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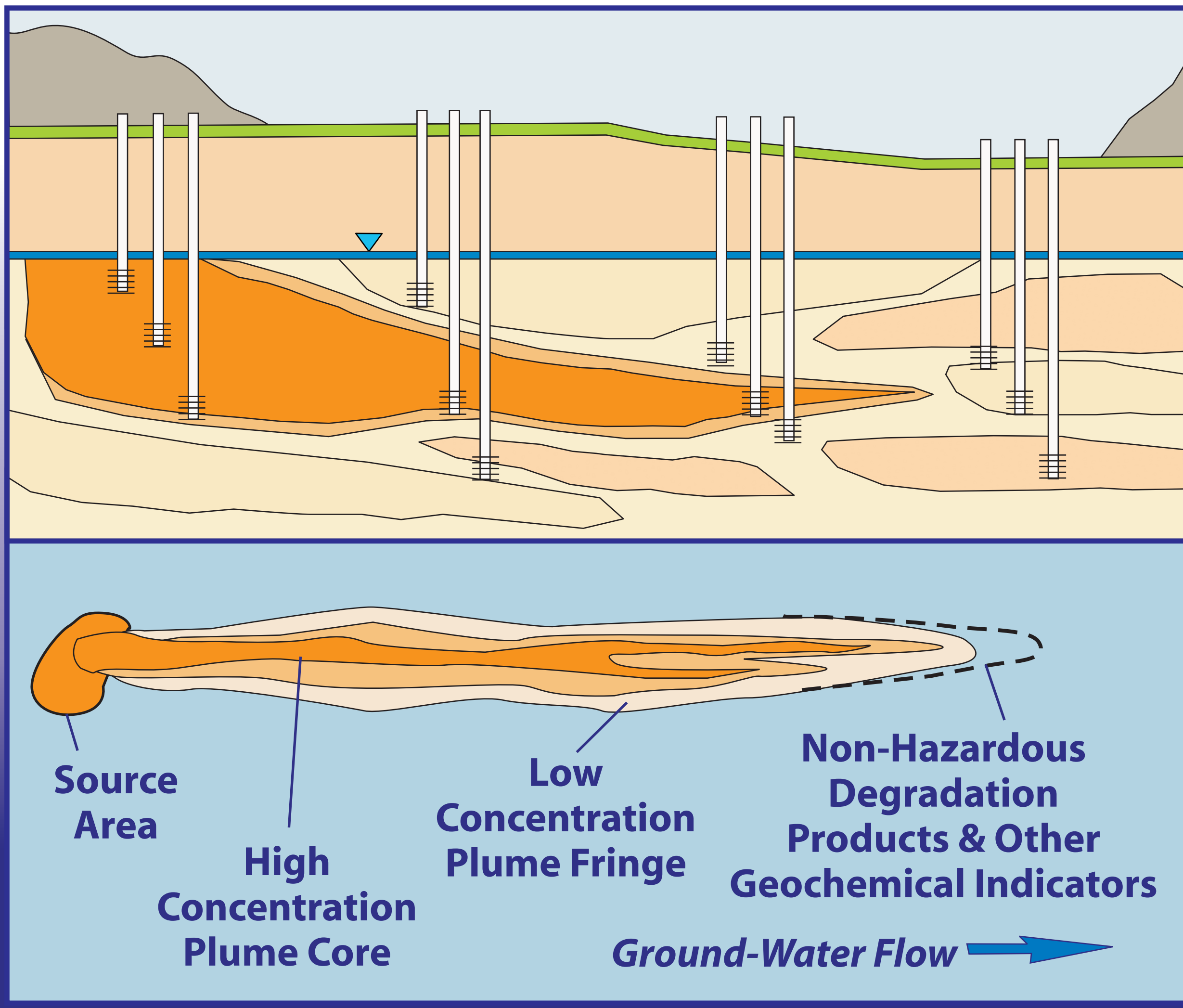
Performance Monitoring of MNA Remedies for VOCs in Ground Water



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Performance Monitoring of MNA Remedies for VOCs in Ground Water

Daniel F. Pope
Dynamac Corporation
3601 Oakridge Boulevard
Ada, OK 74820

Steven D. Acree
U.S. EPA, Office of Research and Development
National Risk Management Research Laboratory
Ground Water and Ecosystems Restoration Division
Ada, OK 74820

Herbert Levine
U.S. EPA, Region 9
Superfund Division
San Francisco, CA 94105

Stephen Mangion
U.S. EPA, Region 1
Office of Research and Development
Boston, MA 02114

Jeffrey van Ee
U.S. EPA, Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Las Vegas, NV 89193

Kelly Hurt and Barbara Wilson
Dynamac Corporation
3601 Oakridge Boulevard
Ada, OK 74820

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Project Officer
David S. Burden
Ground Water and Ecosystems Restoration Division
National Risk Management Research Laboratory
Ada, OK 74820

NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

NOTICE

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here under EPA Contract Nos. 68-C-99-256 and 68-C-02-092 to Dynamac Corporation, Ada, Oklahoma. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Plan.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

Effective performance monitoring for remedies that rely on the natural attenuation of contaminants is a crucial element of remedial design and implementation. Effective monitoring system designs are formulated from an enhanced understanding of the migration and ultimate fate of the contaminants in the site-specific environment. This document provides technical recommendations regarding the types of monitoring parameters and analyses useful for evaluating the effectiveness of the natural attenuation component of ground-water remedial actions. The information will be helpful during the design of the performance monitoring plan as well as during its implementation.

