
     - Bottle type and volume will depend on instructions from the laboratory at which the samples will be analyzed (table 7.5–7).
  5. Protect the sample from light and immediately place it on ice. If the sample bottle is glass, first put it into a protective foam sleeve to prevent breakage. Loose ice is preferred over block ice to reduce the chance of breakage during shipping.

Clear communication with the analyzing laboratory is critical to ensuring proper sample handling for the analysis to be performed.

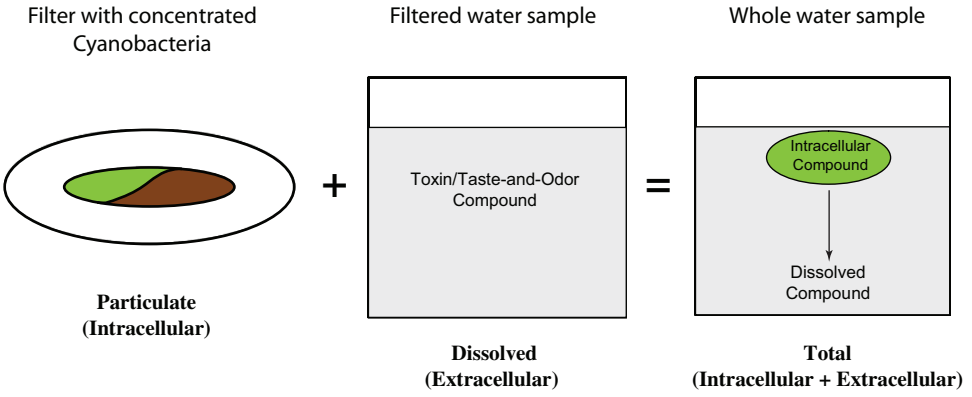


Figure 7.5–9. Schematic showing the partitioning of cyanobacterial toxins and taste-and-odor compounds among the total, particulate, and dissolved phases in different types of samples. From Graham and others (2008).

▶ **Particulate-Concentration Samples**. Particulate samples measure only the intracellular phase of cyanobacterial toxins and (or) taste-and-odor compounds. Particulate concentrations are measured by concentrating cyanobacteria from a known volume of water onto a filter. Alternatively, particulate concentrations also may be calculated by taking the difference between total and dissolved concentrations (fig. 7.5–9).

To process particulate-concentration samples:

1. Follow the general USGS procedures for processing raw (unfiltered) samples (NFM 5.1), using CH/DH protocols (NFM 4.0.2 and NFM 5.0.1).
2. Wear disposable, powderless gloves throughout sample collection and processing.
3. Homogenize the water sample by churning as directed above, and withdraw a subsample.
4. Process the subsample in the same manner as phytoplankton chlorophyll samples (the procedure is described in NFM 7.4, section 7.4.5.A) using 0.7-micrometer (μm) glass fiber filters and a glass or metal filter funnel and glass receiving flask. The maximum pressure of the filtering apparatus must not exceed 15 pounds per square inch (NFM 7.4.5); greater pressure may rupture cyanobacterial cells. For particulate analysis, the material retained on the filter is kept for analysis. The sample filtrate may be discarded or analyzed for dissolved concentration.
5. Record the filtered volume on the field sheet and on the sample label.
6. Label the sample. The label must include the station name and number, date, time, type of sample (for example, integrated photic zone), sample depth (for example, 0 to 5 m) type of analysis (for example, particulate toxin), and volume filtered.
7. Keep the sample chilled until it is shipped by immediately placing it on ice. Pack the sample on dry ice for shipping (it is not necessary to place the sample immediately on dry ice after processing). If samples are not shipped immediately upon return to the office laboratory, place them in the freezer.

▶ **Dissolved-Concentration Samples.** Samples for analysis of dissolved concentrations are used to measure only the extracellular phase of cyanobacterial toxins and (or) taste-and-odor compounds.

To process dissolved-concentration samples:

1. Follow the general USGS procedures for processing raw (unfiltered) samples (NFM 5.1), using CH/DH protocols (NFM 4.0.2 and NFM 5.0.1).
2. Wear disposable, powderless gloves throughout sample collection and processing.
3. Prelabel the sample bottle. The label must include the station name and number, date, time, type of sample (for example, integrated photic zone), sample depth (for example, 0 to 5 m) and type of analysis (for example, dissolved toxin).
4. Homogenize the water sample by churning as directed by USGS protocol, and withdraw a subsample.
5. Filter the subsample in the same manner as phytoplankton chlorophyll samples (see the procedure described in NFM 7.4, section 7.4.5.A) using 0.7-µm glass fiber filters and a glass or metal filter funnel and glass receiving flask. The filtrate from preparation of particulate toxin samples or chlorophyll samples may be used for dissolved-concentration analysis.
6. Pour the filtrate from the glass receiving flask into the sample bottle. Be sure to filter enough volume to fill the sample bottle. If samples will be frozen, bottles should be filled only to two-thirds full to allow for expansion. Bottle type and volume will depend on instructions from the laboratory at which the samples will be analyzed (table 7.5–7).
7. Protect the sample from light and immediately place on ice. If the sample bottle is glass, first put it into a protective foam sleeve to prevent breakage. Loose ice is preferred over block ice to reduce the chance of breakage during shipping.

Toxin and taste-and-odor concentrations typically are expressed volumetrically as micrograms per liter (µg/L) because volumetric concentrations are easily related to drinking-water and recreational- guideline values. Concentrations also may be expressed gravimetrically as micrograms per gram (µg/g) ash-free dry weight.

To estimate ash-free dry weight:

1. Prepare an additional sample for particulate analysis using the same volume of water.
2. Immediately place the sample on ice. Samples should be shipped on dry ice (it is not necessary to place the sample immediately on dry ice after processing if it is being shipped the same day). If samples are not shipped immediately upon return to the office laboratory place them in the freezer.
3. USGS employees send the sample to the National Water Quality Laboratory for phytoplankton ash-free dry weight analysis (Lab Code 2190).
4. Use ash-free dry weight to calculate gravimetric concentrations:
   Particulate toxin (µg) ÷ ash-free dry weight (g) = µg toxin/g of ash-free dry weight.

TECHNICAL NOTE: Gravimetric concentrations must be interpreted with caution. When collected from dense accumulations of cyanobacteria, gravimetric expression of toxin or taste-and-odor concentration often is directly related to cyanobacterial abundance; however, when collected in open-water areas, ash-free dry weight will incorporate all suspended organic material including other phytoplankton, zooplankton, and detritus (Chorus and Bartram, 1999).

Cyanobacterial (Phytoplankton) Samples

Cyanobacteria are considered to be part of the phytoplankton community, and there is no difference between samples collected for cyanobacterial analysis and phytoplankton analysis. Cyanobacteria and phytoplankton samples typically are analyzed for community composition, abundance (cells or natural units per milliliter or liter), and biovolume (cubic micrometers per milliliter or liter) (Blomqvist and Herlitz, 1998; Olrik and others, 1998). Because there can be great variability among analysts, it is important to confirm counting and processing methodologies before the analysis, including subsample preparation, counting threshold, taxonomic references, and the experience of the analyst. This is particularly important when using multiple laboratories for analysis. Because of variability among laboratories, any interpretation based on data from different laboratories must be undertaken with great caution and several split replicate samples collected from a range of environmental conditions must be analyzed to assess analytical variability. **Switching laboratories during the course of a study is strongly discouraged.**

TECHNICAL NOTE: Some cyanobacterial colonies or filaments may exceed the maximum particle size (250 micrometers) recommended for use of a churn splitter (NFM 2.2.1); however, particle size is not an important criterion for churn-splitter use when dealing with cyanobacteria. In contrast to sediment processing, settling is not an issue for cyanobacteria or algae. Churning velocity will maintain all cyanobacterial and algal size classes within the sample, regardless of buoyancy. Although some colonies and filaments may break apart during the churning process, individual cell integrity should not be affected by churning. Use of the churn splitter is inappropriate, however, when collecting samples from thick surface accumulations with little water content.

To process cyanobacterial (phytoplankton) samples for identification and enumeration:

1. Follow the general USGS procedures for processing raw (unfiltered) samples (NFM 5.1), using CH/DH protocols (NFM 4.0.2 and NFM 5.0.1).
2. Wear disposable, powderless gloves throughout sample collection and processing.
3. Prelabel the sample bottle. The label must include the station name and number, date, time, type of sample (for example, integrated photic zone), sample depth (for example, 0 to 5 m), and type of analysis (for example, dissolved toxin). Bottle type and volume will depend on instructions from the laboratory at which the samples will be analyzed (table 7.5–7).
4. Homogenize the water sample by churning as directed by USGS protocol and fill the sample bottle, leaving enough room to add the preservative.

5. Add the required amount of preservative to the sample. The type of preservative selected depends on the requirements of the laboratory doing the analysis. Lugol's iodine and glutaraldehyde are commonly used preservatives. Because of its toxicity (see ***CAUTION*** below), handle glutaraldehyde with care and follow all safety precautions.
   - Handle these preservatives only under good ventilation, wearing gloves and safety glasses.
   - Keep the Material Satety Data Sheets (MSDS) for Lugol's iodine and glutaraldehyde close at hand.
   - Disposal of these chemicals must conform to local ordinance and governmental regulations.
6. Protect sample from light and immediately place on ice. If sample bottle is glass, first put it into a protective foam sleeve to prevent breakage. Loose ice is preferred over block ice to reduce the chance of breakage during shipping.

CAUTION: **Glutaraldehyde is highly toxic. Handle glutaraldehyde only as directed and at the recommended concentration. For a 5 to 25 percent aqueous solution, the MSDS states that glutaraldehyde is corrosive; causes eye burns; is harmful if inhaled, absorbed through skin, or swallowed; causes severe skin irritation and irritation to the respiratory tract (*http://www.jtbaker.com/msds/englishhtml/g4404.htm*, accessed 05/06/2008). Inhalation can be fatal at higher concentrations (*http://msds.chem.ox.ac.uk/GL/glutaric_dialdehyde.html*, accessed 05/06/2008).**

Detailed information on how to collect and preserve phytoplankton samples can be found in Britton and Greeson (1987), American Public Health Association (2005), Wetzel and Likens (2000), and from the laboratory at which samples will be analyzed.

Because the variability among laboratories can be substantial, any interpretation of data base on data from a variety of laboratories must be undertaken with great caution, and only if the appropriate quality-control measures have been incorporated so that analytical variability can be assessed.

7.5.6.C SAMPLE SHIPPING

Before shipping, check the samples to ensure that labels include:

1. Station name and number
2. Date
3. Time
4. Type of sample (for example, integrated photic zone)
5. Sample depth (for example, 0 to 5 m)
6. Type of analysis (for example, particulate toxin)
7. Volume filtered (for particulate toxin analysis only)

Place clear tape over the completed sample label to protect it during shipping from direct contact with cube or loose ice (not block ice) or dry ice.

Samples must be kept chilled (on ice or refrigerated) and in the dark until shipped. Ideally, samples should be shipped on the same day they are collected, following the instructions provided by the analyzing laboratory.

- Samples, other than those for particulate analysis, typically are placed in a cooler, packed in double bags on ice, and shipped using priority overnight mail to arrive at the analyzing laboratory the next morning.
- Particulate samples are packed with dry ice and double bagged, and should be shipped separately from other samples. (For guidance on shipping samples on dry ice see NFM 7.4, section 7.4.6.B.) Appropriate sample documentation should be placed in a separate resealable plastic bag and attach to the inside lid of the shipping cooler. The documentation required will depend on the requirements specified by the analyzing laboratory.

Be aware of sample holding times when shipping to areas of the country that may be experiencing adverse weather. It is better to hold samples under controlled conditions than to have samples exposed to extreme temperatures if shipments get delayed; however, **unprocessed toxin samples need to be shipped within 24 hours**. Once preserved, samples for cyanobacterial and phytoplankton analysis may be stored for longer periods of time (weeks to months); nevertheless, they should be shipped to the analyzing laboratory as soon as possible.

ANALYTICAL TECHNIQUES 7.5.7

A variety of analytical techniques can aid in the determination of cyanobacterial toxins (Graham and others, 2008). Relative advantages and disadvantages of common analytical techniques utilized for analysis of cyanobacterial toxins and taste-and-odor compounds are shown in table 7.5–9. Bioassays, such as enzyme-linked immunosorbent assays (ELISA) typically are easy to learn and use, and are relatively cost effective when used as a screening tool or, when appropriate, for toxicity assessment (Chorus and Bartram, 1999; Msagati and others, 2006); however, cross-reactivity can lead to a lack of specificity for the target analyte(s) (Metcalf and others, 2002). If toxin-specific information is required, the chromatographic techniques are more appropriate, but the cost is greater per sample in comparison to bioassays. Researchers are utilizing multi-toxin liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) methods more frequently because of the ability to distinguish a larger variety of individual toxins more readily, and avoid the derivatization that would be required for any gas chromatography (GC)-based technique. LC/MS and LC/MS/MS can suffer from matrix effects (the influence of other chemical constituents in a sample that impacts quantitation of the analyte of interest leading to signal enhancement or suppression) more than the other techniques, but it is possible to compensate for this problem through standard addition (a laboratory "spike" sample).

Fewer analytical options are available for determining taste-and-odor compounds. Closed- and open-loop stripping techniques combined with a GC flame ionization detector or GC-MS have been used previously, but stripping techniques largely have been replaced by solid-phase microextraction (SPME) where phase transfer of the semivolatile compounds to the gas phase is followed by separation and detection by GC/MS. Typical method reporting levels range from 1 to 5 nanograms per liter (ng/L), the lower threshold for human detection of these compounds through smell (Zimmerman and others, 2002; Taylor and others, 2005). Currently, there are no commercially available ELISA methods for taste-and-odor analysis sensitive enough to be of practical use.

Table 7.5–9. Advantages and disadvantages of common analytical techniques used for the analysis of cyanobacterial toxins and taste-and-odor compounds.

Analytical techniques	Advantages	Disadvantages
Bioassays		
Enzyme-linked immunosorbent assays (ELISA), inhibition assays, and radioassays	• Relatively easy to use • Cost per analysis lowest of all techniques • Can be useful as screening tools • Can indicate toxicity in some cases	• Data interpretation can be difficult • Inhibition assays and radioassays not always available • Bioassays frequently possess some reactivity towards compounds other than the intended target • Radioassays require permits to work with radioisotopes • Research objectives may require a chromatographic technique for compound-specific quantitation
Gas Chromatography (GC)		
Flame ionization detector (GC/FID) and mass spectrometry (GC/MS)	• Compound specific • Cost per analysis is intermediate • Compound identification by GC/MS is superior to GC/FID	• Toxins will most likely require derivitization[1] • Not all compounds are amenable to derivitization • GC/FID may require further confirmation • Sample concentration techniques may be necessary
Liquid Chromatography (LC)		
Ultraviolet-Visible (LC/UV-Vis), fluorescence (LC/Fluorescence), mass spectrometry (LC/MS), tandem mass spectrometry (LC/MS/MS), and ion trap mass spectrometry (LC/ITMS)	• Derivitization typically not necessary • Compound specific • Greatest number of toxins are amenable to LC techniques • Cost per analyte can be lowest in a multi-analyte method • Compound identification is superior by LC/MS/MS or LC/ITMS	• Matrix effects can be substantial • Cost per sample most expensive • Spectroscopic techniques may require further confirmation • Sample concentration techniques may be necessary

[1]Derivitization is the chemical modification of an analyte to improve identification, to enhance analyte response, and (or) improve compatibility with a particular analytical technique.

SAFETY CONSIDERATIONS 7.5.8

Cyanobacterial toxins are known to cause human illness, and skin contact may result in irritation and rash.

- Always wear gloves when collecting samples for cyanobacterial toxin and taste-and-odor analysis. If dense surface accumulations are going to be sampled, gloves that extend to the shoulder are recommended.
- Avoid skin and eye contact with dense surface accumulations. If contact with dense surface accumulations occurs, wash the affected area with soap and water and rinse immediately with clean water.
- Inhalation of aerosols may be a problem for those with respiratory illness. Personnel having a recent history of asthma or respiratory disease should take the necessary precautions when collecting or processing samples.
- General safety considerations for water sampling are described in NFM 9.

REPORTING OF CYANOBACTERIAL POPULATIONS, TOXINS, AND TASTE-AND-ODOR COMPOUNDS 7.5.9

Many of the cyanobacterial toxin and taste-and-odor compounds already have parameter codes available for entry into the USGS National Water Information System (NWIS) and updates are made as new compounds and analyses become available.

- USGS personnel should check the NWIS parameter code dictionary to see what codes are available for toxin and taste-and-odor compounds. The parameter code dictionary is available online at: *http://waterdata.usgs.gov/*nwis/help?codes_help #Table8, accessed 7/15/2008.
- Analyzing agency and method codes also need to be entered into NWIS because of the many different extraction and analysis techniques used for toxins and taste-and-odor compounds.

Most cyanobacterial and phytoplankton data are not entered into NWIS, because the system is not amenable for use with biological data. A system for storing cyanobacterial/phytoplanktonic data (for example, possibly using a MicroSoft Access Database) is necessary, and should be developed for each project until a centralized database is available.

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7.5.12 GLOSSARY

Actinomycetes bacteria—A group of aerobic, gram-positive bacteria that are largely terrestrial organisms associated with soils. The actinomycetes bacteria play a major role in the mineralization of organic matter in soils. Actinomycetes bacteria are not photosynthetic and are not part of the phytoplankton community in lakes and reservoirs.

Acute—Single exposure to a relatively high dose of a toxic substance.

Algae—Unicellular or simple multicellular photosynthetic organisms containing chlorophyll-*a*; there are numerous groups of algae, most of which are eukaryotic aquatic organisms.

Allelopathy—Inhibition or suppression of growth by one species of algae or plant by chemicals produced by another species.

Aphotic zone—Region where there is not enough light to support photosynthesis; extends from below the photic zone to the lake or reservoir bottom.

Benthic—Associated with the bottom of a lake or reservoir. After benthos, a term used to describe the bottom of a lake or reservoir.

Bioactive—Indicates that a substance has an effect on living tissue.

Biovolume—The volume of an organism or group of organisms.

Bloom—The term bloom, not specific to cyanobacteria, is inexact and subjective. Common definitions include (1) a large population or extremely high cell densities of phytoplankton (extremely high densities are typically defined as greater than 20,000 to 100,000 cells per milliliter); (2) a proliferation of phytoplankton dominated by a single or a few species; and (3) a visible accumulation of phytoplankton at the water surface.

Blue-green algae—See cyanobacteria.

Cell lysis—The death of a cell due to rupture of the cellular membrane; cell lysis may be caused by natural processes, such as viruses, or artificial processes, such as application of algicides.

Chronic—Repeated exposure to relatively low doses of a toxic substance over an extended period of time.

Cyanobacteria—Cyanobacteria are true bacteria with a prokaryotic cell structure; however, cyanobacteria also have chlorophyll-*a*, a photopigment characteristic of eukaryotic algae and higher plants. Structurally the cyanobacteria are bacteria-like but functionally the cyanobacteria are algae-like. Cyanobacteria are typically sampled and analyzed as part of phytoplankton (algal) assemblages rather than bacterial assemblages in aquatic ecosystems. Cyanobacteria are often called blue-green algae.

Cyanotoxins—Any of a number of toxins produced by the cyanobacteria. The cyanotoxins include dermatoxins, hepatotoxins, and neurotoxins and impact a wide range of aquatic and terrestrial organisms, including humans.

Derivitization—A chemical modification of an analyte to improve identification, to enhance analyte response, and (or) improve compatibility with a particular analytical technique.

Dermatoxin—A toxin that affects the skin and membrane tissues.

Diel—Regular cycle over a 24-hour period.

Epilimnion—The warm, buoyant upper layer of a stratified lake.

Enzyme-linked immunosorbent assay (ELISA)—A biological assay that is based on immunological principles where antibodies specific to an analyte are utilized in a competitive manner with a corresponding antigen resulting in a measureable response. ELISA's typically are not specific to a single compound, but respond to a class of compounds to varying extents and therefore are frequently used to screen samples with further confirmation by an independent technique with specificity such as chromatography.

Eukaryotic—Having cells with a distinct membrane-bound nucleus; characteristic of all organisms except bacteria, cyanobacteria, and other primitive organisms.

Eutrophic—High nutrient content and levels of production.

Eutrophication—Nutrient enrichment (particularly nitrogen and phosphorus) in aquatic ecosystems leading to increased productivity.

Extracellular—Occurring outside of a cell.

Hepatotoxin—A toxin that affects the liver.

Hypereutrophic—Very high nutrient content and levels of production.

Hypolimnion—The cold, dense bottom layer of a stratified lake; the hypolimnion often becomes anoxic (little or no dissolved oxygen) in productive systems.

Icthyotoxin—A toxin that affects fish or is specific to fish.

Incident light—The light that actually falls on a surface.

Intracellular—Occurring within a cell.

Intraperitoneal—Within the abdominal cavity.

Kemmerer bottle sampler—A type of thief sampler used for collecting water samples at discrete depths. The sampler is held open at both ends and lowered vertically through the water column. At the desired depth a mechanism triggers the sampler and it closes, capturing the water at depth. The main difference between a Kemmerer bottle and a Van Dorn bottle is the mechanism used to open and close the bottle. See figure 2–2*A* in NFM 2.

Matrix effects—A general term used to describe the influence of other chemical constituents in a sample that impacts quantitation of the analyte of interest leading to signal enhancement or suppression. This is typically discussed when analyses are conducted by liquid chromatography with spectroscopic detection (fluorescence and ultraviolet visible wavelengths) and mass spectrometry.

Mesotrophic—Moderate nutrient content and levels of production.

Metalimnetic bloom—An algal population that develops at the interface between the epilimnion and metalimnion in a stably stratified lake. Metalimnetic blooms most commonly occur in mesotrophic lakes where light penetrates into the metalimnion.

Metalimnion—The middle layer of a stratified lake; the metalimnion is characterized by substantial decreases in temperature with depth.

Mixed depth—The depth of turbulent mixing; may include all or only a portion of the water column depending on stratification, solar irradiance, and wind.

Neurotoxin—A toxin that affects the central nervous system.

Oligotrophic—Low nutrient content and levels of production.

Photic (euphotic) zone—Region of water column where there is enough light to support photosynthesis; extends from the surface to the depth were light is approximately one percent of that at the surface.

Phycocyanin—An accessory pigment to chlorophyll that is unique to the cyanobacteria.

Phytoplankton—Algae, including the cyanobacteria, suspended in the water column.

Plankton, planktonic—Drifting or weakly swimming organisms (phytoplankton, zooplankton, or bacteria) that are suspended in the water column in lakes, reservoirs, and other fresh and marine water bodies.

Prokaryotic—Having cells that lack a distinct membrane-bound nucleus; characteristic of bacteria, cyanobacteria, and other primitive organisms.

Secondary metabolite—Cellular products that are not directly involved in primary cellular processes that support growth and development.

Senesce (senescence)—The process of growing old; aging.

Species—A distinct kind of organism; the major division of genus.

Standard addition—A quantitative technique used to minimize the impacts of matrix effects where the response of a known mass of the analyte of interest is amended into a split of the sample. This allows for matrix effect compensation against a known mass of analyte.

Strain—A group of organisms of the same species that have distinctive characteristics but are not considered a separate species.

Taste-and-odor compounds—Compounds that produce objectionable tastes and odors in finished drinking water.

Thermocline—The region where temperature change is greater than or equal to 1°C per meter; the terms thermocline and metalimnion often are used synonymously.

Trophic status—Level of productivity in an ecosystem.

Turnover—Complete isothermal mixing of a previously stratified lake.

Van Dorn bottle sampler—A type of thief sampler used for collecting water samples at discrete depths. The sampler is held open at both ends and lowered either vertically or horizontally through the water column. At the desired depth a mechanism triggers the sampler and it closes, capturing the water at depth. The main difference between a Van Dorn bottle and a Kemmerer bottle is the mechanism used to open and close the bottle. In addition, the Van Dorn bottle may be held either vertically or horizontally, while the Kemmerer bottle can be used only in the vertical position. See figure 2–2*B* in NFM 2.

APPENDIXES

APPENDIX 7.5–A. Example Design and Approach for a Regional Reconnaissance Study to Determine the Occurrence of Cyanobacterial Toxins and Potential Toxin Producers

APPENDIX 7.5–B. Example Design and Approach for a Study to Monitor a Recreational Beach for Cyanobacterial Toxins

APPENDIX 7.5–C. Example Design and Approach for an Interpretive Study to Develop a Real-Time Model to Estimate Geosmin and 2-methylisoborneol (MIB) Concentrations

For all lake and reservoir field work:

- **Wear a personal floatation device (PFD) and appropriate protective clothing when sampling in water or from a boat.**
- **Use sampling methods appropriate for the collection of samples to be analyzed at parts-per-billion to parts-per-trillion concentrations.**

APPENDIX 7.5–A. Example Design and Approach for a Regional Reconnaissance Study to Determine the Occurrence of Cyanobacterial Toxins and Potential Toxin Producers

Objective

Document the occurrence of cyanobacterial toxins and potential toxin producers in all primary recreational and drinking-water-supply lakes and reservoirs within a State.

Design and Approach

Sampling frequency. Samples will be collected monthly during June through September, the period when cyanobacterial populations typically peak.

Site location. In small lakes and reservoirs, samples will be collected at a single, representative open-water site near the deepest part of the lake or reservoir. In large lakes and reservoirs, samples will be collected at representative open-water sites in each of the main basins (lakes) or tributary arms, including a site near the outlet or dam (for manmade reservoirs). If present, samples from surface accumulations of cyanobacteria also will be collected.

Sample type. Integrated photic-zone samples will be collected from open-water sites. Surface grab samples will be collected from surface accumulations.

Sampler used. Samples will be collected every meter throughout the photic zone using a vertical Van Dorn bottle. The samples from each depth will be composited in a churn. An open-mouth bottle sampler will be used for surface grab samples.

Type of toxin analysis. Cyanobacterial toxin samples will be analyzed for total (particulate plus dissolved) toxin concentrations for anatoxins, cylindrospermopsins, and microcystins.

Ancillary data. At each sampling site, photographs and global positioning system (GPS) coordinates will be recorded and Secchi disc depth and vertical profiles of light (irradiance), water temperature, dissolved oxygen, specific electrical conductance, pH, turbidity, and in situ fluorescence will be measured. In addition to cyanobacterial toxins, each sample will be analyzed for cyanobacterial (phytoplankton) community composition (enumeration, biovolume, and identification); chlorophyll; total phosphorus and nitrogen concentrations; and suspended sediment.

Quality-control samples. Equipment blanks and field blanks will be collected during each monthly sampling trip. Sequential replicates (true field replicates) will be collected for 20 percent of all samples. Split replicates will be collected for 10 percent of all samples.

Results. The results from this study can give an indication of how frequently cyanobacterial toxins occur in the State, which toxins are most common, and the range of typical concentrations. Potential cyanobacterial toxin producers also will be identified. General water-quality conditions in the State during peak periods of cyanobacterial abundance will be described. **This study will not, however, give a good indication of maximum toxin concentrations; monthly samples may miss periods of peak cyanobacterial toxin abundance.**

Field Form for a Regional Reconnaissance Study for Occurrence of Cyanobacterial Toxins and Potential Toxin Producers

Station Information		
Station Name:	Date: (MM/DD/YY) _____/_____/_____	Time: ___ ___ ___ ___
Station Identification Number:		
Project Name:		
Sampled By:	Samples Shipped By:	Date: (MM/DD/YY) _____/_____/_____

Sampling Information
Sample Type: Regular Concurrent Replicate Sequential Replicate Split Replicate Field Blank Laboratory Blank Other:_____
Sample Collection: Integrated Photic Zone Sample Surface Accumulation Sample Photic Depth: Sample Depths: Sampling Device: Vertical Van Dorn Open Mouth Bottle Sampler Sampling Method: Multiple Vertical Grab Sample

Physical Site Conditions
Lake Color: Brown Green Blue Clear Other_____
Surface Accumulation Present: Yes No Accumulation Sample Collected: Yes No Location:
Sky: Clear Cloudy _____% Precipitation: Light Medium Heavy Rain Mist Fog
Wind: Calm Light Breeze Gusty Windy
Other Observations:

Related Sampling Activities		
Variable	Supporting Information	Collected (Check)
Total Cyanobacterial Toxins	Bottle Type: HDPE Amber Glass	
Phytoplankton	Preservative: Preservative volume:_____	
Chlorophyll	Volume Filtered:	
Nutrients		
Suspended Sediment		
Remarks:		

Field Form for a Regional Reconnaissance Study for Occurrence of Cyanobacterial Toxins and Potential Toxin Producers—*continued*

Field Measurements		
Latitude: __ __°__ __' __ __" N	Secchi Disc Depth:	Air Temperature:
Longitude: __ __°__ __' __ __" W	Surface Irradiance:	Barometric Pressure:
	Photic Depth:	Other:

Vertical Profile

Depth	Irradiance	Water Temperature	Dissolved Oxygen	Specific Conductance	pH	Turbidity	In situ Fluorescence

Photographs/Observations:

APPENDIX 7.5–B.
Example Design and Approach for a Study to Monitor a Recreational Beach for Cyanobacterial Toxins

Objective

Monitor a recreational beach to determine if cyanobacterial toxins pose an acute exposure risk.

Design and Approach

Sampling frequency. Samples will be collected weekly between Memorial Day and Labor Day, the periods of peak recreational use. If cyanobacteria accumulate in the beach area, daily samples will be collected until the accumulation dissipates.

Site location. Samples will be collected from nine locations within the designated recreational area and composited. The nine locations will be determined by evenly dividing the recreational area into three transects that begin at the beach and extend into the water. Samples will be collected from three locations (ankle, knee, and chest deep) along each transect. Sample collection starts at the waters edge in ankle-deep water and continues into the water to approximately chest depth. Ankle-deep water samples will be collected approximately 0.15 meters (m) below the surface. Knee- and chest-deep water samples will be collected approximately 0.30 m below the surface. If dense cyanobacterial accumulations are present outside of transect locations, an additional sample will be collected from the accumulation.

Sample type. Surface grab samples will be collected. At knee- and chest-deep locations, samples will be collected approximately 15 centimeters below the water surface. Dense cyanobacterial accumulations will be sampled at the water surface.

Sampler used. Grab samples will be collected with an open-mouth bottle at each transect location and composited into a churn.

Type of toxin analysis. Cyanobacterial toxin samples will be analyzed for total (particulate plus dissolved) toxin concentrations for anatoxins, cylindrospermopsins, and microcystins.

Ancillary data. At each sample transect, global positioning system (GPS) coordinates will be recorded. In addition, photographs will be taken, and Secchi disc depth, water temperature, dissolved oxygen, specific electrical conductance, pH, turbidity, and in situ fluorescence will be measured at one central location in the recreational area.

Quality-control samples. Equipment blanks and field blanks will be collected monthly. Sequential replicates (true field replicates) will be collected for 20 percent of all samples. Split replicates will be collected for 10 percent of all samples.

Results. The results from this study will give an indication of when cyanobacterial toxin concentrations are elevated enough to cause human health concerns. Data collected may be used to post warnings or close recreational areas. Study results also will give an indication of the range of cyanotoxin concentrations in the recreational area and when peak values typically occur.

Field Form for a Study to Monitor a Recreational Beach for Cyanobacterial Toxins

Station Information		
Station Name:	Date: (MM/DD/YY) _____/_____/_____	Time: ___ ___ ___ ___
Station Identification Number:		
Project Name:		
Sampled By:	Samples Shipped By:	Date: (MM/DD/YY) _____/_____/_____

Sampling Information
Sample Type: Regular Concurrent Replicate Sequential Replicate Split Replicate Field Blank Laboratory Blank Other:_____
Sample Collection: Surface Grab Sample Surface Accumulation Sample Sampling Device: Open Mouth Bottle Sampler Sampling Method: Grab Sample

Physical Site Conditions
Lake Color: Brown Green Blue Clear Other_____
Surface Accumulation Present: Yes No Accumulation Sample Collected: Yes No Location:
Sky: Clear Cloudy _____% Precipitation: Light Medium Heavy Rain Mist Fog
Wind: Calm Light Breeze Gusty Windy
Other Observations:

Field Measurements		
Latitude: __ __°__ __' __ __" N	Secchi Disc Depth:	pH:
Longitude: __ __°__ __' __ __" W	Water Temperature:	Turbidity:
Air Temperature:	Dissolved Oxygen:	In Situ Fluorescence:
Barometric Pressure:	Specific Conductance:	Other:
Photographs/Observations:		

Sample Locations		
Transect 1	Transect 2	Transect 3
Ankle Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W	Ankle Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W	Ankle Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W
Knee Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W	Knee Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W	Knee Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W
Chest Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W	Chest Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W	Chest Depth: Latitude: __ __°__ __' __ __" N Longitude: __ __°__ __' __ __" W
Remarks:	Remarks:	Remarks:

Related Sampling Activities		
Variable	Supporting Information	Collected (Check)
Total Cyanobacterial Toxins	Bottle Type: HDPE Amber Glass	
Remarks:		

APPENDIX 7.5–C.
Example Design and Approach for an Interpretive Study to Develop a Real-Time Model to Estimate Geosmin and 2-methylisoborneol (MIB) Concentrations

Objective

Describe the environmental factors that are associated with taste-and-odor episodes caused by cyanobacteria in a drinking-water supply reservoir and develop a real-time model to estimate the probability of geosmin and MIB concentrations exceeding the human detection threshold of 10 nanograms per liter.

Design and Approach

Sampling frequency. Samples will be collected monthly from November through April and bi-weekly from May through October, when cyanobacteria typically are abundant in the drinking-water supply reservoir. The sampling regime may need to be adjusted depending on potential ice cover. During a taste-and-odor event, sampling frequency will be increased to weekly or semi-weekly. Sample collection will continue for 5 years.

Site location. The main study site will be located within the vicinity of the drinking-water intake. Other locations also may be sampled if surface accumulations of cyanobacteria develop.

Sample type. The type of samples collected will depend on the vertical structure and distribution of cyanobacteria. Generally, when the water column is stratified, integrated samples will be collected from the epilimnion, metalimnion, and hypolimnion; when the water column is not stratified, integrated photic-zone samples will be collected. Surface samples and discrete-depth samples also may be collected depending on cyanobacterial distribution.

Sampler used. A pump will be used to collect depth-integrated samples and discrete-depth samples. An open-mouth bottle sampler will be used to collect surface samples. All sample types will be composited in a churn for sample processing.

Type of taste-and-odor analysis. Cyanobacterial taste-and-odor samples will be analyzed for total and dissolved concentrations of geosmin and MIB.

Ancillary data. Real-time water-quality monitors will be installed in the photic zone near the drinking-water intake, and will measure lake level, light (irradiance), water temperature, dissolved oxygen, specific electrical conductance, pH, turbidity, and in situ fluorescence. An anemometer (wind meter) also will be installed at the site. Other meteorological data will be obtained daily from a local weather station and the timing of inflow events will be recorded.

During each sampling, site photographs and global positioning system (GPS) coordinates will be recorded and Secchi disc depth and vertical profiles of light (irradiance), water temperature, dissolved oxygen, specific electrical conductance, pH, turbidity, and in situ fluorescence will be measured. In addition to taste-and-odor compounds, each sample will be analyzed for total and dissolved cyanobacterial toxins, cyanobacterial (phytoplankton) community composition (enumeration, biovolume, and identification), chlorophyll, actinomycetes bacteria, nutrients, suspended sediment, major ions, and alkalinity.

Quality-control samples. Equipment blanks and field blanks will be collected quarterly. Sequential replicates (true field replicates) will be collected for 20 percent of all samples. Split replicates will be collected for 10 percent of all samples.

Results. The results of this study will describe the seasonal patterns in the occurrence of taste-and-odor compounds and give an indication of when taste-and-odor episodes are most likely to occur. In addition, the relations between environmental variables, cyanobacterial community composition, and the occurrence of taste-and-odor compounds will be described, and may indicate potential management options. Real-time data and discrete water-quality samples will allow the development of a real-time model to estimate the probability that taste-and-odor compound concentrations will exceed the human detection threshold. This model can allow the drinking-water treatment facility to adjust treatment accordingly and minimize the effects of taste-and-odor occurrences on drinking-water quality.

Field Form for a Study to Develop a Real-Time Model to Estimate Geosmin and 2-methylisoborneol (MIB) Concentrations

Station Information		
Station Name:	Date: (MM/DD/YY) _____/_____/_____	Time: ___ ___ ___ ___
Station Identification Number:		
Project Name:		
Sampled By:	Samples Shipped By:	Date: (MM/DD/YY) _____/_____/_____

Sampling Information

Sample Type: Regular Concurrent Replicate Sequential Replicate Split Replicate Field Blank
Laboratory Blank Other:_____

Sample Collection: Integrated Epilimnion Integrated Metalimnion Integrated Hypolimnion
Integrated Photic Zone Discrete Depth Surface Accumulation

Photic Depth:
Integrated Sample Depths:
Discrete Sample Depth:

Sampling Device: Pump Open Mouth Bottle Sampler

Sampling Method: Multiple Vertical Point Sample Grab Sample

Physical Site Conditions

Lake Color: Brown Green Blue Clear Other_____

Surface Accumulation Present: Yes No Accumulation Sample Collected: Yes No

Location:

Sky: Clear Cloudy _____% Precipitation: Light Medium Heavy Rain Mist Fog

Wind: Calm Light Breeze Gusty Windy

Other Observations:

Related Sampling Activities

Variable	Supporting Information	Collected (Check)
Total Taste-and-Odor		
Dissolved Taste-and-Odor		
Total Cyanobacterial Toxins	Bottle Type: HDPE Amber Glass	
Dissolved Cyanobacterial Toxins	Bottle Type: HDPE Amber Glass	
Phytoplankton	Preservative: Preservative volume:_____	
Chlorophyll	Volume Filtered:	
Actinomycetes Bacteria		
Nutrients		
Suspended Sediment		
Major Ions		
Alkalinity		

Remarks:

Field Form for a Study to Develop a Real-Time Model to Estimate Geosmin and 2-methylisoborneol (MIB) Concentrations—*continued*

Field Measurements		
Latitude: __ __°__ __'__ __" N	Secchi Disc Depth:	Air Temperature:
Longitude: __ __°__ __'__ __" W	Surface Irradiance:	Barometric Pressure:
	Photic Depth:	Other:

Vertical Profile

Depth	Irradiance	Water Temperature	Dissolved Oxygen	Specific Conductance	pH	Turbidity	In situ Fluorescence

Photographs/Observations:

CONVERSION FACTORS, SELECTED TERMS, SYMBOLS, CHEMICAL FORMULAS, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
micrometer (μm)	3.937×10^{-5}	inch (in.)
	3.3×10^{-6}	foot (ft)
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
square centimeter (cm^2)	0.155	square inch (in^2)
meter (m)	3.281	foot
nanometer (nm)	3.93×10^{-8}	inch
liter (L)	0.264	gallon (gal)
milliliter (mL)	0.0338	ounce, fluid (oz)
gram (g)	0.03527	ounce, avoirdupois
microgram (μg)	3.527×10^{-8}	ounce, avoirdupois
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois
kilopascal (kPa)	0.1450	pound per square inch (lb/in^2)

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$
$$°C = (°F/1.8) – 32$$

SELECTED TERMS

Distilled or deionized water: ASTM type 1 water or better.

Equipment blank: A quality control sample that consists of a blank solution processed sequentially through each component of the equipment system to be used in sample collection, processing, preservation, and handling in a controlled environment. The sample is prepared by passing sterile water or buffer through the sampling equipment (if applicable) and into a sterile sample container. Positive results for the equipment blank indicate sampling and analytical bias caused by contamination from equipment and supplies.

Field blank: A quality-control sample that consists of a laboratory-certified blank solution processed through all the equipment used in the various stages of sample collection, processing, preservation, and handling under field conditions. **For quality control of water samples for microbial analyses,** the blank sample is prepared by passing either sterile deionized or distilled water (DIW) or sterile buffered water through the sampling equipment (if applicable) into a sterile sample container. Positive growth on the field blank indicates sampling and analytical bias caused by contamination from equipment, supplies, and (or) ambient environmental conditions.

Field-generated sequential replicate and split replicate: Quality-control samples that measure the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or higher multiples and collected close in time and space—are considered identical in composition and are analyzed for the same properties. **For quality control of water samples for microbial analyses,** two samples are collected sequentially in the field (sequential replicates) and each sample is analyzed twice (split replicate). The relative percent difference between the results is calculated as a measure of variability.

Filter blank (membrane-filtration): As applied to the quality control of water samples for microbial analyses, the filter blank measures the sterility of the equipment and supplies used during the membrane-filtration procedure for bacterial indicators. A 50- to 100-mL sample of sterile buffered water is passed through the filtration apparatus onto a sterile membrane filter before processing the sample. Positive growth on the filter after incubation on selective media indicates poor technique in analysis and positive bias (contamination) of results.

Matrix spike (laboratory matrix spike): A quality-control sample that determines the effect of the sample composition (matrix) on the recovery efficiency of the analytical method. For quality control of water samples for microbiological analyses, a sample is prepared in the laboratory by adding a known quantity of organisms to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available.

Micrometer (µm): The millionth part of the meter. The pore diameter of filter media is expressed in micrometer units.

Negative control: A quality-control sample that measures the selectivity of the membrane-filtration medium for the test organism. A pure culture of nontarget organisms is passed through the filtration apparatus onto a membrane filter and cultured on a selective medium. The absence of growth on the filter after incubation on a selective medium indicates the selective medium is meeting its specifications for culture of the target organism.

Normality, *N* (equivalents per liter): The number of equivalents of acid, base, or redox-active species per liter of solution. Examples: a solution that is 0.01 *F* (formal) in HCl is 0.01 *N* in the hydronium ion (H^+). A solution that is 0.01 *F* in H_2SO_4 is 0.02 *N* in acidity.

Positive control: A quality-control sample that ensures the analytical method is correctly performed and that target organisms are correctly identified and detected. A pure culture of the target organism is passed through the filtration apparatus onto a membrane filter and cultured on a selective medium. Positive growth within a recommended range is considered indicative of the quality of the test medium and procedures to support growth under typical working conditions.

Procedure blank: A quality-control sample that measures the effectiveness of the analyst's rinsing technique during the membrane-filtration procedure for bacterial indicators. A 50- to 100-mL sample of sterile buffered water is passed through the filtration apparatus onto a sterile membrane filter after processing the sample. Positive growth on the filter after incubation on a selective medium indicates poor rinsing technique.