Stephen G. Schmelling, Director
Ground Water and Ecosystems Restoration Division
National Risk Management Research Laboratory

TABLE OF CONTENTS

Page

Page

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS AND ABBREVIATIONS

Acronym	***Definition***
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
COCs	Contaminants of Concern
DCE	Dichloroethene
DNAPL	Dense Nonaqueous Phase Liquid
DQA	Data Quality Assessment
DQO	Data Quality Objectives
EPA	U.S. Environmental Protection Agency
LNAPL	Light Nonaqueous Phase Liquid
MCL	Maximum Contaminant Level
MTBE	Methyl-t-Butyl Ether
MNA	Monitored Natural Attenuation
NAPL	Nonaqueous Phase Liquid
OSWER	Office of Solid Waste and Emergency Response
PCE	Perchloroethene (tetrachloroethene)
PRGs	Preliminary Remediation Goals
QA/QC	Quality Assurance/Quality Control
RAOs	Remedial Action Objectives
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
TCE	Trichloroethene
TEA	Terminal Electron Acceptor
TICs	Tentatively Identified Compounds
VC	Vinyl Chloride

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ABSTRACT

Environmental monitoring is the major component of any remedy that relies on natural attenuation processes. The objective of this document is to identify data needs and evaluation methods useful for designing monitoring networks and determining remedy effectiveness. Effective monitoring of natural attenuation processes involves a three-dimensional approach to network design and clearly defined performance criteria based on site-specific remedial action objectives. Objectives for the monitoring program will be met through routine evaluations of institutional controls and measurements of contaminant, geochemical, and hydrologic parameters. These data are used to evaluate changes in three-dimensional plume boundaries, contaminant mass and concentration, and hydrological and geochemical changes that may indicate changes in remedy performance.

Data interpretation focuses on detection of spatial and temporal changes, and assessment of their impacts on the achievement of site-specific goals. Particular changes of interest include:

- Progress toward contaminant removal objectives and indications of additional contaminant releases,
- Contaminant detections at the horizontal and vertical plume boundaries that may indicate plume expansion,
- Geochemical changes (e.g., oxidation-reduction (redox) conditions) indicative of possible changes in contaminant transformation rates,
- Changes in ground-water flow rates or directions such that contaminants may move into previously unimpacted areas, and
- Changes in land and resource uses that threaten the effectiveness of institutional controls.

Decisions regarding remedy effectiveness and the adequacy of the monitoring program will generally result in either continuation of the program, program modification, implementation of a contingency or alternative remedy, or termination of the performance monitoring program. Such decisions are appropriately based on specific, quantifiable performance criteria defined in the monitoring plan. Continuation of the program without modification would be supported by contaminant concentrations behaving according to remedial expectations while ground-water flow and geochemical parameters remain within acceptable ranges. Modification of the program, including increases or decreases in monitoring parameters, frequency, or locations, may be warranted to reflect changing conditions or improved understanding of natural attenuation processes at the site. Situations that may trigger implementation of a contingency or alternative remedy include:

- Increasing contaminant concentrations or trends not predicted during remedy selection or indicative of new releases,
- Contaminant migration beyond established plume or compliance boundaries,
- Contaminants not decreasing at a rate sufficient to meet remediation objectives,
- Changes in land or ground-water use that have the potential to reduce the protectiveness of the remedy, and
- Contaminants observed at locations posing or having the potential to pose unacceptable risks to receptors.

Chapter 1
INTRODUCTION

1.1 Purpose

The term "monitored natural attenuation," as used in this document and in the Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P (U.S. EPA, 1999a), refers to "the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods." Performance monitoring will be an essential component of the remedy to ensure site-specific objectives are achieved.

This document is designed to be used during preparation and review of long-term monitoring plans for sites where MNA has been or may be selected as part of the remedy. Performance monitoring system design depends on site conditions and site-specific remedial objectives; this document provides information on technical issues to consider during the design process. Discussions include details of issues concerning monitoring parameters, locations (i.e., three-dimensional monitoring locations relative to the plume), and monitoring frequencies. This document does not provide details of particular methodologies for sampling, analysis, modeling, or other characterization tools.

Nothing in this document changes Agency policy regarding remedial selection criteria, remedial expectations, or the selection and implementation of MNA. This document does not supercede any guidance. It is intended for use as a technical reference in conjunction with other documents, including OSWER Directive 9200.4-17P, "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (U.S. EPA, 1999a), and "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (U.S. EPA, 1998a).

1.2 Scope

This document focuses on chlorinated solvent compounds and common fuel-related aromatic compounds (*i.e.,* benzene, toluene, ethylbenzene, and xylenes (BTEX)) dissolved in ground water within porous media. These compounds comprise a significant portion of current ground-water pollution problems, and there is a considerable body of information available concerning their behavior in the subsurface. It is necessary to have a detailed understanding of the behavior of a contaminant in the subsurface in order to properly evaluate natural attenuation processes and develop an adequate monitoring plan. The limited data that may be available on subsurface behavior of other contaminants increase the difficulty of conducting adequate evaluations of remedy performance. Contaminants such as inorganic compounds, radionuclides, fuel oxygenates (*e.g.,* methyl-t-butyl ether (MTBE)), explosives, and wood treating chemicals are not specifically addressed in this document. Many of these contaminants behave differently from those on which this document is focused. Such compounds may not be attenuated at rates sufficient to be protective of human health and the environment while other compounds associated with a given release may be rapidly attenuated. For example, MTBE has been used as a common fuel component (U.S. EPA, 2003a). At many sites, the potential for significant migration of MTBE may be greater than that of the BTEX contaminants. The determination of conditions under which MTBE may be readily attenuated in the subsurface is an area of ongoing research. Although the details of an appropriate performance monitoring program are specific to the contaminant under consideration, the type of monitoring and evaluation methods that are discussed will often be applicable to contaminants such as MTBE that are not explicitly considered in this document. Soils and/or sediment-only remedies are discussed only in reference to contaminant sources for ground water.

This document will focus on contaminants in the aqueous-phase plume. As stated in U.S. EPA (1999a), it is expected that source control will be a fundamental component of any MNA remedy. The degree to which contaminant sources are removed or controlled directly affects the effectiveness and remedial time frame for MNA remedies. In general, the discussions provided in this document will be most applicable to sites with controlled sources or no materials that provide continuing sources for ground-water contamination (*e.g.*, NAPL). Accordingly, the contaminant release scenario used in figures throughout the document is one in which only a small volume of NAPL was released to the subsurface and effective source removal actions were subsequently implemented.

This document is limited to evaluations performed in porous-media settings. Detailed discussion of performance monitoring system design in fractured rock, karst, and other such highly heterogeneous settings is beyond the scope of this document. Ground water and contaminants often move preferentially through discrete pathways (e.g., solution channels, fractures, and joints) in these settings. Existing techniques may be incapable of fully delineating the pathways along which contaminated ground water migrates. This greatly increases the uncertainty and costs of assessments of contaminant migration and fate and is another area of continuing research. As noted in OSWER Directive 9200.4-17P (U.S. EPA, 1999a), "MNA will not generally be appropriate where site complexities preclude adequate monitoring." The directive provides additional discussion regarding the types of sites where the use of MNA may be appropriate.

This document focuses on monitoring the saturated zone, but site characterization and monitoring for MNA or any other remedy typically would include monitoring of all significant pathways by which contaminants may move from source areas and contaminant plumes to impact receptors (e.g., surface water and indoor air).

Chapter 2
PERFORMANCE MONITORING SYSTEM DESIGN

2.1 Introduction

Designing a monitoring system to assess natural attenuation processes and the effectiveness of those processes with respect to achieving remedial objectives involves making site-specific decisions regarding:

- Monitoring parameters,
- Number and location of monitoring points,
- Monitoring frequency, and
- Methods to analyze and interpret the data obtained from monitoring points.

Sections 2.2 and 2.3 of this chapter discuss typical objectives of performance monitoring and ways to develop site-specific objectives and performance criteria such that an MNA remedy can be evaluated based on measurable criteria.

Sections 2.4 and 2.5 discuss general principles of development of the MNA conceptual site model and the monitoring network design, based on data collected during the site characterization efforts. These general principles provide a framework for understanding the controlling factors that guide the monitoring decisions listed above. The data that generally should be available from the site characterization effort are discussed in detail.

Section 2.6 of this chapter addresses the specific application of these general principles to demonstrating effectiveness of MNA for attaining the performance monitoring objectives in Table 1.

The final section of this chapter (Section 2.7) provides suggested content and format for performance monitoring plans.

2.2 Objectives of Performance Monitoring

The OSWER Directive 9200.4-17P (U.S. EPA, 1999a) provides eight specific objectives for the performance monitoring program of an MNA remedy (Table 1). This document will discuss the technical aspects of monitoring systems typically used to meet these and similar objectives. The objectives usually will be met by implementing a performance monitoring program that routinely evaluates the effectiveness of institutional controls and measures contaminant concentrations, geochemical parameters (e.g., oxidation-reduction (redox) parameters, dissolved organic carbon, pH), and hydrologic parameters. These data will be used to evaluate the dynamic behavior of the plume over time, including:

Table 1. Objectives for Performance Monitoring of MNA (U.S. EPA, 1999a)

1)	Demonstrate that natural attenuation is occurring according to expectations,
2)	Detect changes in environmental conditions (*e.g.,* hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes,
3)	Identify any potentially toxic and/or mobile transformation products,
4)	Verify that the plume(s) is not expanding downgradient, laterally or vertically,
5)	Verify no unacceptable impact to downgradient receptors,
6)	Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy,
7)	Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors, and
8)	Verify attainment of remediation objectives.

- Changes in three-dimensional plume boundaries,
- Changes in the geochemical setting (*i.e.*, as indicated by the geochemical parameters, especially the redox parameters such as redox potential, dissolved oxygen, nitrate/nitrite, manganese (II), iron (II), sulfate, and methane) that may be indicative of changes in biotic or abiotic processes affecting the rate and extent of natural attenuation, and
- Contaminant mass and/or concentration reductions indicative of progress toward contaminant reduction objectives.

Plume behavior can then be evaluated to judge the effectiveness of the MNA remedy, the adequacy of the monitoring program, and the adequacy of the conceptual site model for MNA. On the basis of these judgements, decisions may be made for subsequent phases of site operations, including:

- Continue the performance monitoring program without change,
- Modify the performance monitoring program,
- Modify the institutional controls,
- Implement a contingency or alternative remedy, or
- Terminate performance monitoring.

As is the case for other remedies, performance monitoring for MNA remedies continues until all remedial action objectives have been met (*e.g.*, contaminant concentrations throughout the site meet remedial requirements). The last phase of performance monitoring (verification monitoring) may involve changes to the performance monitoring program as appropriate to verify remedial goals have been met (*e.g.*, a period of more frequent monitoring and/or more spatially dense monitoring, especially if monitoring locations or frequency had been reduced over an extended performance monitoring period).

2.3 Developing Site-Specific Monitoring Objectives and Performance Criteria for MNA

Site-specific performance monitoring objectives for MNA are derived from site-specific remedial action objectives (RAOs) and preliminary remediation goals (PRGs). RAOs provide a general description of what the cleanup will accomplish (*e.g.*, restoration of ground water). PRGs are the more specific statements of the desired endpoint concentrations or risk levels, for each exposure route, that are believed to provide adequate protection of human health and the environment based on preliminary site information. For guidance concerning remedial objectives refer to current, program-specific documents (*e.g.*, U.S. EPA, 1997a; U.S. EPA, 2004).