SELECTED SYMBOLS AND CHEMICAL FORMULAS

>	greater than
≥	equal to or greater than
<	less than
≤	equal to or less than
±	plus or minus
g/L	gram per liter
µm	micrometer
µg/L	microgram per liter (equivalent to parts per billion)
$CaCl_2$	calcium chloride
Cu	copper
$FeCl_3$	ferric chloride
H_2SO_4	sulfuric acid
K_2HPO_4	potassium hydrogen phosphate
KH_2PO_4	potassium dihydrogen phosphate
$MgSO_4$	magnesium sulfate
Na_2SO_3	sodium sulfite
$Na_2S_2O_3$	sodium thiosulfate
$NaHPO_4$	sodium phosphate
NaOH	sodium hydroxide
Ni	nickel
NH_4Cl	ammonium chloride
Zn	zinc

ABBREVIATIONS

BOD	biochemical oxygen demand
BOD_5	biochemical oxygen demand (5 day)
CBOD	carbonaceous biochemical oxygen demand
$CBOD_u$	ultimate carbonaceous biochemical oxygen demand
col/100mL	colonies per 100 milliliters
DIW	deionized or distilled water
DO	dissolved oxygen
E. coli	*Escherichia coli*
EDI	equal-discharge increment

EDTA	ethylenediaminetetraacetic acid
EIA	enterococcus confirmation medium (esculin substrate)
+ ETFE	ethylenetetraflouroethylene
EWI	equal-width increment
FEP	fluorinated ethylene propylene
GWUDISW	ground water under the direct influence of surface water
IPR	initial precision recovery
KF	streptococcus medium
mCP	*Clostridium perfringens* medium
mE	membrane filter—Enterococci medium
mEI	enterococcus medium
mENDO	membrane filter—total coliform medium
mF	membrance filter technique
mFC	membrane filter—Fecal Coliform medium
MI	total coliform and *Escherichia coli* medium
MPN	most probable number
mTEC	membrane filter—Thermotolerant *Escherichia coli* media
N	normal
NA–MUG	nutrient agar-4-methylumbelliferyl-b-D-glucuronide
+ NFM	National Field Manual (*National Field Manual for the Collection of Water-Quality Data*)
NWIS	National Water Information System of the U.S. Geological Survey
OPR	ongoing precision recovery
OWQRL	USGS Ocala Water Quality & Research Laboratory, Ocala, Florida
PDF	personal flotation device
PFA	perflouroalkyoxy polymers
PTFE	polytetraflouroethylene polymers ("Teflon")
QC	quality control
TCMP	2-chloro-6-(trichloro methyl) pyridine
TD	to deliver
TNTC	Too Numerous To Count
TTC	triphenyltetrazolium chloride
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

+

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APPENDIX A7-A.

Parameter Codes Used in the National Water Information System (NWIS) of the U.S. Geological Survey

Table 1. Parameter code for 5-day biochemical oxygen demand

Determination	Parameter code	Comments
Five-day biochemical oxygen demand (BOD)	00310	Parameter codes for methods other than the 5-day BOD can be found by accessing "Support Files" in the QWDATA database and searching for "Parameter Code Dictionary."

Table 2. Parameter codes for fecal indicator bacteria

[mENDO, total coliform medium; MI, total coliform and *Escherichia coli* medium; mFC, fecal coliform medium; µm, micrometer; mTEC, *Escherichia coli* medium; NA-MUG, *Escherichia coli* medium; mEI, enterococcus medium; EIA, enterococcus confirmation medium; mE, enterococcus medium; KF, fecal streptococcus medium; mCP, *Clostridium perfringens* medium]

Fecal indicator bacteria type[1]	Medium	Parameter code[2]
Total coliform bacteria	mENDO	31501
	MI	90900
Fecal coliform bacteria	mFC, 0.65-µm pore-size filter	31625
	mFC, 0.45-µm pore-size filter	31616
Escherichia coli	mTEC followed by urea phenol	31633
	Modified mTEC	90902
	MI	90901
	NA-MUG	50278
Enterococci bacteria	mEI followed by EIA	90909
	mE	31649
Fecal streptococci bacteria	KF	31673
Clostridium perfringens	mCP	90915

[1]Membrane-filtration method: all units are in colonies per 100 milliliters.
[2]The parameter codes listed are those that are in common (2003) use in the National Water Information System (NWIS) of the U.S. Geological Survey.

Table 3. Parameter codes for somatic and F-specific coliphages

[SAL, single-agar layer; *E. coli*, *Escherichia coli*; mL, milliliter; L, liter]

Type of coliphage	*E. coli* host strain[1]	Parameter code[2]	Unit of measurement[3]
SAL method			
Somatic	*E. coli* CN-13	90903	plaques/100 mL
F-specific	*E. coli* F-amp	90904	plaques/100 mL
Somatic	*E. coli* C	90905	plaques/100 mL
Two-step enrichment method			
Somatic	*E. coli* C	99328	Presence or absence/100 mL
Somatic	*E. coli* C	99329	Presence or absence/1 L
Somatic	*E. coli* C	99330	Presence or absence/4 L
Somatic	*E. coli* CN-13	99331	Presence or absence/100 mL
Somatic	*E. coli* CN-13	99332	Presence or absence/1 L
Somatic	*E. coli* CN-13	99333	Presence or absence/4 L
F-specific	*E. coli* F-amp	99334	Presence or absence/100 mL
F-specific	*E. coli* F-amp	99335	Presence or absence/1 L
F-specific	*E. coli* F-amp	99336	Presence or absence/4 L

[1]Bacterial host strain used to detect the specified coliphage type.
[2]The parameter codes listed are those that are in common use (2003) in the National Water Information System of the U.S. Geological Survey.
[3]Parameter codes vary by the sample volume associated with the unit of reporting.

Table 4. Parameter codes for *Cryptosporidium* and *Giardia*

[**Parameter code:** Analysis by U.S. Environmental Protection Agency Method 1623]

Parameter name	Parameter code	Unit of measurement
Cryptosporidium	99599	oocysts per 10 liters
Cryptosporidium—spike efficiency	99600	percent recovery
Giardia	99597	cysts per 10 liters
Giardia—spike efficiency	99598	percent recovery

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A8. BOTTOM-MATERIAL SAMPLES

By
Dean B. Radtke

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
P. PATRICK LEAHY, *Acting Director*

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192
This report is accessible online at http://pubs.water.usgs.gov/twri9A/

Foreword

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and quality-assured data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that the data collected are of the quality required to fulfill our mission.

(signed)

Robert M. Hirsch
Associate Director for Water

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BOTTOM-MATERIAL SAMPLES

National Field Manual for the Collection of Water-Quality Data

Chapter A8

Tables

Chapter A8. BOTTOM-MATERIAL SAMPLES

By **Dean B. Radtke**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) describes protocols (requirements and recommendations) and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This release of Chapter A8 provides guidelines for the equipment and procedures needed to collect and process samples of bottom material for the evaluation of surface-water quality.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters are posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed April 2005).

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources.

The *National Field Manual* is Section A of Book 9 of the USGS publication series Techniques of Water-Resources Investigations (TWRI). The *National Field Manual* is comprised of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*.

Chapter A8 on bottom-material samples includes procedures and guidelines for selection of sampling sites, selection and decontamination of equipment, and the collection, processing, packaging, and shipping of samples. Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this report.

PURPOSE AND SCOPE

Chapter A8 of the *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to the collection and processing of bottom-material samples. The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures; (2) provide citable documentation for USGS water-quality data-collection protocols; (3) encourage consistent use of field methods for the purpose of producing nationally comparable data; and (4) provide methods that minimize biasing the data and, when properly applied, that result in data that are reproducible within defined limits of variability.

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. The fundamental responsibility of field personnel is to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. However, whenever a standard procedure is modified or an alternative procedure is used, a description of the procedure used and supporting quality-assurance information are to be reported with the data.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to: NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to: nfm-owq@usgs.gov). Newly published and revised chapters are posted on the World Wide Web under "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed April 2005).

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BOTTOM-MATERIAL A8. SAMPLES

Bottom-material samples are routinely analyzed to assess the occurrence, abundance, and distribution of chemical constituents in surface-water systems. The chemical analysis of bottom materials addresses a broad spectrum of objectives in water-quality studies, including surveillance monitoring, mass-transport loading, remediation effectiveness, presence or absence of contaminants, and spatial extent and temporal change of chemical constituents.

Bottom material consists of living and non-living, organic and inorganic material of varying physical, chemical, and biological composition that has been transported by water, ice, and wind and deposited in aquatic systems.

Obtaining samples that are representative of the environment being monitored is essential to the data-collection process and of primary importance to the accuracy of the final result. Data are no better than the confidence that can be placed in sample representativeness (Feltz and Culbertson, 1972). Conscientious scrutiny and quality-control checks applied during laboratory analyses of samples, while necessary, cannot compensate for data that are biased because of samples that are nonrepresentative of the environmental system or that were collected improperly.

A representative bottom-material sample is a sample that:

- Typifies ("represents") all possible samples within the study environment determined within the objectives and scope of the investigation.
- Results from minimizing all sampling biases.

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FIELD TRIP PREPARATIONS 8.1

Preparation for bottom-material sampling starts with an understanding of the scientific approach of the study. The quality of the data to be collected depends on a field team that has the knowledge and experience needed to select sites, equipment, and methods for collecting and processing samples that will fulfill study objectives.

Before each field trip plan carefully for field activities:

- Schedule adequate time to review data requirements.
- Select a protocol for bottom-material data-collection activities.
- Develop and use checklists of activities, equipment, and supplies to ensure that field activities will be completed efficiently (see section 8.7).
- Create or update a field folder for each site at which samples and ancillary data will be collected. Review the information before starting field work.

Before selecting sampling sites and equipment:

- Review the project work plan, especially noting the types of measurements and samples required.
- Make reconnaissance field trips.
  - Note conditions that would affect sampling operations (such as high flow versus low flow in streams, or unusual aspects of the site that might be sources of contamination).
  - Evaluate potential sources and sinks of contaminants or other chemical constituents of interest.
- Review site files and field folders (note site location and description and site-access instructions; review any previously collected physical, chemical, and biological data).
- Obtain (and update) training needed to perform routine and special procedures.
- Understand the limitations of each piece of equipment. Verify and test, if possible, the operational range and potential for contamination of sampling equipment.

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SITE SELECTION 8.2

The study sites selected for sampling bottom material will affect the quality of the data collected. Guidelines are provided in this section for selecting the location and number of subareas or sampling points at a site. Apply these guidelines as appropriate for meeting study objectives.

LOCATION OF SAMPLING SITES 8.2.1

For most studies, in most bodies of water, a single site or sampling point is not adequate to represent the physical properties, distribution, and abundance of chemical constituents and biologic communities in a water body. Each body of water, whether flowing or still, has a unique set of conditions to be identified for the site-selection process. These conditions must then be evaluated with respect to study objectives for sampling bottom material. Mudroch and MacKnight (1994) state, "There is no formula for design of a sediment sampling pattern which would be applicable to all sediment sampling programs."

Before selecting a site location, review the historical information available about the site, such as flood history, land use, and type and source of any previous contamination. Delineate in three dimensions the environmental system or portion of that system to be studied. When selecting a sampling site, consider the safety of field personnel and the type of equipment and sampling methodology that will be needed. After the site has been selected, map the area from which samples will be collected. Consider using global-positioning equipment (for site positioning), a side-scan sonar sub-bottom profiler, and (or) acoustic survey (such as echo, seismic reflections, and refraction) to characterize the configuration of the stream bottom, and photography to help identify sampling location(s).

Data quality begins before the first sample is collected.

As part of the process for selecting site locations, consider study objectives with respect to:

- The proximity to the sampling site of manmade structures such as bridges, roads, and piers—selecting sites near such structures can interfere with data-collection objectives and therefore such sites normally are avoided.
- Locating sites near a water discharge-stage gaging station—such site locations are advantageous for data interpretation.
- **Perennial flowing streams**—Sample during low-flow periods. **Ephemeral and intermittent streams**—Sample immediately after water recedes, while bottom material is still wet.
- The geomorphology, geology, and geography of the area, such as its size and shape, tributary and runoff patterns, streambank structure and lithology, land use, and climate.
- The chemical, physical, and biological character of the water column above the sample-collection site (for example, water depth and hydraulics, fluvial-sediment transport characteristics, and especially the presence or absence of oxygen).
- The chemical, physical, and biological character of the bottom material to be sampled.
  - Chemical characteristics include geochemistry/mineralogy, oxidation state, colloidal/noncolloidal fractions, inorganic/organic composition, spatial and temporal heterogeneity, bioassay data, and data from reconnaissance sampling.
  - Physical characteristics include size fraction, texture, structure, thickness, pore-water content, horizontal and vertical spatial heterogeneity, and temporal heterogeneity.
  - Biological characteristics include population densities, and community structure and diversity of aquatic organisms.
- The use of either statistical or deterministic methods to select the location and number of sampling sites.

NUMBER OF SAMPLING SITES 8.2.2

The number of sampling sites or subareas at a site is determined when the scientific approach to the study is designed.

Statistical or deterministic methods can be used to select the distribution and number of sampling sites. Deterministic methods for selecting sampling sites for bottom material are based on professional judgment alone. Shelton and Capel (1994) discuss use of deterministic models to determine the presence or absence of chemical constituents, carry out surveillance monitoring, identify the occurrence and extent of target constituents, and for environmental reconnaissance. Statistical approaches are used for the more rigorous analyses frequently required for study objectives that address environmental assessments of chemical mass-transport loading and remediation, and temporal and spatial change and magnitude of chemical constituents. Statistical methods applied to the selection of sites for bottom-material sampling include stochastic random, stratified random, systematic regular, and fixed transect methods (table 8–1) (Horowitz, 1991; Mudroch and Azcue, 1995).

Table 8–1. Applications and limitations of selected statistical methods for selection of sites for collection of bottom-material samples

Stochastic random method

- Commonly used in reconnaissance surveys where little is known about local conditions.
- Most unbiased method of site selection.
- Efficient in areas with homogeneous bottom material.
- Potentially ineffective in areas with heterogeneous bottom material.

Stratified random method

- Often permits elucidation of subtle but real differences.
- Requires knowledge of local conditions.

Systematic regular method

- Randomness achieved through selection of initial sampling site using a number chosen from a random numbers table or from electronically generated random numbers.
- Produces biased results.

Fixed-transect method

- Sites not chosen randomly, therefore any inferences are site specific, and areal conclusions may not be valid.

To determine the number of subareas on the basis of homogeneity of bottom material and the accuracy required by study objectives, see TECHNICAL NOTE, below. Without knowledge of sample variation, the degree to which the data accurately represent the bottom material cannot be known.

TECHNICAL NOTE: Detailed information on estimating sample size using statistical methods can be found in Natrella (1966), Crepin and Johnson (1993), Mudroch and Azcue (1995), and other statistics texts. To determine the number of subareas using equations (1) and (2), obtain a "***t***" table from any statistics textbook. Knowledge of statistics also is required for calculating the standard deviation and understanding how to determine the degrees of freedom:

$$n' = (t_{1-a/2}\ s)^2 / d^2 \qquad (1)$$

$$n_1 = (t'_{1-a/2}\ s)^2 / d^2 \qquad (2)$$

where:

- t = a number chosen from a "***t***" table for a desired confidence interval using an estimated value for degrees of freedom (estimate of subareas needed is based on experience),
- $1-a/2$ = two-sided confidence interval where a is chosen confidence interval,
- s = standard deviation,
- d = standard error or variability, in mean concentration, assuming sample mean is normally distributed,
- n' = first estimate of number of subareas to sample,
- n_1 = final estimate of minimum number of subareas needed to meet required sampling objectives.

Step 1. Compute n' from equation (1) as follows:

a. Choose d (the allowable margin of error) and a (the risk that the estimate of mean will not be off by ± d or more).

b. Choose the number of degrees of freedom appropriate to study needs. Degrees of freedom (*df*) for t are chosen arbitrarily using experience gained from other areas where bottom material has been sampled for the same target constituents.

c. Calculate s from actual data from study area, or estimate s using the formula $s = (R/4)$ at the 95-percent confidence interval where R = expected range of concentrations.

d. Determine t from a t table by calculating $t_{1-a/2}$ using chosen a. For example, if a = 95%, then $t_{1-a/2} = t_{0.975}$.

e. Compute n' where $n' = (t_{1-a/2}\ s)^2 / d^2$.

Step 2. Compute n_1 from equation (2) as follows:

a. Use same values of a, d, and s as in step 1.

b. Determine t from calculating $t'_{1-a/2}$ and using $n'-1$ degrees of freedom.

The computed n_1 value should be less than computed n' value. Adjust the various estimated variables—variance (s^2), standard error (d), or confidence interval—accordingly, if greater accuracy is required, or lesser accuracy is acceptable, in meeting study objectives. **Remember, this is an estimate.**

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SAMPLING EQUIPMENT 8.3

Equipment used to collect and process bottom-material samples is described below. Field personnel must understand the limitations of the equipment selected, decide which equipment will give the best results for the procedures selected, and be thoroughly familiar with equipment operation before starting field work. The decontamination and storage procedures for sampling equipment described in 8.3.2 are necessary to prevent contamination of samples.

EQUIPMENT SELECTION 8.3.1

Equipment selected must meet data-collection objectives. Be aware that no bottom-material sampling equipment is appropriate for every objective and environmental setting. Most bottom-material samplers were designed primarily for the collection of bottom-material samples for benthic-invertebrate or particle-size analysis and generally are not adequate for collecting undisturbed samples for chemical and mineralogical analysis. Most bottom-material samplers are particularly unsuited for collecting samples from the critical water-sediment interface. Characteristics of the more common bottom-material samplers are listed in table 8-2. Additional information on bottom-material samplers and sampling equipment is provided in Sly (1969), U.S. Geological Survey (1978), Plumb (1981), Edwards and Glysson (1988), Norris (1988), Ward and Harr (1990), Horowitz (1991), Mudroch and MacKnight (1994), and Mudroch and Azcue (1995).

When selecting bottom-material sampling equipment, consider:

- Safety of the field team—Safety always takes precedence.
- Sampling platform and (or) access to sampling site (boat, ship, float plane, helicopter, ice, bridge, scuba, wading, cableway).
- Physical character of cross-sectional area (such as size, velocity, slope, bathymetry, and sampling area depth).
- Physical character of bottom material (such as particle size, organic content, degree of consolidation).

- Sampling equipment limitations (with respect to physical disturbance of bottom, retention of fines, degree of sample compaction or induration, penetration depth, grain-size sampling efficiency, portability).
- Winch system operation (ideally should be capable of free-fall and controlled descents).
- Sample size and weight.
- Target analytes (materials used to construct equipment can leach or be abraded and can measurably affect results of sample analysis). Determine appropriate construction materials based on target analytes.
  - **Inorganic analytes.** All equipment parts that come in contact with a sample must be composed of uncolored or white polypropylene, polyethylene, polyfluorocarbon, or other suitable non-metallic material.
  - **Organic analytes.** All equipment parts that come in contact with a sample must be composed of uncolored polyfluorocarbon, metal, or glass.

Data from bottom-material samples collected with different devices may not be comparable.

8.3.1.A Samplers

Two commonly used samplers for collecting bottom materials are grab samplers and core samplers (table 8–2). Dredge samplers are not recommended for use in water-quality studies, primarily because they provide inadequate control of sample location and depth.

Grab Samplers

- Grab samplers are recommended for only very slow-flowing and still water.
- Grab samplers are used for collecting surficial bottom material for temporal and spatial comparisons.
- Grab samplers are susceptible to washout of fine material and dispersion of material in front of the pressure wave created by the sampler.

Core Samplers

- Core (hand, gravity, and piston) samplers are used to collect bottom material for temporal and spatial comparisons.

- Core samplers are susceptible to washout of material, dispersion of material in front of the pressure wave created by the sampler, and compaction of material.

Sieves 8.3.1.B

Bottom-material samples collected for chemical analysis are typically sieved to separate them into various target particle-size fractions. Size-fractionation equipment and procedures vary depending on whether target analytes are inorganic or organic and on the size fraction targeted. Typically, sieves are available with approximately a 76-, 203-, or 305-mm (3-, 8-, or 12-inch) diameter in half, full, or deep stacking height. Sieves usually are constructed with a brass frame and brass or stainless steel wire fabric mesh, stainless steel frame and wire fabric mesh, or high-density polyethylene or nylon frame with either nylon, polyethylene, or polyester monofilament fabric mesh. Nylon fabric mesh can stretch in water. Metallic sieves generally are available with sieve openings from 100 to 0.0020 mm (or approximately 4 to 0.00008 inch). Plastic sieves generally are available with sieve openings from 3.35 to 0.0020 mm (0.132 to 0.00008 inch). Sieves that meet American Society for Testing and Materials (ASTM) E-11 specifications are recommended. Monofilament fabric mesh, however, can have thread diameters and average openings that can vary substantially from ASTM E-11 specifications for metallic fabric.

- **Inorganic analytes.** Use a non-metallic sieve frame and polyester, polyethylene, or nylon monofilament mesh to process bottom material for samples that will be analyzed for metals and metalloids. Use utensils and containers composed of non-metallic material (polyfluorocarbon or other uncolored plastic) for metal and metalloid sample processing.

- **Organic analytes.** Use stainless steel equipment (frame and mesh of sieve, utensils, and containers) to process bottom-material samples that will be analyzed for organic compounds. Brass sieves are acceptable but brass is not the preferred construction material.

Table 8–2. General characteristics of selected grab and core samplers

[Penetration depth, sample volume, and applications are presented in English units because equipment is constructed to English-unit specifications: 1 inch = 2.54 centimeters, 1 pound = 0.4536 kilogram, 1 foot = 0.3048 meter. D, diameter; L, length; W, width; PDC, plastic dip coated; *, trade name; I.D., inside diameter; na, not applicable; mm, millimeter; ft, feet; SS, stainless steel; PVC, polyvinyl chloride; ft/s, feet per second; <, less than]

Sampler designation	Sampler construction material	Sampler dimensions (inches)	Sampler weight (pounds)	Suspension	Penetration depth (inches)	Sample volume (cubic inches)	Application
Grab Samplers							
USBMH-53	SS body, brass piston	2 D x 8 L	7.5	46-inch-long rod	0–8	0–25	Wadable water, loosely consolidated material less than 0.063 mm.
USBMH-60	Cast aluminum body, SS rotary scoop, rubber gasket	8 x 4.5 x 22	32	Hand line or winch and cable	0–1.7	0–10.7	Wadable to water of slow velocity (<1 ft/s) and moderate depth; firm unconsolidated to loosely consolidated material, less than 16 mm; PDC version available; sampler must be equipped with safety yoke.
USBMH-80	SS rotary scoop	2.75 D x 3.25 W	8	56-inch-long rod	0–1.75	0–10.7	Wadable water; unconsolidated to loosely consolidated material, less than 16 mm.
USBM-54	Cast steel body, SS rotary scoop, rubber gasket	8.5 x 7 x 22	100	Winch and cable	0–1.7	0–10.7	Water of moderate velocity and depth; firm unconsolidated to loosely consolidated material, less than 16 mm; PDC version available, sampler must be equipped with safety yoke.
Ponar * (2 sizes)	SS body, zinc-plated steel weights and neoprene flaps	6x6 or 9x9	15–22 or 45–60	Hand line or winch and cable	0–4	0–146.4 or 0–500	Weight dependent; wadable to water of slow velocity (<1 ft/s) and moderate depth; unconsolidated to loosely consolidated material, less than 16 mm; susceptible to loss of fines.
Petersen*	Zinc-plated steel	12 x12	39–93	Hand line or winch and cable	0–12	600	Weight dependent; wadable to water of slow velocity and moderate depth; unconsolidated to consolidated material, less than 16 mm; susceptible to loss of fines.

Table 8–2. General characteristics of selected grab and core samplers—*Continued*

Sampler designation	Sampler construction material	Sampler dimensions (inches)	Sampler weight (pounds)	Suspension	Penetration depth (inches)	Sample volume (cubic inches)	Application
Grab Samplers—*Continued*							
Birge-Ekman* (4 sizes)	SS or brass	6x6x6 or 6x6x9 or 9x9x9 or 12x12x12	16–25 or 21–35 or 47–68 or 100–150	Rod, hand line, or winch and cable	0–3 or 0–4 or 0–5 or 0–6	0–216 or 0–323 or 0–729 or 0–1,726	Wadable to water of slow velocity (< 1 ft/s) and moderate depth; soft unconsolidated material, less than 0.25 mm; susceptible to loss of fines; must penetrate perpendicular.
Shipek*	Cast alloy steel	4 x 6 x 6 or 18.6 5 25.1 5 17.4	11 or 135	Hand line or winch and cable	0–1.2 or 0–4	0–30.5 or 0–183	Wadable to water of moderate velocity and depth; unconsolidated to consolidated material, less than 0.50 mm; susceptible to loss of fines; PDC version available.
Van Veen* (2 sizes)	SS body, zinc-plated steel chain, neoprene flaps	13.8 x 27.6 or 19.7 x 39.4	66–88 or 143–187	Cable	0–12	0–11 or 0–46	Wadable to water of moderate velocity and depth; soft unconsolidated material less than 0.25 mm.
Core Samplers							
Hand	SS or SS core tubes; Lexan* or SS nose piece and SS or plastic core catcher	2 I.D. 20–96 L	10–60	Handle 0–15 ft. L	0–96	0–300	Wadable to diver application, water of slow velocity (< 1 ft/s); soft to semi-firm unconsolidated material less than 0.25 mm; 2-inch core liners available in plastic and SS.
Ogeechee* (sand corer)	SS or SS core tubes; Lexan or SS nose piece and SS or plastic core catcher	2 I.D. 20–96	10–60	Hand corer	0–96	0–300	Wadable to diver application, water of slow velocity (< 1 ft/s) and depth; soft to firm unconsolidated material less than 0.50 mm; 2- inch core liners available in plastic and SS.
Kajak-Brinkhurst [K-B]* (gravity corer)	SS, Lexan, or SS core tubes; Lexan or SS nose piece; SS or plastic core catcher; neoprene valve	2 I.D. 20, 30 L	15–48	Hand line or winch and cable	0–30	0–90	Water with very slow velocity (< 1 ft/s); loosely consolidated material less than 0.063 mm; 2- inch core liners available in plastic and SS.

Table 8–2. General characteristics of selected grab and core samplers—*Continued*

Sampler designation	Sampler construction material	Sampler dimensions (inches)	Sampler weight (pounds)	Suspension	Penetration depth (inches)	Sample volume (cubic inches)	Application
Core Samplers—*Continued*							
Phleger* (gravity corer)	SS core tube, nose piece, core catcher; neoprene valve	1.4 I.D. 20 L	17.6–33	Hand line or winch and cable	0–20	0–40	Water with very slow velocity (< 1 ft/s); soft to firm unconsolidated material less than 0.50 mm; core liners available in plastic.
Ballchek* (gravity corer)	Bronze head, SS or PVC core tubes; Lexan* or SS nose piece and SS or plastic core catcher; plastic/ polyurethane valve	2–5 I.D. 30–96 L	Variable depending on size and construction material	Hand line or winch and cable	0–96	0–750	Water with very slow velocity (< 1 ft/s); loosely consolidated material, less than 0.063 mm; core liners available in plastic and SS.
Benthos* (gravity corer)	Steel core tube, nose piece, and core catcher	2.6 I.D. 120 L	55–320	Winch and cable	120	0–490	Water with very slow velocity (< 1 ft/s); loosely consolidated material less than 0.063 mm; core liners available in plastic.
Alpine* (gravity corer)	Steel core tube, nose piece, core catcher, and neoprene valve	1.6 I.D. 72 L	242–342	Winch and cable	72	0–180	Water with very slow velocity (< 1 ft/s); loosely consolidated material, less than 0.063 mm; core liners available in plastic; inconsistent vertical penetration.
Box	SS with optional acrylic box liner	6 x 6 x 9	31–100	Winch and cable	9	0–300	Water of slow velocity (< 1 ft/s) and moderate depth; unconsolidated material, less than 0.25 mm.
Piston	SS or plastic core tubes; Lexan or SS nose piece; SS or plastic core catcher	1–5 I.D. 40–800 L	25–500	Hand line or winch and cable	0–80	0–6,200	Water with very slow velocity (< 1 ft/s); loosely consolidated material, less than 0.25 mm; core liners available in plastic.
Vibracorer*	Variable	2–3 I.D. 40–500 L	100–300	Frame	0–500	0–2,300	Water with very slow velocity (< 1 ft/s); loosely consolidated material, less than 16 mm; assembly might require scuba divers.

DECONTAMINATION 8.3.2

Decontamination is the cleaning process used to remove potential contaminants from equipment. **Do not collect, process, or handle samples until the equipment has been completely decontaminated.**

Decontaminate all new and used equipment to be used for sample collection, processing, and handling. Equipment also should be decontaminated in the field immediately after completion of sampling. If complete equipment decontamination is not possible in the field, rinse equipment thoroughly with water at the field site and store for complete decontamination. Document decontamination procedures in study notes or on the field form.

Before starting equipment decontamination, check the construction material of field equipment, cleaning equipment, and supplies:

- If your samples will be analyzed for metals and metalloids, do not use metallic equipment and supplies. Use nonreactive cleaning equipment and supplies composed of uncolored or white polypropylene, polyethylene, polyfluorocarbon, or some other suitable non-metallic material.

- If your samples will be analyzed for organic compounds, do not use reactive plastic equipment and supplies. Use nonreactive cleaning equipment and supplies composed of metal, glass, or polyfluorocarbon materials.

- A list of equipment and supplies used to clean and maintain equipment is given in section 8.7.

Use the following three-step decontamination procedure *(put on disposable gloves and other appropriate protective clothing before starting):*

1. Wash equipment thoroughly with **phosphate-free detergent.**
2. Rinse with copious quantities of **tap water.**
   - If equipment has recalcitrant mineral residues, rinse **nonmetallic equipment** with a dilute acid solution.
   - If equipment has recalcitrant oily residues, rinse **nonplastic equipment parts** with pesticide-grade methanol.
3. Rinse with copious quantities of **deionized water.**

Store cleaned equipment inside sealable polyfluorocarbon or other uncolored plastic bags.

Improperly cleaned equipment is a source of sample contamination.

CAUTION: Before handling chemicals, refer to Material Safety Data Sheets for proper precautions.

- **Wear appropriate safety gloves, glasses, and protective clothing.**
- **Clean chemical spills immediately.**
- **Dispose chemical solutions according to regulations.**

SAMPLE COLLECTION 8.4

The field team is responsible for determining what will comprise a representative sample with respect to study objectives and site characteristics. The bottom-material sample must resemble the native bottom material without loss of physical, chemical, and biological structure. The degree to which a single sample can be considered representative depends on many factors, including:

- Temporal and spatial homogeneity of the water body.
- Number and distribution of subareas sampled at a site.
- Method (statistical or deterministic) used to select sampling sites and subareas.
- Size of individual samples.
- Technique used to collect samples and results from the quality-control sample analysis.

Errors introduced by sampling can be the most significant in the entire data-collection process: always collect replicate samples for quality control.

Generic USGS data-collection efforts typically take a whole-system approach, meaning that data are collected using methods to ensure that an entire stream reach is represented. Special studies may require an approach for which samples are representative of a specific, targeted environment or portion of an aqueous system, instead of the entire system. Criteria and considerations for collecting a representative sample are summarized in table 8–3.

CAUTION: Do not jeopardize personal safety when working from boats, planes, bridges; on ice; or in flowing water.

Table 8–3. Criteria and considerations for collecting a representative sample of bottom material

Aspects of sample collection	Criteria and considerations
Equipment	• Sampling equipment penetration must be deep enough to provide a sample that meets project objectives. • Sampling equipment must be completely closed after proper penetration. • Weight of sampler (too light could produce improper deployment of sampler).
Techniques and methods	• Bottom-material disturbance prior to equipment deployment must be avoided. • Quantities of bottom material enclosed each time sampling equipment is deployed should be approximately equal. • Speed of sampler through water column (too fast will produce too large a shock wave in front of descending sampler and greater potential for sampler malfunction, but too slow could produce insufficient penetration, especially with core samplers).
Sampling environment	• Depth of water column (ensure adequate cable length to control speed of sampler deployment and personal safety when wading). • Physical, chemical, and biological character of water column above sample-collection site (especially presence or absence of oxygen). • Velocity of water currents (too fast could produce improper deployment of sampler). • Sampling platform stability (such as boat, ice, float plane).

8.4.1 SAMPLING PROCEDURES

Bottom-material samples must meet the sampling objective of the study. Use procedures that minimize sample disturbance and prevent contamination. Be aware that no procedure for collecting bottom-material samples can be used for every type of study objective and environmental setting.

Complete the following steps before beginning to sample:

1. Select sampling locations (refer to section 8.2 and table 8–4).

   a. Examine each site to be sampled in a manner that minimizes the site's problematic characteristics and maximizes its beneficial characteristics.

      - For perennial flowing water, consider collecting bottom-material samples after extended low-flow periods.
      - For ephemeral flowing water, consider collecting bottom-material samples just after a runoff event.

b. Inspect the body of water visually and bathymetrically.
   - Observe (or refer to historical information on) size and shape of the area, land use, tributary and runoff characteristics, geology, point and diffuse sources of contamination, hydraulics, water depth, and fluvial-sediment transport characteristics.
   - Use aids for site inspection, such as side-scan sonar, sub-bottom profiler or acoustic survey (echo, seismic reflections and refraction), or reconnaissance sampling.

c. Determine number of subareas according to the accuracy required by study objectives.
   - If a transect is split by natural or manmade barriers, treat each channel as a separate entity.
   - Use the two-step method described in the TECHNICAL NOTE in section 8.2.2 to obtain a statistically based estimate of the appropriate number of subareas.

d. If using statistical design methods, divide the site into numbered subareas with a sampling point located in each subarea. Collect samples in the center of numbered sites that correspond to random numbers when using stratified random, stochastic random, or systematic regular methods for design of a sample-collection network.

e. Use global positioning equipment and detailed maps to indicate site location and subareas or their sampling points.

2. Select, assemble, and set out the proper sampling, support, and safety equipment (such as floatation jackets, cable cutter, cones, signs, buoys).
   - Use quality-assured sample containers (jars, bottles, or cartons) supplied by the USGS National Water Quality Laboratory (NWQL) through One-Stop Shopping for USGS studies.
   - Ensure that the weight of a sampler is sufficient to allow proper penetration into the bottom and deployment.
   - Sampler cable or line must be properly secured to sampling platform and sampler in order to avoid losing the sampler.
   - Limitations of using scuba gear are depth, visibility, currents, and personal safety.

Great care must be exercised when using multipurpose equipment for bottom-material sampling and sample processing. Consider following the Clean Hands/Dirty Hands technique described in NFM 4.0.1 and Horowitz and others (1994) when using metal support equipment.

Table 8–4. Procedures for selecting sampling locations using selected nonstatistical and statistical methods

Method	Procedure
Nonstatistical method	
Deterministic	1. Divide total area to be sampled into subareas, using site-characteristics information, study objectives, and professional judgment. 2. Select location and number of subareas within total area on predetermined non-random, biased criteria.
Statistical methods	
Stratified random	1. Divide total area to be sampled into numbered subareas, using site-characteristics information, study objectives, and professional judgment. 2. Determine number of subareas required for sampling. 3. Select subareas using random numbers. 4. Collect sample in center of subarea (sampling point) that corresponds to a random number.
Stochastic random	1. Divide total area to be sampled into equally sized and numbered subareas. 2. Determine number of subareas required for sampling. 3. Select subareas using random numbers. 4. Collect samples in center of numbered subareas (sampling point) that correspond to random numbers.
Systematic regular	1. Divide total area to be sampled into regularly spaced subareas. 2. Determine number of subareas required for sampling. 3. Select subareas using random numbers. 4. Sample at center of each subarea (sampling point), keeping a constant distance between sampling locations.
Fixed transect	1. Sample along a transect at fixed and predetermined subareas (sampling points). These do not need to be at constant intervals. Sampling points can be established to coincide with the location of equal-width-increment (EWI) water sampling verticals. 2. Visually inspect body of water from bank to bank, observing and noting velocity, width, and depth distribution, as well as apparent distribution of sediment in cross section. 3. Determine width from a tagline or from increment markings on cableways or upstream bridge railings. 4. Decide minimum number of increments needed to adequately define bottom material through the transect and also to satisfy study needs and objectives. Where feasible, use a minimum of 10 EWI increments.

Begin sampling after sampling points have been located and equipment set up:

1. Move sampling and support equipment to the first station (sampling point) to be sampled and to each subsequent sampling point, in order, as samples are collected.

   - Avoid disturbance to bottom material at sampling points, caused by wading, movement of vessel and motor, and mixing or compaction of bottom material. Sample disturbance can result from a pressure wave from sampler, frictional resistance during penetration of bottom by sampler, skewed sampler penetration of bottom, and loss (washout) of sample during retrieval.
   - If wading, always approach sampling point from downstream.

2. Make field measurements in water column above sampling point to determine physical, chemical, and biological character of water (especially presence or absence of oxygen). To minimize disturbance to bottom material, make such measurements after collecting bottom-material samples (this precaution applies especially if transect will be waded).

3. Collect samples.

   If using a grab sampler:

   a. Cock bucket in open position.

   b. Steadily lower sampler to bottom, avoiding any jerking motions that would cause the cable to slacken and the bucket to close prematurely.

   c. Upon impact with bottom, tension on suspension cable or handline will be released, allowing spring-loaded sample bucket to scoop a sample. (With some grab samplers, sample bucket most often scoops sample from bottom as sampler is lifted. Therefore, sampler should be lifted slowly to allow bucket to close on the sample before raising it quickly to water surface.)

   d. Discard sample and resample if grab sampler did not close completely or if there was an obvious loss of fine material.

CAUTION: Keep hands away from the opening of the sampling bucket at all times!

If using a core sampler:

a. Use box corers in a similar manner as grab samplers and use gravity, piston, and vibracorer samplers as described by the manufacturer. (Gravity corers generally are not recommended for flowing waters.)

b. Use hand coring when wading or when using scuba gear in nonwadeable water.

- When wading, place sampler on bottom and capture bottom material by pushing sampler into bottom. Avoid hammering.
- Carefully retrieve hand corer and immediately cap it to prevent loss of sample.
- If a core liner is used, remove liner from corer and stopper both ends.

4. Resample if much of the fine-grained material is lost during sampler retrieval.

5. Transfer samples from sampler to either an appropriate sample container or appropriate compositing device using nonreactive utensils and containers and the instructions in section 8.5. Before transferring any extruded core material to an appropriate container, proceed as directed in section 8.5. Repeat for samples collected from each sampling point. **Field extrusion is not recommended.**

- When transferring sample from sampler to a nonreactive, appropriate sample container or compositing device, ensure that all particles are removed and transferred.
- When transferring sample aliquots from sampler to sample container, ensure that each subsample is "representative."

6. Repeat sample-collection procedure at each sampling point across the transect.
   - You will need to collect and homogenize at least three replicate grab samples or three subsamples from a core at each sampling point to make defensible statistical inferences. More replicates may be necessary to achieve a desired level of precision.
   - **A composite of an entire core length generally is not recommended.**
7. Label each sample container with the following information:
   - Station/sampling point number and name.
   - Date.
   - Mean time and gage height (or discharge) for period of sample collection.
   - Station/sampling point location, such as bridge and tagline.
   - Depth of water at sampling point.
   - Sample collection method, sampler used, analyses requested, and other information requested by laboratory performing sample analysis.
   - Number of samples in container if samples are composited.
   - Initials of sample collector.
8. Read and record gage height and time at which sample collection was completed.
9. Complete sample processing and preservation, where applicable. Refer to section 8.5.
10. Calculate and record in field notes the mean time and gage height for the period of sample collection. In field notes, record texture, color, odor, and any other characteristics of the bottom material.
11. Disassemble samplers for decontamination or routine cleaning. Decontaminate samplers as described in section 8.3.2. Always store grab samplers in the closed position.

8.4.2 QUALITY-CONTROL PROCEDURES AND REQUIREMENTS

Quality-control samples are a requisite for any sample-collection and analysis program. Quality-assurance procedures involving quality-control samples are not to be viewed as an option. Quality-control procedures for bottom-material sampling will entail use of split field samples and concurrent replicate field samples.

- **The recommended minimum quality-control samples is 10 percent of the total number of samples collected per year** (total for all field-collected quality-control samples).
- For long-term projects that entail multiple sampling sites, an attempt should be made, during the life of the project, to collect at least one set of field quality-control samples at every sampling site used for that project.
- If seasonal variations are suspected, an attempt also should be made to collect field quality-control samples under various seasonal conditions.

8.4.2.A Split Samples

Split samples are designed to determine analytical precision for chemical constituents in a "real-world" sample matrix. A split sample is an aliquot of an already collected, homogenized, processed, and preserved sample. Split samples are prepared by partitioning a larger volume of processed sample from one container into equal subsamples; samples are split in an enclosed environment and using equipment and methods that preclude sample contamination.

Concurrent Replicate Samples 8.4.2.B

Concurrent replicate samples are two samples that are collected using identical methodology, as closely together in time and space as possible (Horowitz and others, 1994). Concurrent sample data are intended to provide the user with a measure of sampling precision and (or) are intended to indicate inhomogeneities in the system being sampled.

To collect and process concurrent replicate samples:

1. Starting with the first sampling point, collect a sample for compositing and place it in a field-rinsed compositing device.
2. Reoccupy (in close proximity) the first sampling point, collect a second sample, and place it in a second field-rinsed compositing device.
3. Go to the second sampling point, collect a sample, and place it in the second compositing device.
4. Reoccupy (in close proximity) the second sampling point, collect a sample, and place it in the first compositing device.
5. Continue to sample remaining sampling points in this manner, continuing to alternate placement of samples in first and second compositing devices.
6. After all sampling points have been visited, two compositing devices will contain an approximately equal volume of representative samples.
7. Process the first composited sample (see section 8.5); if a split field sample is needed, partition the sample into two appropriate sample containers, with one labeled “Site x, Sample 1, Split A” and the other labeled “Site x, Sample 1, Split B.”
8. Process the second sample, and then if a split field sample is needed, partition it into two appropriate sample containers, with one labeled “Site x, Sample 2, Split A” and the other labeled “Site x, Sample 2, Split B.”

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SAMPLE PROCESSING 8.5

Sample processing includes compositing and subsampling, sieving, phase separation, and sample preservation. Sample preservation normally consists of keeping the sample chilled to 4°C during shipping and storage, but also can involve processing oxygen-sensitive material under an inert-gas atmosphere or freeze drying the sample.

- Use nonreactive equipment. Components of processing equipment need to be made of materials that will not contaminate or adsorb target analytes, and that will withstand cleaning solutions.
  - **Inorganic analytes.** Use utensils, bowls, pans, and containers composed of non-metallic material (polyfluorocarbon or other white or clear plastics).
  - **Organic analytes.** Use utensils, bowls, pans, and containers composed of polyfluorocarbon, glass, or stainless steel.
- Decontaminate all processing equipment as instructed in section 8.3.2.

Prepare for sample processing:

1. Park the field vehicle as far away from any nearby road(s) as possible and turn off motor (road dust and vehicle emissions can contaminate samples) in order to isolate the sample-processing area from potential contaminants.
2. Set up field-processing area. Appropriate areas include a bench set up in a van or a building conveniently located near the sampling site.
   - Spread a large, uncolored or white plastic (non-metallic) sheet over the area where inorganic sample processing is taking place.
   - Use heavy-duty aluminum sheeting over the area where organic sample processing is taking place.
   - Keep sample-processing equipment covered (when not processing sample), and keep all sample containers covered or capped.

3. Field rinse processing equipment to ensure that all cleaning solution residues are removed, and to equilibrate equipment with sampling environment.

4. Wear powderless, disposable gloves while processing sample. Avoid contact with any potential source(s) of contamination. For example, keep gloved hands off any reactive (metal or plastic) objects when processing samples.

8.5.1 COMPOSITING AND SUBSAMPLING

Depending on study objectives, bottom-material sampling methods generally produce a composite sample. When sampling for chemical constituents, the sample usually is subdivided at the field site into a number of subsamples, each equivalent in constituent concentrations.

Use the following procedures when sample compositing and subsampling *(programmatic protocols might supersede some of the following procedures):*

1. Transfer sample (or core segments) from each sampling station to an appropriate compositing device, sieve, or sample container. Be sure to remove and transfer all particles (use nonreactive utensils).