The site-specific performance monitoring objectives are general statements of what is to be required of the monitoring network (*e.g.*, detect plume expansion). Performance criteria are detailed statements that set forth standards or requirements based on specific measurements. For instance, it might be specified that the monitoring system be able to detect a contaminant concentration of 1 μg/L in ground water in the area between the known contaminated aquifer and a receptor. Clearly stated performance monitoring objectives, accompanied by specific, quantifiable performance criteria, are useful for designing and evaluating the performance monitoring system, and assessing MNA remedy effectiveness. RAOs, PRGs, performance monitoring objectives, and performance criteria may be specified in remedy decision documents (*e.g.,* Record of Decision, Corrective Action Plan) to provide the basis for development of the performance monitoring plan.

Common remedial objectives include lack of plume expansion and reduction of contaminant concentrations to established limits. Examples of performance criteria for monitoring such objectives include:

- The ability of the monitoring network to detect a specified contaminant at a specified concentration at specified sampling locations (*e.g.,* detect the occurrence of vinyl chloride at a transect of wells located between the plume boundaries and potential receptors at a concentration of 2 μg/L), and

- The ability of the monitoring network to detect a specified decrease in contaminant concentrations throughout the site within a specified time frame (*e.g.,* detect a 50 % decrease in concentrations throughout the plume by the end of ten years).

In order to develop such performance criteria and realistic means of evaluating performance with respect to these criteria, a systematic process should be followed. This process should take into account the data needs and the methods available to obtain the data. For example, if statistical tests are to be used to assess MNA performance, a systematic process can be used to select the appropriate tests, and to choose the type of data and data collection techniques necessary to obtain data required for the test. One such systematic development process that is highly effective and is endorsed in current guidance (U.S. EPA, 2000a) is the Data Quality Objectives (DQO) Process.

The DQO process is a systematic planning approach for data collection that is based on the scientific method. The DQO process identifies goals of the data collection and decision-making process, and assesses consequences of incorrect decisions. Although the process is typically described in linear terms (Figure 1), it is really a flexible process that relies on iteration and modification as the planning team works through each step, allowing earlier steps to be revised considering new information. The basic steps in the process begin with identification of the problem to be solved and the resources available to support the solution. Based on a statement of the problem, a specific decision that requires the acquisition of new data is formulated. Once the specific question to be answered has been stated, the data needed to make the decision can then be specified. Decisions regarding the boundaries of the study required to answer the question of concern are then made. Such boundaries may include spatial boundaries (*e.g.*, the boundaries of the contaminated aquifer) and time boundaries (*e.g.*, the time frame for data collection). The decision to be made is then simplified through development of a logical "if-then" statement describing the conditions under which different alternatives would be chosen. At this point, acceptable limits on errors in the decision and methods for limiting uncertainty in the data are established. Finally, cost-effective sampling designs to provide the needed data are produced. Although these steps are largely intuitive, steps may be overlooked if a specified framework is not used.

The DQO process provides a framework for addressing the issues of subsurface heterogeneity and data variability (Appendix A) that cause uncertainty about site characteristics, and often present obstacles to development of monitoring plans and data interpretation. Subsurface geology, hydrology, geochemistry, biology, and contaminant distribution may be highly variable and interact in complex ways. Therefore, it is important to have a defined process for dealing with the variability in order to design an appropriate monitoring system, and interpret the data derived from the monitoring system within an acceptable range of uncertainty. Uncertainty may be expressed mathematically using statistical techniques, if feasible, and it may be expressed qualitatively as "professional judgement" concerning the reliability of a certain interpretation of the data. The DQO process involves identification of data gaps that may cause an erroneous decision to be made, and assessment of the cost-benefit ratio of filling those gaps to reduce uncertainty.

When the DQO process identifies additional data needed to reduce uncertainty and facilitate development of the performance monitoring plan, further investigation of a site is warranted. Use of the Triad approach (U.S. EPA, 2001a) to planning and conducting the investigation can provide the information rapidly and cost-effectively, allowing the performance monitoring plan to be developed and deployed expeditiously. The Triad approach combines systematic planning to ensure that the characterization goals are clearly defined with dynamic work plans (U.S. EPA, 2003b) and quick-turnaround analytical techniques, including field analytical techniques (U.S. EPA, 2003c), to provide data meeting site-specific requirements in a condensed time frame. The approach promotes the use of new science and technology tools to identify and manage information gaps (*i.e.*, uncertainties) that could lead to unacceptable decision errors. The Triad approach is particularly effective where site heterogeneity increases uncertainty about the representativeness of isolated data points. The Triad approach is intended to produce an accurate conceptual site model. Using the dynamic work plan element of the Triad approach allows efficient refinement of the model in real time by specifying sampling locations and analyses based on data from previous samples.

Examples of typical problems and concerns that may be addressed using the DQO process during development of a performance monitoring plan are listed in Table 2. Important outcomes from the DQO process include the spatial and temporal scales for the collection of data, sample collection methods, acceptable decision error rates, and number of samples needed to support decision-making.