   If using a grab sampler—Go to step 2 if sample is anaerobic and should not be aerated:

   a. With a clean, nonreactive spatula, carefully homogenize the composite sample until texture and color appear uniform.

   b. Using a nonreactive spatula, transfer a homogenized subsample to sieve (see 8.5.2) or sample container.

   If using a core sampler—Go to step 2 if sample is anaerobic and should not be aerated:

   a. If pore water is not a concern, carefully siphon off water overlying material in the corer or liner without disturbing the bottom-material/water interface. Leave a small amount of water at the bottom-material/water interface.

   b. Use a core extruder to gently and slowly force core material out of the corer or core liner.

      • If a core liner is used, visually inspect before extruding, sectioning, or slitting liner and core. Record features observed in field notes.

- Remove core catcher and check valve before extrusion process.
- Begin extrusion process from cutting end of barrel.
- Vertical extrusion is recommended.

c. Split the core lengthwise; visually inspect and make careful measurements of the core length and any layers that appear different.
   - Note deformation and compaction.
   - Note sloping layers, indicating possible nonperpendicular penetration of bottom.
   - Note changes in stratigraphy, such as color and texture.

d. As core is extruded, carefully remove (section) required material with clean, non-reactive utensils and transfer material into an appropriate compositing device or sample container. Transfer only material that meets project and sampling objectives. **It is recommended that only undisturbed core material (material from the interior of the core) be transferred.**

e. If compositing core material or segments, follow procedures listed above for the grab sampler.

2. To process sample in an oxygen-free atmosphere:

   a. Composite samples or extrude core under an oxygen-free atmosphere, such as a portable glove box filled with inert gas.

   b. Extrude cores in an oxygen-free glove box.

   c. Leave no headspace in sample containers.

   d. Pack sample containers in airtight bags and maintain at 4°C.

3. Complete sample processing (and preservation, where applicable).

4. Calculate and record in field notes the mean time and gage height for the period of sample collection. Record in field notes the bottom-material texture, color, odor, and any other characteristics.

5. Disassemble and clean samplers, sieves, and other equipment.

Splitting and subsampling core material are best done in a controlled environment—not in the field.

8.5.2 SIEVING AND SAMPLE HANDLING

To provide a better understanding of the environmental fate of inorganic and organic constituents, bottom-material samples collected for chemical analysis are typically sieved to separate them into various targeted particle-size fractions. **Sieving of bottom material is known to disrupt chemical equilibrium of the sample.**

Study objectives will dictate if sieving or another method of phase separation (such as centrifuge) is used. Data-collection needs will determine the type and construction of equipment, including the type, construction, diameter, and pore size of the sieve. Because sieving can be a labor-intensive process, it is very important to determine, in advance, the mass of sample required for chemical analysis so as not to over or under sieve. The type and quality of equipment used for processing of samples can affect quality of results (section 8.3).

> **TECHNICAL NOTE:** Check with the NWQL before sending bottom-material samples to determine if the samples need to be pre-sieved through a 2.0-mm or smaller sieve. When sieving, use a minimal volume of native water.

Use the following procedures for sample sieving and subsampling:

1. Put on a pair of disposable gloves.
2. Homogenize the composited sample, using appropriate, nonreactive processing equipment:
   a. Decant excess water from sample into an appropriate, nonreactive wash bottle, being careful not to lose fine material.
   b. Visually inspect homogenized composite and record color and texture information in field notes.
3. Select an appropriate, nonreactive sieve or nest of sieves:

   Inorganic constituents.

   - Pre-sieve through a 2.0-mm or smaller sieve.
   - Nest sieves to facilitate sieving process for finer fractions.
   - Use uncolored or white non-metallic sieve and utensils to process bottom material for samples that will be analyzed for metals and metalloids.
   - Use a stainless steel, uncolored, or white non-metallic sieve and utensils to process bottom material for samples that will be analyzed for nutrients, major ions, and radioisotopes.

Organic compounds.

- Pre-sieve through a 2.0-mm or smaller sieve.
- Nest sieves to facilitate sieving process for finer fractions.
- Use a stainless steel sieve and stainless-steel or polyfluorocarbon utensils to process bottom material for samples that will be analyzed for organic compounds. Brass is acceptable but not recommended.

4. Wet sieve an aliquot of the composite as follows:

   a. Place an appropriate, nonreactive container under selected sieve or nest of sieves.

   b. Place an aliquot of composite sample on top of sieve(s).

   c. Using a decontaminated squirt bottle, apply a minimal (<100 mL) amount of native water and any supernatant from the composite to remaining material on sieve(s).

      - If native water has a conductivity of greater than 3,000 µS/cm, use deionized water or dry sieve. (Water other than native water may alter ion-exchangeable solute concentrations.)
      - If necessary and without compromising sieve openings, shake sieve(s) from side-to-side to allow passage of material less than or equal to target particle-size fractions through sieve(s). Use an appropriate, nonreactive utensil to gently work target particle-size fractions through sieve(s).
      - At sites with no native water, sieving should be done dry.

   d. When all wash water has passed through the sieve, allow the material in the catchment container to settle.

   e. Decant the supernatant into a wash bottle constructed of appropriate material and continue to reuse the wash water to sieve any additional material until the required amount of material for analysis is obtained.

   f. When the required amount of material is obtained, allow material in catchment container to settle.

      - Allow sufficient time (while at the field site) for most, if not all, material in supernatant to settle.
      - If fine, colloidal, or organic material fails to settle from supernatant, decant supernatant into a separate sample container and take container back to the lab for additional settling time or centrifugation.
      - **Do not discard supernatant until all fine or organic material has settled from supernatant.**

5. Visually inspect >2-mm fraction.

   a. Record information in field notes:

      - Relative volume of >2-mm fraction.
      - Relative volume of organic matter.
      - Relative abundance of shell fragments or other biological material.
      - Relative abundance of grain coatings of red, yellow, and black oxides.

   b. Retain >2-mm fraction for analysis if germane to study objectives; otherwise, discard.

6. If a 63-µm sieve is used, visually inspect >63-µm fraction.

   a. Record information in field notes:

      - Relative volume of >63-µm fraction.
      - Relative volume of organic matter.
      - Relative abundance of grain coatings of red, yellow, and black oxides.
      - Relative abundance of shell fragments or other biological material.

   b. Retain >63-µm fraction for analysis if germane to study objectives; otherwise, discard.

7. If subsamples are needed for several types of analytical requirements, thoroughly mix the sieved material with an appropriate, nonreactive utensil before subdividing into subsamples.

8. Transfer an appropriate amount of subsample to the appropriate sample container. It is recommended that all bottom-material samples be maintained at 4ºC during shipping and until analysis.

   - **Inorganic constituents.** Use polypropylene container, chill, and maintain at 4ºC.
   - **Organic compounds.** Use glass container with polyfluorocarbon cap liner, chill, and maintain at 4ºC for shipment; 1-L baked glass bottles are needed for most organic analyses—check with the analyzing laboratory for the appropriate sample containers and sample designations.

9. Place samples on ice immediately after collection and again after processing.

SAMPLE PACKAGING AND SHIPPING 8.6

Generally, the shorter the time elapsed between sample collection and analysis, the more reliable will be the analytical results. Ship carefully packed samples as expeditiously as possible. Follow the packaging and shipping requirements of NWQL or other analyzing laboratory. For more information on shipping to NWQL, review NWQL Technical Memorandum 95.04 and Office of Water Quality Technical Memorandum 92.06 (see "Selected References and Technical Memorandums").

SAMPLE IDENTIFICATION AND PACKAGING 8.6.1

For USGS studies:

- Use quality-assured sample containers (jars, bottles, or cartons) supplied by NWQL.
- Analytical Services Request (ASR) forms must be completed in the field and included with each shipping container (cooler or carton).
- Do not seal the package without completing and including a laboratory analytical services request (ASR) form, as described in 8.6.3.

The following instructions apply to all studies:

1. Label each sample container using a permanent, waterproof marker, or use preprinted labels that will remain securely attached. Protect labels from water to prevent smearing.
   - Each label must, at a minimum, include
     - – Site ID number
     - – Date and time (MM-DD-YY @ HHMM) of collection
     - – Sample designation code

- **Do not put analytical requests such as schedule number and lab code adds or deletes on sample container instead of on the ASR form.**
- Field personnel might find it more convenient to pre-label sample containers with preprinted labels before going into the field.

2. Securely fasten each cap. **Do not use tape or paraffin on lids of jars containing organic samples—tape can contaminate the sample.**

3. **For chilled samples:**

   a. Pack samples in fresh ice for shipping with a volume of ice equal to at least the volume occupied by samples, but preferably twice the volume of ice to samples. The amount of ice necessary will vary depending on the length of time in transit from the field to lab and the time of year. During summer, in particular, the cooler and samples should be prechilled.
      - **Do not** send samples chilled with "blue ice" or other types of commercial, refreezable containers.
      - **Do not** chill sample containers with dry ice or with other substances that have a freezing point below 0ºC; this may cause sample containers to freeze and can result in ruined samples and (or) broken sample containers.
      - **Do not** mix ice/water with packing materials. Keep ice/water and packing materials totally separate. Do not mix foam peanuts with ice for shipping.

   b. Line all coolers with doubled (a bag within a bag) heavyweight trash bags. After samples and ice are placed in a doubled bag, seal each bag with a knot, or by gathering the top of the bag, folding it over, and securing with filament tape.

4. All samples can be shipped in coolers; samples not requiring chilling can be shipped in sturdy boxes, but these also should be lined with doubled heavyweight trash bags.

5. Always use adequate packaging materials to prevent breakage. NWQL will not accept samples shipped in vermiculite. **Ship all glass jars in foam sleeves.**

6. When sending multiple sets of samples in one shipping container, label each set of samples with a letter of the alphabet (for example, A, B, C, and so forth) with each sample container in a set having the same letter as others in the set.
   - Add this letter to the upper right hand corner of the ASR form.
   - Recommended procedure is to place all samples from a sample set in a separate bag to keep them together.
7. Package all sample sets for a particular schedule in the same cooler/carton.
8. **Do not ship nutrient samples in coolers with samples that have been treated with nitric-acid preservative.** Contamination from the acids used in sample preservation may create false readings for some nutrient species.
9. When shipping a single set of samples or subsamples in multiple coolers (or other shipping containers), indicate the number of samples being shipped on the outside shipping label.
10. Remember to include an ASR form for each sample sent to the laboratory.
    - **Do not** send samples in a shipping container without an ASR form.
    - ASR forms must not be separated from samples.
    - The ASR forms in different shipping containers may refer to the same site or station identification number, but the schedule and lab code information should apply only to samples shipped with the ASR form.

A sample container with an unreadable label results in a wasted sample.

8.6.2 SHIPPING CONTAINERS AND SAMPLE SHIPMENT

To prevent degradation of analytes by biological metabolism, it is recommended that bottom-material samples be shipped in ice-filled coolers (section 8.5 mentions possible exceptions to this recommendation).

The following instructions pertain to most bottom-material samples.

1. Ship chilled samples in coolers that are free of leaks.
    - Carefully inspect cooler for leaks or damage.
    - Spouts must be sealed, preferably with silicone or epoxy.
    - Broken and/or leaky coolers must be replaced.
    - Insulated water coolers, from 1 to 5 gallons in size, make good shipping containers.
    - Larger volumes of chilled samples can be sent in ice chests as long as maximum weight restrictions of the carrier are not exceeded.
    - NWQL will return, when feasible, recyclable packing materials (mesh bags, foam sleeves, and so forth) that are shipped to NWQL in coolers. **NWQL will not return disposable packing materials.**
2. To prevent leakage and maintain the integrity of the cooler, wrap tape around the cooler in order to secure the lid and seal the spigot.
3. With a permanent waterproof marker, label the inside of the cooler and cooler lid with your current return address and telephone number in case the shipping label is separated from the cooler.
4. Provide return address shipping labels in the cooler, along with an ASR form.
    - The account to be billed for return shipment must be clearly marked on the shipping label.
    - If no label is provided, or an incorrect account is on the label, the District's default account will be charged a shipping fee.

5. If possible, samples should be sent to NWQL on a daily basis. (Mailing samples daily by **PRIORITY MAIL** is usually an adequate means of ensuring a minimum transit time to NWQL.)

6. Whatever means of transportation is used, do not exceed restrictions on package size and weight.

   - If the U.S. Postal Service is used, the shipper is responsible for compliance with postal laws and regulations.
   - Preauthorization from the Postal Service may be needed to ship samples packed in ice.

7. Shipment of samples from hazardous waste sites must be authorized by the NWQL and must comply with Postal Service regulations.

Each shipping container (cooler or carton) must contain at least one ASR form and all the samples associated with that form.

ANALYTICAL SERVICES REQUEST FORM 8.6.3

A NWQL Analytical Services Request (ASR) form must be included with each sample. To ensure correct processing of samples, all shipments must include an ASR form that refers only to samples in that shipment. It is mandatory to identify on the form highly contaminated or potentially hazardous samples so that proper precautions can be taken at the NWQL. Mandatory information on the ASR is indicated by an asterisk.

If samples might contain hazardous chemicals, note this in clear, bold letters on the comment line at the bottom of the ASR form.

Complete the ASR form as follows:

1. Use permanent, waterproof ink or laser-printed forms.
2. Each form must include:
    - station id or unique number
    - telephone number of study chief
    - study chief/collector's name
    - state, district/user
    - study account number
    - begin date and time
    - schedules and lab codes required to initiate analytical work for samples shipped with the form.
3. Check all ASR forms carefully for correct/current lab codes and schedules and compare with sample containers being shipped with the form.
4. At the bottom of each ASR form, indicate the total number of samples being sent to NWQL with the form.
5. At the bottom of each ASR form, include sample-designation codes of samples sent with the form.
6. When shipping multiple containers, include copies of the original ASR form with the appropriate lab codes and schedules to correspond with sample containers shipped in that container.
7. Prevent water damage to the ASR form from melting ice.
    - Place the form inside a sealable plastic bag (doubled ziplock or whirlpack).
    - Tape the bag containing the ASR form to the inside of cooler lid with filament tape.
8. Be sure to keep a carbon copy of the ASR form in study files.
9. Indicate the appropriate Sample Medium, Analysis Status, Analysis Source, Hydrologic Condition, Sample Type, and Hydrologic Event on ASR forms if analytical results are to be stored in the USGS National Water Information System (NWIS).

8.7 CHECKLIST OF FIELD EQUIPMENT AND SUPPLIES

Equipment and supplies commonly used to collect and process bottom-material samples are listed in table 8–5. The list may be modified to meet specific study needs.

Much of the equipment used in stream-gaging procedures also is used as support equipment for sampling bottom materials. A thorough description of the various types of support equipment is beyond the scope of this manual although some support equipment is listed on table 8–5. More detailed descriptions of support equipment can be found in Corbett and others (1943), Rantz and others (1982), Mudroch and MacKnight (1994), and Mudroch and Azcue (1995).

- Equipment must be cleaned and tested before each field trip.
- It is advisable to prepare a checklist so that essential and proper sampling equipment, including backup equipment and chemical reagents, are not forgotten.

Table 8–5. Checklist of field equipment and supplies

✓	Item
	Sampling Devices and Equipment
	Bottom-material (core or grab) sampler
	Bridgeboard, non-metallic; and nylon rope for bridgeboard
	Core catchers
	Core extractor/extruder
	Core liners
	Core liner caps
	Core nose pieces
	Support Equipment for Sampling
	Cranes: Type A designed for weights of 150 pounds or less.
	Crane bases:
	• Four-wheel base should always be used when samplers weighing 75, 100, and 150 pounds are used with the Type A crane. • Three-wheel base can be used with Type A crane.
	Reel, hanger bars, and pins: (selection of type of reel should be based largely on maximum length and strength of cable that would be required) • Type A reel has a fixed crank and no brake. Will accommodate 80 feet of 0.10-inch cable. The estimated practical maximum recommended load for this reel and cable combination is 100 pounds. • Type B reel has a brake and two interchangeable handles. Will accommodate 144 feet of 0.10-inch cable, or 115 feet of 0.125-inch cable. The estimated practical maximum recommended load for this reel and cable combination is 200 pounds. • Type E reel has a brake and two cranks for a 2-person operation. Will accommodate 200 feet of 0.10-inch cable, or 165 feet of 0.125-inch cable. The estimated practical maximum recommended load for this reel and cable combination is 200 pounds.
	Sheeting, plastic for covering bridge rail
	Winch and cable
	Processing Equipment and Supplies
	Sample containers, plastic, assorted [125, 250, 500, 1,000 milliliters (mL)]
	Sample containers, glass or polyfluorocarbon, assorted (125, 250, 500, 1,000 mL)
	Bottom-material splitting equipment: • Containers, plastic or glass, large, sealable, wide mouth, polyfluorocarbon lined caps • Funnel, large: plastic, stainless steel or glass • Mixing bowls: flat bottom, large: polyfluorocarbon, plastic, or stainless steel • Sieve cloth: stainless steel, brass, or plastic mesh • Sieve frame: plastic, brass, or stainless steel • Spoons, scoops, and spatulas: polyfluorocarbon, plastic, and/or stainless steel

Table 8–5. Checklist of field equipment and supplies—*Continued*

✓	Item
	Cleaning Equipment and Supplies
	Acid spill kit
	Apron
	Basins, clear/white plastic (three per site)
	Brushes, non-metallic
	Deionized water
	Detergent, phosphate free, 0.2 percent by volume
	Eyewash
	Gloves, noncontaminating (nonpowdered, disposable)
	Safety glasses
	Sealable plastic bags without colored closure strips
	Tap water
	Inorganic compounds: • Bottles, wash, for deionized water • Gloves, vinyl or latex, nonpowdered • Tissues, lint free, extra large • Tube or pipet jar, non-metallic
	Organic compounds: • Aluminum foil • Glass bottles, baked (check with laboratory) • Gloves, latex or nitrile, nonpowdered, disposable
	Shipping Supplies
	Bags, plastic ziplock, for Analytical Services Request forms
	Bags, plastic, large
	Boxes, sturdy
	Coolers, 1 and 5 gallons
	Forms, Analytical Services Request
	Ice
	Mailing labels (public and private shipping labels and return labels)
	Pens, pencils, noncontaminating, waterproof, permanent
	Sample container labels
	Sleeves, foam or bubble wrap
	Tape, fiber

Table 8–5. Checklist of field equipment and supplies—*Continued*

✓	Item
	Miscellaneous Equipment and Supplies
	Boat, motor, paddles/poles/oars, trailer
	Boots, hip
	Bug repellent, non-aerosol
	Calibration log books for all instruments
	Calculator
	Camera with film
	Drinking water
	Fire extinguishers
	First aid kit
	Flashlight with extra batteries
	Forms, field documentation
	Fuel
	Gloves, vinyl or latex, nonpowdered
	Historical discharge data for determining transit rates, verticals, depths
	Highway emergency kit
	Ice auger
	Keys for security locks
	Paper towels
	Personal flotation device
	Rain gear
	Safety vest
	Schedules, analytical with sample container requirements
	Shovel
	Soap, antibacterial
	Spray, plastic dip coating
	Station analysis and historical field measurement plots
	Station description files and detailed site location map
	Sunscreen
	Tag line
	Tape, polyfluorocarbon
	Tool kit
	Waders, chest

CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
meter (m)	3.281	foot
micrometer (μm)	3.3×10^{-6}	foot
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
liter (L)	0.2642	gallon
milliliter (mL)	0.0338	ounce, fluid
	2.64×10^{-4}	gallon
foot (ft)	0.3048	meter
pound, avoirdupois (lb)	0.4536	kilogram

Temperature: water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

Specific electrical conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (μS/cm). This unit is equivalent to micromhos per centimeter (μmho/cm) at 25 degrees Celsius.

ABBREVIATIONS

ASR	Analytical Services Request
lab	Laboratory
NWIS	National Water Information System
NWQL	National Water Quality Laboratory, Denver, Colo.
TWRI	Techniques of Water-Resources Investigations
USCG	U.S. Coast Guard
USGS	U.S. Geological Survey
WRD	Water Resources Discipline of USGS

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Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data

Chapter A9. SAFETY IN FIELD ACTIVITIES

By
Susan L. Lane and Ronald G. Fay

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Mark Schaefer, *Acting Director*

For additional information write to:

Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

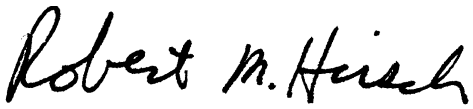
Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

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SAFETY IN FIELD ACTIVITIES A9.

National Field Manual for the Collection of Water-Quality Data

Chapter A9.

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Chapter A9. SAFETY IN FIELD ACTIVITIES

By **Susan L. Lane and Ronald G. Fay**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) describes protocols (requirements and recommendations) and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter of the manual addresses topics related to personal safety to be used in the collection of water-quality data, including: policies and general regulations on field safety; transportation of people and equipment; implementation of surface-water and ground-water activities; procedures for handling chemicals; and information on potentially hazardous environmental conditions, animals, and plants.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://pubs.usgs.gov/publications/index.html>.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources.

The *National Field Manual* is Section A of Book 9 of the USGS publication series Techniques of Water-Resources Investigations (TWRI). A complete list of TWRI publications is included at the end of this report. The *National Field Manual* is comprised of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*.

Chapter A9 has been designed to assist field personnel in the safe execution of water-quality data collection. This report provides general guidance and information on common safety issues, promotes awareness of preventive measures, identifies hazards that might threaten safety, and stresses a panic-free and common-sense approach when confronted with field hazards. The USGS also provides training, equipment, and medical programs that address a variety of safety situations. The references cited in this report and safety officers in local, district, or regional offices of the USGS can provide additional detailed information.

PURPOSE AND SCOPE

Chapter A9 provides USGS personnel with information about hazards they may encounter during field work, and describes procedures that, when implemented properly, will help ensure the safety and health of field personnel. The report is designed to be taken to the field as an immediately available reference.

Chapter A9 addresses only the most common safety issues in water-quality sampling. Safety guidelines of a general nature are included regarding basic policies, protocols, and regulations adhered to by the USGS, including use of vehicles, surface-water and ground-water field activities related to the collection of water-quality data, handling of chemical substances, and appropriate response when confronted by environmental (weather, animals, plants) hazards. Each USGS office is unique and has special safety requirements. An exhaustive discussion of detailed safety issues is beyond the scope of this chapter. Chapter A9 is meant to be used in conjunction with more comprehensive manuals cited in the references that provide details on rules, regulations, remedies, and recommendations that apply to the myriad of specific locales, climates, field conditions, and circumstances.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to: NFM-QW, USGS, National Center 412, Reston, VA 20192 (or send electronic mail to: nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://pubs.usgs.gov/publications/index.html>.

ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. Special thanks is extended to Maynard Cox for suggestions for improving the sections on animals and plants and for generously allowing the use of his material.

The authors wish to acknowledge the following individuals in the USGS who provided valuable contributions as technical reviewers that improved the accuracy and quality of this document: F.L. Andrews, C.E. Arozarena, D.J. Cowing, R.D. Gist, G.J. Hwang, T.A. Muir, and K.R. Thompson. F.D. Wilde was the managing editor, with editorial and publication assistance from I.M. Collies, L.S. Rogers, C.T. Mendelsohn, and A.M. Weaver.

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SAFETY IN FIELD ACTIVITIES A9.

"Safety first" is the motto for all USGS personnel involved in field activities. This chapter of the *National Field Manual* is required reading for USGS personnel who will be involved in the collection of water-quality data. Using the information in this chapter, field teams are responsible for establishing and implementing safety procedures appropriate for their field activities.

Safety: the condition of averting or not causing injury, danger, or loss.

To ensure safety, field work requires an awareness of potential hazards and a knowledge of regulations and recommended procedures. The collection of water-quality data in the field brings field personnel in touch with numerous hazards. Personnel routinely work in extreme environmental conditions and in remote locations. Many assignments require working with, or around, heavy machinery. Water-quality studies involve the transportation and use of equipment and chemicals. Personnel routinely come in direct and indirect contact with waterborne and airborne chemicals and pathogens, and with potentially dangerous animals and plants.

- You are the first line of defense for on-the-spot evaluations of situations that may compromise your safety. Be aware of your environment, use common sense, do not exceed your limits (for example, operation of equipment; lifting heavy objects and equipment; physical tolerance to exertion, heat, and cold), and trust your instincts. Listen to that "little voice" inside you if you feel uneasy about your situation.
- Remain calm if you find yourself in danger.
- Use the information in this manual to help you take appropriate actions.

The only worthwhile safety protocol is an implemented one.

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SAFETY POLICIES, REGULATIONS, AND REQUIREMENTS 9.1

The information presented has been summarized from more detailed reports (referenced below) and from field experience, in order to make essential safety guidelines readily accessible to the field team at the time of sampling. USGS employees are encouraged to become familiar with the policies, regulations, and requirements provided in documents published by the U.S. Department of the Interior, the USGS, and other Federal agencies.

USGS AND FEDERAL POLICIES 9.1.1

The USGS, as a bureau of the U.S. Department of the Interior (DOI), structures its safety program using DOI safety guidelines. These guidelines are described in the Departmental Manual handbook titled *Safety and Health Handbook* (*485 DM*) (U.S. Department of the Interior, 1991), which is updated periodically to reflect current DOI policies. USGS safety policies and regulations are found in USGS Handbook 445-1-H, the *Safety and Environmental Health Handbook* (U.S. Geological Survey, 1989), and in USGS Handbook 445-2-H, the *USGS Occupational Hazards and Safety Procedures Handbook* (U.S. Geological Survey, December 1993). Additional safety requirements are described in *A Guide to Safe Field Operations* (U.S. Geological Survey, 1995), and in Water Resources Division (WRD) numbered memorandums (see "Selected References and Internal Documents"). A safety officer is designated in each District and Region of the USGS, Water Resources Division, to provide additional information and guidance.

Consult the DOI and USGS publications cited above for detailed information on safety issues, including the following topics:

- Chemical hygiene plan.
- Hazard communication, handling of waste materials, and hazardous waste sites.
- Exposure to ionizing radiation.
- Blasting and firearms.
- Hearing conservation.
- Reporting accidents and unsafe conditions.

You are required to know and follow safety policies and requirements.

Numerous safety and environmental laws are regulated and enforced by Federal, State, and local governments. Recent congressional acts, such as the Federal Facility Compliance Act of 1991, require Federal agencies to comply with Federal, State, and local regulations. Many USGS and DOI policies reflect compliance with U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), U.S. Environmental Protection Agency (EPA), and U.S. Department of Transportation (DOT) regulations. State and local governments and USGS and DOI safety programs can supplement but cannot supersede Federal OSHA, EPA, or DOT regulations.

- OSHA policies are found in the *U.S. Code of Federal Regulations* (CFR) title 29—Labor, parts 1900-1910 (U.S. Department of Labor, 1995). This volume defines general industry safety requirements. For example, 29 CFR 1910.132 describes Federal requirements for personal protective equipment.
- EPA policies are described in the *U.S. Code of Federal Regulations* (CFR) title 40 (U.S. Environmental Protection Agency, 1995). For example, 40 CFR 260-272, under direction of the Resource Conservation and Recovery Act (RCRA) of 1976, regulates toxic substances control and hazardous waste disposal (including small-quantity exemptions). Many USGS memos concerning handling and disposal of chemicals reference 40 CFR.
- DOT policies are found in the *U.S. Code of Federal Regulations* (CFR) title 49 (U.S. Department of Transportation, 1995). DOT regulates transportation of hazardous materials by authority of the Hazardous Materials Transportation Act (HMTA) of 1974. For example, 49 CFR, parts 171-177, give transportation guidelines which include material description and classification, packaging and package labeling, and quantity limitations.

JOB HAZARD ANALYSIS 9.1.2

Many accidents and injuries can be prevented by analyzing and communicating hazards. A job hazard analysis (JHA) identifies hazards and describes actions to avoid mishaps. For example, JHA's are used to determine and document the proper personal protective equipment required for the job. JHA program requirements are given in DOI Departmental Manual 485, chap. 14, and in USGS Handbook 445-2-H, chap. 2.

JHA components include:

- The sequence of steps associated with an activity.
- Identification of hazards involved for each step.
- Determination of controls needed to eliminate or reduce the hazard.

Visit the field site, if possible, to be sure that you and your equipment can get to, sample at, and leave the site safely. Talk to employees who may have visited the site—you might receive your most valuable safety information from them. **Always check the study workplan, field folder and site records, and other available information before departure.**

PERSONAL PROTECTIVE EQUIPMENT 9.1.3

Personal protective equipment (PPE) is defined as safety equipment for your skin, eyes, ears, face, head, extremities, and respiration (see USGS Handbook 445-1-H, chap. 9 and OSHA 29 CFR 1910, Subpart I). **The USGS is required to supply PPE, and you are required to use it!**

Proper PPE selection is based on the hazards likely to be encountered, as well as compliance with regulatory safety requirements. Examples of PPE are cited throughout this chapter (see sections 9.4, 9.6, and 9.11.1).

> TECHNICAL NOTE: Respirators might be required to ensure protection from some chemical and biological hazards. **You must be medically approved, trained, and tested for fit before using a respirator.** If one is needed, follow USGS policy given in USGS Handbook 445-2-H, chap. 5. Do not share a respirator.

9.1.4 TRAINING

Field personnel must be aware of safety training requirements and certification or recertification needed to perform specific tasks. For example,

- Personnel who operate government-owned or leased vehicles must be certified and periodically recertified in defensive driving.
- Cardiopulmonary resuscitation (CPR) and other first-aid certification and recertification are mandatory for field personnel.

Safety training and certification requirements, recommendations, and opportunities are subject to change—check with your safety officer periodically to keep current with prevailing requirements.

Complete safety training and certification requirements before beginning field work.

FIELD TRIP PREPARATIONS AND EMERGENCY CONTACTS 9.2

Before leaving for the field, obtain the information shown on figures 9-1 and 9-2, and carry this with you in the field—either at the front of Chapter A9 or in the field folder. Put Chapter A9, or the sections of it that are applicable to your work, in a binder and keep it with you. **Become familiar with the information provided here before you are in the field and confronted with an emergency.**

Certain types of data-collection activities require a field team of two or more people (Horowitz and others, 1994). While the multi-person field team also might be important to carrying out technical procedures, the field team or buddy system can be a life-saving practice. Mobile telephones provide a minimum precaution if personnel will be unaccompanied. Satellite communication services might be available for remote areas where cellular service is not available.

Don't forget to leave names of emergency contacts and their phone numbers at work and (or) with family or colleagues.

Basic preparations that should become routine before every sampling activity:

- Use safety checklists when preparing for a field trip. Examples of checklists are in section 9.11. Develop your checklists from existing site safety information and site reconnaissance (job hazard analysis or site safety plan).
- Keep a field folder for each surface-water and ground-water site at which water-quality data will be collected. The safety-related contents of a field folder include:
  - Copies of the checklists mentioned above.
  - Site type (hazardous waste, confined space, cableway, wading site, bridge site, boat site) and site description.
  - Site location (include map, site sketch, and description).
  - Locations and phone numbers of emergency facilities, such as a hospital or first aid station, police and fire departments, utility companies.
  - Additional information specific to the site: for example, if it is open to hunting, and season dates; appropriate clothing (such as orange safety vests).
- Make an itinerary for every field trip and leave a copy at the office and with family or colleagues. Schedule times to check in at work and with family or colleagues when field trips require overnight stays. Follow the established schedule. Notify all concerned parties if your schedule changes.
- Obtain or reserve communication equipment, such as a cellular phone or two-way radio.

Emergency Contacts

Personal contacts

Name: _____ Phone: (home) _____ (work) _____

Name: _____ Phone: (home) _____ (work) _____

U.S. Geological Survey contacts

District Office _____

Safety Officer _____

National Water Quality Laboratory, Arvada, CO.

Emergency coordinator (303) 467-8000 _____

Local emergency contacts (or call 911)

Hospital _____ Phone: _____

Address: _____

Other medical facility (24-hour care) _____ Phone: _____

Address: _____

Police _____

Fire _____

Utility _____

Health Information Centers

Center for Disease Control

Information Hotline: (404) 329-3311 _____

Fax: Disease Directory: (404)-332-4565 _____

Other

_____

_____

Figure 9-1. Example of emergency contact form to be completed and taken on field trips.

Medical Information for Office Personnel

Employee name: _____ Home phone: _____

Treatment preference: medical _____ other (specify) _____

Doctor: _____ Phone: _____

Other emergency contact: _____ Phone:

Allergies and other medical conditions	Medications being taken	Medications to avoid

Relevant medical history:

Allergies and other medical conditions:

Special instructions:

Figure 9-2. Example of medical information form to be completed and taken on field trips.

TRANSPORTATION 9.3

Various modes of transportation are used to reach field sites. Each type of transportation comes with specific guidelines for safe operation, for which appropriate training must be completed before leaving for the field. Training requirements are described in the USGS Handbook 445-2-H and are provided by office or regional safety officials. Perform a safety inspection on all transportation equipment before using. Safety inspection checklists are found in USGS Handbook 445-1-H, chap. 12.

ROAD VEHICLES AND TRAILERS 9.3.1

Passenger cars, vans, and 4-wheel-drive vehicles can differ in operation and in safety features, depending on the vehicle's age, make, and model. Become familiar with all operating systems of the vehicle before you leave for the field—test operation of lights, locks, seat belts, windows, 4-wheel drive and winch, and hood release.

"Musts" that apply to all USGS employees driving government vehicles:

- Have a valid U.S. State driver's license.
- Take a course in driver safety—the current requirement is to take the course every 3 years.
- Inspect all vehicles before use.
- Tie down or otherwise secure all cargo.
- Wear a seat belt.
- Obey all traffic regulations and operate your vehicle safely.

Inspect each vehicle thoroughly before departing from the office (USGS Handbook 445-I-H, chap. 12): discovering that the 4-wheel drive is not working when you are in the backwoods can result in considerable inconvenience and place you in a dangerous situation.

- Check that your vehicle is equipped with the proper safety equipment (see 9.11.2).
- Create checklists specific to each vehicle and (or) each type of sampling trip to make the inspection process routine.
  - Towing a trailer or equipment with your vehicle requires additional planning, caution, and proficiency in driving.
  - Vehicles and trailers vary in maximum load capacity.
  - Vehicles and trailers must be compatible and have a matching hitch ball and coupling.
  - Trailers are required to have standard safety equipment such as safety chains (placed in an "x" under the coupling), lights, brakes (if applicable), and load-securing devices.
  - Be aware that air turbulence from passing vehicles can cause your trailer to sway.
  - Before towing, consult USGS Handbook 445-1-H, chap. 14, p. 14-5, for additional guidance.
- Drive slower.
- Disengage the vehicle's automatic "overdrive gear" option when towing.
- Maintain extra following and stopping distance to allow for the increased load. Loads must be balanced.
- **Do not exceed the maximum recommended load capacity.** (Check owner's manuals or contact vehicle or trailer manufacturers for this information).

Never permit anyone to ride in or on trailers.

Obtain the training that will help you handle potentially dangerous driving conditions; for example, wet, icy, or snow-filled roads; high wind velocity; glare from bright sunshine; poor visibility from dust storms, fog, or heavy precipitation. In very hot climates, keep the windows slightly open when the vehicle is parked to avoid shattering windows from the heat. **To avoid asphyxiation from carbon monoxide, never sit or work in a closed vehicle with the engine running for more than a few minutes.**

WATERCRAFT 9.3.2

Boats are used extensively by USGS personnel for sampling the quality of water in rivers and lakes. All boats must carry equipment as required by the U.S. Coast Guard. Checklists are useful for ensuring that all the proper equipment is in place (see 9.11.3). WRD Memorandum No. 96.25 and the DOI Departmental Manual 485 provide regulations for watercraft safety.

Head back to harbor in the event of a storm. You are required to follow U.S. Coast Guard regulations for waterway safety and etiquette. Carry extra lines, foul-weather gear, and backup equipment. Remember, all cargo must be secured. For additional information see USGS Handbook 445-1-H, chap. 17, and USGS Handbook 445-2-H, chap. 16.

AIRCRAFT 9.3.3

Airplanes and helicopters are sometimes used for sampling trips to remote areas. Pilots and passengers must follow stringent guidelines when using these means of transportation. Any sampling activity involving the use of aircraft must be carefully planned and coordinated with USGS safety officials, the DOI Office of Aircraft Services, and appropriate local and regional safety officials, as described in USGS Handbook 445-1-H, chap. 16, and USGS Handbook 445-2-H, chap. 13. WRD Memorandum No. 95.49 provides an example of a safety plan for aircraft use.

OTHER METHODS OF TRANSPORTATION 9.3.4

Additional methods of transportation include snowmobiles, all-terrain vehicles, horses or mules, and backpacking. Evaluate and practice these methods before use, taking care to consider the measures necessary for a safe trip and making sure to obtain proper training. USGS Handbook 445-1-H, chap. 14, and USGS Handbook 445-2-H, chap. 14, provide more detailed information.

9.4 SURFACE-WATER ACTIVITIES

Collection of water-quality samples can be as simple as hand dipping water from a slow moving stream to as complex as using heavy power equipment while working from a cableway. Know the safety steps needed for any sampling method used.

9.4.1 WADING

Examine the section of a stream or river you plan to wade. Check the field folder for information relating to safety, including maximum depths in relation to stage, wading-section anomalies such as slippery conditions and drop-offs or holes (a wading rod can be used to help assess streambed conditions), and velocity curves for determining wadable stages. **Do not attempt to wade a stream for which values of depth multiplied by velocity equal or exceed 10 ft²/s.** For example, a stream only 2 ft deep but with velocities of 5 ft/s or more can be dangerous to wade.

While wading to collect a water sample:

- Wear a personal flotation device (PFD) during wading activities.
  - Approved PFDs for wading include the standard jacket type and the suspender type. The PFD must fit properly, be rated for your weight, and be in good condition.
  - The PFD should be dried and kept indoors between trips.
- Wear hip boots or chest waders. Boots and waders provide protection from cold and pollutants, as well as from underwater objects. Be aware of the possibility of slipping and going underwater (feet up, head down) while wearing them. Practice wearing hip boots and waders in a controlled, group-training situation before using for field work. The following recommendations are the result of experiments with boots (Joseph, 1957) and field experience.
  - Hip boots with a strap at the top are better than boots that are open. The strap should be pulled closed. This allows air to be trapped in the boot in case you are submerged. The air cushion can be used as a partial mechanism for flotation until you reach shore or are rescued.

  - Avoid hip boots with tight ankles. These are difficult to remove in an emergency situation.
  - Avoid chest waders that are tight fitting at the top. Like tight-ankled hip boots, they are difficult to remove in an emergency situation. Whenever chest waders are worn, a PFD also must be worn.

- Be aware of surrounding conditions.
  - Watch for debris floating downstream, such as logs, aquatic vegetation, or "rafts" of animals seeking higher ground.
  - Watch for sand channels that can shift under foot and become quicksand.
  - Watch the stream stage, especially when it could rise rapidly.
  - When wading below a dam or control structure, contact the gate operator before entering the stream.

Rule of Thumb: Don't wade a stream if (Stream Depth) × (Velocity) ≥ 10 ft²/s.

WORKING ON BRIDGES 9.4.2

A bridge safety plan is required by WRD Memorandum No. 95.17. For every bridge site, develop and diagram a detailed procedure that conforms to State and Federal regulations. Keep this procedure and diagram in the field folder. The bridge procedure includes plans for safety cones and signs, lane blockage, and traffic control.

Equipment used for sampling from a bridge can be heavy and unwieldy. Practice assembling and using the equipment before starting field activities, and make sure the equipment is operational before leaving the office. When using a bridge crane, keep a pair of heavy-duty wire cutters readily available for cutting the cable in case debris snags the sounding line.

Be aware of boat traffic. The bridge crane cable should have strips of bright plastic flagging attached in intervals to make it easily visible to all boat traffic.

- **A PFD must be worn when working on bridges.** The suspender type PFD is approved for bridge work.
- Workers involved in peripheral activities should wear high-visibility vests with reflective tape.

9.4.3 WORKING FROM BOATS

Safety regulations for the various types of boats used by the USGS when obtaining water-quality samples are comprised of U.S. Coast Guard (USCG) and OSHA rules, and are supplemented by USGS requirements.

Before working from a boat, obtain the appropriate training for the vessel being used, as specified in WRD Memorandum No. 96.25. This training should cover all the specifics regarding boat operation as per USCG regulations. Before taking a boat on the water, ensure that the vessel is in operating condition. Boats are to be inspected annually. If a vehicle is being used to trailer the boat to the site, the vehicle and trailer are to be included in the preliminary inspection. Equip the boat with all USCG-required equipment (see the checklist in 9.11.3) as well as items that the study team deems appropriate for emergencies or equipment failures. Some Districts[1] keep a duffel bag on each boat stocked with standard emergency supplies such as flashlights, air horns, and whistles.

A float plan for each field trip must be left with the supervisor or other designee. The plan should include, at a minimum:

- Date and purpose of trip.
- Name(s) of operator(s) and name(s) of passengers.
- Destination and route to be taken.
- Time of departure and estimated time of return.
- Radio frequency or cellular designation, if applicable.
- Type of watercraft, and its length, color, identification number, and other unique features.

Check weather conditions before departure. In coastal areas, pay particular attention to tidal cycles.

[1]The term "District" as used in this report refers to an organizational unit of the USGS located in any of the States or Territories of the United States.

Each person on the boat must wear an orange USCG-approved PFD, which should have at least 200 cm^2 of retroreflective material on the front, back, and reversible sides. Inspect all PFDs for damage before and after each use. Store PFDs properly and discard damaged PFDs.

- Do not wear hip boots or waders in a boat. Wearing boots or waders could be a safety hazard if the boat should tip or you are thrown out.
- **Don't panic if you fall out of a boat!** Think through and execute the basic safety procedures that you have been taught.

Attach bright colored plastic flagging in intervals to the tag line used to designate the transect along which samples will be collected, so as to make it easily visible to boat traffic. In areas of frequent boat traffic, station a member of the field team on shore who can drop the tag line rapidly, should it present a hazard to boats.

All boat passengers should be practiced in emergency procedures and the location of emergency equipment. Boat operators are required to have current training in first aid and CPR. They must also know how to use the type(s) of fire extinguisher(s) on the watercraft.

Head back to shore if a storm is approaching.

WORKING FROM CABLEWAYS 9.4.4

Water-quality sampling from a cableway requires extensive measures that are described in *Streamgaging Cableways* (Wagner, 1991) and in WRD Memorandum No. 91.42. These guidelines must be followed. Become familiar with cableway procedures and requirements and obtain the necessary training before attempting to work from a cableway. Check the field folder for special considerations pertaining to each cableway. Cableways must be inspected by trained professionals at prescribed intervals. At the site, always:

- Visually inspect each cableway before use.
- Wear a PFD, hard hat, and work gloves.
- Take an extra cable-car puller and heavy-duty cutting pliers to the site.

9.4.5 SCUBA DIVING

Scuba diving to collect samples is permitted only after every requirement of OSHA 29 CFR 1910.401-441, Subpart T, has been met. Diving activities are regulated by the USGS Diving Control Board and the Diving Safety Officer.

Extensive training is required to be certified in scuba diving and sufficient skill must be demonstrated before diving is permitted for any USGS activity. If diving is necessary for sample collection, personnel involved must coordinate the endeavor with the USGS Diving Officer through district and regional safety officials. Guidance is provided in Departmental Manual 485, chap. 28, and in the USGS Diving Safety Manual (U.S. Geological Survey, July 1994).