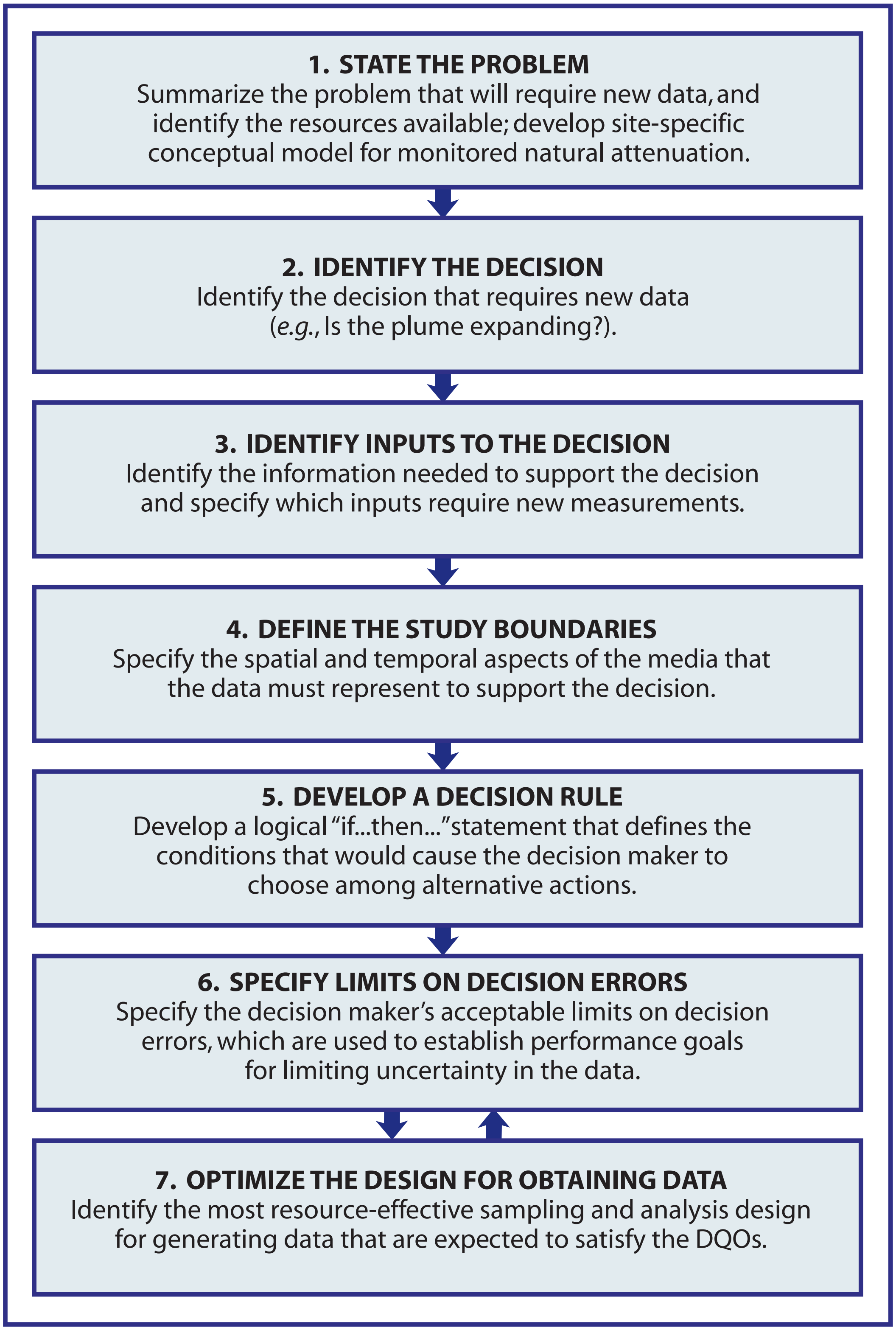


Figure 1. Steps in the establishment of data quality objectives (modified from U.S. EPA, 2000a).

Table 2. Examples of MNA-Relevant Decisions to be Addressed Using the DQO Process

Is natural attenuation occurring according to expectations?

- ❑ Determine that plume is behaving as specified in decision documents.
- ❑ Determine that contaminant mass reduction is proceeding as specified in decision documents.
- ❑ Determine that contaminant concentrations in source areas and the downgradient plume are declining at sufficient rates to meet RAO's.

Are there any changes in conditions that may affect the efficacy of natural attenuation?

- ❑ Determine that there are no changes in ground-water flow rates and directions that would impact plume stability.
- ❑ Determine that there is no change in the geochemical environment (*e.g.*, redox conditions) that would impact plume stability or contaminant reduction.

Are there potentially toxic and/or mobile transformation products?

- ❑ Determine if naturally-occurring arsenic, manganese or other potentially problematic species are being transformed and mobilized due to changes in the geochemical environment.
- ❑ Determine if previously unrecognized toxic and/or mobile transformation products are present.

Is the plume expanding?

- ❑ Determine that the plume is not migrating beyond current horizontal or vertical boundaries.
- ❑ Determine that no contaminants are found in the wells placed between the downgradient edge of the plume and receptors at concentrations above a specified limit.

Are there any unacceptable impacts to receptors?

- ❑ Determine that there is no unacceptable impact to surface-water bodies, wetlands, or other ecological receptors.
- ❑ Determine that there is no impact to indoor air in adjacent buildings.
- ❑ Determine that there is no impact to water-supply wells.

Are there any new contaminant releases that may impact remedy effectiveness?

- ❑ Determine that there are no new releases of contaminants from the source area.

Are the specified institutional controls effective?

- ❑ Determine that institutional controls are currently effective in eliminating exposure to contaminants.

Have remedial objectives been met?

- ❑ Verify that contaminant concentrations are below required levels.

2.4 The MNA Conceptual Site Model

The monitoring network design is based on the data derived from site characterization and any other site studies. These data are used to develop a conceptual model of the site before remedy selection; the conceptual model can then be used to facilitate the performance monitoring design process. The conceptual site model for natural attenuation is the site-specific qualitative and quantitative description of the migration and fate of contaminants with respect to possible receptors and the geologic, hydrologic, biologic, geochemical, and anthropogenic factors that control contaminant distribution. Essentially, the conceptual site model expresses an understanding of the site structure, processes, and factors that affect plume development and behavior. It is built on assumptions and hypotheses that have been evaluated using site-specific data, and is continually reevaluated as new data are developed throughout the site lifetime. The conceptual model typically should be developed and evaluated using a team approach (*i.e.*, using a team of subject-matter experts including hydrogeologists, microbiologists, statisticians/modelers, chemists and other experts as appropriate for the specific site).