9.4.6 ELECTROFISHING

Electrofishing involves applying an electrical charge in water to stun and capture fish. The requirements for this procedure, as stated in WRD Memorandum No. 93.19, include:

- Field teams must consist of at least two people, one of which will have been trained and certified in a USGS-approved course in the safety and technical procedures of electrofishing.
- At least two individuals in each team must be trained and currently certified in CPR.
- Each member of the field team must use proper personal protective equipment.

Field team members must obtain all necessary immunizations before electrofishing (WRD Memorandum No. 96.29).

GROUND-WATER ACTIVITIES 9.5

Each well site is unique. Site hazards may not be known before, or be evident during the site visit. Check the field folder for site information relating to safety to prepare for the field trip.

WELL SITES 9.5.1

Wells can be located in open, unprotected areas as well as in enclosures such as shelters, well houses, or vaults. These sites and enclosures can contain dangerous chemicals and fumes, animals and plants, and large machinery with high-capacity power systems.

Before departing for the field site, obtain permission, oral or written, from the well owner or an authorized representative to enter the site. Entering a privately owned site without permission is considered trespassing. Inventory the safety equipment you will need for your sampling trip using the standard checklists as described in section 9.11, adding items specific to your program or study.

When arriving at the site, use your senses. Do you see warning signs posted or animals grazing? Hear gunshots? See exposed electrical connectors and wires? Smell fumes? Decide how to handle such circumstances to ensure the safety of the field team.

- Well houses or shelters constructed over wells often are havens for bees, wasps, spiders, snakes, and rodents. Snakes have been found inside shelters and in well casings.
  - Check your surroundings carefully for signs of animals before starting work.
  - If you smell, hear, or see signs of animal infestation, proceed only after taking necessary precautions (see 9.9.6). Before entering, the enclosure should be ventilated, disinfected, and cleaned.

- Check the well house or shelter carefully for chemical fumes and for faulty power systems.
  - Poorly ventilated shelters are especially hazardous and can be classified as "confined spaces," which are defined and regulated by OSHA and USGS policies. Confined spaces are discussed in detail in USGS Handbook 445-2-H, chap. 11, and in OSHA 29 CFR 1910.146.
  - Use testing devices such as a portable photoionization detector ("sniffer") if the site has potential for chemical or radioactive contamination.
- Never turn on or remove a well-owner's pump without permission. The system may be turned off for a safety reason. Not only could you cause yourself great harm, you could injure someone who might be near or working on the system.

Before leaving the well site, minimize any hazard to yourself, others, and the environment from field activities:

- Clean and decontaminate yourself and all sampling and processing equipment.
- Channel or contain purge and waste water to avoid transforming the site into a slippery swamp.
- Contain all trash and chemical wastes.
- Follow Federal, State, and local safety regulations for handling and disposal of contaminated waste materials.

Before putting your hands or feet into a confined space, visually inspect the area.

MACHINERY, PUMPS, AND OTHER EQUIPMENT 9.5.2

Ground-water samples usually are collected from a well using suspension and (or) pumping equipment. Water and formation samples also could be collected during site reconnaissance or well installation, which requires working around heavy machinery and, often, large industrial systems. Heavy machinery, equipment, and power supplies are potentially dangerous, whether permanently installed or transported to the sampling site.

- USGS and OSHA have general safety requirements for working around heavy machinery and power supplies. USGS Handbooks 445-1-H and 445-2-H cover electrical safety, lockout/tagout procedures, and personal protective equipment (see section 9.1.3). OSHA 29 CFR 1910 covers, in great detail, industry requirements for working with machinery.
- Since equipment and power systems vary greatly, knowledge of their operation is paramount to a safe and successful sampling trip. Use the correct equipment for the job. Keep instruction manuals readily available.

When working with permanently installed pumps or sample-collection systems:

- Watch for unguarded moving parts, exposed and ungrounded wiring, hazardous fuels, and faulty or inadequate repairs.
- Use caution when lowering a well tape down a well to measure water level. Lines can get caught around rotating parts of pumps and be wrenched from your hands. Wells with electrically powered submersible pumps can be energized by a short in the electrical circuit, and in turn can conduct the power surge to you through the steel tape.

When using portable pumps or sample-collection systems:

- Make sure power systems are compatible with the equipment and are used correctly. Portable pumps or systems usually require portable power. Most power is supplied by a gasoline, diesel, or natural gas engine to run a generator or compressor.
  - Store fuel in appropriate containers and refill engines carefully.
  - Make sure electrical generators are properly grounded—refer to the system's instruction manual for proper grounding procedures.
- Do not attempt a multi-person task alone. Portable pump systems can be heavy and awkward to use. Remember that the suspended weight of the pump increases as it is lowered down the well.
- Avoid lodging a pump in a well. Construct a "dummy probe" which is slightly larger than the pump. Make sure it can safely reach the desired depth and be retrieved before lowering the pump into the well.

When working around well-drilling operations, you are subject to all the hazards and safety requirements associated with working around a drill rig:

- Wear personal protective equipment such as steel-toed boots, hardhat, hearing protection, and a respirator if necessary (see 9.11.1).
- Communicate with the drilling crew and heed their instructions on safety.
- Be aware that heat generated from friction between drill rods or auger flights and earth materials can cause the escape of volatile organic compounds, posing a possible health hazard if inhaled.

CHEMICALS 9.6

USGS employees are routinely exposed to chemicals during the water-quality sampling process. Chemicals—as solids, liquids, or gases—range from dilute salt solutions to strong acids, bases, dyes, and organic compounds. Field measurements and the processing of sample water can cause chemical reactions that generate dangerous fumes and by-products.

Be cognizant of the regulations that govern the use, transportation, and disposal of chemicals and wastes. Because regulations vary greatly from state to state, contact your safety officer or state agency for the proper procedures in your locality.

USE AND HANDLING 9.6.1

For safe use of chemicals, follow the guidelines given below, communicate hazards to all members of the field team, use proper personal protective equipment, and apply common sense when working with dangerous substances.

- **Obtain information about the chemical or compound.**
  - Material Safety Data Sheets (MSDS) supply material characteristics such as chemical description, fire and explosion data, chemical compatibility and reactivity, protection precautions, and spill procedures. These documents are required by OSHA 29 CFR 1910.1200 (hazard communication) and usually are shipped with chemicals when purchased. Your safety officer or chemical supplier also can provide the MSDS needed.
  - Chemical safety information is available from many Federal and private sources. For example, the Permissible Exposure Limit (PEL) of a given chemical is listed by OSHA 29 CFR 1910.1000, subpart Z, and in the *Pocket Guide to Chemical Hazards* published by the National Institute for Occupational Safety and Health (June 1994).
  - DOI and USGS internal memorandums describe chemical usage and handling policies of our most commonly used chemicals. For example, refer to:

    DOI Departmental Manual 485, chap. 29, for general guidelines on chemical safety in laboratories.

    USGS Handbook 445-2-H, chap. 7, for Hazard Communication Program goals.

WRD Memorandums No. 93.44, 94.06, and 94.07 for storage, transportation, handling, and disposal of formaldehyde, hydrochloric acid, and methyl alcohol, respectively.

Office of Water Quality Technical Memorandums 94.02 and 94.16 for information on discontinuing field use of mercury-filled thermometers and mercury-based sample preservative, respectively.

Do not use mercury thermometers in the field.

- **Use Personal Protective Equipment (PPE) (see sections 9.1.3 and 9.11.1).**
  - Wear protective clothing, including gloves, glasses, lab coat, and if necessary, use a respirator. **Remember that you must be certified before using a respirator** (see USGS Handbook 445-2-H, chap. 5).
  - Select PPE appropriate to the chemical(s) to be contacted. PPE can be designed for specific chemicals. For example:

    Respirator cartridges are ineffective if they fail to filter the chemical hazard encountered.

    Wear gloves that will provide adequate protection. Gloves become ineffective if they are dissolved by the chemical you are using. Vinyl gloves are used for handling inorganic acids and bases. Latex gloves are used for handling relatively mild organic solvents, such as methanol and acetone; nitrile gloves can be used for some stronger organic solvents.

- **Use the following standard procedures.**
  - Avoid unnecessary exposures and spills. Never place chemical containers where they can be knocked over. For example:

    Clean up chemical residues or spills immediately and appropriately.

    Keep chemical spill kits near the work area.

- Work with adequate ventilation or under a hood when working with hazardous or reactive chemicals and gases.
- Keep eye wash kits readily accessible while working with chemicals.
- Handle and mix chemicals and compounds appropriately (check the MSDS). For example:

  When transferring flammable liquids, all metal containers must be grounded to eliminate igniting the liquid with an electrical spark.

  When preparing a hydrochloric or nitric acid cleaning solution, the sequence is to put water in the vessel first and then add the acid.

Remember the rhyme: "Add acid to water, like you ought-ter!"

- Open chemical containers slowly and carefully, wearing proper PPE. Allow hot containers to cool before opening. Open frozen or encrusted lids with caution. For example:

  To open fused-glass ampules, break the ampule at the base of neck, in a direction away from you and others. Use an ampule breaker if it is safer for you, and wear gloves.

  Check containers and ampules for contents lodged near the container top or neck. Dislodge trapped material by gently tapping the container at the top.
- Properly dispose of all parts of the spent ampule (Office of Water Quality Technical Memorandum 92.11). Temporarily store used ampules in an appropriate container. Do not let these wastes accumulate in your vehicle or work area—they produce corrosive and potentially explosive fumes.

9.6.2 TRANSPORT

The USGS must follow applicable Federal, DOT, EPA, and supplemental State guidelines when transporting chemicals and chemical wastes. References include the *Emergency Response Guidebook* (U.S. Department of Transportation, 1990) and the *Driver's Pocket Guide to Hazardous Materials* (J.J. Keller & Associates, 1993). USGS chemical transportation guidelines are summarized below.

- The USGS transports small quantities of chemicals for use in field and office-laboratory procedures. The USGS is not considered a commercial carrier which, by definition, transports materials in commerce or in the furtherance of a commercial enterprise (transporting for profit).
- Because the USGS transports small quantities of chemicals and wastes, the Federal EPA and DOT small-quantity exemption rules apply. According to these guidelines, the USGS is exempt from many industry handling and shipping regulations and training requirements. Check your State's laws on intrastate transport of small quantities of chemicals in a Federal government vehicle.
- It is not necessary to placard your vehicle when transporting small quantities of chemicals. Placarding a vehicle informs enforcement and emergency response personnel that the vehicle contains large amounts of the placarded material. For their own safety, first-response teams might not immediately approach a wrecked vehicle that is placarded for a highly dangerous or reactive material.

For safe containment and transport of chemicals:

- Protect yourself and passengers in the vehicle by stowing and securing chemicals away from the passenger compartment and behind a safety screen or barrier.
- Stow compressed gas cylinders securely and in a vertical position, if possible. Never transport cylinders with regulators attached, or with safety caps missing.

- Try to transport chemicals in their original DOT-approved shipping containers with the package correctly sealed. If the original packaging is not available, use a container that will resist and contain the material in the event of an accident. Use of an overpack container, such as an ice chest, is recommended to further protect against breakage and spills.
- Carry spill kit(s) appropriate for the chemicals being transported.
- Label packages as to their contents, and remove old, inappropriate labels from containers that are being reused.
- Keep a chemical inventory list in the glove box or side door pocket of the vehicle. This list should also have an emergency contact name and phone number. Keep a copy of each chemical's Material Safety Data Sheet (MSDS) here, as well.
- Waste products should be transported in the same safe and approved manner as other hazardous materials. The container must be of adequate composition and strength and must be labeled with the type and concentration(s) of chemical(s).

STORAGE AND DISPOSAL 9.6.3

Chemicals require strict storage procedures for safety reasons, as well as to avoid chemical degradation, volatilization, and contamination. Specific storage areas should be designated in your vehicle and office laboratory. Use appropriate, approved chemical storage cabinets. Never store incompatible materials together. Refer to USGS Handbook 445-1-H, chap. 8, for chemical compatibility and storage.

- Separate storage is needed for acids, corrosives, and flammables.
- High purity, laboratory-grade flammables should be stored apart from other flammables, such as gasoline and solvents.

Chemical and waste disposal requirements, and exemptions, are regulated federally by the EPA. Supplemental State guidelines must also be followed. Contact your safety officer or waste disposal representative for details, and follow these general disposal guidelines:

- Do not indiscriminately dump chemicals or pathogens down sinks, toilets, or drains.
- Do not let chemical wastes accumulate in your vehicle, office, or laboratory. Waste disposal storage areas should be established and used.
- Do not mix incompatible wastes. Waste disposal companies have strict and costly requirements for accepting mixed wastes.
- Always label the storage container of a waste product to indicate its contents.
- Put chemical containers, such as spent ampules containing chemical preservative, in chemically separated storage containers and dispose of properly. Instructions are given in Office of Water Quality Technical Memorandum 92.11, and in Horowitz and others (1994).
- The dilute acid solution used for equipment cleaning can be prepared for safe disposal by following procedures described by Horowitz and others (1994, p. 12).

Do not discard wastes into the environment.

CONTAMINATED WATER 9.7

Water being sampled could be contaminated with pathogens and hazardous chemicals. Use caution and extra protection when working with water known or suspected to contain high concentrations of pathogens. Sample containers, shipping containers, and paperwork must indicate the type and severity of the contamination. This alerts personnel to the appropriate personal protective equipment and procedures needed. **Communicate known or suspected contamination to all personnel who could come in contact with the sample.**

Waterborne, disease-causing organisms (pathogens) are found in nearly all surface-water systems, and occur in some ground-water systems as well. Most pathogens originate from the body fluids and feces of animals and humans. Pathogens enter surface-water resources primarily through sewage discharges and spills, storm and agricultural runoff, and direct contact. Microorganisms also are transported on small particles such as dust or aerosols (gaseous suspension of very fine particles). Pathogens enter ground water through infiltration from septic tank effluent, leachate from fields and ponds, and from faulty well seals and casings. Bacteria, viruses, and other pathogenic organisms can occur in the most pristine environments. **Never drink sample water, no matter how pristine the environment appears.**

To minimize exposures to and effects from contaminated water:

- Receive required inoculations. The USGS immunization program requires inoculations for field personnel working around polluted water (WRD Memorandum 96.29). Employees receive inoculations for waterborne pathogens such as typhoid, tetanus, hepatitis, polio, and rabies at USGS expense. Contact your safety officer about receiving appropriate inoculations before you sample.

- Use personal protective equipment, including respiratory equipment (certification required) when working over turbulent, polluted flows, and in shelters containing evidence of excrement (see WRD Memorandums 94.30 and 95.06). Pathogens can enter your body through many openings such as your mouth, eyes, nose, cuts, scrapes, or chapped skin.
- Wear rubber boots, coveralls or aprons, gloves, and splash protection (a disposable dust mask offers splash and dust protection at a very low cost).
- Do not ingest pathogens or other contaminants. Never eat or drink while sampling or put pencils or other items in your mouth, and do not store food or drink in sample coolers.
- Carry antibacterial soap; wash before leaving the site. Remember to wash again after unloading supplies.
- Disinfect all contaminated surfaces as soon as possible.
- Handle bacteria plates carefully and autoclave them before disposal. An aseptic technique for bacteria enumeration is described in Chapter A7.1 of this *National Field Manual*.

Alert colleagues and laboratory if samples could contain large concentrations of hazardous materials.

ENVIRONMENTAL CONDITIONS 9.8

Field work often is necessary under adverse atmospheric and other environmental conditions. Unpredictable occurrences, such as earthquakes, require event-response planning. Prepare for extreme conditions that might be experienced in your area of the country. Before leaving for the field, check the weather forecast using one or more of these options: the local television station, the national weather channel, the local land/marine weather band channel that constantly repeats current and future weather conditions, or computer networks such as the World Wide Web at http://www.intellicast.com.

TEMPERATURE AND SUN EXPOSURE 9.8.1

Extremes of air temperature occur in all parts of the country. The ideal comfort range for humans is between 16 to 32°C (60 to 90°F). Hypothermia and hyperthermia normally occur in temperatures outside this range.

Hypothermia is a condition of reduced body temperature caused by exposure to cold, and aggravated by wet clothes, wind, hunger, and exhaustion. Hypothermia in extremities can lead to frostbite. Hypothermia can occur with air temperature above 16°C (60°F) under wet and (or) windy conditions. The best way to avoid hypothermia is to dress warm and stay dry. Refer to Denner (Revised 1993) for information on cold-weather clothing.

The warning signals of hypothermia are uncontrollable fits of shivering, incoherence, listlessness, fumbling hands, frequent stumbling, drowsiness, and inability to get up after resting. Victims of hypothermia must be treated immediately by removing them from exposure to the elements, replacing wet clothes with dry ones, and giving them warm, non-alcoholic drinks. Seek emergency facilities as soon as possible.

To prevent hypothermia:

1. Put on rain gear before it starts to rain or snow.
2. Put on additional clothes before starting to shiver.
3. Seek shelter immediately if conditions become severe.

Always carry a complete change of dry clothes. This simple procedure could save a life!

Hyperthermia is a condition of increased body temperature caused by exposure to excessive heat. Contributing factors are physical exertion, clothing, humidity, lack of air movement, and temperature, but the most important factor is body hydration. The normal body requirement for fluids in temperate regions is 2 1/2 quarts per day; desert conditions require more fluid. Early warning symptoms of hyperthermia are chilling, a throbbing pressure in the head, unsteadiness, dizziness, nausea, dry skin (either hot and red or cool and pale), rapid pulse, and muscle pains and spasms.

Persons suffering from hyperthermia should seek medical attention immediately. First aid involves cooling down and rehydrating.

To avoid hyperthermia:

1. Drink water in moderate amounts on a scheduled basis—do not wait until you are thirsty.
2. Avoid alcohol, caffeine, and soda—these liquids are not water substitutes.
3. Wear lightweight clothing and a wide-brimmed hat.
4. Schedule activities that require the most exertion in early morning or late afternoon, if possible, and not when air temperature is at its highest.

Sun exposure can have painful and dangerous short-term and long-term effects. Regardless of the region in which you are working, take the proper precautions to protect your skin and eyes from excessive sun exposure.

To prevent excessive sun exposure:

1. Wear sunscreen on all exposed skin to avoid burning and skin cancer.
2. Wear sunglasses with polarized lenses to protect eyes, reduce glare, and improve vision, especially when working on water or snow.

THUNDERSTORMS, TORNADOES, AND HURRICANES 9.8.2

Thunderstorms, which can be accompanied by hail, are common throughout the United States. Some are predicted by weather forecasters. Others can move into an area with almost no advance warning. Watch the sky for signs of thunderstorms, and seek shelter before the weather deteriorates. Lightning is extremely dangerous and should be respected.

To protect yourself during thunderstorms, heed the following advice from Lockhart (1988):

- Seek shelter inside a vehicle or building; keep away from open doors and windows, plugged in appliances, and metal. Avoid contact with metal objects in a vehicle.
- Do not use a telephone.
- If outside, do not congregate. In case of a lightning strike, someone must be able to begin revival techniques immediately, such as cardiopulmonary resuscitation (CPR).
- Put on rubber boots or rubber-soled shoes.
- Do not work on electrical lines, pipes, cableways, or steel structures.
- Do not use metal objects such as wading rods, bridge cranes, and well-logging equipment.
- If caught in the open, crouch down low, but do not lie flat on the ground.
- Avoid standing near isolated trees.
- Avoid working on streams and lakes.
- Seek lower elevations such as valleys or canyons—avoid being on peaks or ridges.
- If you feel your hair standing on end and your skin tingling, this is a sign that lightning might be about to strike—crouch immediately (feet together, hands on knees).

Tornadoes sometimes accompany thunderstorms. Tornadoes are violently rotating columns of air that descend from the clouds in a funnel formation. A weather channel or weather-band radio will sometimes provide advance warning of possible tornadoes.

To protect yourself during a tornado, heed the following advice from Lockhart (1988):

- Seek shelter immediately if there is a sudden, violent change in weather involving wind, rain, hail, or funnel-shaped clouds.
- Avoid occupying vehicles or mobile homes.
- If you are caught outside, find a ravine, ditch, or culvert and lie flat.
- If inside, go to the basement or lowest interior reinforced part of the structure, such as a closet or bathroom. Stay away from windows.

Hurricanes are severe tropical cyclones with winds exceeding 74 miles per hour, and also can contain heavy rain. Stay informed as to the projected path of an approaching hurricane. Sampling activities should not be conducted until the hurricane has moved out of the area.

Get out of and off of water bodies if you are in or expect a thunderstorm, tornado, or hurricane.

FLOODS 9.8.3

Rain can fall at a rate of several inches per hour and rapidly create dangerous flash flood conditions, either in the area where you are working or several miles away. Weather forecasts will be helpful in planning your activities accordingly to ensure your safety. Maintain an updated copy of your district floodplan. Always be aware of rapidly rising stages in rivers and creeks. Beware of dry creekbeds that can become raging rivers in a short period of time.

EARTHQUAKES 9.8.4

Although earthquakes occur more frequently in tectonically active areas, an earthquake can occur anywhere and without warning.

- **Do not panic and run during an earthquake.** The greatest danger is from falling objects and walls (including rock formations). If possible, take cover under a solid structure, such as a table, to protect yourself from falling objects until the shaking stops. If you are out in the open, sit down to avoid losing your balance.
- If an earthquake occurs while driving, slow down and pull over to the side of the road, avoiding overhead structures such as bridges and signs. If on a bridge, try to drive onto solid ground.

9.8.5 FIRE

Fire can spread out of control rapidly—call 911 if you notice a brush fire or other type of threatening fire or smoke. Working inside your field vehicle or outside at your field site requires fire prevention measures. Do not smoke. Keep matches stored in a metal container. Keep fire extinguishers visible and accessible.

- Know how to operate fire extinguishers.
- Know the type of fire for which an extinguisher is designed (extinguishers are different for ordinary combustibles, flammable liquids, and electrical equipment).
- Never point an extinguisher at a person's face.
- **Recharge fire extinguishers according to the schedule provided with the extinguisher.**

9.8.6 SNOW AND ICE

Snow and ice are dynamic mediums that change quickly in structure and strength. Snow and ice can accumulate rapidly, hiding hazards, and creating slippery conditions. Heavy snowfall (white-outs) can be disorienting and can produce avalanche conditions in steep terrain. Working on ice requires experience, training, and knowledge of the water body over which the ice has formed. Wear layers of appropriate clothing and work in teams. Refer to USGS Handbook 445-1-H, chapters 14 and 15, for detailed information.

ANIMALS 9.9

Most sampling activities take place in and around areas inhabited by animals. Before a field trip, try to find out which species inhabit the area and how to deal with them. Table 9-1 summarizes guidelines on what to do if faced with dangerous animals. Note that such guidelines can vary from expert to expert; the right way to deal with encounters could well be what works at the time.

- Most animals will vigorously protect their young and should not be approached or disturbed.
- If a threat or an injury occurs, the most important action is to remain calm and focus on taking the appropriate steps to relieve, remedy, or rescue yourself or another victim. Call for medical advice before transporting the victim, if possible.

ARACHNIDS AND INSECTS 9.9.1

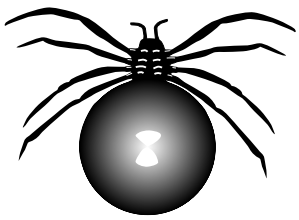
The most common remedy for bites and stings usually involves basic first aid, followed by immediate medical attention if symptoms warrant. If a member of the field team is allergic to insect bites or stings, this should be made known to all members of the team and noted in the emergency information section of the field folder. Treatment procedures should be reviewed before field activity begins. Persons with known allergic reactions to insects should wear or carry on their person medical alert identification, and carry sting kits for use in emergencies.

Scorpions, spiders, and ticks

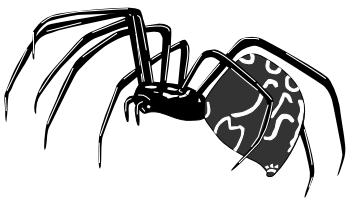
Arachnids such as scorpions, spiders, and ticks are cause for caution by the field team. Spiders and scorpions are known to inhabit enclosed, dark spaces; for example, inside shoes or the corners of well houses and shelters.

Scorpions. Scorpions are known to frequent the desert, but also have been found frozen in ice. Scorpions are not easily seen in the wild. They are nocturnal creatures that are sensitive to vibrations, either in the air or on the ground. When humans are stomping around, scorpions usually run for cover. Scorpion stings often involve an encounter between a big toe and a scorpion that has crawled into a shoe. Check shoes and boots left in the field vehicle before putting them on. **Beware of putting your hands and feet into small, dark spaces (table 9-1).**

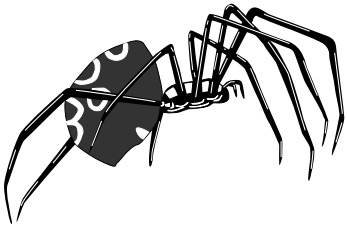
Spiders. Although few spiders in North America bite people, and the venom of most is harmless (Audubon Society, 1980), exceptions include the black widow and the brown recluse (fig. 9-3). The black widow (*Latrodectus mactans*) has a fairly large geographical range. Red and brown widow spiders are found mainly in the Gulf Coast region of the United States. The brown recluse (*Loxosceles reclusa*) frequents areas of human habitation and prefers dark spaces such as equipment shelters, as well as areas in the wild. It is advisable to be familiar with the area in which you are working and take care when walking and when reaching into small spaces.



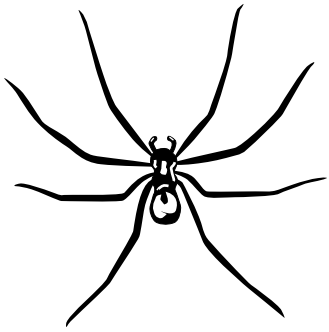
Southern black widow spider
(underside view)



Brown widow spider



Red widow spider



Brown recluse spider

Figure 9-3. Sketches of selected spiders found in North America. (From M.H. Cox, 1994, p. 38-39.)

Ticks. Ticks are found nearly everywhere in North America, and can transmit diseases such as Rocky Mountain spotted fever, Lyme disease, human ehrlichiosis, and human granulocytic ehrlichiosis (HGE). To reduce your chances of being exposed to ticks, wear long pants and tuck the pants legs into your socks; use a repellant containing the compound DEET (N-diethyl-meta-toluamide) on exposed skin, except for the face; check your body regularly for ticks, including inspection of the neck and scalp. Remove attached ticks immediately (table 9-1).

Bees and wasps

Venomous insects of common concern include bees and wasps. Bee stingers are equipped with barbs that should be scraped off if a person is stung—using forceps or tweezers to pull the stinger out can force more venom into the wound (table 9-1). A wasp stinger has no barb; the venom is injected and the stinger usually slides out. The yellow jacket (a vespid wasp) nests in the ground and will aggressively defend the nest if disturbed, particularly in the late summer and early fall. Stings in the mouth or throat sometimes result when a bee or wasp has flown into a can of soda. Seek medical attention if symptoms warrant.

Do not disturb bee hives or wasp nests.

9.9.2 SNAKES

DISTINGUISHING FEATURES OF POISONOUS AND NONPOISONOUS SNAKES OF NORTH AMERICA

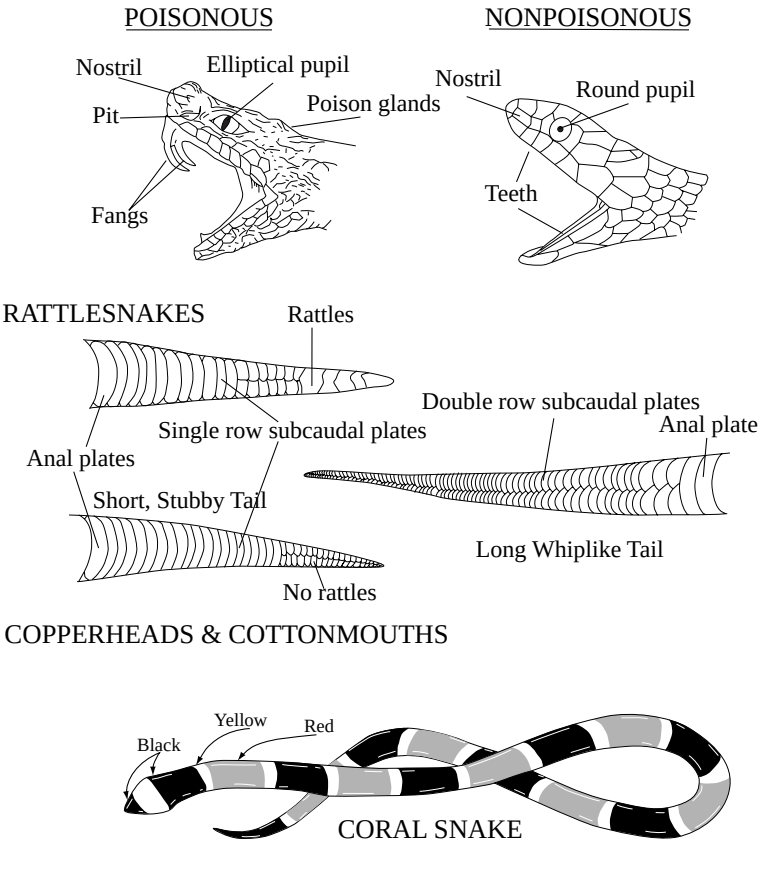


Figure 9-4. Sketches of selected poisonous and nonpoisonous snakes of North America. (From M.H. Cox, 1994.)

SNAKES 9.9.2

Snakes deserve our respect, but they do not have to be feared. Only about 10 percent of the approximately 3,000 species of snakes in the world are poisonous. Differences between poisonous and nonpoisonous snakes of North America are illustrated in figure 9-4.

In the event of snakebite, take the victim to the nearest medical facility as soon as possible. Call the medical facility first if time allows. Even a person who has been bitten by a nonpoisonous snake should be treated by medical personnel, because some people are allergic to the foreign protein in snake saliva. Refer to table 9-1 for procedures to follow if bitten. The best advice regarding snake bites is to prevent them in the first place.

Snake expert Maynard Cox (1994) recommends:

- Do not put your hands or feet where you cannot see.
- Never handle a snake unnecessarily, dead or alive, poisonous or nonpoisonous.
- If you come upon a poisonous snake, turn and run. A snake normally can strike up to one-half or two-thirds of its body length, but if provoked it can strike up to its full body length.

A common symptom of a poisonous snakebite from pit vipers (copperheads, cottonmouths or water moccasins, and rattlesnakes) is a burning, fiery, stinging pain at the bite site. Other symptoms could include swelling; skin discoloration; nausea and vomiting; a minty, metallic, rubbery taste in the mouth; sweating and chills. If the pain does not get any worse and remains localized, venom probably was not passed. If the pain becomes severe, venom was probably injected.

Copperheads (*Agkistrodon contortix*) have a wide distribution throughout the central, mid-Atlantic, and southern United States. They can be found on wooded hillsides or in areas near water. Although the bite of a copperhead can be painful, it is unlikely to result in an adult human death.

Cottonmouths or water moccasins (*Agkistrodon piscivoros*) are found in the southeastern United States and are never far from water. Cottonmouths usually swim with their entire body on top of the water (Huegel and Cook, undated). Cottonmouths might be seen in the daytime, but they are more active at night. They are an extremely aggressive snake and should not be approached.

Rattlesnakes have been found in every state except Alaska, Delaware, Hawaii, and Maine. All other states have at least one species of rattlesnake, and many have three or four. Arizona, for example, has 17 species or subspecies of rattlesnakes (Kauffeld, 1970). A rattling sound usually alerts that a nearby rattlesnake has been disturbed and can be preparing to strike, but if the snake is sufficiently disturbed, it might not rattle at all.

Coral Snakes. Symptoms are different for bites from coral snakes. The coral snake's venom is extremely toxic, but little or no pain may occur from the bite. Look for teeth marks at the puncture wound. Other symptoms could include euphoria, excess salivation, convulsions, weakness, and paralysis (Cox, 1994).

The **Eastern coral snake** (*Micrurus fulvuis*) is found in the southeastern United States. It is identified by wide red and black bands separated by a narrow, bright yellow band. The red and black bands never touch. The **Arizona coral snake** (*Micruroides euryxanthus*) is located in the southwestern United States. The red and black bands also never touch.

9.9.3 ALLIGATORS

The American alligator (*Alligator mississipiensis*) is found in swamps, rivers, and lakes, primarily of the southeastern United States. Alligators are fairly inactive in the winter months when the water temperatures are cool; their metabolism slows down and there is little need for food. The breeding season is mostly during April and May; male and female move around more during this time.

Treat alligators with extreme caution. Some can become a nuisance when they lose their fear of humans and usually have to be destroyed by licensed trappers. **Never approach an alligator, either on land or in the water.** Alligators can outrun humans for short distances. If your sampling involves fish collection, get the specimens out and away from the water as soon as possible.

BEARS 9.9.4

Bear behavior is unpredictable. According to *Guidelines for Safe Geologic Fieldwork in Alaska* (U.S. Geological Survey, May 1978), bears fiercely defend any carcasses and will often bury or partially cover such prizes for later. Contrary to popular belief, bears can see almost as well as people, but trust their noses much more than their eyes or ears.

Avoiding contact with a bear is the best defense:

- Avoid game trails that bears might use.
- Avoid carrion (dead and decaying flesh), fresh kill, or gut piles.
- Avoid berry patches, or other areas abundant with plants that bears use for food.
- Avoid willow and dry grass patches; bears sometimes use these areas for daybeds.
- Avoid areas with fresh bear tracks.
- Make noise or wear bells when moving through the woods so as not to surprise bears.
- Avoid carrying food that a bear can smell. Always keep food sealed and in a backpack, not in a pants pocket.
- Work in teams of two or larger groups to help deter a bear from attacking.

If you meet a bear on the trail, effective methods of defense can vary:

- If you see the bear before it sees you, decide on your route of escape and leave the area at once.
- If you find yourself close to a bear, give the bear all the room you can.
- Let the bear know you are human—talk in a normal voice and wave your arms. Try to back away slowly, but if the bear follows, stop and hold your ground.
- **Do not run!** Bears often make bluff charges, sometimes within 10 feet of their adversary, without making contact.
- If a bear actually makes contact, surrender! Fall to the ground and play dead. Typically, a bear will break off its attack once it feels the threat has been eliminated. If the bear continues to bite after you assume a defensive posture, the attack is predatory and you should fight back vigorously.

9.9.5 MOUNTAIN LIONS

Mountain lions (*Felis concolor*) are a species of larger cats found in North America (also called cougar, puma, and panther). The primary habitat for these members of the cat family is west of the Rocky Mountains and south of the Yukon, although Florida has a small population. Mountain lions are active during the day and night, and search a wide territorial range for food. The main food source is deer and smaller animals.

Be alert to reports of mountain lion attacks or sightings. Healthy mountain lions do not usually attack humans, but when this occurs, it is usually because the person panicked and ran. Turning and running can evoke a predatory response from mountain lions.

9.9.6 RODENTS AND OTHER SMALL MAMMALS

Rodents and other small mammals can be disease carriers as well as be a nuisance. The best policy is to avoid them; know what animals are in your particular area and take appropriate precautions. Two diseases of concern carried by such animals are hantavirus and rabies.

Mice, rats, and chipmunks are the primary hosts of hantaviruses (Center for Disease Control, 1994a and b). Known carriers include the deer mouse (*Peromyscus maniculatus*), piñon mouse (*P. truei*), brush mouse (*P. boylii*), cotton rat (*Sigmodon hispidus*), and western chipmunk (*Tamias*). Hantavirus does not cause apparent illness in the host, but the infected individual sheds the virus in saliva, urine, and feces for many weeks. Rabies infection is another hazard of contact with small animals, especially skunks, raccoons, foxes, coyotes, bats, cats, and dogs.

The best way to eliminate the chance of infection from rodents and other small mammals is to secure the areas in which you will be working against an animal population. In gage houses and recorder shelters, make sure all openings have been blocked before leaving the site. Subsequent inspections must be made on a routine basis to ensure that rodents have not found other means of access into the structure.

Structures with heavy rodent infestation must be treated with extreme caution and may require specific training to ensure proper precautions are used. Persons involved in cleanup should wear disposable coveralls, rubber boots or disposable shoe covers, rubber or plastic gloves, protective goggles, and appropriate respiratory protection, such as a half-mask air-purifying (or negative pressure) respirator with a high-efficiency particulate air (HEPA) filter or a powered air-purifying respirator (PAPR) with HEPA filters (Center for Disease Control, 1994b). Immediately after the clean-up operation, this personal protective equipment should be decontaminated or discarded using appropriate methods.

If the gage house or recorder shelter is suspected of being inhabited by rodents, the following steps are to be followed before entering the structure:

1. Open the door or shelter lid and allow to air out for at least 30 minutes before entering.
2. Wear rubber or plastic gloves when working in the previously enclosed area.
3. Spray dead rodents, rodent nests, droppings, or other potentially tainted areas with a general-purpose household disinfectant. Soak the materials thoroughly with disinfectant and place in a plastic bag. Seal the bag and place it inside another plastic bag and then bury or burn. If this is not possible, contact the local or State health department for alternative disposal methods.
4. After removing the above items, disinfect the area with a solution of water, detergent, and disinfectant. Do not vacuum or sweep dry surfaces prior to disinfecting with a liquid solution.

DOMESTIC ANIMALS 9.9.7

Sampling often involves working in urban or rural areas where cats, dogs, cows, horses, and other domesticated animals can be carriers of disease or exhibit unpredictable and aggressive behavior. Before entering private property, contact the owner and obtain permission to enter. Ask about any animals that might be on or around the property. Do not pet, feed, or otherwise contact these animals.

Table 9-1. Guidelines on potentially dangerous animals

[mm, millimeter; in., inch; cm, centimeter; ft, foot; lb, pound; mph, mile per hour]

Animals	Description/ Characteristics	Procedure
Arachnids and Other Insects		
Black widow spiders (Black, brown and red widow spiders are illustrated in figure 9-3.)	Female (only one that bites) is black with abdomen almost spherical, usually with red hourglass mark below or with 2 transverse red marks separated by black. Spiderling is orange, brown, and white, gaining more black at each molt. Habitat among fallen branches and under objects, such as well shelters, furniture, and trash.	**If bitten, seek medical attention as soon as possible.**
Brown recluse spiders	Orange-yellow thorax with dark violin pattern. Bases of legs orange-yellow, rest of legs grayish to dark brown. Abdomen grayish to dark brown with no obvious pattern. Habitat outdoors in sheltered corners, among loose debris; indoors on the floor and behind furniture in houses and outbuildings.	
Scorpions	Nocturnal, sensitive to vibrations. Field boots are a favorite hiding place.	
Ticks	Small, less than 3 mm (<1/8 in.). Clamps to host using a dart-like anchor located just below the mouth.	**Do** • Check for ticks during and after field work. • Remove with tweezers within 24 hours. **Don't** • Leave the head imbedded. • Extract using matches or applying petroleum jelly or other coating.
Bees	Bees vary in size from 2 mm (0.08 in.) long to 4 cm (1.6 in.) long; divided into a number of family classifications which are determined by mouthparts and other characteristics that are difficult to see without dissection.	**Do** • Avoid all bee hives and wasp nests. • Scrape off the bee stinger with a knife or other flat object. • Use an over-the-counter sting ointment or a solution of baking soda, meat tenderizer, and ammonia. **Don't** • Use forceps or tweezers to pull the bee stinger out.
Wasps	Wasps vary in size from minute up to 5 cm (2 in.) long; adults distinguished by a narrow waist between the first and second abdominal segments.	
Snakes and Alligators		
Copperhead snake Cottonmouths or water moccasin snakes Rattlesnakes Eastern coral snakes and Arizona coral snakes	Elliptical eyes; short, stubby tail. Elliptical eyes; short, stubby tail. Usually swim with their entire body on top of the water. Never far from water. Most active at night. An extremely aggressive snake. Elliptical eyes; short, stubby tail. The rattle is a sign of fear, but if the snake is sufficiently disturbed, it might not rattle at all. Wide red and black bands separated by a narrow, bright yellow band; the red and black bands never touch; round pupils; short, stubby tail.	**Do not confront a snake—turn and run** **If bitten:** **Do** • Reassure victim. • Treat for shock. Keep victim lying down; elevate feet 10 to 12 in. • Seek medical attention as soon as possible. Call medical facility while en route, if possible. **Don't** • Cut and suck affected area. • Apply ice or a tourniquet. • Leave victim unattended.

Table 9-1. Guidelines on potentially dangerous animals–*Continued*

Animals	Description/ Characteristics	Procedure
Snakes and Alligators—*Continued*		
Alligators	Fairly inactive when water is cool. Most active during breeding season (mostly April and May). Alligators can run quickly for short distances.	**Don't** approach an alligator.
Mammals		
Polar bears	White, 8-10 ft in length, male 600-1,200 lb, female 400-700 lb, carnivores (primarily).	**Do** • Make your presence known (sing, talk, tie bells to pack). • Travel with a group. • Give bears plenty of room. • Play dead if attacked. Lie flat on stomach or curl up in a ball with hands behind neck. Remain motionless as long as possible, until the bear is gone. If bear continues attack long after you play dead, it is probably a predatory attack. FIGHT BACK VIGOROUSLY! **Don't** • Run. Bears can run up to 35 mph. • Imitate bear sounds or make a high-pitched squeal.
Black bears	Brown to black, white patch in front of chest, 5 ft in length, male 150-400 lb, female 125-250 lb, herbivores (primarily).	
Brown bears	Dark brown to blonde, 7-9 ft in length, male 400-1,100 lb, female 200-600 lb, herbivores (primarily).	
Mountain lions	Active during the day and night. Healthy mountain lions do not usually attack humans.	**Do** • Stand your ground. • Shout and wave your arms. • Throw rocks at the animal. **Don't** • Turn your back. • Panic and run.
Rodents and small mammals: mice, chipmunks, rats, skunks, squirrels, raccoons, bats, foxes, coyotes	Animals infected with hantavirus show no signs of illness. Virus is transmitted from being bitten, or when infective saliva or excreta are inhaled as aerosols produced directly from the infected rodent, or when dried or fresh material contaminated by rodent excreta are disturbed, directly introduced into broken skin, introduced onto the conjunctivae (mucous membrane covering the eyeball), or possibly ingested in contaminated food or water. Signs of an animal infected with rabies are nervousness, aggressiveness, excessive drooling and foaming at the mouth, abnormal behavior, such as wild animals losing their fear of humans or nocturnal animals being seen in the daytime.	**Do** • Wash the wound from a bite or scratch thoroughly with soap and water. • Seek medical attention. • Notify game warden or health department. **Don't** • Capture animal. • Pet or feed wild or domestic animals.
Domestic animals: cats, dogs, cows		

9.10 PLANTS

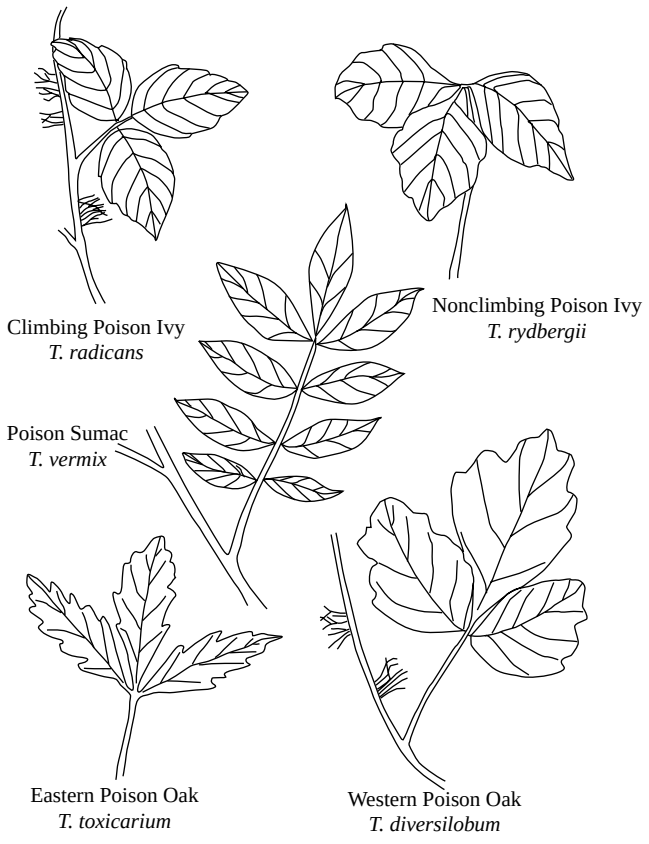


Figure 9-5. Shapes of leaves in five species of *Toxicodendron* found throughout the continental United States (except Alaska and Nevada). (From Frankel, 1991.)

PLANTS 9.10

The most common poisonous plants are the *Toxicodendrons*, or poison ivies, and include climbing and nonclimbing poison ivy, eastern and western poison oak, and poison sumac (fig. 9-5). Resins and secretions from these species are capable of inflicting a mild to serious skin rash on susceptible individuals (Frankel, 1991).

The best defense against *Toxicodendrons* and other poisonous plants is proper clothing. Long pants and sleeves will protect you in most cases, but plant poisons have been known to penetrate clothing. In the field, always wear shoes that protect your whole foot.

The oily resin of the plant is only slightly soluble in water, and the best treatment is to flush the area of skin contact with copious amounts of cold water (table 9-2). A little water spreads the poison; lots of water washes it away. Soap can remove natural skin oils that protect against penetration of the resins; warm water can also hasten the absorption.

Table 9-2. Guidelines on poisonous plants

Plant	Description/Characteristics	Procedure
Poison ivy *(Toxicodendron rydbergii)*	• Climbing poison ivy has alternate, trifoliate leaves, tiny greenish-white flower clusters or white berries, and aerial roots that grow straight and are fuzzy. Ubiquitous in most environments (seldom found in deep, dark forests or at heights above 4,000 ft) (Frankel, 1991). • Non-climbing poison ivy lacks aerial roots. The leaves are larger and broader than the climbing variety, but the pattern is still alternate and trifoliate.	**In case of skin contact:** **Do** • Flood the affected area with copious amounts of **cold** water as soon as possible. **Don't** • Use soap. • Use warm water.
Eastern poison oak *(Toxicodendron toxicarium)*	Prefers the sandy soil of the Atlantic and Gulf coasts. Distinguished by trifoliate fuzzy leaves, fuzzy fruits, and leaflets with rounded tips.	
Western poison oak *(Toxicodendron diversilobum)*	Strictly a Pacific coast species. Usually grows as a short shrub but can grow as a vine, due to aerial roots. Trifoliate leaves.	
Poison sumac *(Toxicodendron vernix)*	A tree that prefers a moist habitat such as bogs or swamps. Ranges in height from 6 to 20 feet. The alternate leaves are compound with 7 to 13 lobeless, toothless leaflets arranged in a featherlike fashion with a single leaflet on the end. Can have white berries. The fruits of poisonous varieties of sumac droop downward.	

9.11 CHECKLISTS FOR STANDARD SAFETY EQUIPMENT

Checklists are helpful for ensuring that personnel have the appropriate safety equipment available during field trips. Each study team needs to consider the specific needs for their work and should customize these checklists as necessary.

9.11.1 CHECKLIST FOR PERSONAL PROTECTIVE EQUIPMENT

✓	Personal Protective Equipment[1]
	Chemical and disease protection
	Aprons
	Eye/Face splash guards
	Gloves (vinyl and/or latex or nitrile). Sizes: S M L XL
	Protective suits. Sizes: S M L XL
	Respirators (certification required for use)
	Climatic and UV protection
	Boots
	Fluids (for example, water and sports drinks)
	Hat, wide-brimmed
	Insect repellent (unscented)
	Rain gear
	Sunglasses
	Sunscreen
	Temperature-modifying clothing
	Flotation and reflective protection
	Orange flotation vests and jackets
	Safety harness
	Protection for working around heavy objects and machinery
	Back belt
	Hardhat
	Hearing protection
	Safety glasses
	Steel-toed safety boots
	Work gloves

[1] PPE must be selected based on the hazards likely to be encountered. The USGS is required to supply appropriate PPE, and field personnel are required to use it.

CHECKLIST FOR VEHICLES AND VEHICULAR LABORATORIES 9.11.2

✓	Items for Field Vehicles
	Chemical protection and storage
	Chemical spill kit
	Eye wash kit (replace old or expired wash solution)
	Material Safety Data Sheets (MSDS)
	Chemical reagents (stored in appropriate area)
	Flammable solvents (stored in appropriate dedicated area)
	Pressurized gases (stored in appropriate area)
	Communications and instructions
	Field folder (including maps, emergency phone numbers for medical facilities, office contacts, family contacts)
	Cellular phone/communication equipment (check that the service is operational for the area to be traveled)
	First aid and protective equipment
	Complete change of clothes (stored in dry area)
	Fire extinguisher (safely secured)
	First aid kit and manual (check for missing or old, expired items and replace if necessary)
	Orange reflective vest
	Miscellaneous equipment
	Bungie cords (to secure loose articles)
	District flood plan (most current version)
	Flagging
	Flares
	Flashlight (including fresh batteries)
	Flexible hose (to vent exhaust away from vehicle)
	Safety cones
	Tool kit

9.11.3 CHECKLIST FOR WATERCRAFT

✓	Watercraft Items
	Instructions and navigation
	Field folder, with float plans
	Charts and maps
	Compass (in working order)
	Depth finder (if appropriate)
	Dead-man's switch
	Navigation lights
	Ring buoy with line
	Distress and external communication
	Radio (VHF, AM, FM, and WEATHER)
	Special lighting/flagging (if boat activities might pose a hazard to the public, such as tag line measurements)
	Visual distress signals (Coast Guard approved)
	Whistles or horns
	Type IV throwable rescue device
	Personal flotation devices for each passenger (Coast Guard approved)
	Anchor and lines (spare)
	Bucket for use as a bailer
	Paddle (extra paddle for each canoe or rowboat)
	First aid kit (Coast Guard approved)
	Flashlights and batteries
	Fire extinguishers
	Spare parts (anchor, fuel, propeller, extra lines)
	Tool and repair kits
	Extra clothes (hat, foul-weather gear)
	Food and water
	Sunscreen

CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
milligrams (mg)	3.52×10^{-5}	ounce
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
square centimeter (cm^2)	0.155	square inch
liter (L)	0.2642	gallon
meter (m)	3.281	foot
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
square foot (ft^2)	2.590	square kilometer
mile	1.609	kilometer
pound, avoirdupois (lb)	0.4536	kilogram
quart	0.9464	liter

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8\ (°C) + 32$$

ABBREVIATIONS

CFR	Code of Federal Regulations
CPR	Cardiopulmonary resuscitation
DOI	U.S. Department of the Interior
DOT	U.S. Department of Transportation
EPA	U.S. Environmental Protection Agency
MSDS	Material Safety Data Sheet
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit
PFD	Personal flotation device
PPE	Personal protective equipment
TWRI	Techniques of Water-Resources Investigations
USCG	U.S. Coast Guard
USGS	U.S. Geological Survey
WRD	Water Resources Division of the USGS

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The reports listed below are for sale by the U.S. Geological Survey, Branch of Information Services, Box 25286, Federal Center, Denver, CO 80225 (authorized agent of the Superintendent of Documents, Government Printing Office). Prepayment is required. Remittance should be sent by check or money order payable to the U.S. Geological Survey. Prices are not included because they are subject to change. Current prices can be obtained by writing to the above address. When ordering or inquiring about prices for any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations."

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National Field Manual for the Collection of Water-Quality Data

Chapter A10.
LAKES AND RESERVOIRS: GUIDELINES FOR STUDY DESIGN AND SAMPLING

By W. Reed Green, Dale M. Robertson, and Franceska D. Wilde

Techniques of Water-Resources Investigations Book 9, Chapter A10

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

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Cover Photo: The Annie. "First Boat Ever Launched on Yellowstone Lake." Reported to first be used on June 29, 1871. James Stevenson and H.W. Elliott, 5th annual report, page 96. William Henry Jackson, photographer (Yellowstone National Park). U.S. Geological and Geographical Survey of the Territories, Yellowstone Series, 1871, Vol. III (Hayden Survey). Image file: *http://library.usgs.gov/photo/#/item/51dca2c7e4b097e4d383aebd*.

Preface

One of the missions of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and quality-assured data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a national field manual for the U.S. Geological Survey is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that the data collected are of the quality required to fulfill our mission.

The purpose, scope, and revision process for the *National Field Manual for the Collection of Water-Quality Data* are described on the home page of this chapter (chapter 10) at *http://water.usgs.gov/owq/FieldManual/Chapter10/Ch10_contents.html*.

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Contents

Figures

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Conversion Factors

Multiply	By	To obtain
micrometer (µm)	3.937×10^{-5}	inch (in.)
	3.3×10^{-6}	foot (ft)
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
nanometer (nm)	3.93×10^{-8}	inch
liter (L)	0.264	gallon (gal)
milliliter (mL)	0.0338	ounce, fluid (oz)
gram (g)	0.03527	ounce, avoirdupois
microgram (µg)	3.527×10^{-8}	ounce, avoirdupois
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois

Temperature: Water and air temperatures are reported in degrees Celsius (°C).

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C=(°F–32)/1.8.

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8x°C) +32.

Vertical coordinate information is referenced to "North American Vertical Datum of 1988."

Specific electrical conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Selected Symbols

>	greater than
<	less than
µm	micrometer
µg/L	microgram per liter (equivalent to parts per billion)
mg/L	milligram per liter
mm^3/L	cubic millimeter per liter
$µm^3/L$	cubic micrometer per liter

Chapter 10. Lakes and Reservoirs: Guidelines for Study Design and Sampling

By W. Reed Green, Dale M. Robertson, and Franceska D. Wilde

Abstract

The National Field Manual for the Collection of Water-Quality Data (National Field Manual, NFM) is an online report with separately published chapters that provides the protocols and guidelines by which U.S. Geological Survey personnel obtain the data used to assess the quality of the Nation's surface-water and groundwater resources. Chapter 10 reviews limnological principles, describes the characteristics that distinguish lakes from reservoirs, and provides guidance for developing temporal and spatial sampling strategies and data-collection approaches to be used in lake and reservoir environmental investigations.

Within this chapter are references to other chapters of the NFM that provide more detailed guidelines related to specific topics and more detailed protocols for the quality assurance and assessment of the lake and reservoir data. Protocols and procedures to address and document the quality of lake and reservoir investigations are adapted from, or referenced to, the protocols and standard operating procedures contained in related chapters of this *National Field Manual*.

Introduction

Lakes and reservoirs constitute the largest source of the usable freshwater on Earth. With approximately 97 percent of the water on Earth being saline and stored primarily in the oceans, only 3 percent of Earth's remaining water resource exists as freshwater (*http://water.usgs.gov/edu/watercyclefreshstorage.html*; accessed 02/03/2015). An estimated 68.7 percent of that freshwater is contained in glaciers and ice caps and thus is not readily or practicably available for human use, 30.1 percent resides in groundwater, and about 0.3 percent is surface water. Of that 0.3 percent surface water, about 2 percent is found in rivers, 11 percent in swamps, and about 87 percent is contained in lakes and reservoirs.

Limnology is the study of all inland waters, including streams and rivers. In this chapter, however, the term **limnology**[1] refers only to the study of lakes and reservoirs. Limnological studies are typically conducted by the U.S. Geological Survey (USGS) to gain an understanding of ecosystem dynamics in order to develop effective strategies to monitor, assess, and prevent deterioration of lake and reservoir structure and function. Commonly collected data for limnological studies include field characteristics and other observational data, general conditions of the water body, water chemistry, aquatic biology, and living and nonliving bottom material (tables 10–1 and 10–2). The specific set of data collected depends on objectives of the study.

Purpose and Scope

This chapter of the National Field Manual for the Collection of Water-Quality Data (National Field Manual or NFM) is designed to provide the general information, considerations, preparations, and

[1] Terms in bold are among the terms defined in the glossary at the end of this chapter.

USGS-specific sampling guidelines needed to design and implement studies in which lake or reservoir environmental quality can be reliably monitored and evaluated. To this end, this chapter includes a review of the basic principles of limnological (lake and reservoir) science, provides an explanation of the distinguishing characteristics of lakes and reservoirs, and places special emphasis on the appropriate temporal and spatial sampling strategies and approaches needed to account for differing data requirements (depending on characteristics of the water body under investigation). The discussion of study design in section 10.3 refers to standard USGS methods and quality-assurance protocols in the sampling and collection of water, bottom material, and biological components that are more fully described in other sections of the *National Field Manual* (table 10–1).

Topics related to stream and groundwater systems and their interactions with lakes or reservoirs are not addressed in this report. Also beyond the scope of this chapter are guidelines specific to sampling saline lakes or seas, the Great Lakes, ponds and stormwater detention or retention basins, and subsurface water bodies (such as those found in karst environments).

Table 10–1. Primary references for commonly collected data for limnological studies.

[NFM, National Field Manual for the Collection of Water-Quality Data; GPS, global positioning system; USGS, U.S. Geological Survey]

Data group	Description	Primary references[1] consulted
Field characteristics and observational data	General field observations, such as water color and clarity, current meteorological conditions, presence of visible algae, presence of surface accumulations or scums of cyanobacteria	NFM 1 NFM 4 NFM 7.4 Wetzel and Likens, 2000 Wetzel, 2001
	Quality-assurance procedures and policies GPS coordinates Photographs of current conditions Meteorological conditions several days before sampling Occurrence of recent inflow events Water residence time Lake or reservoir pool elevation	
General conditions and properties of the water body	Light attenuation Secchi disk Solar radiation	NFM 7.4 NFM 7.4.1.B
	Standard field measurements, such as water temperature, specific conductance, pH, dissolved oxygen, and **turbidity**	NFM 6 Wetzel and Likens, 2000 Wetzel, 2001 Wagner and others, 2006
Water chemistry: Inorganic constituents and organic compounds	Nutrients, such as phosphorus and nitrogen	NFM 4 NFM 5 Hem, 1989 Wetzel, 2001
	Alkalinity and acid neutralizing capacity (ANC)	NFM 6.6
	Suspended sediment (solids)	NFM 4 NFM 5
	Major ions	NFM 2 NFM 4 NFM 5 Hem, 1989
	Carbon	NFM 2 NFM 4 NFM 5 Hem, 1989

Table 10–1. Primary references for commonly collected data for limnological studies.—Continued

[NFM, *National Field Manual for the Collection of Water-Quality Data*; GPS, global positioning system; USGS, U.S. Geological Survey]

Data group	Description	Primary references[1] consulted
	Trace elements	NFM 2 NFM 4 NFM 5 Hem, 1989
	Trace organic compounds	NFM 2 NFM 4 NFM 5
Aquatic biology, including **benthic fauna**	Fecal indicator bacteria	NFM 7.1
	Chlorophyll	NFM 7.4
	Phytoplankton	NFM 7.4 NFM 7.5 Britton and Greeson, 1987 Wetzel and Likens, 2000 Wetzel, 2001 American Public Health Association, 2005
	Periphyton	NFM 7.4 Britton and Greeson, 1987 Wetzel and Likens, 2000 Wetzel, 2001 American Public Health Association, 2005
	Zooplankton	Britton and Greeson, 1987 Wetzel and Likens, 2000 Wetzel, 2001 American Public Health Association, 2005
	Fish	Britton and Greeson, 1987 Wetzel and Likens, 2000 Wetzel, 2001
	Macrophytes	Britton and Greeson, 1987 Wetzel and Likens, 2000 Wetzel, 2001
	Actinomycetes bacteria density	NFM 7.5
	Cyanobacteria	NFM 7.5
Nonliving material	Bottom-material sampling strategies and procedures	NFM 8 Britton and Greeson, 1987 Wetzel and Liken, 2000 Wetzel, 2001 American Public Health Association, 2005

[1]For description of and guidance for specific USGS protocols and methods for collecting selected types of data, refer to NFM chapters or chapter sections (available from *http://water.usgs.gov/owq/FieldManual/*) and to other reports, as noted.

10.1 Basic Limnology

Limnology is the study of the physical, chemical, and biological interactions within inland waters. Limnological studies include the movements and biogeochemical changes that occur as water moves through drainage basins and within lakes and reservoirs. Relatively static lake and reservoir waters (collectively referred to as **lentic** waters) are functionally linked with the surrounding landscape, including the flowing waters in streams (collectively referred to as **lotic** waters) (Wetzel, 2001). The term "lakes" commonly is used to encompass both natural water bodies and manmade impoundments (reservoirs) of inland waters that are relatively stable (standing or still waters), open to the atmosphere, and nonflowing or low-flowing (relative to free-flowing rivers and streams). In the context of conceptualizing and designing studies for environmental assessments, however, reservoirs are distinguished from lakes by differences in structural, as well as functional, characteristics. To serve the purpose of this guidance, therefore, the terms "**lake**" and "**reservoir**" are defined as shown below.

Some natural lakes have been engineered with elevated modified spillways to increase or decrease pool elevation and storage; in this respect, they function as a reservoir but have many hydrologic, geologic, and physical characteristics/features in common with lakes. A continuum exists from lakes to reservoirs, from the basic seepage lake (no inlets or outlets), to a natural drainage lake (with inlets and outlets), to a slightly impounded system, to a full-blown drinking water supply or flood-risk reduction reservoir. Typical characteristics and properties along this continuum between lake and reservoir are listed in table 10–2.

Table 10–2. Comparative characteristics and properties between reservoirs and natural lake ecosystems (modified from Wetzel, 1990).

Properties[1]	Natural lakes	Reservoirs
Geographical distribution	In the United States, predominantly in the northern glaciated regions	In the United States, predominantly in the southern nonglaciated regions
Climate	Precipitation commonly close to or exceeds evaporative losses	Precipitation often low and evaporation high or greater than precipitation
Drainage basins	Generally circular, lake basin usually central; usually small in comparison to lake area (around 10:1)	Usually narrow, elongated lake basin in base or drainage basin; area large in comparison to lake area (around 100:1 to 300:1)
Shoreline development	Relatively low; stable	High, astatic
Water level fluctuations	Small, stable	Large, irregular
Thermal stratification	Natural regime; often dimictic or monomictic	Variable, irregular; often too shallow to stratify in riverine and **transitional zones**; often can temporarily stratify in lacustrine zones
Inflow	Runoff to lake via small tributaries (low stream orders) and diffuse sources; penetration into stratified waters small and dispersive	Most runoff to lake via river tributaries (high stream orders); penetration into stratified strata complex (over-, inter-, underflows); often flow is directed along an old riverbed valley
Outflow (withdrawal)	Relatively stable; surface water	Highly irregular with water use; withdrawal from surface layers or from hypolimnion
Flushing rates	Long, relatively constant (one to many years)	Short, variable (days to several weeks); increase with surface withdrawal, disruption of stratification with hypolimnetic withdrawal

Table 10–2. Comparative characteristics and properties between reservoirs and natural lake ecosystems (modified from Wetzel, 1990).—Continued

Properties[1]	Natural lakes	Reservoirs
Sediment loading	Low, limited dispersal; relatively constant rates seasonally	High with large drainage basin area; flood plains large; deltas large, channelized, gradation rapid
Deposition of sediments	Low, limited dispersal; relatively constant rates seasonally	High in riverine zone, decreasing exponentially down reservoir; greatest in old river valley; highly variable rates seasonally
Suspended sediment in water	Low to very low; turbidity low	High, variable; high percentage clay and silt particles; turbidity high
Allochthonous particulate organic matter (POM)	Low to very low	Moderate, especially fine POM during spates and inundation of floodplains
Water temperature	Generally lower (because lakes are concentrated in more northern climate regions)	Somewhat higher (because reservoirs are concentrated in more southern climate regions)
Dissolved oxygen	Somewhat higher solubilities (lower temperatures); small horizontal variability; metalimnetic oxygen maxima more common than minima	Somewhat lower solubilities (higher temperatures); greater horizontal variability with inflow, withdrawal, and **particulate organic matter** loading patterns; metalimnetic oxygen minima more common than maxima
Light extinction	Vertical light gradients predominate over the scale of meters; variable but relatively low extinction from dissolved organic compounds and biogenic particulate matter	Horizontal gradients predominate over the scale of kilometers; light extinction irregular and often very high, particularly in riverine and transitional zones from abiogenic particulate matter; euphotic zone commonly increases in lacustrine zones
External nutrient loadings	Variable but relatively predictable; loadings often moderated by biogeochemical influences of wetland/**littoral** interface zones	Generally higher than in natural lakes (larger drainage basin, more human activity, greater water-level fluctuations); variable, often unpredictable
Nutrient dynamics	Vertical gradients dominate; often low internal loading, particularly in lakes without severe culturally induced eutrophication	Horizontal gradients predominate; dependent upon sedimentation rates, **residence times**, and flow regimes; concentrations in water decrease with distance from headwaters; irregular internal loading
Dissolved organic matter (DOM)	Allochthonous and littoral/wetland sources predominate; relatively constant, often high; refractory DOM predominates	Allochthonous and benthic sources predominate; irregular, often high; refractory DOM predominates
Littoral zone/wetland	Dominates primary production in most lakes; important to regulation of nutrient and dissolved particulate organic matter loadings	Irregular and limited by severe water-level fluctuations
Phytoplankton	Vertical and seasonal gradients predominate; small horizontal gradients; light and inorganic nutrient limitations predominate	Marked horizontal gradients; volumetric primary productivity (or P_{max}) decreases from headwaters to dam; areal primary productivity relatively constant horizontally; light and inorganic nutrient limitations predominate

Table 10–2. Comparative characteristics and properties between reservoirs and natural lake ecosystems (modified from Wetzel, 1990).—Continued

Properties[1]	Natural lakes	Reservoirs
Bacterial heterotrophy	Benthic and littoral/wetland bacterial heterotrophy predominates in most lakes	**Pelagic**, particle-associated, and benthic bacterial heterotrophy predominates in riverine zones
Zooplankton	Vertical and seasonal gradients predominate; horizontal patchiness moderate; phytoplankton is a predominate food source	Maximal development common in transition zone; horizontal patchiness high; particulate **detritus** (including adsorbed DOM) variably augments phytoplankton as food source
Benthic fauna	Moderate to high diversity; productivity moderate to high	Low diversity with minimal and irregular littoral zone; productivity low to moderate; initially high with inundated terrestrial vegetation
Fish	Warm- and coldwater species composition; spawning success good, egg mortality lower, larval success good; moderate productivity	Predominantly warmwater species composition; differences often related to initial stocking; spawning success variable (low with low water levels), egg mortality increases with siltation, larval success reduced with less **refugia**; productivity initially (5 to 20 years) high, then decreasing
Biotic community relationships	Diversity high; niche specialization moderately narrow; growth selection variable, relatively homeostatic; immigration-extinction processes slow; production low to moderate, relatively constant	Diversity low; niche specialization broad; growth selection rapid; immigration extinction processes rapid; net production high soon after inundation, then decreasing
Ecosystem succession rates	Similar to reservoirs but greatly protracted	Similar to lakes but greatly accelerated; greatly stressed by human manipulations of basin and drainage basin

[1]See the glossary at the end of this chapter for the definition of selected terms.

The residence time of water in reservoirs is usually considerably less than in lakes (Wetzel, 2001). Compared to natural lakes, reservoirs generally exhibit a larger degree of spatial heterogeneity with respect to water quality. This heterogeneity results from longitudinal gradients in basin morphology, flow velocity, flushing rate, and the loading rates of sediment, nutrients, and other constituents that usually enter at the upstream end of the reservoir. Typically, three zones occur in reservoirs along the downstream gradient, which differs from natural lakes (fig. 10–1; from Kimmel and others, 1990).

- An upstream **riverine zone** is characterized by higher flow velocity, shorter residence time, high concentrations of bioavailable nutrients and suspended solids (higher turbidity), and greater light extinction relative to the downstream portions of the reservoir.
  - Inorganic (silt and clay) turbidity often limits the depth to which light can penetrate, which is referred to as the **photic zone**.
  - Often the depth of the **mixed layer** exceeds the depth of the photic zone; consequently, primary production (algal photosynthesis) is often light-limited.

- A transitional zone is characterized by increasing phytoplankton productivity and biomass occurring in conjunction with increasing basin width, decreasing flow velocity, increasing residence time, increasing sedimentation of fine silt and clay particles near the surface (lower turbidity), and increasing light penetration. Because both light and nutrients are more available in the transition zone, this area can be the most productive and fertile region in a reservoir.
- A **lacustrine zone** occurs nearest the dam.
  - This zone usually has the lowest flow velocity, longer residence time, lower nutrient and suspended sediment concentrations, higher water transparency, and a deeper photic zone than the transition zone.
  - Primary production in the lacustrine zone is often nutrient-limited during most of the growing season and often supported by internal nutrient cycling rather than nutrients transported from upstream.

Riverine Zone	Transitional Zone	Lacustrine Zone
• Narrow, channelized basin	• Broader, deeper basin	• Broad, deep, lake-like basin
• Relatively high flow velocities	• Reduced flow velocities	• Little flow velocities
• High suspended solids, turbidity, low light availability, photic zone less than mixing zone	• Reduced suspended solids, less turbidity, light availability increased	• Relatively clear, light more available at depth, photic zone greater than mixing zone
• Nutrient supply by advection, relatively high nutrients	• Adjective nutrient supply reduced	• Nutrient supply by internal recycling, relatively low nutrients
• Light-limited primary production	• Primary production relatively high	• Nutrient-limited primary production
• Cell losses primarily by sedimentation	• Cell losses by sedimentation and grazing	• Cell losses primarily by grazing
• Organic matter supply primarily allochthonous	• Intermediate between allochthonous and **autochthonous** organic matter sources	• Organic matter supply primarily autochthonous
• More eutrophic	• Intermediate	• More oligotrophic

Figure 10–1. Longitudinal zonation and environmental factors controlling light and nutrient availability for phytoplankton production, algal productivity and standing crop, organic matter supply, and trophic status in an idealized reservoir (modified from Kimmel and others, 1990, figure 6.1).

The riverine, transition, and lacustrine zones in a reservoir are not discrete, invariable entities, but result from the combined effects of a number of overlapping gradients. These zones are transient and usually dynamic and expand and contract in response to inflow volumes, density flow characteristics, and reservoir operating schedules. In general, the principles of limnology apply equally to lakes and reservoirs, although the physical and chemical structure and biological processing of reservoirs are temporally and spatially more variable than those of lakes. Reservoirs, therefore, can behave differently than lakes.

10.1.1 Physical and Chemical Limnology

Fluctuations in light penetration, temperature, pH, and concentrations of dissolved oxygen and nutrients, such as phosphorus and nitrogen, interact to exert important influences on the chemical composition and quality of lake water and the lacustrine ecosystem. An understanding of these properties and their short- and long-term effects on lake systems is briefly covered below. This understanding is necessary for developing a sound lake-monitoring strategy and for interpreting the data collected. Comprehensive explanations of water-quality data and lake processes are provided in Hem (1985) and Wetzel (2001). Techniques to measure physical and chemical properties are described in sections 10.5 and 10.6 below.

10.1.1.A Light and Water Clarity

The attenuation of light through a water column provides an estimate of the extent of the photic zone; that is, the depth of water that is exposed to sufficient sunlight to allow photosynthesis to occur. The thickness of the photic zone is typically measured from the water surface down to where light intensity decreases to 1 percent of that at the surface. Measurement of light attenuation is a routine part of data collection for most USGS lake and reservoir investigations (NFM 7.4). Light attenuation is commonly determined by using one of two methods: (1) direct measurement of surface and underwater solar radiation, or (2) measuring water clarity, generally with a Secchi disk (section 10.5).

The amount of direct solar radiation that reaches the water surface varies with the angular height of the sun and, therefore, with time of day, season, and latitude (Wetzel, 2001). The quantity and quality of light also vary with the transparency of the atmosphere and the distance the light must travel through it; therefore, it varies with altitude and meteorological conditions (Wetzel and Likens, 2000). Much of the light is reflected from the water surface and is, therefore, unavailable to the aquatic system, although some can be backscattered to the water surface indirectly.

Water clarity or transparency is also used to estimate the light extinction coefficient, which is a measure of how quickly light is attenuated (Wetzel and Likens, 2000; NFM 7.4.1.B). Water clarity commonly is measured using a Secchi disk (section 10.5) and is referred to as the "Secchi depth." A simple rule of thumb is that the photic zone is approximately 2.5 times the Secchi depth.

Many factors influence water clarity, such as water color and the abundance of **algae**, zooplankton, and suspended sediment. Diminished clarity in lakes often occurs with an increase in phytoplankton abundance in summer. In reservoirs, inorganic turbidity composed of suspended solids, such as silts and clays, typically affect water clarity, especially at the upper end of the reservoir. At the lower end of the reservoir, however, phytoplankton generally exerts the most dominant influence on water clarity.

10.1.1.B Temperature and Stratification

In freshwater lakes and reservoirs, water density is primarily a function of water temperature. This relation is highly nonlinear; water is most dense at approximately 4 degrees Celsius (~4 °C) and becomes less dense with either warming or cooling. In addition, small changes in water temperature further from

4 °C have greater changes in density than small changes near 4 °C (fig. 10–2). This nonlinear relation results in wind being inadequate to completely mix the water column as water temperatures increase or decrease from 4 °C, and, therefore, lakes often stratify or freeze. During the annual cycle, many lakes and reservoirs thermally stratify for extended periods and later destratify either once (during winter if there is no ice cover), referred to as **monomictic**, or twice (during the spring and fall and restratify under the ice), referred to as **dimictic**.

During winter months, water temperatures in lentic waters often decrease to near or below 4 °C. If ice cover does not occur, the density differences between different temperatures around 4 °C are small, allowing complete (wind) mixing of the water column. During warm, calm days, however, as air temperatures and daylight hours increase during spring, the water at the surface (in deeper lakes) heats more quickly than it can be mixed by the wind with the deep, cooler (denser) waters below. As water near the surface warms, the density difference between two successive warm water temperatures, for example 29 and 30 °C, is greater than cooler water, for example 4 and 5 °C (fig. 10–2). The density difference between 29 and 30 °C is 37.25 times greater than the density difference between 4 and 5 °C. The wind energy needed to mix 29 and 30 °C water would be proportionally greater than the energy needed to mix 4 and 5 °C water. Relative thermal resistance to mixing (Wetzel, 2001) is the phenomenon that allows a **thermocline** to set up and the water body to stratify. At warmer water temperatures, a difference of only a few degrees is sufficient to prevent complete mixing.

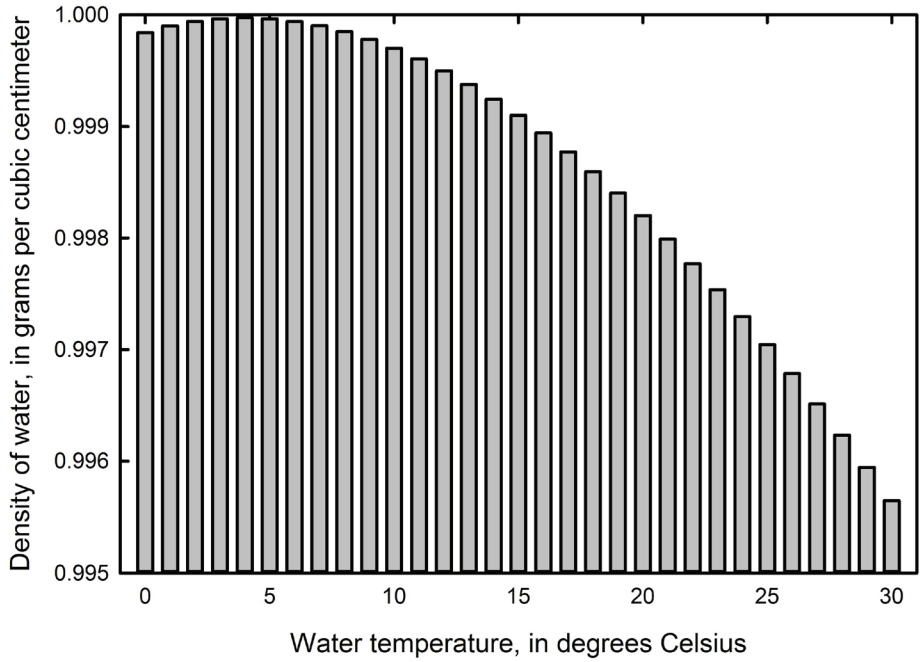

Figure 10–2. Density of water distribution by water temperature.

Over time, the water column in deeper lakes and reservoirs, typically greater than 6 meters (m), will be divided into three layers (fig. 10–3): the **epilimnion**—the warmer, more buoyant water near the lake surface; the **hypolimnion**—the cooler, more dense water near the lake bottom (having the temperatures close to the final spring temperature before stratification); and the **metalimnion** (middle layer)—where the thermocline (the plane of maximum rate of temperature change with depth) exists. The metalimnion ranges from warm to cold between the epilimnion and hypolimnion.

Annually, a lake or reservoir will cycle from being **isothermal** in the spring to being thermally stratified at variable thermocline depths in the summer (fig. 10–4). Shallow lakes, defined as having a maximum depth less than about 6 m (Osgood and others, 2002), typically experience only short periods of thermal stratification—when the cooler, more dense bottom water (hypolimnion) does not mix with the warmer, less dense surface water (epilimnion)—rather than a single extended period of stratification from early summer through early fall. This difference in the extent of mixing results in three types of lakes:

- Polymictic lakes: Lakes in which water frequently mixes to the bottom in the deepest areas throughout the open-water period.
- Dimictic lakes: Lakes in which water mixes to the bottom in the deepest areas only during the spring and again in the fall (autumn), referred to as spring and fall turnover. These lakes have extended periods of stratification in summer and are under ice in winter.
- Monomictic lakes: Lakes in which water mixes to the bottom in the deepest areas over one extended period throughout late fall and winter. These are deeper lakes that typically do not freeze.

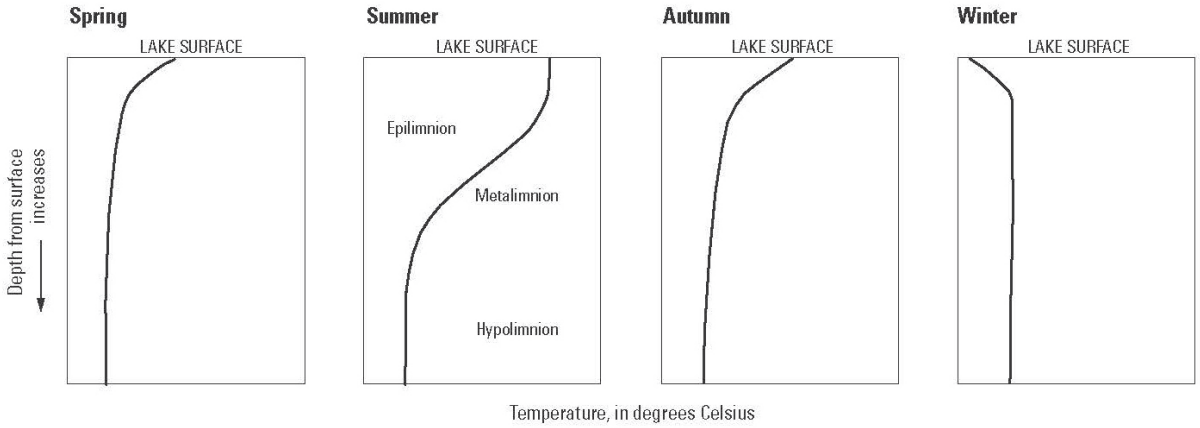

Figure 10–3. Water-temperature profiles for a classical deep, temperate-zone lake by seasons of the year (from Averett and Schroder, 1994, fig. 12).

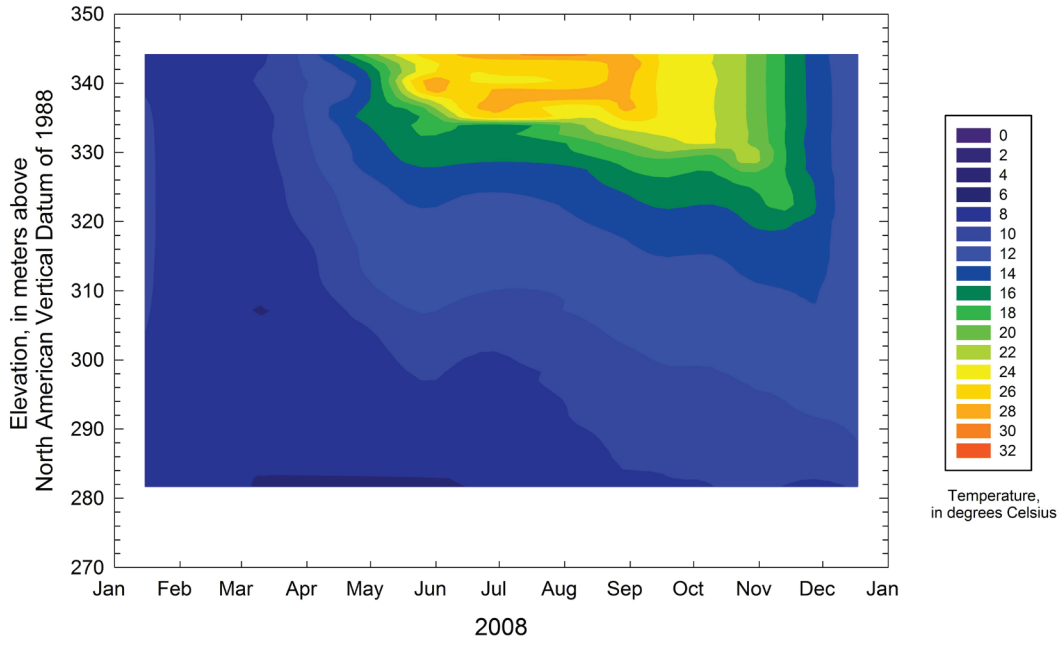

Figure 10–4. Depth and time plot of water-temperature contours from Beaver Lake, a deep reservoir in Arkansas (De Lanois and Green, 2011, appendix).

10.1.1.C pH

pH is a measure of the acidity of water. pH is defined as the negative logarithm of a hydrogen-ion (H^+) concentration and varies, generally, over a 14-unit log scale (refer to NFM 6.4) with a pH value of 7 being defined as neutral. Values less than 7 indicate acidic conditions; the lower the value the stronger the acidity. Values greater than 7 indicate alkaline conditions. The pH of water is important because it affects the solubility of many chemical constituents, and because aquatic organisms have limited pH tolerances.

Lake pH is influenced in part by photosynthesis and respiration of planktonic algae and aquatic plants. Phytoplankton and aquatic plants produce oxygen and consume carbon dioxide through photosynthesis during the daytime, causing pH to increase. These plants consume oxygen and produce carbon dioxide through respiration, which is the dominant metabolic process during nighttime when photosynthesis is not occurring. Carbon dioxide combines with water molecules to form carbonic acid; therefore, nighttime respiration causes a decrease in pH. The result is a daily cycle in the pH of a lake. Because phytoplankton are generally more concentrated near the water's surface, changes in pH in the epilimnion, where photosynthesis usually occurs, are more extreme than in the hypolimnion. Productive lakes with high algae and fish populations generally have a pH between 6.7 and 8.2. Values of pH greater than about 8.5 have been shown to cause the release of phosphorus from lake sediments (James and Barko, 1991), often triggering additional phytoplankton growth.

10.1.1.D Dissolved Oxygen

Dissolved-oxygen concentration is one of the most critical factors affecting lake and reservoir ecosystems because oxygen is an essential element for most aquatic life, and it is involved in many chemical reactions (see section 10.4 for information on the measurement of dissolved oxygen). Very low dissolved-oxygen concentrations can control some types of chemical reactions. The solubility of oxygen in water is inversely related to temperature. That is, oxygen solubility decreases as water temperature increases. This relation is important because at warmer temperatures the metabolic rate of an organism increases

but less oxygen is available for respiration. The primary sources of dissolved oxygen are from the air and photosynthesis. The minimum dissolved-oxygen concentration specified in national water-quality criteria for early life stages of warm-water aquatic life is 5.0 milligrams per liter (mg/L) (U.S. Environmental Protection Agency, 1986).

In early summer, if thermal stratification develops, the metalimnion restricts the surface supply of dissolved oxygen to the hypolimnion (fig. 10–5). The hypolimnion can become isolated from the atmosphere. Thus, as summer progresses, the dissolved-oxygen concentration can decrease in response to decomposition of dead algae that settle from the epilimnion and in response to the biological and chemical oxygen demand of the sediments. The oxygen demand from these processes may completely deplete the oxygen in the water near the lake bottom, creating a condition of anoxia. Oxygen depletion then progresses upward but usually is confined to the hypolimnion (fig. 10–6).

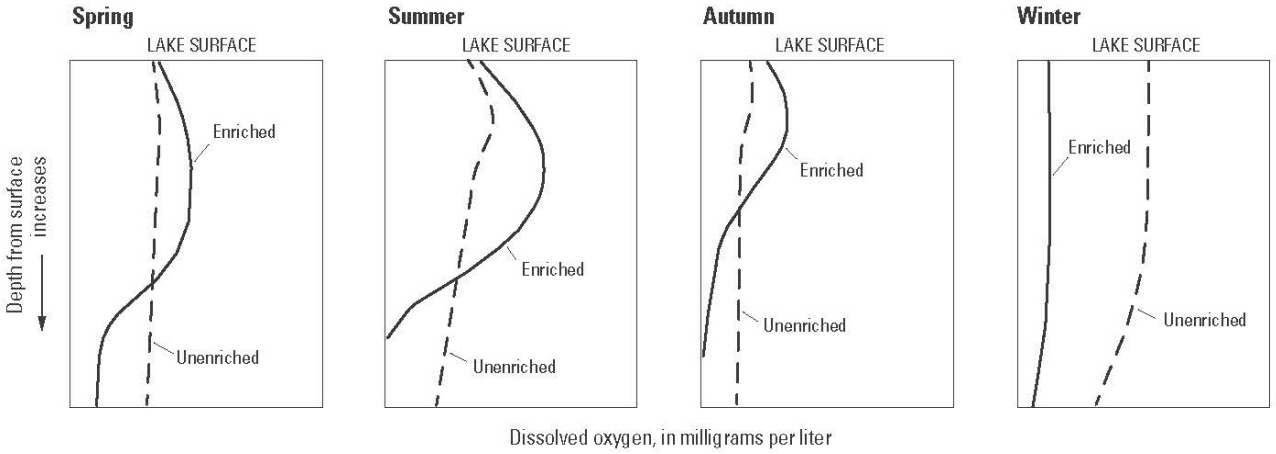

Figure 10–5. Dissolved-oxygen profiles for classical deep (stratified) temperate-zone lakes by seasons of the year and nutrient enrichment (from Averett and Schroder, 1994, fig. 13).