A three-dimensional conceptual site model that incorporates temporal changes is often needed to provide a framework for interpreting the site data, judging the significance of changes in site conditions, and predicting future behavior of the source and plume. Understanding plume formation and behavior is the basis for predicting future plume behavior, and therefore, predicting whether the MNA remedy will be able to achieve site remedial goals within specified time frames. Conceptual models are expressed tangibly in text, site maps (*e.g.,* contaminant isoconcentration maps and potentiometric surface maps), cross sections (*e.g.,* hydrogeologic and chemical distributions), and other graphical presentations, and in terms of mathematical calculations describing the plume and site.

The development of quantitative models (*i.e.*, mathematical representations of site conditions) based on the conceptual site model generally is an essential part of site characterization, remedy selection, and performance monitoring for MNA. Quantitative models may be as simple as linear regressions for estimation of contaminant attenuation rates, or as complex as numerical models of ground-water flow and contaminant fate and migration. These mathematical representations are used to help understand site processes, locate monitoring points, estimate attenuation rates, and evaluate possible effects of different conditions on plume behavior. Quantitative assessments require particular types of data. The data collection effort should be designed with the chosen evaluation methods, calculations, and model(s) in mind.

The data and analyses necessary for formulation of an adequate three-dimensional conceptual site model for MNA depend on site-specific conditions. However, the types of information and analyses that are generally needed for model development are illustrated in Figure 2 and described below.

2.4.1 *Hydrogeology*

Hydrogeology is the foundation of the conceptual site model for natural attenuation (National Research Council, 2000). Detailed knowledge of site hydrogeology is crucial to understanding how ground water flows and contaminants may be transported in the subsurface. A general discussion of the effects of geology and hydrology on ground-water flow follows.

Much of the spatial variability in observed contaminant concentrations is the result of geologic heterogeneity. In a sedimentary geologic setting, spatial changes in geology are present at scales that can vary from fractions of an inch to miles. Sedimentary facies (*i.e.,* sedimentary bodies that are internally similar in characteristics) determine the three-dimensional geometries, connectivity, and heterogeneity (*i.e.,* variability) of transmissive zones and barriers to flow (Galloway and Sharp, 1998). These characteristics and the resulting variability in hydraulic properties (*e.g.,* hydraulic conductivity and porosity) are generally the result of the original geologic depositional processes. In similar fashion, anthropogenic features such as buried utility corridors and

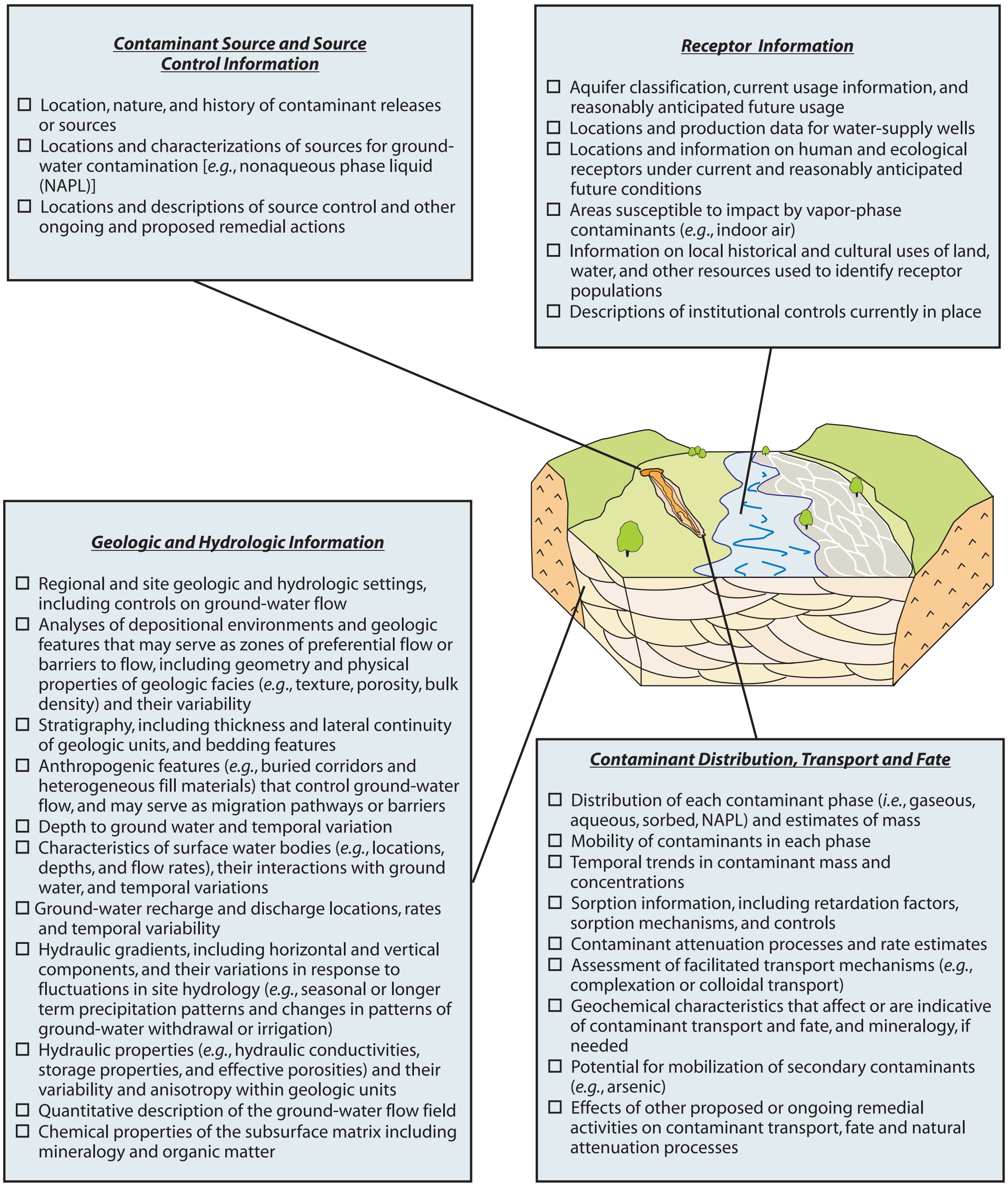


Figure 2. Elements of a conceptual site model for monitored natural attenuation.

heterogeneous fill materials may also result in the formation of transmissive zones and flow barriers. Transmissive zones are subsurface units where ground water flows in paths constrained or bounded by lower hydraulic conductivity materials (*i.e.*, geologic impediments to flow) or hydrologic barriers (*e.g.*, hydraulic head boundaries). An example of a transmissive zone is a deposit of discontinuous, interbedded sands and silt bounded above by the water table and below by a thick, locally continuous clay of low hydraulic conductivity. These bounds act to keep ground water flowing within the transmissive zone. However, even within a given transmissive zone, ground water may move in sinuous paths due to small-scale differences in hydraulic conductivity resulting from heterogeneous geologic materials or to temporally variable, three-dimensional hydraulic gradients.

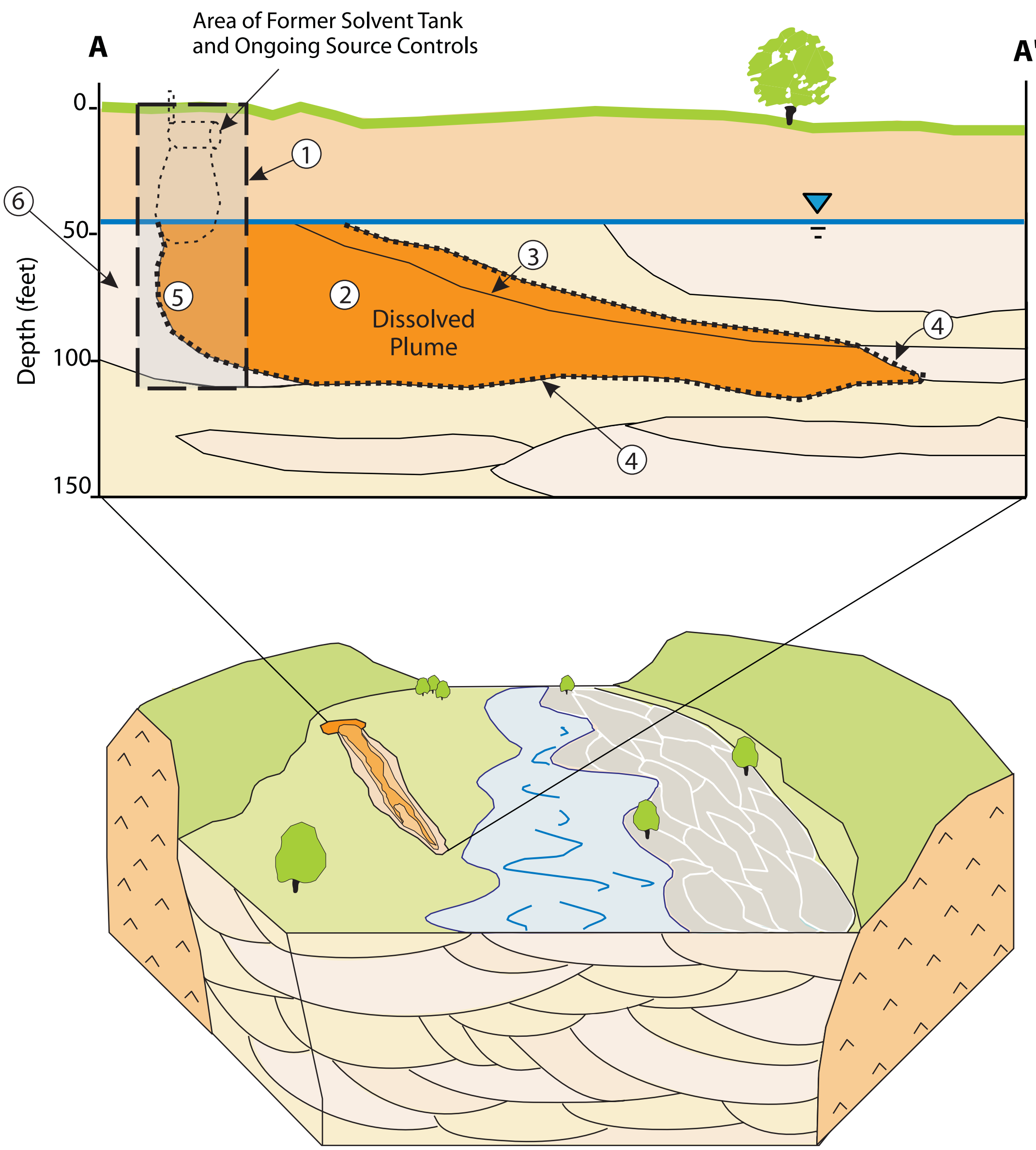
Transmissive zones may be separate and distinct pathways for contaminant movement. For example, the degree of hydrologic connection between different sedimentary facies depicted in Figure 3 is small. Monitoring points in different sedimentary facies may appear to be similar and may be hydraulically downgradient of one another without significant ground-water flow and contaminant migration from one unit to the next. A reduction in contaminant concentrations between two monitoring points that are not in the same flowpath may not accurately represent contaminant attenuation in either flowpath. Inferences about natural attenuation based on apparent decreases in contaminant concentration in the downgradient direction are likely to be incorrect in these situations unless ground-water flow paths are determined and monitored. Determining flow paths is often difficult to accomplish, especially when using small numbers of monitoring points.

Differentiation of the ground-water flow field by means of a detailed characterization of site geology is crucial for effective performance monitoring of a natural attenuation remedy. In this respect, evaluation of sedimentary depositional environments is an especially useful framework for the understanding of site stratigraphy and the distribution of lithologic controls on ground-water flow. Three-dimensional characterization is used to evaluate and predict the effects of natural attenuation processes (*e.g.,* advection, dispersion, sorption, and transformation processes) on contaminants. Requirements for monitoring transmissive zones of interest typically should be considered in the development of the site-specific DQOs for a performance monitoring plan.