Anoxia in the hypolimnion is common in stratified (nutrient rich, eutrophic; described below) lakes and reservoirs. During anoxic conditions, many aquatic organisms cannot survive, but many other species (primarily bacteria) can only function in such conditions. Therefore, a shift from oxic to anoxic conditions produces a rapid and dramatic change in the biological community and chemical environment. Anoxia also can increase the release of phosphorus from the bottom sediments. This phosphorus then mixes throughout the water column during spring and fall turnover.

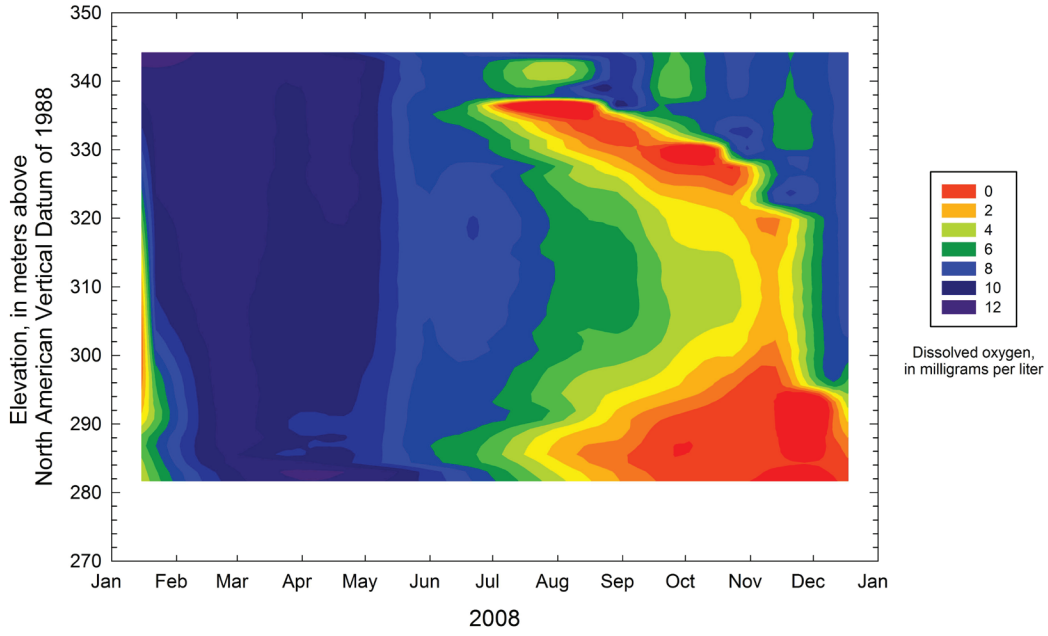

Figure 10–6. Depth and time plot of dissolved-oxygen contours (in milligrams per liter) from Beaver Lake, Arkansas (De Lanois and Green, 2011, appendix).

10.1.1.E Phosphorus and Nitrogen

Phosphorus is one of the essential nutrients for plant growth. High phosphorus concentrations, however, can cause dense algal populations (**blooms**) and, therefore, can be a major cause of increased lake productivity, referred to as **eutrophication**. When phosphorus concentrations exceed about 0.025 mg/L at the time of spring overturn in lakes and reservoirs, these water bodies may occasionally experience excess or nuisance growth of algae or other aquatic plants (U.S. Environmental Protection Agency, 1986). In many regions of the country other nutrients, particularly nitrogen, can lead to eutrophication. Phosphorus is often the nutrient in shortest supply, therefore, limiting or controlling plant growth. In water, dissolved orthophosphate is that part of total phosphorus that is most readily available for use by algae.

Internal phosphorus recycling occurs in many lakes. Phosphorus used by algae, aquatic plants, fish, and zooplankton is stored within these organisms. As these organisms die and decompose, this phosphorus is returned to the lake water and sediment. Anoxia in the hypolimnion makes phosphorus more soluble, adding further to the release of phosphorus from the falling particulate matter and lake sediments. During spring and fall mixing/turnover events, the phosphorus that was released from decomposing matter and the bottom sediments into the hypolimnion during anoxia mixes throughout the lake. As mentioned earlier, pH values of 8.5 and greater can also cause the release of phosphorus from lake sediments even if anoxia is not present. These phenomena are part of the internal-recycling processes of lakes. The phosphorus is then available for algal growth.

Nitrogen, like phosphorus, is an essential nutrient for plant and algal growth; however, nitrogen is often in abundant supply from the atmosphere and other sources. If phosphorus is abundant relative to algal needs, nitrogen can become the limiting nutrient. In that case, algal blooms are more likely to be triggered by increases in nitrogen than by increases in phosphorus. Some blue-green algal species (**cyanobacteria**) can fix nitrogen from the atmosphere (Wetzel, 2001). Therefore, in situations where other types of algae are excluded because of a shortage of nitrogen, the nitrogen-fixing cyanobacteria algae have a competitive advantage and may be present in abundance.

Lakes and reservoirs with total nitrogen-to-phosphorus ratios larger than 15 to 1 near the surface may generally be considered phosphorus limited; a ratio from 10 to 1 to 15 to 1 indicates a transition situation, and a ratio smaller than 10 to 1 generally indicates nitrogen limitation. Total nitrogen is the sum of ammonia, organic nitrogen, and nitrate-plus-nitrite nitrogen. Near-surface concentrations are commonly used to compute the total nitrogen-to-phosphorus ratio because most algal species grow near the lake surface.

10.1.1.F Chlorophyll *a*

Chlorophyll *a* is a photosynthetic pigment found in algae (Wetzel, 2001) and other green plants. The concentration of chlorophyll *a*, therefore, is commonly used as a measure of the density (biomass) of the algal population in a lake or reservoir. Chlorophyll *a* concentrations are generally highest during summer when algal populations are highest. Moderate populations of desirable algae are important in the food chain; however, excessive populations or algal blooms are undesirable. Algal blooms can cause taste and odor problems and limit light penetration needed to support the growth of submerged aquatic plants. Certain species of blue-green algae (cyanobacteria) can produce toxins.

10.1.2 Trophic Classification

One method of classifying the water quality of a lake is with trophic state index (TSI) values based on near-surface concentrations of total phosphorus, chlorophyll *a*, and Secchi depths, as developed by Carlson (1977) (table 10–3). The indices were developed to place these three characteristics on similar scales to allow comparison of different lakes. TSI values based on total phosphorus concentrations (TSI_P), chlorophyll *a* concentrations (TSI_C), and Secchi depths (TSI_{SD}) are computed for each open-water sampling by use of equations 1 through 3. The individual index values can be averaged monthly, and the monthly average values can then be used to compute summer (May through September) average TSI values:

$$TSI_P = 4.15 + 14.42\ [\ln \text{total phosphorus (in micrograms per liter)}] \quad (1)$$

$$TSI_C = 30.6 + 9.81\ [\ln \text{chlorophyll } a \text{ (in micrograms per liter)}] \quad (2)$$

$$TSI_{SD} = 60.0 - 14.41\ [\ln \text{Secchi depth (in meters)}] \quad (3)$$

The TSI approach to lake classification developed by Carlson (1997) assigns numerical ranges to the three or four trophic conditions that are generally used to describe the wide range of lake and reservoir water-quality conditions. **Oligotrophic** lakes have TSI values less than 40; have a limited supply of nutrients; typically have low phosphorus concentrations, low algal populations, and high water clarity; and contain oxygen throughout the year in their deepest zones (Wisconsin Department of Natural Resources, 1992). **Mesotrophic** lakes have TSI values between 40 and 50, a moderate supply of nutrients, a tendency to produce moderate algal blooms and have moderate clarity, and occasionally have oxygen depletions in the deepest zones of the lake. **Eutrophic** lakes have TSI values greater than 50; a large supply of nutrients; severe water-quality problems, such as frequent seasonal algal blooms and poor clarity; and oxygen depletion being common throughout the deeper zones of the lake. Eutrophic lakes with TSI values greater than 60-70 are often further classified as **hypereutrophic** lakes, and they typically have even more severe water-quality problems, including frequent and extensive algal blooms.

The transition of lakes from being classified as oligotrophic to hypereutrophic is a natural process as lakes age as a result of the addition of nutrients and organic materials, including the loading of silt and organic matter from their watersheds. This process is referred to as eutrophication. Lakes and reservoirs

enriched by human activities are said to be culturally eutrophic. Mesotrophy is a term often used to position a lake or reservoir in between the low, oligotrophic, and high eutrophic status.

Table 10–3. Trophic state index values (Chl, SD, TP), trophic state attributes, and possible changes to the water supply that might be expected in a temperate lake as the amount of algae changes along the trophic state gradient (from *http://www.secchidipin.org*, accessed February 3, 2015).

[TSI, trophic state index; Chl, chlorophyll; SD, Secchi depth; TP, total phosphorus; µg/L, microgram per liter; m, meter; <, less than; >, greater than]

TSI	Chl (µg/L)	SD (m)	TP (µg/L)	Trophic state attributes	Water supply
<30	<0.95	>8	<6	**Oligotrophy:** Clear water, oxygen throughout the year in the hypolimnion, often referred to as ultraoligotrophic	Water may be suitable for an unfiltered water supply
30–40	0.95–2.6	8–4	6–12	Hypolimnia of shallower lakes may become anoxic	
40–50	2.6–7.3	4–2	12–24	**Mesotrophy:** Water moderately clear; increasing probability of hypolimnetic anoxia during summer	Iron, manganese, taste, and odor problems worsen. Raw water turbidity requires filtration
50–60	7.3–20	2–1	24–48	**Eutrophy:** Anoxic hypolimnia, macrophyte problems possible	
60–70	20–56	0.5–1	48–96	Blue-green algae dominate, algal scums and macrophyte problems	Episodes of severe taste and odor possible
70–80	56–155	0.25–0.5	96–192	**Hypereutrophy (light-limited productivity):** Dense algae and macrophytes	
>80	>155	<0.25	192–384	Algal scums, few macrophytes	

10.1.3 Biological Limnology

Lakes and reservoirs have three distinct and interacting biological communities or zones: (1) littoral zone (shallow areas) and its sediments, (2) open-water pelagic zone—deep areas with sufficient light penetration to support photosynthesis (photic zone), and (3) **profundal zone**—deep areas below effective light penetration and its sediments (Cooke and others, 2005; fig. 10–7). Eutrophication and other ecological processes that occur in one zone directly or indirectly affect processes in other zones. For example, nutrients that cause algal blooms may come from lake sediments and decomposition of littoral zone plants, as well as from external loading (Cooke and others, 2005). When setting up a water-quality monitoring strategy, it may be necessary to collect data from all nutrient sources in each of the zones (fig. 10–7) in order to determine and understand the major processes that are occurring in the water body.

The bottom sediments of a lake or reservoir can be divided into littoral and profundal sediments (fig. 10–7). The littoral zone encompasses that shoreline region commonly influenced by the disturbances of breaking waves (Wetzel, 2001). Below the littoral zone is a transitional zone, the littoriprofundal zone, occupied by scattered photosynthetic algae and bacteria. The littoriprofundal zone is often adjacent to the metalimnion of stratified lakes and reservoirs. The remainder of the sediments, free of vegetation, is referred to as the profundal zone (Wetzel, 2001).

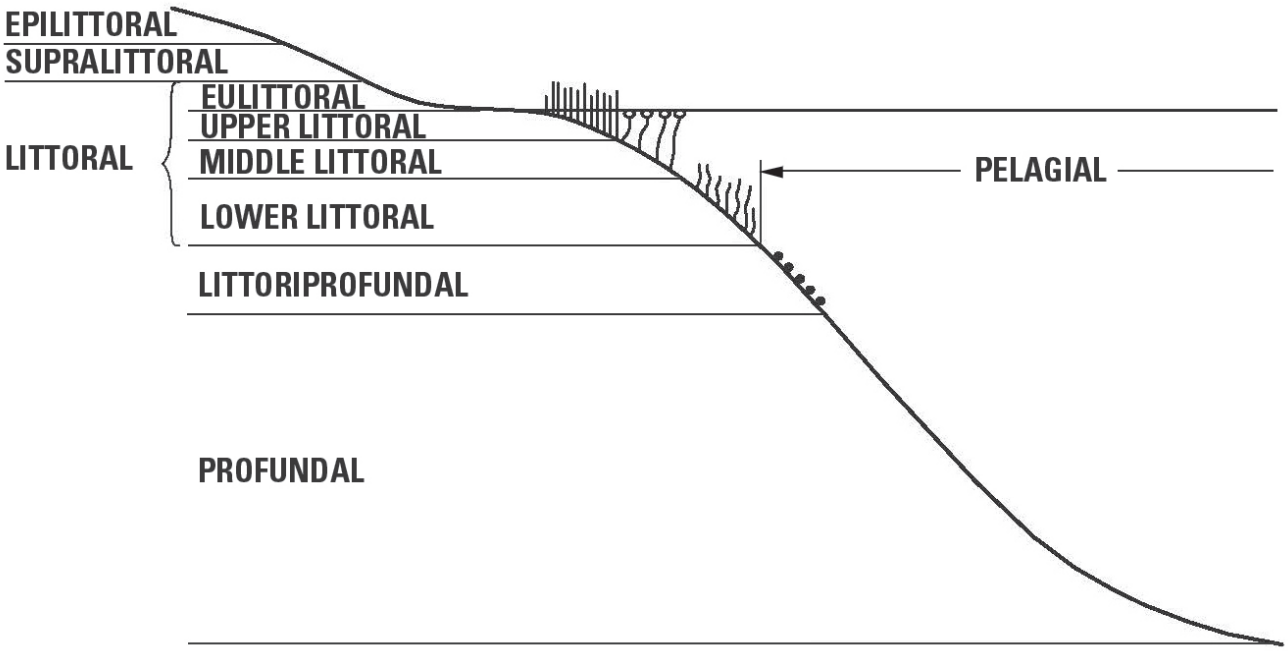

Figure10–7. Lateral zonation in lakes and reservoirs (from Wetzel (2001) modified from Hutchinson (1967)).

Macrophytes (emergent, floating, and submersed vascular plants) and their attached flora and fauna dominate the wetland-littoral zone (Cooke and others, 2005). In very productive systems, the macrophytes may often have large masses of filamentous algae attached to them as thick mats. Shallow, lighted sediments often have highly productive epilithic, epipelic, and epiphytic flora (algae growing on surfaces of rocks, sediments, and vascular plants) (Cooke and others, 2005). These plants are distinctly different from the microscopic, floating (planktonic) cells and colonies of algae.

10.1.3.A Littoral Zone

The littoral zone often has high species diversity and is commonly the area of a water body where fish reproduction and development occur (Cooke and others, 2005). This area is also usually important waterfowl habitat. Plant biomass in the littoral zone typically replaces itself two or more times per summer in productive lakes and reservoirs, leading to inputs of nonliving dissolved and particulate organic matter termed “detritus” to the water column and sediments. Detritus, whether from the watershed or from in-lake productivity, is a stable source of energy and nutrients for lake and reservoir **autotrophic** and **heterotrophic** production.

10.1.3.B Pelagic Zone

Plankton (phyto- and zooplankton), and the fish grazing on them, dominate the pelagic zone (Cooke and others, 2005). The phytoplankton includes algae that can produce unsightly “blooms” and low water clarity. The pelagic community obtains energy from sunlight and from detritus transported to it from stream inflows and the littoral zone. The phytoplankton of most enriched lakes and reservoirs is often dominated by one or a few species of highly adapted algae and bacteria (for example, green algae and the nuisance blue-green algae (cyanobacteria)). Zooplankton include the primary grazers of detritus, bacteria, and algae, though their abundance may be regulated by complex interactions with the algal community and predators, such as fish and insects (Cooke and others, 2005).

10.1.3.C Profundal Zone

The profundal community receives nutrients and energy from organic matter loaded to or produced in the lake or reservoir (Cooke and others, 2005). Inorganic forms of nutrients can settle from the water column to the profundal zone and its bed sediments. In enriched lakes and reservoirs, large areas of the profundal sediments are continuously anoxic during thermal stratification due to intense microbial respiration from the decay of deposited detritus. Anoxic conditions can cause high rates of nutrient release from the bed sediments to the water column—referred to as internal loading (Cooke and others, 2005). In lakes and reservoirs that are not impacted by nutrient enrichment, anoxic conditions in the profundal sediments have less of an impact. Internal nutrient loading in oligotrophic lakes and reservoirs is less than in enriched, eutrophic lakes and reservoirs.

10.2 Comparative Properties of Lakes and Reservoirs

When designing a lake or reservoir monitoring study, it is important to first gather as much historical, morphometric, hydrologic, and water-quality information as possible related to the water body and its watershed. Examination of the existing information is often useful for describing current conditions, determining the existence and extent of a problem, and identifying appropriate techniques and approaches for assessment. The types of study-design considerations and preliminary information-gathering processes should reflect the structural and functional differences that distinguish lakes from reservoirs.

- ► Common to all lake and reservoir studies is the need to assemble currently available data to help describe the following information:
  - — Morphometry – basin length, width, perimeter (shoreline length) and bottom shape
  - — Drainage area
  - — Hydrologic data network (for example, locations of stream gages)
  - — Land use and land cover
  - — Topography and land slope
  - — Soil type(s) and erosion potential
  - — Climactic data (for example, seasonal precipitation patterns; annual maximum, minimum, and average air temperature; and wind speed and direction)
  - — Annual runoff
  - — National Pollutant Discharge Elimination System-permitted discharges
  - — Hydraulic residence time and (or) flushing rate
  - — Morphometric characteristics that are useful for planning a study include:
    - Surface area
    - Volume
    - Mean and maximum depth
    - Maximum effective length and width (distance wind can blow across the water body without landscape obstructions)
    - **Shoreline development ratio** (ratio of shoreline length to that of a circle with the same surface area)

Areas of potential lake or reservoir sediment erosion or accumulation and other such hydromorphometric characteristics are important to identify in the context of study objectives. When developing the approach for either a lake or a reservoir study, it is important to identify areas of sediment deposition, as these are areas of potential chemical enrichment and influence. Distinct biological zones should be identified as well: the littoral zone is the most biologically productive area in the water body; the epilimnion and metalimnion are the most productive phytoplankton zones. Chemical qualities in these zones are influenced by biological activity. For example, in many eutrophic lakes and reservoirs, the hypolimnion is isolated from the atmosphere and reaeration. Bacterial respiration can remove all the dissolved oxygen over time and anaerobic conditions can develop, causing the dissolution of phosphorus, iron, manganese, and other elements. Also, decomposition of settling organic matter is reduced under these anaerobic conditions. Of course, other lake and reservoir conditions can be important depending on study objectives. What is important in one study may not be that important in another.

For reservoirs, the study approach should consider factors such as demands on the reservoir for flood-risk reduction, potable and industrial water supply, irrigation, hydroelectric power supply, navigation, fish and wildlife habitat, recreation, and aesthetics.

► These considerations can affect the proposed methods of data collection and interpretation that also may rely on determining an expanded set of physical characteristics, including:

- Length and slope of the main channel
- Sinuosity ratio
- Normal pool elevation
- Spillway elevation
- Shoreline length
- Ratio of drainage to surface area
- Volume contained in the normal pool and flood pool
- The length and mean, maximum, and relative depth to bottom (normal pool)
- Outlet elevation(s)

Consequently, depending on whether a lake or reservoir is to be studied, differing considerations and guidelines should be considered when designing the approach and selecting the methods to be used for collecting samples and data for water, sediment, and biological analyses, such as spatial and temporal heterogeneities in the water body and long-term changes in the system.

Basin characteristics such as drainage area, annual runoff, topography and slope, land use/land cover, soil types, and erosion potential are all characteristics that influence discharge and constituent loading into lakes and reservoirs.

10.2.1 Spatial and Temporal Heterogeneity

Reservoirs typically have larger and more elongated drainage basins than natural lakes and are usually located at the mouth of a relatively large drainage basin (Thornton, 1990). Reservoirs may receive only a small proportion of their total inflow as direct runoff from the adjacent watershed, with the majority of water, nutrient, and sediment load entering from one or two major tributaries located a considerable distance from the dam. Most of the variability in physical conditions and water quality in natural lakes occurs in the vertical dimension, such as light, temperature (stratification), dissolved substances, productivity, and decomposition

(Hutchinson, 1957; Wetzel, 1983; Kimmel and others, 1990). This vertical heterogeneity results from density gradients that are set up because of differences in water temperature and possibly salinity/specific electrical conductance. In winter, if a lake is not ice covered, the water column is typically mixed from top to bottom; the wind is usually capable of mixing the entire water column because of the low resistance to mixing resulting from the density similarities. If a lake freezes, the water column typically stratifies with slightly warmer, denser water near the bottom and cooler less dense water near the surface.

In reservoirs, similar vertical heterogeneities exist, but downstream (horizontal) gradients in water quality also occur, typically resulting in reservoirs being divided into the riverine, transition, and lacustrine zones described earlier in figure 10–1. The relative productivity of the mixed, near-surface water generally decreases down-reservoir as the advected nutrient supply is reduced with increasing distance from tributary inflows and as phytoplankton production becomes more dependent on internal nutrient regeneration (Kimmel and others, 1990; fig. 10–8). The **trophic state** (as reflected by clarity, phosphorus supply, algal content, phytoplankton productivity, dissolved oxygen depletion, or indices based on these physical and chemical properties) usually shifts from conditions that are more eutrophic to more oligotrophic along the riverine-transition-lacustrine gradient. Temporal variation in lakes and reservoirs also occurs due to seasonal climatic events and related tributary inflows (fig. 10–9).

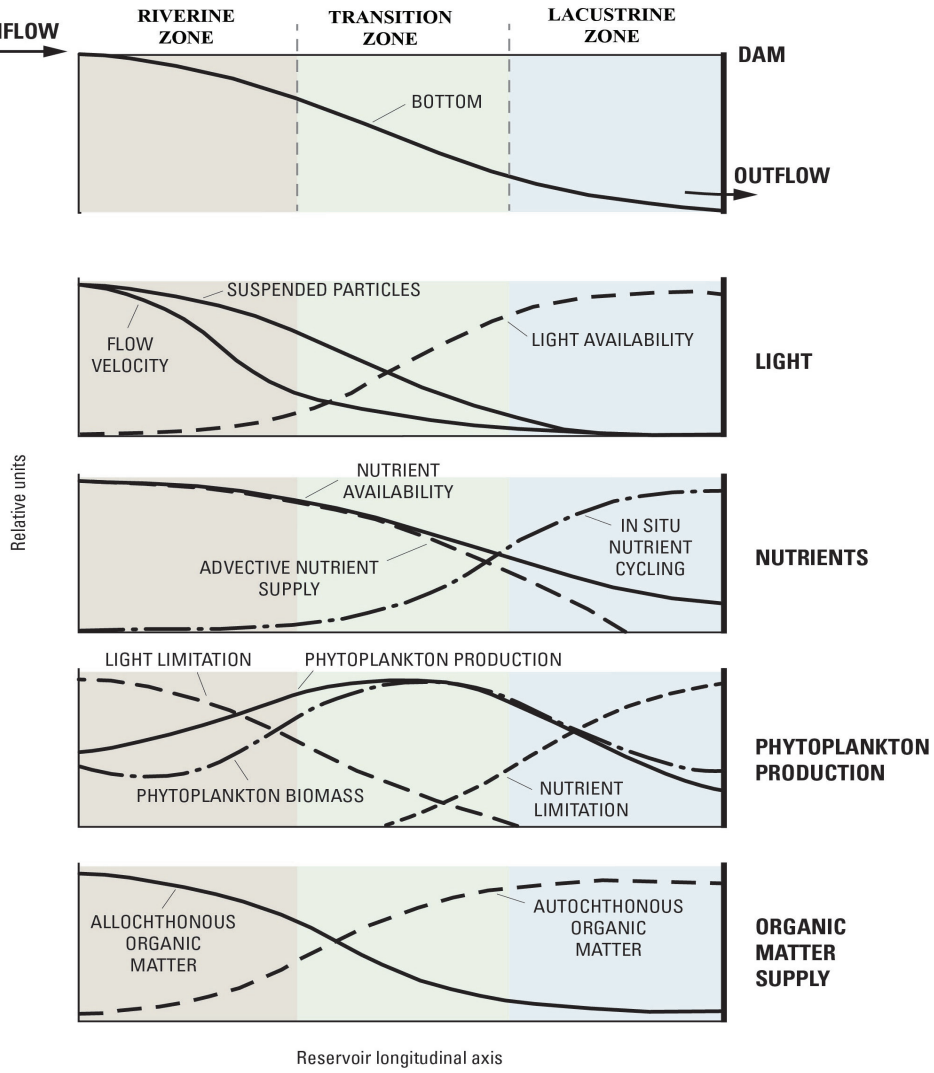

Figure 10–8. Cross-sectional view of gradients showing environmental factors that affect phytoplankton productivity and biomass, and the relative importance of allochthonous organic matter along the longitudinal axis of an idealized reservoir (from Kimmel and others, 1990, fig. 6.2).

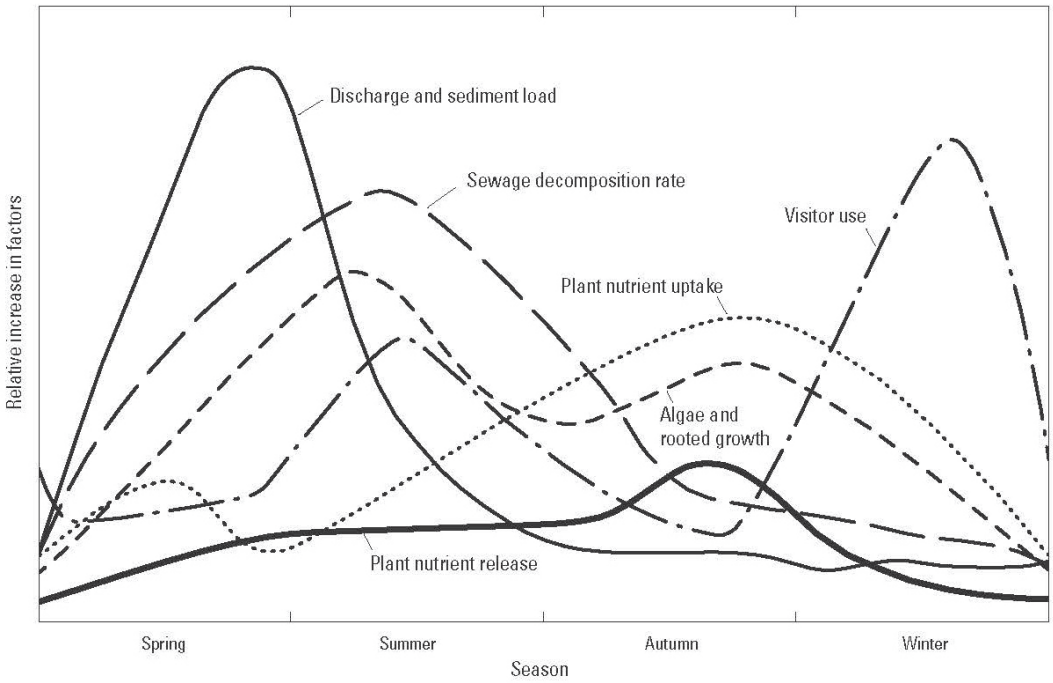

Figure 10–9. An example of different combined impact factor curves by seasons of the year (from Averett and Schroder, 1994, fig. 11).

Depending on the relative importance of inputs from the watershed, inflow characteristics, and flushing rates, the three zones may not always be distinguishable within a particular reservoir (fig. 10–10). For example, in a rapidly flushed, run-of-the-river reservoir receiving turbid inflow, conditions characteristic of the riverine zone may persist throughout most of the reservoir. On the other hand, in a long-residence-time storage reservoir, both the riverine and transition zones may be compressed into a small up-reservoir portion of the basin.

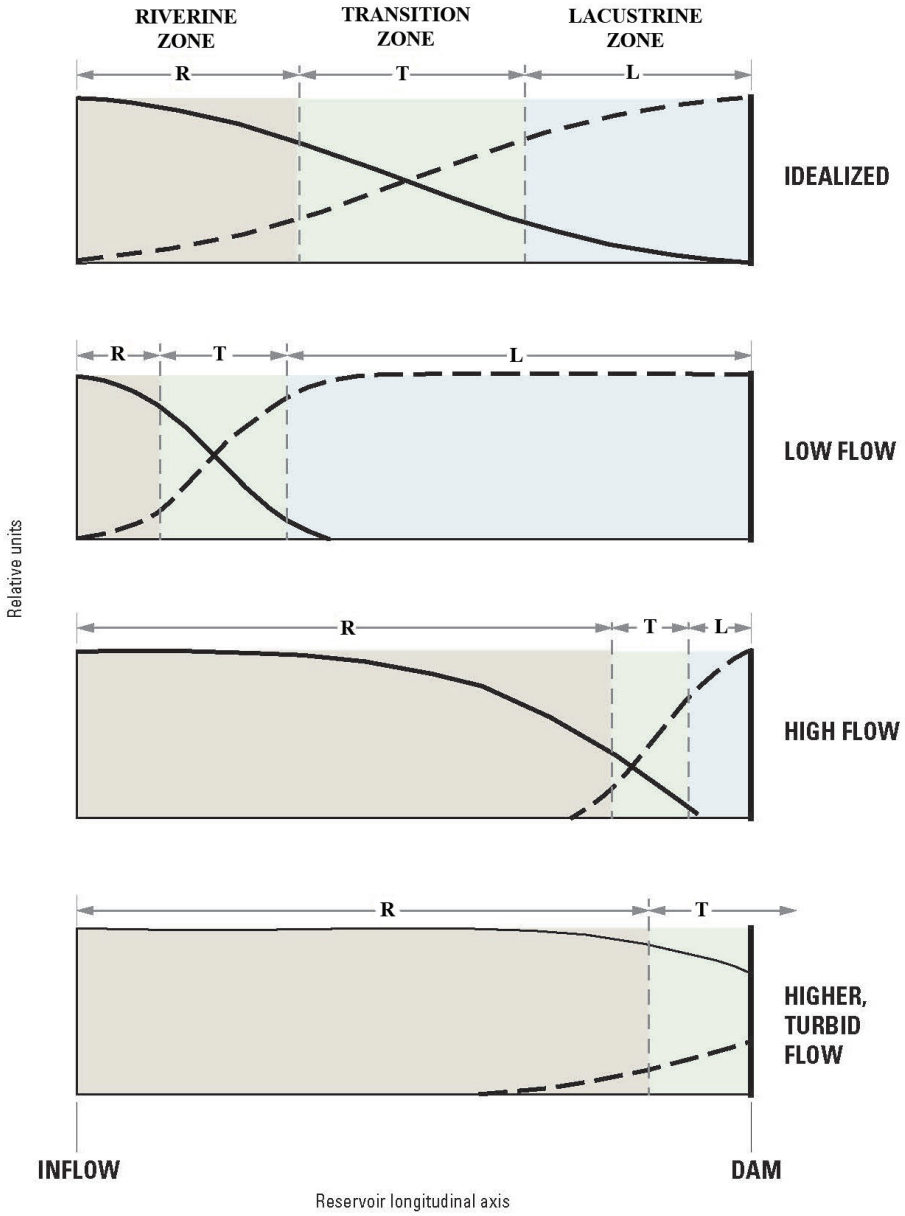

Figure 10–10. Variation in the longitudinal zonation of environmental conditions within reservoirs. Solid and dashed lines represent the prevalence of riverine and lacustrine conditions, respectively. The longitudinal zonation is dynamic spatially and temporally and fluctuates in response to watershed runoff, inflow characteristics, density-flow behavior, and reservoir operations. R, riverine; T, transition; and L, lacustrine (from Kimmel and others, 1990, fig. 6.3.)

Inflow into lakes and reservoirs can vary dramatically. In natural lakes with small tributaries, inflow generally flows through diffuse sources, and flow into stratified waters is small and dispersive. In reservoirs and lakes with large tributary inputs, inflows into the stratified waters can occur as over-, inter-, or underflow (fig. 10–11), based on density differences between tributary and reservoir waters, which are primarily driven by differences in water temperatures. When flows are high, inflows may pass through the reservoir in a few days to weeks as a plunging inter- or underflow, carrying the suspended sediment and other constituents with it. If flows are very high, inflows may completely push the water in the reservoir downstream, resulting in the reservoir acting as a slow-moving river.

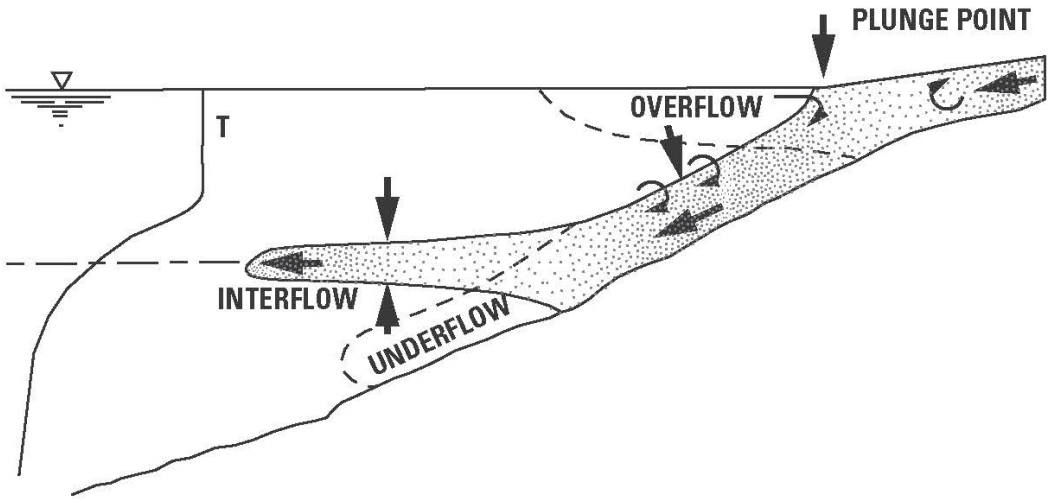

Figure 10–11. Density inflows (over-, inter-, and underflow) into lakes and reservoirs. T, water temperature (from Ford, 1990, fig. 2.10).

Other sources of horizontal spatial heterogeneity are often related to the dendritic nature (shoreline) of lake and reservoir basins and to tributaries of differing water quality. This spatial heterogeneity due to dendritic shorelines can result in embayments having limnological characteristics unique from adjacent main channel areas (Kimmel and others, 1990). These embayments may be quite important to game-fish and forage-fish populations as food sources and nursery areas. Differences in primary and secondary productivity between embayments and the main basin areas may be further enhanced if extensive areas of macrophytes occur in the embayments.

In summary, there are many functional similarities between natural lakes and reservoirs. Nevertheless, because of their differences in size, shape, drainage basin, quantity, and quality of inflow and outflow, the physical and chemical structure and biological processing in reservoirs are generally more variable in both space and time than they are in natural lakes. This variability should be considered when designing a program to collect water, sediment, and biological samples. Lake and reservoir systems vary widely in their complexity and similarity to each other. Shallow reservoirs can often be considered a slow-moving river and have longitudinal, as well as lateral, gradients resulting from tributaries entering along the main downstream axis. Vertical gradients also can occur as a result of thermal stratification and density-driven inflows.

10.2.2 Reservoir Aging

Reservoirs naturally age (natural eutrophication) and the aging process can be accelerated depending on the level of human-derived development in the drainage basin (cultural eutrophication). It is important to know what position the reservoir being investigated is in within the aging process in order to better

interpret the results of the study. Reservoirs typically experience a highly productive period, termed the "trophic upsurge," shortly after construction (Baranov, 1961; Kimmel and Groeger, 1986). This trophic upsurge is the result of a combination of several factors: (1) a large influx of organic detritus and inorganic nutrients from the recently inundated reservoir basin, (2) an abundance of high-quality habitat and food for benthic organisms, and (3) a rapidly expanding lacustrine environment (Baxter, 1977; Ploske, 1981; Benson, 1982). The trophic upsurge is followed by a trophic depression, which is, in fact, the initial approach of the reservoir ecosystem toward its natural equilibrium level (Kimmel and Groeger, 1986; fig. 10–12).

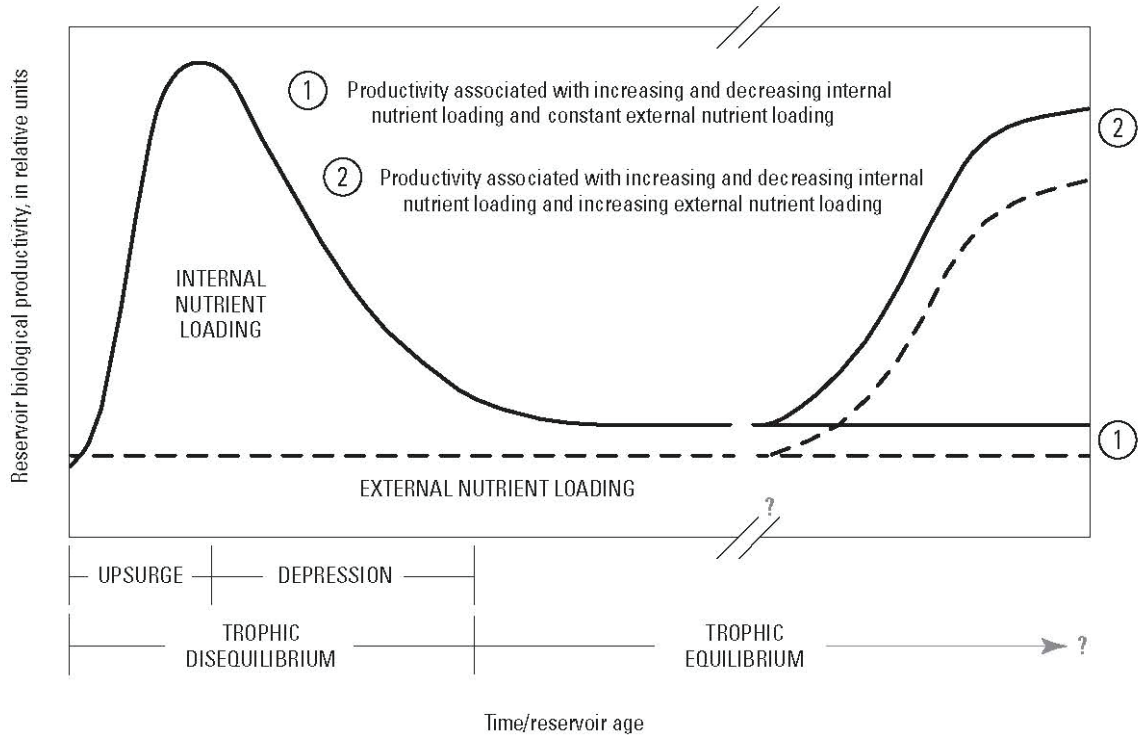

Figure 10–12. Conceptual model showing changes in factors influencing reservoir water quality and biological productivity as a reservoir matures and ages (modified from Kimmel and Groeger, 1986, fig. 2).

The magnitude and duration of each of these phases (fig. 10–12) is quite variable among reservoirs because of differing basin inundation rates, internal and external nutrient loading rates, flushing rates, the quantity and quality of new habitat, the fish assemblages present, and reservoir operations (Ploskey, 1981; Kimmel and Groeger, 1986). The brief initial periods of trophic upsurge and depression result from changes in internal nutrient loading (see 1 in fig. 10–12).

Following the trophic depression, the magnitude and variability in biological production within the maturing reservoir become dependent on external inputs of nutrients and organic matter from the watershed, as in natural lakes (Kimmel and Groeger, 1986). Because the drainage-basin area relative to surface area and volume is large, fluvial inputs are usually the most important sources of nutrients for most reservoir ecosystems (Gloss and others, 1980; Kimmel and Groeger, 1986; Kimmel and others, 1990). Nutrients in the tributaries result from a combination of nonpoint sources (runoff from many diffuse sources within the watershed) and point sources (municipality and commercial and industrial facilities). The amount of nutrients in runoff typically depends on land use within the watershed (Likens, 1972; Hutchinson, 1973). Undisturbed terrestrial ecosystems usually are characterized by runoff that is low in dissolved and particulate substances, while, pastures, croplands, and urban areas contribute much greater nutrient loads to

aquatic systems (Likens, 1975). Therefore, land-use patterns in the watershed have long-term effects on reservoir productivity and water quality (Kimmel and Groeger, 1986).

If lakes or reservoirs are permitted to age without the water body or watershed being otherwise disturbed, one would expect (based on present understanding of the relations between basin morphology, nutrient loading rates, and lacustrine productivity) that biological productivity would either remain relatively constant over time or gradually increase (Kimmel and Groeger, 1986). Because the construction of reservoirs often promotes additional land-use changes and technological development within the watershed, water-quality and productivity changes attributable to "natural" reservoir aging are usually small compared to the effects of human-induced changes to watershed-reservoir interactions.

10.3 General Considerations for Study Design

Eight distinct steps are involved in the design, implementation, and analysis of any lake or reservoir sampling program: (1) problem identification (purpose of the study), (2) statement of scope and objective(s), (3) formulation of the approach (sampling strategy and design), (4) implementation of the sampling design (data and sample collection), and (5) data management, (6) analysis, (7) interpretation, and (8) dissemination of the results. Following this structure helps ensure that data collection, results, and conclusions will be clearly presented.

Defining the study (project) objectives involves identifying the water-quality issues of concern and developing an approach to differentiate the potential factors or causes of the symptoms or concerns. The U.S. Army Corps of Engineers (1987) provides a useful table of water-quality concerns and possible contributing factors used in establishing objectives (table 10–4). Once the study objectives have been defined, the scientific approach and specific methods for the study can be identified and an implementation plan can be developed. As data and information are collected and water-quality processes and concerns become better understood, the water-quality objectives can be refined and the sampling program can be modified to better identify the areas of uncertainty and concern.

Table 10–4. Water-quality concerns and the possible contributing factors or causes in lakes and reservoirs (modified from U.S. Army Corps of Engineers, 1987).

[Fe, iron; Mn, manganese; NH_3, ammonia; H_2S, hydrogen sulfide; N_2, nitrogen gas; X, indicates water-quality concern can be present]

Possible Contributing Factors	Water-Quality Concerns																							
	Large Flow Variations	Scour	Erosion	Mudflats	Cold Release Temperatures	Unnatural Release Temperature	Low Release Dissolved Oxygen	High Release Metals (Fe, Mn, and others)	High Release NH_3 and H_2S	N_2 Supersaturating	High Turbidity	High Suspended Solids	Total Dissolved Solids/Salinity	High Nutrient Concentrations	High pH	Low pH	Contaminants	Organics	Taste and Odor Compounds	Disinfection Byproduct Precursors	Algae Blooms	Aquatic Weeds	Pathogenic Bacteria	Fish Stress
Bottom Withdrawal					X		X	X	X								X	X	X	X				X
Plunging Spillway Flow		X								X														X
Hydropower Operation	X	X			X		X	X	X	X							X	X	X	X				X
Fluctuating Water Level			X	X							X	X												X
Stable Water Level																					X	X		
Large Fetch/Waves		X	X								X	X												
Limited Mixing														X							X	X	X	
Extensive Littoral Areas																					X	X		
Watershed Land Use (Agri/Urban)							X				X	X	X	X		X	X	X	X	X	X		X	X
High Sediment Inflow							X				X	X		X			X	X				X		X
High Nutirent Inflow							X							X							X			
High Total Organic Carbon Inflow							X										X	X	X	X				
Point Source Discharges											X	X		X	X	X	X	X	X	X	X		X	X
Stratification					X	X	X																	
Ice Cover							X																	
High Evaporation													X	X										
Sediment Oxygen Demand							X																	X
Organic Decomposition							X	X	X					X			X	X	X	X	X			
Hypolimnetic Anoxia							X	X	X					X			X	X	X	X				X
Reduced Chemical Species								X	X								X	X	X	X				X
Internal Nutrient Loading									X					X							X			
High Algal Production							X				X				X			X	X	X	X			
High Macrophyte Production							X							X	X			X						

10.3.1 Common Study Types

The design of lake and reservoir water-quality studies varies depending on the purpose, scope, and objectives of each study. Most studies can be broadly categorized into one of three common types: reconnaissance, diagnostic (also commonly referred to as monitoring), or interpretive (Averett and Schroder, 1994).

- In many cases, little data and information are available for a given lake or reservoir and a **reconnaissance or pilot study** may be required to gather baseline information to determine the need for, or objectives and scope of, a future environmental investigation or assessment.
- A **diagnostic study** is appropriate when the water quality within a lake or reservoir has already reached the problem state and specific data and analyses are needed to describe or explain its condition. If regulatory compliance information is needed, a diagnostic study can be designed to gather data and information that specifically relate to the regulated constituents.
- An **interpretive study** typically has an expanded scope that can include, for example, identifying and developing an understanding of biogeochemical processes or causes of a specified problem, determining trends in the water-quality data collected or the problem that was identified, and performing simulations to help diagnose and forecast future water-quality conditions based on various potential solutions to the problem.

10.3.1.A Reconnaissance Studies

Reconnaissance studies are common for a lake or reservoir for which either very little to no relevant data or information have been collected, or for which data are needed to establish the boundaries and scope of a more in-depth investigation. A common purpose for reconnaissance studies is to gather baseline information that can be used to determine current water-quality conditions (such as the trophic status), or provide water-resource managers the information needed for developing resource-management strategies.

Reconnaissance studies often are limited in resources and time, which constrains the objectives, scope, and approach of the investigation to target only the immediate questions of concern so as to provide a foundation or rationale for future investigations. The information gathered should be sufficient to fill in where historical data or other data essential to addressing the purpose of the investigation are absent (table 10–5). The data collected should provide, depending on the purpose, scope, and objectives, a basis on which to describe the physical, chemical, and biological conditions and variability of the water body. Care should be taken to determine what specifically needs to be sampled (water, bed material, and biological components), the onsite data to be collected, the number and location of possible sampling sites, and the constituents for which samples will be analyzed. Multiparameter instruments can be used to determine vertical and horizontal physical and limited chemical variations among different areas in the lake or reservoir (table 10–5). In addition to the environmental properties that are determined routinely, these instruments can be equipped to measure such properties as pigment fluorescence and photosynthetic active radiation.

- Depending on the size of the lake or reservoir, longitudinal and cross-sectional transects can be made with the multiparameter instruments to determine the spatial variability associated with physical and basic chemical and biological characteristics to identify discrete locations or sampling sites for further water-quality sampling and assessment.
- After the lake or reservoir is divided into one or more sections for water-quality sampling and assessment, specific locations within each section should be identified and marked by buoys or recorded

using a global positioning system so one can return to the same location for additional sampling, as needed.

► Common water (and bed-sediment) components typically include chemical-constituent analyses of nutrients (nitrogen and phosphorus components), major ions, trace elements, organic matter, and targeted contaminants (table 10–5). Common biological components typically include chlorophyll, phytoplankton, macrophytes, and benthic fauna.

The design of a water-quality reconnaissance study should document which media (water, bed sediment, and biological components) and chemical and physical properties and constituents should be measured or analyzed, and the rationale for sampling site locations, so as to provide future study teams a context in which to understand the historical data record and use that insight to inform future study plans.

Table 10–5. Typical physical, chemical, and biological components and their priority in a reconnaissance study.

[Priority 1 variables generally have maximum utility in assessing general water quality and water-quality changes. Priority 2 variables have moderate utility in assessing general water quality and water-quality changes. Priority 3 variables have utility in assessing specific water quality and water-quality changes]

Variable	Priority
Physical	
• Water depth	1
• Water temperature profile	1
• Secchi disk transparency	1
• pH profile	2
• Specific conductance profile	2
• Turbidity profile	3
Chemical	
• Dissolved-oxygen profile	1
• Nutrients (phosphorus and nitrogen species)	1
• Total and dissolved organic carbon	2
• Major ions	3
• Trace elements	3
Biological	
• Chlorophyll	1
• Pathogenic indicators (*Escherichia coli*, fecal coliform)	2
• Phytoplankton: diversity, abundance, and biovolume	3
• Macrophytes	3
• Zooplankton	3
• Littoral macroinvertebrate fauna	3
• Profundal macroinvertebrate fauna	3
• Fish diversity and abundance	3

10.3.1.B Diagnostic Studies

Diagnostic studies often are conducted to provide water-resource managers with the information needed to develop or evaluate the feasibility of specific cost-effective protection and restoration strategies for vulnerable or impaired lakes/reservoirs. For example, building on information gathered from

reconnaissance, a diagnostic water-quality assessment could be developed to determine the sources, causes, and extent of a lake or reservoir being threatened or affected by sediment/nutrient loading, sedimentation, and (or) nutrient enrichment. A diagnostic study could be designed to evaluate the efficacy of potential or in-place controls on water-quality impairment. For these and other study scenarios, a diagnostic assessment often requires an interdisciplinary approach in which the study team includes the expertise of multiple disciplines, such as biology, geology, chemistry, physics, and engineering.

Diagnostic studies often extend beyond the boundary of the water body into the drainage basin. Major tributaries to the lake or reservoir commonly are monitored or otherwise included in the data-collection effort in order to quantify the water quality of the inflow water. Results from diagnostic studies may also be used in interpretive studies that use statistical or mathematical models to simulate and interpret functions and processes in the lake or reservoir and forecast future conditions based on various management options.

In diagnostic studies, it is usually important to determine both the concentrations and the quantity of constituents entering and leaving the lake or reservoir. To accomplish this, continuous stream gages can be installed on the major tributaries to provide the volumetric discharge needed to calculate constituent loads entering the lake or reservoir. It is good to have as much of the watershed gaged as possible to reduce or eliminate assumptions for ungaged flow. Water-quality samples should be collected frequently enough over the entire hydrologic regime in order to calculate constituent loads and quantify the amount of material entering the lake or reservoir.

- A few computer programs that estimate constituent loads and yields include:
  - EGRET (Hirsch and DeCicco, 2014, *http://pubs.usgs.gov/tm/04/a10/*)
  - LOADEST (Runkel and others, 2004, *http://water.usgs.gov/software/loadest/*)
  - Fluxmaster (Hoos and others, 2008, *http://pubs.usgs.gov/of/2008/1163*)
  - FLUX (Walker, 1999; also U.S. Army Corps of Engineers, *http://el.erdc.usace.army.mil/elmodels/emiinfo.html*)
  - GCLAS (Koltun and others, 2006, *http://water.usgs.gov/software/GCLAS/*)
- When developing diagnostic studies, sampling design should:
  - Collect data to describe seasonal variability at specific sites at specific times consistently throughout the year. This allows changes to be identified and verified and trends in annual average conditions to be recognized and validated. In addition to describing variability in vertical conditions in both lakes and reservoirs, horizontal variability, both across and upstream and downstream in a reservoir, should be captured whenever possible.
  - Consistently measure water temperature, pH, specific conductance, dissolved oxygen, and Secchi-disk transparency during each site visit.
  - Use consistent sampling protocols. Physical and chemical data can be augmented with analysis of biological indicators, such as chlorophyll, phytoplankton, macrophytes, and benthic fauna.

Diagnostic studies generally provide results in summary tables, graphic displays, and statistical analyses rather than provide detailed interpretation of the processes causing the changes in water quality. See Helsel and Hirsch (2002) for parametric and nonparametric statistical analyses that are appropriate for various study objectives and sampling strategies.

10.3.1.C Interpretive Studies

Interpretive studies typically have an expanded scope compared to other studies. An example of an interpretive study is one for which the effects of watershed point- and nonpoint-source nutrient enrichment are examined and the changes in extent of lake/reservoir eutrophication after implementation of best-management practices to reduce nonpoint source loading are being forecast. An interpretive study generally is best carried out after completion of a reconnaissance study of the system (Averett and Schroder, 1994). Interpretive studies typically require additional and more detailed data and information to examine processes, assess conditions, interpret trends, and possibly forecast future conditions and resource-management scenarios. Statistical and mathematical simulation tools commonly are used to assess or diagnose current conditions and forecast future conditions, based on changes in watershed management and resultant changes in loading.

Depending on the objectives, interpretive studies may require several years of data collection from various media (water, bed sediment, and biological components) at multiple sites, including inflowing tributaries, in-lake or in-reservoir sites, and sites downstream of the lake/reservoir. On the basis of results from a reconnaissance or diagnostic study (in which the spatial and temporal variability within the system is defined), a monitoring plan can be developed to include collection of water, bed sediment, and biological samples at specific longitudinal, horizontal, and vertical locations (including tributaries) at a specified frequency. The resulting data can then be used in statistical or mathematical models to describe and better understand the physical, chemical, and biological functions and processes within the system.

Some of the statistical, descriptive, and mathematical tools typically used in interpretive studies are briefly described below.

- Trends in water quality can be examined using various statistical methods and software. The statistical methods that are typically used are those designed to overcome common statistical problems encountered by conventional statistical trend techniques in the analysis of water-quality data, including data that are non-normal and seasonally varying, and water-quality records with missing values, “less-than” (censored) values, and outliers. The type of data collected will determine whether parametric or non-parametric statistical trend tests should be used.

- Many data analysis and statistical (empirical) tools are available for describing and interpreting water-quality conditions and forecasting future conditions. Many of the empirical tools are described in detail in Reckhow and Chapra (1983a), as well as in the sources shown below:

  - Phosphorus Loading Models (Vollenweider, 1968, 1976; Vollenweider and Dillon, 1974; Vollenweider and others, 1980; Panuska and Kreider, 2003)
  - USEPA–NES Trophic State Delineation (U.S. Environmental Protection Agency, 1974)
  - Carlson’s Trophic State Index (Carlson, 1977)
  - Nutrient Loading and Lake Response (Rast and Lee, 1978)
  - Simplified Procedures for Eutrophication Assessment and Prediction (Walker, 1985; *http://el.erdc.usace.army.mil/elmodels/emiinfo.html,*accessed 2/4/2015)
  - Phosphorus Loading Concept and the OECD Eutrophication Programme (Rast and Thornton, 2005)
  - Eutrophication Classification According to Trophic Criteria (Klapper, 2005)

- Many mathematical modeling tools are available to help describe and interpret lake and reservoir water-quality conditions and for forecasting future conditions. Many of these models and techniques are described in Reckhow and Chapra (1983b) and more recently in Mooij and others (2010). Some of the most widely used include (accessed between 1/28/2015 and 2/4/2015):
  - BATHTUB, *http://el.erdc.usace.army.mil/elmodels/emiinfo.html*
  - CE-QUAL-W2, *http://www.cee.pdx.edu/w2/*
  - EFDC, *http://www.epa.gov/athens/wwqtsc/html/efdc.html*
  - DYRESM--CAEDYM, *http://tools.envirolink.govt.nz/dsss/dynamic-reservoir-simulation-model-computational-aquatic-ecosystem-dynamics-model/*
  - ELCOM, *http://www.ce.utexas.edu/prof/hodges/site2006/elcom.htm*
  - GLM, *http://aed.see.uwa.edu.au/research/models/GLM/*

10.3.2 Sampling Strategies and Approaches

The purpose of defining a specific sampling strategy is to make data collection more efficient and so that the obtained information is sufficient to meet study objectives. The sampling strategy and design should be as cost effective as possible. Since the purpose of the sampling design is to describe specific water-quality characteristics, a sampling design should consider the variability in the system, such as vertical and longitudinal gradients, and seasonal variability. Study design should consider:

- Vertical and longitudinal gradients (Thornton and others, 1982), different sources and locations of tributary loading, and seasonal patterns that increase the variability in the data.
- Initial conditions - Spatial and seasonal variability at the beginning of the sampling program so that procedures can be incorporated to minimize their impact during the later data analysis and interpretation phases (U.S. Army Corps of Engineers, 1987).

Often a single station is not adequate to characterize lake or reservoir water quality; therefore, the required number and location of sampling stations must be determined. Depending on study objectives, one sample station may be sufficient in a small lake or when trying to characterize a specific location in a reservoir (for example, at the drinking-water intake) rather than collecting fewer samples at several stations. In other cases, many stations may be needed to describe the variability in the system.

10.3.2.A What to Sample

The purpose, objective(s), and scientific approach of a study will determine what media (water, bed sediment, and biological components) should be sampled and what variables should be measured. It is important to keep in mind the various zones or strata in lakes and reservoirs: thermal, light, chemical, depth, littoral, pelagial, profundal, riverine, transition, and lacustrine. The following example provides an idea of what should be sampled in an eutrophication study.

Example: On the basis of the water-quality concerns and possible contributing factors in lakes and reservoirs (table 10–4), data are often collected for many of the physical, chemical, and biological variables listed in table 10–5. Field measurements, including vertical profiles of water temperature, dissolved-oxygen concentrations, pH, specific electrical conductance, and photosynthetic pigments (chlorophyll and others), and Secchi disk transparency usually are collected onsite at the

time of sampling. Common analytes measured in water samples typically include nutrients, dissolved solids, major ions, trace elements, organic carbon, and organic constituents (table 10–6). Biological samples in water and bed sediments are often collected as well. Biological analyses in water samples could include chlorophyll concentrations, pathogen indicator density (fecal coliform, *Escherichia coli*), and possibly phytoplankton and zooplankton diversity, abundance, and biomass/biovolume, aquatic macrophytes, and fish. Bed sediments often are analyzed for nutrients, trace metals, and organic carbon.

Table 10–6. List of selected water-quality constituents that are often measured in water-quality samples.

Sample group	Field-measured property or analytical constituent
Ambient conditions at time of sampling	Temperature
	Dissolved oxygen
	Specific conductance
	pH
	Alkalinity
	Color
	Suspended sediment (suspended solids)
Nutrients	Orthophosphate
	Total phosphorus
	Nitrite plus nitrate nitrogen
	Ammonia nitrogen
	Ammonia plus organic nitrogen
	Total nitrogen
Major ions	Calcium
	Chloride
	Dissolved solids
	Fluoride
	Iron
	Magnesium
	Manganese
	Potassium
Major ions (cont.)	Silica
	Sodium
	Sulfate
Trace elements	Aluminum
	Antimony
	Arsenic
	Barium
	Beryllium
	Cadmium
	Chromium
	Cobalt
	Copper
	Lead
	Manganese
	Molybdenum
	Nickel
	Silver
	Uranium, natural
	Zinc
Organic Carbon	Total organic carbon Dissolved organic carbon

10.3.2.B How Many Samples to Collect

The purpose and objectives of the study will determine how many and how often samples should be collected. The number of samples should be sufficient to represent the variability in water quality that exists at the location the site was chosen to represent and the time period the sample was chosen to represent. In addition to the typical samples that will be used for water-quality analysis, quality-assurance samples should also be collected to identify, quantify, and document bias and variability in the data. Statistical

tools and guidance are available to help design a statistical strategy for sample collection (Thornton and others, 1982; Gaugush, 1987; Averett and Schroder, 1994).

If the project is a reconnaissance study as discussed above, sampling sites are typically located across the lake or reservoir in areas that represent different zones or strata. If the lake or reservoir is thermally stratified, samples are typically collected within each layer, especially the epilimnion and hypolimnion. The number of samples needs to be sufficient to achieve study and data-quality objectives and strengthen an understanding of the limnological system.

10.3.2.C Where to Sample: Systematic, Random, and Stratified Approaches

A sample is a single representation of a particular aspect of a system; a substantial amount of data and information can be gained from a sample or a measurement (Averett and Schroder, 1994; NFM 8). Therefore, it is important that care be taken when selecting the location(s) where samples will be collected and measurements will be made. A single sample may not represent the whole or even define the average condition of the whole system. Therefore, samples typically need to be collected at a variety of locations to define the average and the extremes, as well as other attributes of the system. In some instances, more samples are collected and more measurements are made than are necessary to meet study objectives. Oversampling may provide security, but this is an expensive and poorly designed study approach (Averett and Schroder, 1994). Oversampling at the beginning of a study, however, is often required to understand the variability in the system and to enable a more optimal study design to be established.

Lakes and reservoirs can be complex systems in regard to selecting sampling sites (Averett and Schroder, 1994). In the formation of reservoirs, stream valleys are drowned, and each area may become a miniature reservoir with its own hydrologic patterns. Therefore, keep in mind the different zones in a reservoir described above: riverine, transition, and lacustrine or lake-like. Also consider the biological, light, and thermal zones. There is no single quantitative method for sampling-site selection. Sites should be selected in accordance with the scientific approach that will be used for the analysis and interpretation of the data, as described below, and considering what the data will represent.

In small lakes, sampling is usually conducted at only one location that is near the deepest location in the lake, or near the deepest location in each of the basins of a multibasin lake. Sampling at the deepest location will often provide the best description of the vertical variability in water quality. It is preferred that this location is near the center of each basin to minimize internal mixing processes. In larger lakes and in reservoirs, more than one location is often needed to describe the spatial variability in water quality. Of the various methods used to determine where to sample these more complex systems, the three most common approaches are systematic, random, and stratified approaches; each approach is described, in brief, below. (See also the discussion in NFM 8 on applications and limitations of statistical methods for the selection of bottom-material sampling sites).

- Systematic Approach

  Systematic sampling consists of selecting the first sampling site at random, and then selecting the remaining sampling sites at some predetermined space (Averett and Schroder, 1994). This technique can easily be used in most lake and reservoir studies, but the samples may provide biased results. Systematic sampling is a common sampling method, particularly in a sampling program designed to sample large water bodies (Gaugush, 1987).

- Random Approach

  A random sampling approach requires that the samples be collected without bias and be representative of the entire lake or reservoir (Averett and Schroder, 1994). The basic concept is to estimate the mean and measurement uncertainties, which requires that every sampling unit or other discrete unit that is

selected for sampling has an equal chance of being chosen. For example, when planning to collect samples at three sites, select the three sites using an unbiased procedure. This approach applies to the selection of dates for sample collection as well as sampling locations (see 10.3.2.D). In other words, if you plan on collecting 12 samples in a year, choose the 12 sample collection dates in an unbiased manner. Gaugush (1987) describes in detail the statistical procedure for designing a simple random sampling program.

- Stratified Approach

Stratified random sampling is useful when the strata are distinct; that is, they have known sizes and boundaries (Averett and Schroder, 1994). In this situation, the reservoir could be divided into specific strata (zones). If a simple random sample is drawn from each stratum, then the sampling design is referred to as stratified random sampling (Gaugush, 1987). Strata in lakes and reservoirs can also be vertical zones, such as epilimnion, metalimnion, and hypolimnion. Likewise, in a reservoir, the strata of interest might also be the riverine, transition, and lacustrine zones along the downstream gradient.

Stratified random sampling has two important advantages over simple random sampling. First, it can be advantageous to obtain data on separate subsets of the target population. Second, stratified sampling may produce an increase in the precision (error reduction) of the estimate for the entire population. The estimates for the strata can then be combined into a precise estimate for the target population. The total number of samples used in such a design will often be less than would be required using a simple random sample design (Gaugush, 1987).

10.3.2.D When to Sample: Seasonal and Diurnal Considerations

Just as spatial patterns in lake and reservoir water quality are ultimately determined by flow regime, wind, and the vertical and longitudinal changes in light penetration and temperature, temporal patterns are determined by the dynamics of the flow regime, wind, and seasonal changes in temperature and solar radiation (Gaugush, 1987). Some of the temporal variability may be quite random, such as variability associated with changes in flow, whereas other variability may be quite consistent from one year to the next, such as variability associated with water temperatures. The annual cycle of changes in thermal stratification is well documented in limnology texts, such as Wetzel (2001) and Thornton and others (1990).

- Seasonal

In warm monomictic lakes and reservoirs, the summer stratified period is preceded and followed by a period of fall/winter circulation. In such a case, stratification of the temporal variability into only two seasons may be sufficient to adequately account for the temporal component of variability in the lake or reservoir water quality. In dimictic lakes and reservoirs, the periods of mixing occur during the spring and fall turnover and are preceded and followed by periods of stratification. The duration and extent of these seasonal events can be used to stratify a sampling program temporally (Gaugush, 1987). Typically, monthly sampling is adequate to capture and describe the seasonal variability in water quality of lakes and reservoirs. It is preferable to collect monthly samples at about the same time of month each year to better enable long-term analyses.

- **Diurnal**

Environmental conditions affecting lakes and reservoirs can change over a 24-hour period. Solar radiation varies from high intensity during midday to darkness throughout the night. As a result, surface temperatures may fluctuate between the extremes of day and night, especially in the shallow littoral areas. In addition, light affects productivity, which leads to diurnal patterns in dissolved

oxygen, pH, and phytoplankton production. Organisms like phytoplankton and zooplankton often move vertically and (or) horizontally to relocate themselves in response to these environmental changes. These movements are usually associated with light, food availability, and predation pressures (Wetzel and Likens, 2000).

When sampling a site multiple times during the year or season, most sampling is conducted at a consistent time of day to eliminate much of the **diurnal** variability in water quality. A dissolved oxygen profile at 0500 hours may be quite different from one collected at 1700 hours on the same day. This variability is true also for measurements of pH and chlorophyll measured by **in vivo** fluorescence. The primary causes of diurnal variations in these measures are photosynthesis and aerobic respiration. Photosynthesis is driven by sunlight and produces oxygen, which causes an increase in dissolved oxygen during the day. Large differences in 24-hour dissolved-oxygen minima and maxima can occur. In addition, phytoplankton and zooplankton can migrate up and down in the water column to acquire a position for optimum light intensity or food. Typically, routine sampling should be done at about the same time of day, preferably between 1000 and 1500 hours, when the sun is relatively high in the sky.

- Flow

  In reservoirs, temporal changes in flow regime can also provide a means to temporally stratify sample collection (Gaugush, 1987). Flow regimes can be divided into a high-flow stratum (for example, during the spring season high flows) and a low or base-flow stratum (during the summer and fall low flows).

  Including a combination of thermal and flow stratification considerations can improve a sampling design that will account for a greater proportion of the temporal variability; for example, winter circulation, high flow (March–May), thermally stratified (June–September), and fall/winter mixing low flow (October–February).

10.4 Preparations for Data Collection: Data Management and Safety Precautions

Prior to data collection, specific protocols should be established for setting up site files and for data management. Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (see NFM 1.1.1, fig. 1–1).

It is important that field personnel understand the purpose for which the various types of data are being collected and what the samples are meant to represent. This better enables field personnel to make more informed changes when field conditions are different than expected. Field crews should:

- Review the project sampling-and-analysis, quality-assurance, and work-schedule plans and be trained in how to collect the types of measurements and samples needed.
- Understand the physical and chemical limitations and utility of each piece of equipment to be used with respect to meeting project data-collection objectives and data-quality requirements. The operational range of the sampling equipment to be used should be verified and tested.
- Document conditions that could affect sampling operations (for example, site access, commercial traffic, recreation activities, and potential safety hazards) and the training needed.

- Follow all safety procedures.
  - Review the safety plan.
  - Ensure that personnel have the current Occupational Safety and Health Administration Hazardous Waste Operations and Emergency Response (HAZWOPER) certification, which is required when working at sites designated as hazardous.
  - Personnel operating a motorized vessel must have completed the USGS Motorboat Operator Certification Course (**MOCC**) and maintain current certification (USGS-SAF-MOCC-S1657-UDT).
  - Evaluate potential sources of contamination at the site, based on the target analytes to be collected.

10.4.1 Site Files

USGS field personnel are responsible for establishing site files in the National Water Information System (NWIS)[2] for each station or site that is to be sampled (table 10–7) and for creating field folders for each location (detailed information is given in NFM 4.1). It is the responsibility of project personnel to ensure the functionality of the NWIS files, make updates promptly, and check that the information contained is correct.

A field (or site) folder for each data-collection site should be created and taken on each trip to the site. The field folder should contain information about the site that can be referenced and updated by field personnel to help locate and safely access sites, collect and process water samples and data, and record observations that could be useful for future site visits. Recommended contents for the field folder are listed in NFM 4.1 (see fig. 4–2), but the folder should be customized according to project needs.

Field notes for lake and reservoir samples are recorded on paper and (or) in electronic field forms. The field form typically includes the station identifiers and descriptions; field personnel involved in collecting the sample; information for the laboratory; date, time, record number, and associated water-quality data related to a given water-quality sample; alkalinity titration numbers; meter calibration and field measurements; quality-control information; and the NWIS database information that is required for storage of laboratory and other analytical results.

[2]NWIS is the hydrologic database of the U.S. Geological Survey and is updated periodically.

Table 10–7. Minimum information required for electronic storage of site and lake water-quality data in the U.S. Geological Survey National Water Information System (NWIS).

[GWSI, Ground-Water Site Inventory; USGS, U.S. Geological Survey; QWDATA, Quality of Water Data]

Required information for creation of a surface-water site in NWIS 1, 2		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station identification number	C1	0209799150
Station name	C12	B.E. Jordan Lake AB US Hwy 64 at Wilsonville, NC
Latitude	C9	354430
Longitude	C10	0790109
Coordinate accuracy	C11	S (nearest second)
Coordinate method	C35	R (reported)
Coordinate datum	C36	NAD83
USGS Water Science Center	C66	37 (North Carolina)
Country	C41	US (United States)
State	C7	37 (North Carolina)
County	C8	037 (Chatham)
Time-zone code	C813	EST
Daylight-savings flag	C814	Y (yes)
Agency use[3]	C803	A (Active)
Station type	C802	LK
Required information for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	**Alpha parameter code**	**Example data (Description of code)**
Agency code	AGENCY	USGS
Station identification number	STAID	0209799150
Date (year/month/day)	DATES	20140716
Time (standard 24-hour clock)	TIMES	1530
Sample medium	MEDIM	WS (surface water)
Sample type	STYPE	9 (regular sample)
Analysis status hydrologic	ASTAT	U (unrestricted)
Hydrologic ("Hydro") condition	HSTAT	9 (stable, normal stage)
Hydrologic event	EVENT	9 (routine sample)

[1]Numerous additional data fields are available in NWIS that can be useful for data analysis or mandatory for meeting study objectives (for example, indicating whether a non-USGS agency collected the data).

[2]Modified from Groundwater Site Inventory Schedule Form 9-1904-A, Revised June 2004, NWIS 4.4.

[3]See WRD Policy Memorandum 2009.02/Administrative Policy and Services Instructional Memorandum No. 2009-09 (see wrdpolicy09.02 at *http://water.usgs.gov/admin/memo/policy/policy.html*).

10.4.2 Safety Precautions

The USGS, as a Bureau of the U.S. Department of the Interior (DOI), structures its safety program using DOI safety guidelines. These guidelines are described in the Departmental Manual Part 485 titled "Safety and Occupational Health Program" (*http://elips.doi.gov/elips/Browse.aspx?startid=1594&dbid=0*), which is updated periodically to reflect current DOI policies. USGS safety policies and regulations are found in USGS Handbook 445–3–H, "Safety and Health for Field Operations" (*http://www.usgs.gov/usgs-manual/handbook/hb/445-3-h.pdf*). Additional safety requirements are described in "A Guide to Safe Field Operations" (U.S. Geological Survey, 1995) and in numbered memorandums from the Water Mission Area. A safety officer is designated in each Water Science Center of the USGS to provide additional information and guidance.

National Field Manual chapter 9, "Safety in Field Activities" (*http://water.usgs.gov/owq/FieldManual/Chap9/content.html*), describes hazards commonly encountered when engaged in field activities related to the collection of water-quality data. Each field site is unique and could have special safety requirements that need to be identified. Chapter 9 is meant to be used in conjunction with the DOI manuals, and handbooks cited above. It is the responsibility of the Water Science Center Safety Officer and Project Chief to ensure that the safety courses needed are taken by all field personnel and safety policies and procedures are implemented (table 10–8).

Personnel using sampling equipment should become familiar with the hazards involved and establish appropriate safety practices before using the equipment. Personnel should:

- Make sure all equipment is in safe working condition. All electrical equipment must bear the approval seal of Underwriters Laboratories and must be properly grounded to protect against electrical shock.
- Consider and prepare for hazards associated with the operation of motor vehicles, boats, winches, tools, and other incidental equipment.
  - Boat operators must be up-to-date with their motorboat operator training and certification (MOCC).
  - All boats must be equipped with fire extinguishers, boat horns, throw rope and life ring, extra float cushions and personal floatation devices (PFDs), and flares or other emergency communication devices.
  - Field personnel working on or near water should be able to swim.
- Prepare a job hazard assessment (JHA) and communication plans.
  - All field personnel need to be fully aware of all lines of communication.
  - Field personnel should have a daily check-in safety procedure.
  - An emergency communications plan should be readily accessible that includes up-to-date contacts for police, ambulance, fire departments, hospitals, and search and rescue personnel.

Table 10-8. Standard health and safety practices for U.S. Geological Survey personnel.

Recommended Training
• First aid • Cardiopulmonary resuscitation (CPR) • Vehicle safety • Boating and water safety • Field safety (weather, personal safety, orienteering, and site reconnaissance prior to sampling) • Equipment design, operation, and maintenance • Handling of chemicals, fuel spills, and other hazardous materials
Communications
• Check-in schedule • Sampling itinerary (vehicle used and description, time of departure and return, and travel route) • Contacts for police, ambulance, hospitals, fire departments, and search and rescue personnel • Emergency services available near each sampling site and base location • Cell (or satellite) phone. Mobile telephones and or satellite communication services for remote areas where cellular service is not available should be accessible at all times.
Personal Safety
• Protect the health and safety of all personnel. Always err on the side of personal safety. • Field clothing and other protective gear including personal flotation devices (PFDs) for all field personnel. PFDs are required to be worn at all times when over, in, or near a water body, including when in a boat or on a boat dock. • Medical and personal information (allergies and personal health conditions) • Personal contacts (family, telephone numbers, and other) • Physical exams and immunizations • At least two persons should be present (in a boat) during all sample-collection activities and no one should be left alone while in the field. • Exposure to lake water and sediments should be minimized as much as possible. Use gloves and clean exposed body parts as soon as possible after contact. Wear heavy gloves when hands are used to agitate the substrate during collection of benthic macroinvertebrate samples. • Use appropriate protective equipment (gloves and safety glasses) when handling and using hazardous chemicals. • Be familiar with the symptoms of heat/sun stroke and be prepared to move a suffering individual into cooler surroundings and hydrate immediately. • Be familiar with the symptoms of hypothermia and know what to do in case symptoms occur.

All surface waters and sediments should be considered possible health hazards and potential sources of human or animal wastes and other types of toxic or pathogenic substances. Infectious agents and toxic substances can be inhaled or absorbed through the skin (NFM 9). It is advisable for field personnel to be immunized against tetanus, hepatitis, typhoid fever, and polio. Toxin-producing algae may be present in eutrophic or hypereutrophic waters, and gloves should be worn when coming in contact with such waters (NFM 7.5.8). Many hazards lie out of sight in the bottoms of lakes and reservoirs. Broken glass or sharp pieces of metal embedded in the substrate can cause serious injury if care is not exercised when walking or working with hands.

10.5 Field-Measured Properties

In situ measurements (water properties directly measured within the water body) that describe the general physical, chemical, and biological conditions in a water body are usually referred to as field-measured properties. Understanding the distribution in these properties ensures that the other samples being collected accurately represent the conditions, zones, or strata in the water body for which the sample is supposed to represent. Chapter 6 of the *National Field Manual* establishes USGS protocols, requirements, and recommended practices for collecting field measurements, including sensor calibration, technical specifications of instruments, quality control of the measurement process, and criteria for data reporting (table 10–9). Field-measurement protocols and the required and recommended methods needed to preserve the integrity of the water data being collected are described in other chapters of this field manual and in the USGS Techniques and Methods reports referenced below (table 10–9).

USGS personnel should refer to the *National Field Manual* for instructions relating to calibration, maintenance, measurement criteria, possible measurement interferences, and quality-control procedures that pertain to each of the water properties covered in chapter 6 (NFM 6) and in Techniques and Methods 1–D3 and 1–D5. NFM sections 6.0 through 6.7 provide required and recommended procedures for measurements made when using the same single- or dual-parameter instruments at multiple field sites or stations, while section 6.8 provides that information for use of sensors bundled in multiparameter instruments. "Guidelines and Standard Procedures for Continuous Water-Quality Monitors" (Wagner and others, 2006) provides the basic USGS guidelines and procedures for field-site and water-quality monitor selection, field procedures and compliance with sampling protocols given in the NFM, continuous-monitor calibrations, and record computation, review, and data reporting. Common multiparameter instruments have sondes that typically include sensors for the collection of temperature, specific electrical conductance, dissolved oxygen, and pH data, but can be configured to measure other properties, such as turbidity and fluorescence. Sampling and measuring indicators of algal biomass are described in NFM 7.4, which includes sections on the use of sensors for making direct (in situ) measurements of light availability, chlorophyll, and phycocyanin. When creating a vertical water-quality profile by deploying a multiparameter sonde through a water column, follow the instructions given below under "Multiparameter Instrument Sondes" (section 10.5.2).

Table 10–9. U.S. Geological Survey protocols and guidance documents for in situ or onsite measurements of water-quality properties.

[NFM, National Field Manual for the Collection of Water-Quality Data; USGS, U.S. Geological Survey]

Field methods documentation	Title	Description
NFM chapter/section[1]		
Chapter 6	**Field Measurements**	
6.0	Guidelines for Field-Measured Water-Quality Properties	Sections 6.0 through 6.7 provide general information about the water property and specific protocols, procedures, and recommendations for field-measurement practices, with a primary focus on making discrete measurements using single or dual-parameter instruments.
6.1	Temperature	
6.2	Dissolved Oxygen (DO)	
6.3	Specific Electrical Conductance (SC)	
6.4	pH	
6.5	Reduction-Oxidation Potential – Electrode Method (ORP or Redox)	
6.6	Alkalinity and Acid Neutralizing Capacity (ANC)	
6.7	Turbidity	
6.8	Use of Multiparameter Instruments for Routine Field Measurements	Section 6.8 provides guidance for measuring the properties listed above (sections 6.1–6.4 and 6.7) specific to using a multiparameter sonde.
Chapter 7	**Biological Indicators**	
7.4 7.4.1	Algal Biomass Indicators Pre-sampling considerations	Section 7.4.1.B includes information on measuring light attenuation by Secchi disk, turbidimeter, and light meter.
7.4.2	In vivo measurement of chlorophyll and **phycocyanin**	Section 7.4.2 describes use of fluorescence-based sensors.
Techniques and Methods 1–D3[2]	Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting	Guidelines for site- and monitor-selection considerations; sensor inspection and calibration methods; field procedures; data evaluation, correction, and computation.
Techniques and Methods 1–D5[3]	Optical Techniques for the Determination of Nitrate in Environmental Waters: Guidelines for Instrument Selection, Operation, Deployment, Maintenance, Quality Assurance, and Data Reporting	Information for USGS field operations regarding the selection and use of ultra-violet (UV) nitrate sensors, including instrument types and maintenance of sensor performance, sensor design, sensor characterization techniques and typical interferences, and approaches for sensor deployment.

[1] NFM chapters and chapter sections are available at *http://water.usgs.gov/owq/FieldManual*.

[2]Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting (*http://pubs.usgs.gov/tm/2006/tm1D3/*).

[3]Optical Techniques for the Determination of Nitrate in Environmental Waters (*http://ca.water.usgs.gov/pubs/2013/tm1d5.html*).

10.5.1 Light Attenuation

Measurement methods for estimating the thickness of the upper layer of water that light penetrates (referred to as the photic or euphotic zone) require either use of a Secchi disk or an instrument by which solar radiation is determined directly.

- Secchi Disk Method. The Secchi disk is a weighted disk with alternating black and white quadrants, 20 centimeters (cm; 8 inches) in diameter, and attached to a line with distance marked in meters or feet. The disk is slowly lowered in the water column until it is no longer visible. The depth at which the disk is no longer visible is referred to as the Secchi depth. Secchi depths should be measured on the shady side of the boat. The thickness of the photic zone is measured by multiplying Secchi disk depth by a factor of approximately 2.5 (Welch, 1948; Horne and Goldman, 1994; Wetzel and Likens, 2000). Light penetration, as measured with a Secchi disk, can vary considerably when the sun is at extreme angles. Therefore, if only one sample is to be collected in a day, the Secchi measurement generally is made between the hours of 1000 and 1500 hours. NFM 7.4.1 describes how to measure water transparency using a Secchi disk.

- Surface and Underwater Solar Radiation. Measurements of surface and underwater irradiance (light availability) include shortwave (100 to 400 nanometers (nm)), reflected longwave (infrared radiation; 700 to 3.5x105 nm), and **photosynthetic active radiation** (**PAR**; 400 to 700 nm) and are measured using a pyrheliometer, pyranometer, net radiometer, or quantum sensor (see fig. 10–13 in section 10.5.3.B). Refer to NFM 7.4.1.B for detailed information about measurements of solar radiation.

Light attenuation can be measured using the surface (terrestrial) radiation sensor along with the underwater radiation sensor. The depth where the underwater sensor reaches 1 percent of the surface intensity identifies the bottom or thickness of the photic zone. The extinction coefficient is the absolute value of the slope of the natural log of solar radiation with depth. Refer to NFM 7.4.1.B, Technical Notes and Tips-2, to calculate the portion of the water body in which light is sufficient for photosynthesis (the euphotic depth).

10.5.2 Multiparameter Instrument Sondes

Multiparameter instruments, in which various types of sensors are bundled in a **data sonde**, provide concurrent measurement of various water-quality related properties (sometimes referred to as "parameters" in the industry literature) that should or must be measured onsite, such as water temperature, dissolved oxygen, specific electrical conductance, pH, and turbidity (NFM 6.8; Wagner and others, 2006). Additional sensors could be added to the data sonde to measure light attenuation, chlorophyll, phycocyanin and **phycoerythrin** (cyanobacteria pigments) (NFM 7.4; NFM 7.5), nitrate, and colored fluorescent **dissolved organic matter**. An advantage of multiparameter sondes is that they can be activated manually or be programmed for data collection and storage at defined time steps.

Prior to using a multiparameter instrument, the sensors should be properly calibrated or the calibration checked following the protocols and guidance given in NFM 6.8 (see table 10–9 for relevant sections), and NFM 7.4 and 7.5.5 (for chlorophyll, phycocyanin, phycoerythrin, and cyanobacteria).

10.5.2.A Temperature, Dissolved Oxygen, pH, Specific Electrical Conductance, and Turbidity

- Temperature. Water temperature is important when determining the various strata and zones in a water body. The proper calibration and maintenance of the thermistor or temperature sensor is extremely important for water-quality studies. Refer to NFM 6.1 and 6.8 for USGS guidelines and procedures

related to selection, calibration, maintenance, and measurement criteria for thermistor thermometers. The accuracy of measurements of dissolved oxygen, specific electrical conductance, pH, oxidation-reduction potential,[3] the rate and equilibria of chemical reactions, biological activity, and fluid properties depend on the accuracy of the temperature measurement.

- Dissolved Oxygen. Data that accurately describe dissolved-oxygen concentrations are essential for documenting changes in the water quality of lakes and reservoirs and determining whether or not the changes observed were caused by natural phenomena or human activities. NFM 6.2 and 6.8 provide guidelines and procedures related to equipment selection, calibration, maintenance, and deployment of either optical (luminescence-based technology) or the amperometric (Clark cell) sensors. Optical sensors are recommended for long-term deployment and are replacing the amperometric sensors as the measurement method of choice for most USGS field studies. As is the case of other gases, oxygen solubility often exhibits an inverse relation to temperature.

- pH. The pH, or activity (effective concentration) of hydrogen ions (H^+), in a lake or other aqueous system, is a measure of the acidity of the water. Water with a pH value of 7 is defined as "neutral" at a temperature of 25 °C, when the H^+ concentration is equal to that of the hydroxide (OH^-) concentration. Remember that the chemical equilibrium of hydrogen ions in solution is temperature dependent. Refer to NFM 6.4 for a more detailed definition and informative explanation of pH and how it is measured in accordance with USGS protocols and requirements. Several methods are described in the National Field Manual that can be applied to the measurement of pH in standing waters. NFM 6.4 and 6.8 provide guidelines and procedures related to pH equipment maintenance, calibration, and measurement.

- Specific Electrical Conductance (SC). Electrical conductance is a measure of the capacity of a substance to transmit an electrical current. The SC of water is a function of the types and quantities of dissolved substances it contains, normalized to a unit length and unit cross section at a specified temperature (NFM 6.3). The presence of charged ionic species in a simple solution makes it conductive; that is, as ion concentrations increase, the electrical conductance of the solution increases. SC, therefore, provides a rough indication of the total number of ions present in a solution and thus is related to total dissolved solids (TDS) and ionic strength. Temperature affects the SC value at the time of measuring and must be factored into the measurement. Most instruments report SC adjusted to a common water temperature (25 °C). NFM 6.3 and 6.8 describe USGS calibration and measurement procedures for SC in standing water, using either a contacting-type sensor (dip cell, cup cell, or flow cell) or electrodeless-type sensors.

- Turbidity. Many instruments are available for measuring turbidity, each of which is assigned a USGS parameter and method code (see "Turbidity parameter and methods codes" on the index page for "6.7 Turbidity" at http://water.usgs.gov/owq/FieldManual/Chapter6/6.7_contents.html). The specific calibration instructions and the calibrants needed depend on the instrument being used. NFM 6.7 and 6.8 provide guidance on equipment and sensor types, calibration procedures, reference and turbidity standards, and quality-assurance practices in the measurement of turbidity.

10.5.2.B Algal Biomass: Photosynthetic Pigments

- Depending on the sensor and instrument capability, fluorescence-based sensors can be connected to a multiparameter data-sonde profiler or used individually to measure pigment fluorescence (NFM 7,

[3]See NFM 6.5 "Reduction-Oxidation Potential."

section 7.4.2). Follow the instructions for profiling under "Methods of Sonde Deployment" (section 10.5.3.A) for collecting a measurement profile.

- **Chlorophyll**. Fluorescence-based sensors can be deployed in situ to provide a discrete or continuous measure of total chlorophyll. The chlorophyll sensor produces a relative measure of total chlorophyll and can be adjusted to chlorophyll a concentrations by relating fluorescence values with analytical concentrations extracted from water samples collected at the same site.
- **Cyanobacteria**. **Phycocyanin** and **phycoerythrin** (pigments in cyanobacteria) concentrations also can be estimated by in vivo fluorescence to provide a continuous record. Refer to NFM 7.4.2 for pros and cons and guidance on equipment use, calibration, and measurement of in vivo fluorescence measurements.

10.5.2.C Ultraviolet Nitrate Sensors

Ultraviolet (UV) photometers for in situ determination (discrete or continuous measurements) of nitrate concentrations have been tested and are being employed at selected sampling stations (primarily at USGS stream and river sites). Guidance and detailed information about types and use of UV nitrate sensors is given in Pellerin and others (2013), Techniques and Methods 1–D5 (see table 10–9).

10.5.3 Methods of Sonde Deployment

Multiparameter instruments can be lowered through the water column during sampling (profiling) or they can be installed and configured to provide data continuously at a single station or on a data platform (section 10.5.3.B). For additional information, see Wagner and others (2006), NFM 6.8, and table 10–9).

10.5.3.A Profiling

Prior to lowering the sonde through the water column, the sonde and (or) transducer must be calibrated and weighted properly so that it sinks properly. Consult the manufacturer before adding weight to the instrument.

To manually collect profile data, use the following procedure:

1. Record (automatically or manually) each depth at which a measurement(s) is made.
    a. Some multiparameter instruments may include or can be custom ordered with a pressure transducer that estimates water depth.
    b. For instruments without pressure transducers, the approximate depth of the sonde as it is lowered through the water column can be followed by placing incremental marks along the instrument cable. Alternatively, a single-instrument pressure transducer can be deployed attached to the sonde.
2. Deploy the sonde and record, at the selected depth intervals, the values given from the field-measurement sensors for which the sonde was outfitted (usually temperature, pH, SC, and DO).
    a. Lower the sonde to just under the surface of the water.
    b. Wait for the sensors to stabilize before recording the set of field measurements, in accordance with the USGS field-measurement protocols described in NFM 6. (Note that some instruments and sensors require a longer equilibration time: check the manufacturer's recommendations.)

c. Based on the total depth of the water body and vertical variability within the water column, lower the sonde in 0.5- to 1-m-depth increments (or other depth interval, in accordance with study objectives and requirements).

- Record each depth interval; then wait for all the sensors to stabilize to the new depth conditions before recording the set of field-measurement values for that depth.
- It is usually best for long-term evaluations to lower and record field measurements at consistent depth intervals.

3. Continue to lower the sonde and record depth and field-measurement values until the sonde reaches bottom (avoid stirring bottom sediments).

10.5.3.B Water-Quality Monitoring Platforms with Continuous Sensors or Multiparameter Sondes

Water quality can change frequently in lakes and reservoirs, requiring frequent, repeated measurements to characterize the temporal variations in quality (Wagner and others, 2006). Operation of a water-quality monitoring platform with multiparamter sondes can provide a nearly continuous record of specific water-quality constituents. The data being collected can be recorded on site or distributed directly by telemetry to the Internet. Continuous water-quality monitoring systems can be mounted or moored on fixed structures (such as piers and dam walls), mounted on an anchored barge (fig. 10–13), or suspended from an anchored buoy (fig. 10–14). These systems can operate a single sensor at a fixed depth, multiparameter sondes with multiple sets of sensors at fixed depths (fig. 10–15), or sensors or sondes can be raised or lowered using a mechanical wench or ballast system (fig. 10–16).

► As part of water-quality lake/reservoir studies, temperature and dissolved oxygen are the two properties most often measured. Other field-measured properties can include SC, pH, turbidity, pigment fluorescence, ammonia, nitrate, chloride, and solar radiation (most often PAR).

► Meteorologic stations also often are associated with the continuous water-quality monitoring platforms in order to provide information critical to the interpretation of the water-quality data collected.

Lake and reservoir water quality ranges from clear, pristine, oligotrophic systems to highly productive eutrophic or hypereutrophic systems. Continuous monitoring in highly productive environments can be challenging because of relatively rapid biofouling. In addition, corrosion of electronic components can occur in high humidity areas. The choice and placement of instrumentation in a lake or reservoir is based on the data objectives of the project.

The number of vertical depths at which measurements are made should depend on the extent of vertical mixing, similar to collecting other water-quality samples (Wagner and others, 2006). Measurements can be made at evenly spaced intervals or at points relative to where changes in field-measured properties, such as temperature or salinity gradients, typically occur. If vertical stratification is usually sharply defined, the locations for measurements can be chosen across the transition zone and more closely spaced to adequately represent the position and degree of stratification.

The frequency at which measurements are made is based on the data objectives of the project and should depend on the temporal variation of change in the system. In a stable, stillwater system, hourly data may be adequate to capture the temporal variation. In more dynamic, frequently mixed (polymictic) systems or in rapidly flushed systems, more frequent data collection may be needed. In the former, a single mulitparameter data sonde mechanically positioned at the various depths may be sufficient. In the latter, a string of sensors positioned at different depths, all recording at the same time, may be needed.

Figure 10–17 shows changes in the dissolved-oxygen concentrations in Lake Maumelle, Arkansas, a shallow drinking-water reservoir. The changes in concentration were based on data measured at a 5-minute frequency over a 7-day period using 12 vertically spaced sensors. This figure demonstrates wind-induced upwellings of hypolimnetic water and downwellings of epilimnetic surface water. The upwellings can move hypolimnetic water, rich in reduced iron and manganese, up to a depth where drinking water is withdrawn. The drinking-water treatment facility uses these data to adjust the treatment process in order to reduce the increased concentrations of elements that produce taste and odor problems and clog filters.

Figure 10–13. Barge-mounted continuous water-quality monitoring system on Lake Houston, Texas, station 2295554095093401 (photograph by T.D. Oden, U.S. Geological Survey).

Figure 10–14. Buoyed continuous water-quality monitoring system on Lake Maumelle, Arkansas, station 072623995 (photograph by W.R. Green).

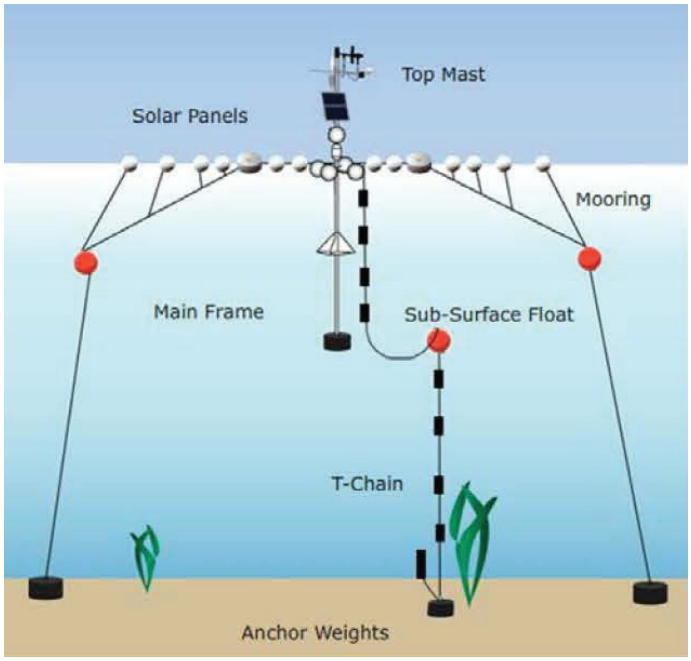

Figure 10–15. Continuous water-quality monitoring system with multiple sensors. (Diagram courtesy of Precision Measurement Engineering, Inc., Vista, California.) The submerged buoys above each anchor allow the buoyed station to rise and fall with the changing pool elevations, keeping a tight mooring all the while.

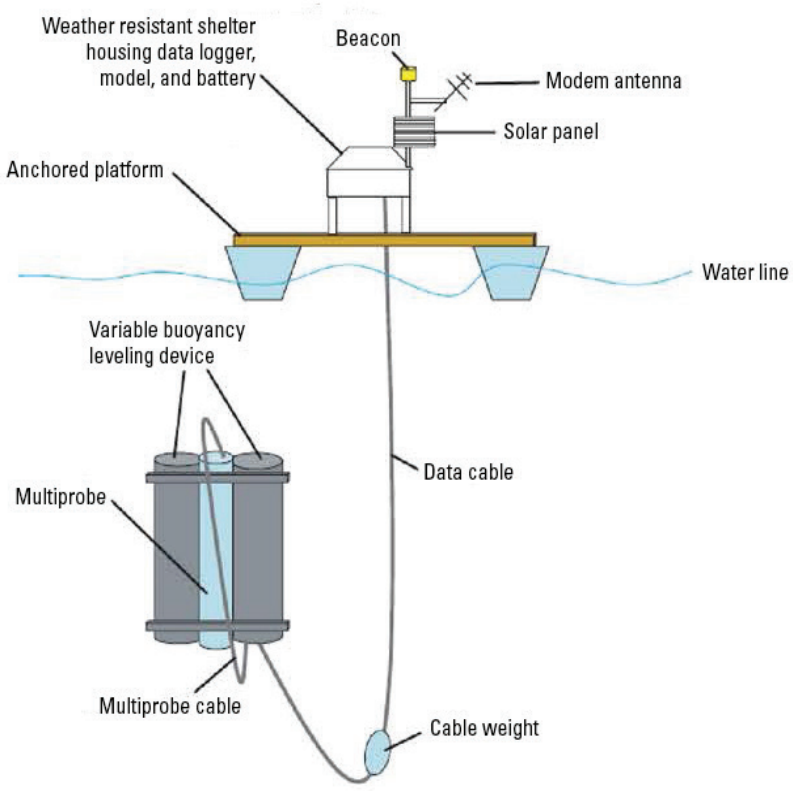

Figure 10–16. Continuous water-quality monitoring system with a single set of sensors that is moved to various depths by use of a variable-buoyancy system (from Rowland and others, 2006, fig. 4).

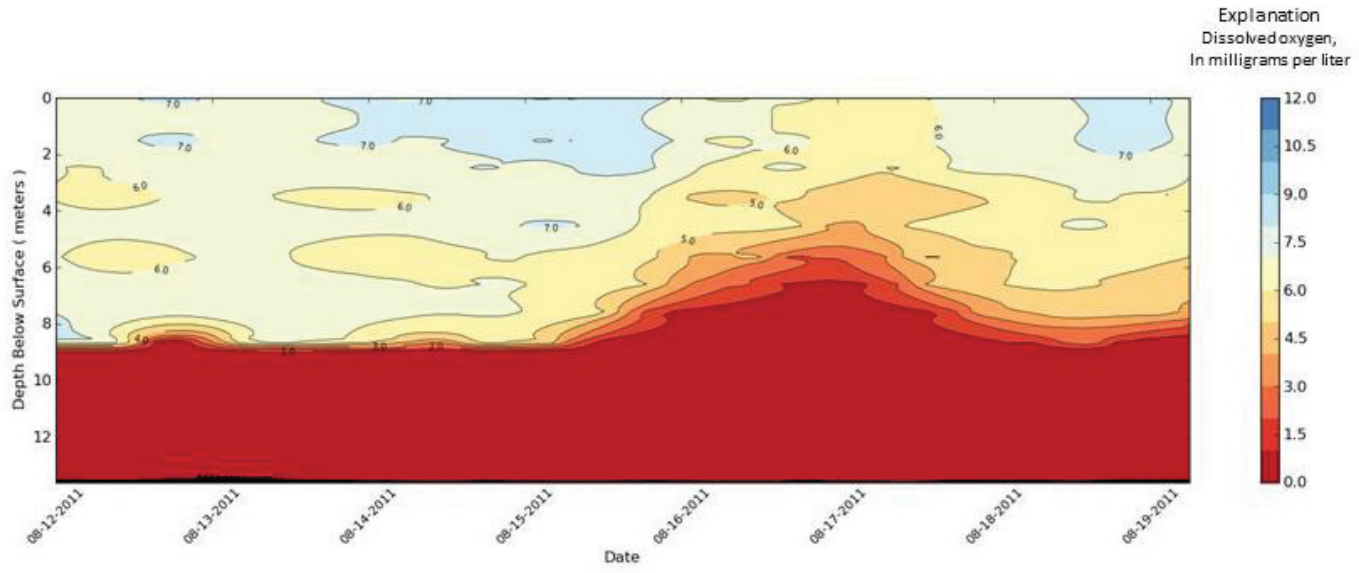

Figure 10–17. Time and depth contour plot of dissolved-oxygen concentrations measured every 5 minutes from a 12-sensor continuous water-quality monitoring platform in Lake Maumelle, Arkansas, station 072632995, August 16–23, 2011. Sensor depths are every 1 meter from 0.5 meter below the surface to 1 meter above the bottom.

10.6 Sampling in the Water Column

Chapters 4 and 5 of the *National Field Manual* describe standard USGS methods (sampling and quality-control strategies, techniques, requirements, and recommendations) for the routine collection and processing of stream and groundwater samples.[4] Analogous sampling strategies, techniques, requirements, and recommendations also apply to USGS studies of lakes and reservoirs, as described in NFM 7.4 and 7.5. NFM 7.5.5 provides specific guidance for sampling cyanobacterial community composition, toxins, and taste and odor compounds, and the use of equipment for various sample types, which are generally applicable for collecting all types of lake and reservoir samples. Studies of cyanobacteria require Teflon-coated samplers but other types of analyses do not necessarily need to use Teflon.

Before sample collection begins, field personnel should take steps to ensure that the samples collected will be representative of the aqueous system being investigated. A representative sample is one that typifies (represents) in time and space that part of the aqueous system to be studied and is delineated by the objectives and scope of the study. Obtaining representative samples is of primary importance for a relevant description of the lake or reservoir condition.

The types of sampling devices (samplers) commonly used to collect surface (NFM 2.2.1.B), discrete-depth (NFM 7.5.5.C), and depth-integrated samples (NFM 7.5.5.D) in lakes and reservoirs are listed in NFM 7.5, table 7.5–6. Detailed descriptions of the samplers and proper uses of these samplers are presented in Britton and Greeson (1987), NFM 2.1.1B, NFM 4.1.3.B, and NFM 4.1.3.C, and U.S. Environmental Protection Agency Standard Methods Sections 1060 and 10200 (American Public Health Association, 2005). The advantages and disadvantages of each sampler type are presented in NFM 7.4, tables 7.4–7 and 7.4–8. The two most common types of instruments used to collect water samples in lakes and reservoirs are the Van Dorn and Kemmerer samplers, each of which consists of a cylindrical tube attached to a depth-labeled rope or wire used to lower the sampler to a specific depth. The Van Dorn sampler has a

[4] NFM chapters 1, 2, and 3 provide information and guidance regarding field preparations, equipment selection, and equipment decontamination for water-quality studies, respectively, that can be applied to or adapted for lake and reservoir water-quality studies.

horizontal cylinder with rubber covers on each end that are kept open until the sampler is lowered to the desired depth. The Kemmerer sampler has a vertical cylinder with stoppers on each end that are held open as the sampler is lowered by a line to a desired depth. These rubber covers or stoppers are triggered to close the ends of the tube using a messenger that is dropped down the line that is holding the sampler.

10.7 Sampling Bottom Material

Bottom material in a lake or reservoir consists of living and nonliving, organic and inorganic material of varying physical, chemical, and biological composition that has been transported from the watershed or produced within the water body. Chemical and biological analysis of bottom materials can address a broad spectrum of objectives in lake and reservoir water-quality studies, such as surveillance monitoring, mass-transport loading, remediation effectiveness, presence or absence of contaminants, and spatial extent and temporal change of chemical constituents. NFM 8 provides information and guidance for selecting sampling site locations, selecting equipment, quality-control samples, and procedures and protocols for the collection, processing, and shipping of bottom-material samples.

Analysis of bottom-material samples can include chemical analysis of the bulk sediment (Braun and others, 2012; Lower Granite Reservoir in eastern Washington; Robertson and others, 2012; Mercer Lake, Wisconsin); chemical (phosphorus) release studies (Robertson and Rose, 2008; Butternut Lake, Wisconsin); and sediment accumulation and reconstruction of past water quality using diatom community analyses (Juckem and Robertson, 2013; Shell Lake, Wisconsin). Field observations are typically recorded to document sample color, texture, odor, benthic organisms, detritus, and other visible characteristics.

Surface grab and core samples in lakes and reservoirs can be collected by wading in the shallow littoral zones. In deeper water bodies, bed-material samples are most often collected by dropping or dragging a sampler from a boat. Sometimes bed material is collected by scuba divers. Grab samples are commonly collected using Ekman, Peterson, or Ponar grab samplers (Lewis and others, 1982). Sediment cores are commonly collected using box, gravity, or piston corers (Van Metre and others, 2004; Juracek, 2011).

10.8 Sampling Biological Components

The ecology of a lake or reservoir system is driven by the ambient physical and chemical conditions, but is often assessed by investigating its biological components. Britton and Greeson (1987), Wetzel and Likens (2000), Moulton and others (2002), American Public Health Association (2005), *National Field Manual* chapter 7 sections 7.1 through 7.5, and the other references cited throughout this chapter provide detailed methods for the collection and processing of aquatic biological and microbiological samples.

- **Phytoplankton** composition and biomass (primary production) provides an integrated assessment water-quality conditions, an indication of eutrophication (nutrient enrichment), and the presence or absence of toxin and taste and odor producing organisms.
- Zooplankton composition and biomass (secondary production) supports both the water-quality and ecological assessment by providing insight to the quality of the food chain and the energy flow through the system.
- Microbial monitoring detects the presence or absence of fecal indicator bacteria and viruses (coliphage) and their pathogens (disease-causing organisms) and the potential contamination from human and animal (wildlife and livestock) waste.

- Benthic (bottom dwelling) invertebrate community composition and abundance, and aquatic macrophyte (native and introduced) distribution and biomass are integrators of past and present water-quality conditions.
- Fish community composition and abundance are integrators of past and present water-quality and ecological health, and they can provide insight into the quality of energy flow through the food chain.

10.8.1 Phytoplankton

Phytoplankton are unicellular photosynthetic organisms existing as single cells, colonies, chains, or filaments that generally are transported passively (some forms are active swimmers) by currents and other mixing processes (Britton and Greeson, 1987; NFM 7.4). Phytoplankton are photosynthetic microorganisms adapted to live partly or continuously in open water (Reynolds, 2006). Photoautotrophic plankton are the major **primary producer** of organic carbon in the pelagic zone of the seas and of inland waters. Phytoplankton blooms can severely affect water quality, either through algal blooms, the production of toxins that lead to fish kills or threats to human health, or through the decomposition of organic matter that can deplete oxygen when the algae die.

Integrated studies of aquatic ecosystems often include measurements of phytoplankton biomass and composition (Britton and Greeson, 1987; NFM 7.4). To maximize the use of phytoplankton data, the sampling sites and methods used for phytoplankton should correspond as closely as possible to those selected for other biological, microbiological, and chemical sampling. Measurements of biomass are described in part above and in the "General Guidelines—Photosynthetic Pigments" section of Britton and Greeson (1987, section 10.4.2.H). The most common measure of the overall amount of algae in a specific area or zone in a water body is a simple chlorophyll *a* concentration. However, phytoplankton identification and enumeration can provide much additional information. Phytoplankton can be identified and quantified using an optical microscope. This method can provide counts (density, number of counting units per milliliter) and the compositional makeup (diversity); it can also provide biomass based on the assumption that the volume of the organisms equals that of water based on displacement (1 mm^3/L = 1 mg/L or 1 μm^3 = 1 µg/L; Wetzel and Likens, 2000). Phytoplankton biomass can then be converted to carbon based on the assumption that the carbon content in different groups of phytoplankton (cyanobacteria, dinoflagellates, diatoms, green algae, and others) is a given portion of their total biomass (for example, carbon = biomass multiplied by 0.11).

- Knowledge of the average chlorophyll a concentration is an indication of the trophic state of a water body.
- Knowledge of species composition can indicate the causes of seasonal changes in biomass and indicate stresses imposed by contaminants that may not be evident from measurements of biomass (chlorophyll a) alone (Britton and Greeson, 1987).
- As bioindicators, phytoplankton and changes in phytoplankton populations can provide two main types of information about water quality (Bellinger and Sigee, 2010)
  - Long-term information—the status quo, and
  - Short-term information—environmental change.
- Changes in phytoplankton communities act as bioindicators and can serve as early warning signals that reflect the "health" status of an aquatic system.

10.8.1.A Sample Collection

A chlorophyll *a* sample is collected by filtering a known amount of sample water (typically collected with a Van Dorn sampler) through a glass-fiber filter (typically 5 μm). The filter is then sealed in aluminum foil and immediately frozen or placed on ice. The filter paper itself is then used for the analysis. The filter is ground up in an acetone solution and either a fluorometer or spectrophotometer is used to quantify the light transmission at a given wavelength, which in turn is used to calculate the concentration of chlorophyll *a*.

Phytoplankton samples can be collected using any of the three general sampling methods described above under "Water Sampling" (section 10.6) and in NFM 7.5.5: surface samples, discrete-depth samples, or depth-integrated samples. For each sample type, a single grab sample may be collected or multiple grab samples may be composited. The types of sampling devices (samplers) commonly used to collect each type of sample are discussed and listed above in table 10–9. A detailed description of the samplers and their proper uses are presented in Britton and Greeson (1987), NFM 2.1.1.B, NFM 4.1.3.B, and NFM 4.1.3.C. Advantages and disadvantages of each sampler type are presented in NFM 7.4, table 7.4–8. Samples should be collected in a manner that does not rupture or deform phytoplankton cells, particularly when species composition is going to be quantified. Generally, sampling devices and **churn splitters** have minimal impact on phytoplankton cell integrity; exceptions are discussed in NFM 7.4, table 7.4–8. See NFM 7.5 for more detail on phytoplankton sample collection and processing.

10.8.1.B Ancillary Data

Ancillary data collected as part of phytoplankton studies depend on the study objectives (NFM 7.5.5). Chlorophyll samples commonly are collected along with the phytoplankton sample. Other commonly measured variables are listed in table 10–1. Generally, all subsamples for laboratory analyses, including phytoplankton community composition, are collected from the same grab or composite sample. The volume of the grab or composite sample must be sufficient for all planned analyses.

10.8.2 Zooplankton

Zooplankton consist of small animals suspended in water that have limited powers of locomotion and that are generally subject to dispersal by the water movements and circulation (Wetzel, 2001). Zooplankton are dominated by four major groups: (1) protists that include **protozoa** and heterotrophic flagellates; (2) rotifers, and two subclasses of crustaceans; (3) cladocerans; and (4) copepods. Zooplankton are major herbivores as well as predators of other zooplankton in lakes and reservoirs (Wetzel and Likens, 2000). In order to better understand lake and reservoir metabolism, it is important to evaluate the composition, biomass, and role of zooplankton within the ecosystem.

10.8.2.A Sample Collection

Britton and Greeson (1987) and Wetzel and Likens (2000) describe in detail collection and processing of zooplankton samples. Zooplankton can be collected with bottles, **bailers** or tubes, water pumps, and plankton nets, followed by filtering the water sample onsite or in the laboratory (Britton and Greeson, 1987; Wetzel and Likens, 2000). Plankton traps, such as tow nets or Schindler-Patalas traps, are often used to collect concentrated zooplankton samples. For more detail on zooplankton sample collection and processing, see Britton and Greeson (1987) and Wetzel and Likens (2000).

10.8.2.B Ancillary Data

Ancillary data collected for zooplankton studies, like phytoplankton samples (above), depend on the study objectives. Commonly measured variables are listed in table 10–1.

10.8.3 Microorganisms

Three groups of potentially pathogenic microorganisms affect the public health acceptability of waters in the United States: fecal indicator bacteria, fecal indicator viruses, and protozoan pathogens. Detailed guidelines for sampling microorganisms that commonly are monitored for environmental assessments are found in NFM 7 and in other references cited in the respective sections below.

10.8.3.A Fecal Indicator Bacteria

Fecal indicator bacteria are commonly used to assess the microbiological quality of water. Detailed guidelines for the collection and processing of fecal indicator bacteria are provided in NFM 7.1, which describes tests that can be completed in the field for identifying and enumerating five types of fecal indicator bacteria: total **coliform** bacteria, fecal coliform bacteria, ***Escherichia coli (E. coli)***, fecal **streptococci**, and **enterococci**. Also included in NFM 7.1 is guidance to collect samples to be analyzed for *Clostridium perfringes* (*C. perfringens*). Although these bacteria are not typically disease causing, they are usually associated with fecal contamination and the possible presence of waterborne pathogens.

The density of indicator bacteria is a measure of suitability of water for body-contact recreation or for consumption. Sterile techniques should be followed and their use documented in field notes when collecting and processing samples for fecal indicator bacteria. The equipment and supplies needed for sample collection, processing, and analysis (presence-absence or most-probable-number analysis) of fecal indicator bacteria in water and sediment are detailed in NFM 7.1.

The areal and temporal distribution of bacteria in the water and bottom sediments of lakes and reservoirs can be as variable as the distribution of suspended material because bacteria commonly are associated with solid particles. Because of this variability, it may be necessary to collect multiple samples throughout the lake to accomplish the data-quality objectives. At least three bottom-material samples should be collected from each site at the same depth and composited (NFM 7.1.2.C) due to the spatial heterogeneity of bacteria. Refer to NFM 7.1 for sampling methods and quality-control and quality-assurance procedures.

10.8.3.B Fecal Indicator Viruses

Detailed guidelines for the collection and analysis of fecal indicator viruses (as indicated by **coliphage** estimates) are provided in NFM 7.2. Coliphages are viruses that are used as indicators of fecal contamination and of the microbiological quality of the water. Coliphages are not pathogenic to humans. Somatic coliphages and F-specific coliphages are used as viral indicators and are abundant in waters polluted with sewage contamination (International Association of Water Pollution Research and Control Study Group on Health Related Water Microbiology, 1991).

In lakes and reservoirs, the hand-dip, grab-sample, or sterile-point-sampler methods can be used to collect the sample (NFM 7.2.1). The specific equipment and supplies used to collect and analyze samples for fecal indicator viruses must be decontaminated and rendered sterile before and after sampling. Sterile conditions also must be maintained during collection, preservation, transport, and analysis of fecal indicator virus samples (NFM 7.2.2). Specific procedures have been developed that must be strictly followed (NFM 7.2.2). After collection, immediately chill samples in an ice chest or refrigerator at 1 to 4 °C, without freezing. To ship samples to the laboratory, double bag the sample containers before placing them into the

bagged ice in a cooler. Seal the analytical services request form and, if required, the chain-of-custody form in doubled plastic bags and tape these forms to the inside lid of the cooler being shipped to the laboratory. Check that the sample identification and relevant information for use by the laboratory have been recorded correctly. The laboratory must begin the analysis of samples within 48 hours of sample collection.

10.8.3.C Protozoan Pathogens

Cryptosporidium and ***Giardia*** are the principal protozoan pathogens that have been identified as the cause of several outbreaks of waterborne diseases and that have compromised the acceptability of public water supplies within the United States (Centers for Disease Control and Prevention, 2012; Xiao and others, 2013). The oocysts and cysts of protozoa survive longer in the environment and have greater resistance to disinfection than fecal indicator bacteria. Detailed guidelines for the collection and analysis of protozoan pathogens are provided in NFM 7.3.

Because there are cyclical and seasonal variations in their concentrations, a sampling program for *Cryptosporidium* oocysts and *Giardia* cysts needs to be conducted over an extended period of time (LeChevallier and Norton, 1995; Wilkes and others, 2009). A summary of requirements for sample-collection equipment, procedures for sample preservation, and holding-time requirements are given in NFM 7, section 7.3, table 7.3–2. In lakes and reservoirs, samples are collected using sterile equipment (see NFM 2, section 2.1.1.B) and adapting the sterile techniques described in NFM 7.1,1, 7.2,1, and 7.3.1.

The field and laboratory procedures for protozoan samples described in NFM 7, section 7.3.3, are specific to analysis by USEPA Method 1623: *Cryptosporidium* and *Giardia* in Water by Filtration/IMS/FA (U.S. Environmental Protection Agency, 2005). Method 1623 should be performed in a certified laboratory by a qualified analyst.

10.8.4 Benthic Fauna

Benthic fauna are animals living on and in the bed sediments and on plants in the littoral zone of lakes and reservoirs; the species are usually highly diverse (Wetzel and Likens, 2000). The segmented worms (oligochaetes and leaches), microcrustacea (ostracods), and macrocrustracea (mysids, isopods, decapods, and amphipods) are the major components of benthic fauna of freshwaters (Wetzel and Likens, 2000). As part of many lake and reservoir studies, reliable quantitative estimates of the amount and distributions of the benthic fauna are needed. The objective of many benthic fauna studies is focused on describing the abundance of insect larvae or other immature insect forms.

10.8.4.A Sample Collection

Wetzel and Likens (2000) describe the collection and analysis techniques for benthic fauna in detail. Britton and Greeson (1987) describe in detail the collection and processing techniques used specifically for benthic invertebrates.

- Benthic invertebrates can be collected using:
  - Ekman, Ponar, VanVeen, and Petersen-type dredges or grabs
  - A smaller Ponar dredge (for example, the “Petite Ponar Grab”)
  - Core samplers, when an undisturbed sample is needed

10.8.4.B Ancillary Data and Sample Processing

Ancillary data typically collected for benthic fauna studies, like other biological samples (above), depend on the study objectives. Some of the common measured variables collected in benthic fauna studies are listed in table 10–1.

10.8.5 Macrophytes

Macrophytes (typically referred to as aquatic plants) include vascular plants, bryophytes, and algae that can be seen without magnification. Characteristic forms of vascular plants found in aquatic habitats are (1) emergent rooted aquatics, (2) floating-leaved rooted aquatics, (3) submersed rooted aquatics, and (4) free-floating aquatics (Britton and Greeson, 1987). The growth of aquatic macrophytes is typically controlled by the availability of nutrients. Nutrient enrichment may result in excessive plant growth that can become a major nuisance, causing water-quality problems. Many nonnative submersed and emergent aquatic macrophytes invade and grow unchecked in many lakes and reservoirs. Some of these plants may form surface mats of vegetation.

The distribution and growth of aquatic macrophytes depend on depth of water, illumination, nutrient availability, water quality, water clarity, substrate, and water velocity (Britton and Greeson, 1987). Different species grow at different depths and light intensities. Sometimes the types of rooted vascular plants are arranged in zones corresponding to successively greater depths. The ability to grow in deeper water is impacted by turbidity. Free-floating aquatic plants may occur anywhere on the water surface, depending on wind direction and intensity and surface flow.

10.8.5.A Sample Collection and Processing

- A quantitative description of the distribution of aquatic macrophytes may be obtained by careful sampling within defined quadrats (Wetzel and Likens, 2000). Sampling sites can be selected using either a stratified random design or along a transect(s). Much of the biomass of rooted aquatic plants can occur below ground; therefore, it is essential to sample biomass from both above and below ground in any quantitative study. Replicate sediment core samples may be used to determine below-ground biomass.
- Aquatic macrophyte samples are typically collected by hand or with grappling hooks, rakes, oyster tongs, or dredges (Britton and Greeson, 1987).
- Entire plants should be collected, including the flowers, seeds, and if present, roots, and rhizomes or tubers, if possible.

For more detail on aquatic macrophyte collection and processing, see Britton and Greeson (1987) and Wetzel and Likens (2000).

10.8.5.B Ancillary Data

Ancillary data typically collected as part of aquatic macrophyte studies, like other biological samples (above), depend on the study objectives. Some of the common variables measured as part of macrophyte surveys are listed in table 10–1.

10.8.6 Fish

Fish are the most common vertebrates in lakes and reservoirs. Their growth and survival depend, in part, on phytoplankton and zooplankton (food web) interactions and energy flow. Therefore, the amount and types of fish present are indicators of the ecological health of a lake or reservoir. Fish are often sampled to assess community structure, examine gut contents, and perform tissue-contaminant analysis. As top predators in the aquatic food chain, they tend to biomagnify and bioaccumulate toxins that move through the food chain, such as methylated mercury.

10.8.6.A Sample Collection and Processing

Collecting fish in a quantitative manner requires knowledge of the selectivity, limitations, and efficiency of the different types of sampling gear (Britton and Greeson, 1987). Because of the nonrandom distribution of fish populations, the choice of sampling method, time of sampling, and frequency depend on the objectives of the particular study. The American Fisheries Society (Zale and others, 2013) recently updated its description of fish-sampling techniques to describe both passive and active capture techniques, as well as acoustical methods. In "Standard Methods for Sampling North American Freshwater Fishes" (Bonar and others, 2009), sections are dedicated to describing sampling of both warm- and coldwater fish in small and large standing waters. Warmwater fish typically occupy the littoral zones of lakes and reservoirs. Warmwater fish are typically of riverine origin and are oriented to the shoreline bottom (Miranda and Boxrucker, 2009). Few warmwater fish in the United States are strictly pelagic. Fish that do occupy the pelagic zone, like white, striped, and hybrid bass, originally were from fish families of marine origin. Coldwater fish typically occupy the hypolimnion of lakes and reservoirs and reservoirs, during stratified periods, but may be found throughout the water body when it is unstratified. Water bodies that support fish (such as trout and salmon) throughout the year are referred to as coldwater lakes and reservoirs (Beauchamp and others, 2009).

The most common active and passive gear used to sample fish in the littoral and pelagic zones include electroshocking boats, shoreline seines, purse seines, gill nets, fyke nets, trawls, and hydroacoustic devices. Miranda and Boxrucker (2009) report that each type of gear is particularly useful for sampling selected species, life stages, or species that occupy distinct habitats. Each type of gear and survey, however, provides only an approximate representation of the fish assemblage inhabiting the lake or reservoir. Miranda and Boxrucker (2009) found that electrofishing and fyke netting were the most useful tools for describing the fish community in the littoral zone, whereas, gill netting and hydroacoustic techniques were best suited to describe fish communities in the pelagic zone.

10.8.6.B Ancillary Data

Ancillary data typically collected as part of fish studies, like other biological studies (described above), depend on the study objectives. Some of the variables commonly measured as part of fish surveys are listed in table 10–1. Some information that is especially useful includes specific electrical conductance to adjust the electrofishing settings, water temperature, turbidity (Secchi depth), and water depth (Miranda and Boxrucker, 2009). To help understand the results from fyke and gill nets, the dissolved-oxygen concentration at 1 m above the bottom and the average bottom slope should be measured. It is also important to document how long each type of gear was used.

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Glossary

Abiotic: Denoting nonliving (physical or chemical) components of the environment.

Algae: Photosynthetic microscopic organisms that may occur as single cells, colonies, or filaments.

Allochthonous: Denoting material or energy stored in organic matter that was brought into a lake or reservoir.

Allophycocyanin: An accessory (blue) pigment to chlorophyll readily found in cyanobacteria (blue-green algae) and red algae.

Autochthonous: Denoting material or energy stored in photosynthetically formed organic matter synthesized within the lake or reservoir.

Autotrophic: Denoting an organism that is capable of synthesizing its own food from inorganic substances using light or chemical energy. Green plants, algae, and certain bacteria are autotrophs.

Bailer: A commonly used **thief sampler** consisting of a cylinder (of various diameters and lengths and types of construction material, such as stainless steel, polyvinyl chloride, or fluorocarbon polymer) with double check-valves (top and bottom), with a bottom emptying device.

Benthic zone: The area of a water body associated with the bottom of a lake or reservoir.

Benthic fauna: The animal community associated with and living on the bottom of lakes and reservoirs.

Biotic: Denoting the living (microbial, plant, and animal) components of the environment.

Bloom: Refers to a large population or extremely high cell densities of phytoplankton; a proliferation of phytoplankton dominated by a single or a few species; or a visible accumulation of phytoplankton at the water surface.

Chlorophyll: The green photosynthetic pigment found in cyanobacteria (blue-green algae) and in the chloroplasts of algae and plants.

Churn splitter(s): A bucket or container (with lid and bottom spigot) used to mix and composite or subdivide a water sample. Churn splitters are of various volumes and types of construction material, such as polypropylene, polyethylene, or fluoropolymer plastic.

Coliform: A broad class of bacteria commonly used as an indicator of the sanitary quality of water.

Coliphage (somatic and F-specific): A type of bacteriophage (bacteria-specific virus) that infects *Escherichia coli* and that is commonly used as a viral indicator.

***Cryptosporidium*:** Oocyst-producing unicellular microorganisms that can cause disease in humans and other animals.

Cyanobacteria: True bacteria with prokaryotic cell structure; however, cyanobacteria also have chlorophyll *a*, a photopigment characteristic of eukaryotic algae and higher plants. Structurally, the cyanobacteria are bacteria-like but functionally, the cyanobacteria are algae-like. Cyanobacteria are often called blue-green algae.

Data sonde: Multiparameter water-quality monitoring instrument used to measure key water-quality parameters (typically temperature, pH, specific electrical conductance, dissolved oxygen, and others) in the field.

Destratification: The development of vertical thermal convection or wind-induced circulation within a thermally stratified lake or reservoir that progressively erodes the metalimnion from above and continues until the water body becomes isothermal—often referred to as "lake turnover." (See also "Thermal stratification.")

Detritus: Nonliving particulate organic matter found in streams, lakes, and reservoirs.

Diagnostic study: A study that typically describes or explains the water quality of a lake or reservoir.

Dimictic: Lakes or reservoirs that have two extended mixing periods in a year, once after summer thermal stratification and the second after winter ice cover.

Dissolved organic matter: A broad classification of organic molecules defined as less than 0.5 μm in diameter.

Diurnal: Having a daily cycle, recurring every day.

Enterococcus: Bacteria normally found in the feces.

Epilimnion: The warm, upper layer of a stratified lake or reservoir.

***Escherichia coli (E. coli)*:** Gram-negative, rod-shaped bacterium that is commonly found in the lower intestine of warm-blooded organisms, some strains of which are pathogenic.

Euphotic zone: See photic zone.

Eutrophic: A water body that has high nutrient content and levels of production.

Eutrophication: The process of nutrient enrichment (particularly nitrogen and phosphorus) in aquatic ecosystems leading to increased production.

Flushing rate: The rate at which the volume of water in a lake or reservoir is displaced—typically computed as the mean annual inflow or outflow divided by the volume (flushes per day or year).

***Giardia*:** Cyst-producing unicellular microorganisms that can cause disease in humans and other animals.

Heterotrophic: Denoting a type of organism that depends on previously formed organic compounds to provide energy for maintenance, growth, and replication. An organism that cannot synthesize its own food and is dependent on complex organic substances for nutrition is a heterotroph.

Hypereutrophic: Denoting a water body that has a very high nutrient content and levels of production.

Hypolimnion: The cold, dense bottom layer of a stratified lake or reservoir; the hypolimnion often becomes anoxic (little or no dissolved oxygen) in productive systems.

Interpretive study: A study that attempts to explain processes, outcomes, and results for a water body.

In vivo: Refers to a measurement made within the natural environmental setting of the organism.

Isothermal: Uniform temperature. In lakes and reservoirs, isothermal refers to the entire water column being of constant temperature (density).

Lacustrine zone: The open water, lentic area in a water body. In reservoirs, the zone is at the downstream end, nearest the dam that resembles lake-like, lentic conditions. The lacustrine zone is

characterized by a longer residence time, lower concentrations of dissolved nutrients and suspended sediment, clearer water, and a deeper euphotic zone.

Lake: A naturally formed inland water body of considerable size, localized in a basin that is surrounded by land and is apart from a river, stream, or other form of moving water that serves to feed or drain the lake.

Lentic: Denoting standing or relatively still water, relating to or living in still water, as opposed to **lotic** (moving water).

Light extinction (attenuation): The reduction of light (radiant energy) with depth from both scattering and adsorption by suspended materials.

Limnology: The study of the physical, chemical, and biological interactions within inland water bodies.

Littoral: The region of the shore of and shallow bottom of a lake or reservoir where rooted vegetation can inhabit.

Lotic: Denoting flowing water, relating to or living in flow flowing water, as opposed to lentic (standing or still water).

Mesotrophic: Denoting a water body that has a moderate nutrient content and levels of production.

Metalimnion: The middle layer of a stratified lake or reservoir; the metalimnion is characterized by substantial decreases in temperature with depth.

Mixed layer: The surface layer of water in a lake or reservoir, stratified or not, that is relatively uniform in temperature and mixes as the result of wind and wave actions. This layer is often referred to as the epilimnion.

Monomictic: Denoting lakes or reservoirs that mix (destratify) for one prolonged period of the year, typically after summer thermal stratification.

MOCC: Motoraboat Operator Certification Course (USGS-SAF-MOCC-S1657-UDT).

Oligotrophic: Denoting a body of water with a low nutrient content and levels of production.

PAR (photosynthetic active radiation): Photosynthetically Active Radiation (PAR) measures irradiance or the amount of sunlight or ambient light that diffuses through water compared to surface light. PAR focuses on the dynamics of the photic zone, typically 1–5 meters below the surface (*http://disc.sci.gsfc.nasa.gov/hydrology/data-holdings/nldas-parameters/photo-active-radiation*).

Particulate organic matter: Organic matter defined as greater than 0.5 micrometers (μm) in diameter.

Pelagic: Denoting the free open water area of a lake or reservoir.

Photic (euphotic) zone: Region of water column where there is enough light to support photosynthesis; typically defined as the region that extends from the surface to the depth where light is approximately 1 percent of that at the surface.

Photosynthetic active radiation: See PAR.

Phycoerythrin: An accessory (red) pigment to chlorophyll that is unique to the cyanobacteria.

Phytoplankton: The assemblage of small plants or photosynthetic bacteria suspended in the water having no or limited powers of locomotion.

Primary producer: Any green plant or any of various microorganisms like phytoplankton and cyanobacteria that can convert light energy (or chemical energy) into organic matter.

Profundal zone: The deeper area of a lake or reservoir that is free of vegetation.

Protozoa: A diverse group of unicellular eukaryotic organisms, many of which are motile.

Reconnaissance study: A study designed to provide a basic description of a water body and help provide information to scope future investigations.

Refugia (plural of refugium): An area of a water body that has escaped ecological changes occurring elsewhere and so provides a suitable habitat for relict species.

Reservoir: Engineered systems (basically consisting of a dam constructed across a topographical constriction in a river valley) for the purpose of water management through planned releases of impounded water.

Residence time: The average time spent by a given water particle in a water body—water body volume divided by mean annual inflow or outflow (days or years).

Riverine zone: The up-reservoir lotic part of a reservoir characterized by higher flow, shorter residence time, and higher levels of nutrients and suspended solids. **Abiotic** turbidity often limits the thickness of the photic zone.

Shoreline development ratio: The ratio of the length of the shoreline to the length of the circumference of a circle whose area is equal to that of the lake or reservoir.

Streptococci: A group of gram-positive bacteria (genus Streptococcus), some strains of which can cause disease.

Thermal stratification: Refers to formation of layers with a vertical change in the temperature in lakes and reservoirs when water temperatures are above 4 ^{o}C (results in warmer water above colder water), or when temperatures are below 4 ^{o}C (results in colder water above warmer water).

Thermocline: The depth in lakes and reservoirs where the temperature gradient is greatest.

Thief sampler: A water-sample collection device used to collect instantaneous discrete water samples. The most commonly used thief samplers are the Kemmerer sampler, Van Dorn sampler, and double check-valve bailer with bottom emptying device. These samplers are available in various sizes and mechanical configurations and are constructed of various types of material (such as stainless steel, glass, polyvinyl chloride, and fluorocarbon polymer).

Transitional zone: The mid-reservoir zone between the up-reservoir riverine zone and the lacustrine zone at the lower end of the reservoir, typically characterized by higher phytoplankton productivity and biomass occurring in conjunction with increasing reservoir size (volume) and residence time, sedimentation of suspended inorganic materials, and increased light penetration.

Trophic state: The level of productivity in a lake or reservoir. The four main trophic states are oligotrophic, mesotrophic, eutrophic, and hypereutrophic.

Turbidity: The cloudiness or haziness of a fluid caused by the presence of suspended and dissolved matter, such as clay, silt, finely divided organic matter, plankton and other microscopic organisms, organic acids, and dyes.

Zooplankton: Small animals that feed on bacteria and phytoplankton, and that are suspended in water with limited powers of locomotion.