Temporal variations in the ground-water flow field due to natural or anthropogenic changes in ground-water recharge or withdrawal may also be important influences on contaminant migration. These fluctuations may lead to changes in the geometry of the plume that will affect monitoring system design and operation. For example, there can be seasonal changes in water elevations that depend upon the temporal patterns of rainfall, and, in the north, snowfall and snowmelt. Because there can be fixed controls on water levels (*i.e.*, the fixed elevation of the oceans or large water bodies), hydraulic gradients can also change seasonally. In addition, there can be longer term fluctuations in water elevations associated with sequences of unusually wet or dry years. With increasing development, land use changes can alter patterns of recharge, discharge, or withdrawal that in turn may impact contaminant migration.

Available ground-water elevation data are used to determine, if possible, the expected range of variation of velocities over the life of the plume that is being treated by MNA. For example, seasonal variations in precipitation may change hydraulic gradients and the depth to ground water resulting in fluctuations in horizontal and vertical plume boundaries, changes in contaminant concentrations in individual wells, changes in direction of plume migration, and plume discharge to intermittent streams and wetlands. Anthropogenic influences on site hydrology such as changes in ground-water withdrawal or irrigation rates and patterns may have similar effects on plume behavior but may occur on frequencies and timing other than those corresponding to precipitation patterns. Temporal variations in plume behavior affect the choice of performance monitoring well locations and the analyses of data obtained from the well network.

Geologic and hydrologic data and interpretations that are used in the development of the performance monitoring plan are shown on Figure 2. The level of detail needed will be site



Target Monitoring Zones

1. Source area
2. Contaminated zones of highest concentrations and mobility
3. Plume fringes exhibiting low contaminant concentrations
4. Plume boundaries
5. Recalcitrant zone determined from historical trends
6. Upgradient locations

Legend

- Gravel, gravel-sand mixtures
- Medium to coarse-grained sand
- Fine-grained silty sand
- Bedrock
- Dissolved Plume

Figure 3. Geologic block diagram and cross section depicting a stream environment in which sediments have accumulated as valley fill. In the figure, there are numerous coarse-grained deposits as well as finer-grained materials with lower hydraulic conductivity.

specific. Much of the geologic information is obtained from geologic cores and supplemented with information from surface and, particularly, borehole geophysical methods. Innovative characterization technologies, such as the cone penetrometer and geologic sampling using direct-push methods, offer the potential for cost-effectively evaluating the geologic controls on ground-water flow and their variability in greater detail than previously possible. Hydrologic information will generally be obtained through hydraulic testing in the field (*e.g.,* pumping tests, slug tests, and tracer tests) and through the measurement of hydraulic heads in wells and piezometers that are appropriately screened in individual hydrostratigraphic units. Additional information regarding geologic and hydrologic site characterization concepts and techniques may be obtained from a variety of sources (*e.g.,* Butler, 1998; Kruseman and de Ridder, 1989; U.S. EPA, 1991a, 1993a, 1993b, 1997b, 2002a).

At a minimum, the hydrogeologic database generally should be sufficient to:

- Define geologic and hydrologic controls on the ground-water flow field (*e.g.,* transmissive units, barriers to flow, and the horizontal and vertical components of hydraulic gradients),

- Quantify ground-water flow rates and directions and their spatial and temporal variations within transmissive units, and

- Support identification of possible receptors and characterization of natural attenuation rates and the relative effects of dominant natural attenuation processes.

It is desirable that the hydrogeologic database be developed and kept in electronic form, for ease of adding, sorting, analyzing and transferring data, developing and publishing reports, and interfacing with geographic information systems. There are no widely-recognized standard formats for such databases, but the interested parties may adhere to a particular format for a given site.

The scale and intensity of the characterization are determined by the variability in site geology and hydrology and the acceptable level of uncertainty in the outcome of the evaluations. Spatial and temporal variability in these parameters and their effects on the performance monitoring network and sampling frequencies typically should be explicitly considered. This process generally should consider the observed variability, the sources of that variability, and the degree to which the variability affects decisions regarding the monitoring network design and monitoring strategies.

2.4.2 *Contaminant Distribution, Migration, and Fate*

Contaminant distribution and behavior should be well characterized within both former source areas and the downgradient plume (*i.e.*, the plume downgradient of all known source materials). Source characterization data (Table 3) are used to help identify appropriate performance monitoring constituents and monitoring locations and depths as well as interpret historical data and predict future behavior of the dissolved plume. Some of the data, such as the history of source release, may be unavailable.

Some of the more common sources for continued ground-water contamination by organic compounds are NAPL and sorbed organic contaminants within the vadose and, especially, saturated zones (Palmer and Fish, 1992; U.S. EPA, 1993c). NAPL infiltration into the subsurface is complex and is influenced by physical properties of the NAPL and by macro- and micro-scale

Table 3. Source Characterization Information for Conceptual Site Model Development

Data Type	***Utility***
Three-dimensional distribution of physical contaminant phases (*e.g.*, nonaqueous phase liquid (NAPL) and sorbed materials) that are continuing sources for ground-water contamination.	Conceptualize, in conjunction with hydrogeologic data, three-dimensional migration pathways of both NAPL and aqueous-phase contaminants. Project possible behavior of dissolved plume. Identify need for source controls and estimate range of possible time frames for restoration of the plume. Identify areas where contaminant attenuation rate may not be sufficient to meet contaminant reduction objectives (*i.e.*, "recalcitrant zone"). Aid in identifying appropriate monitoring locations and depths.
Contaminant release and source removal/control histories (*i.e.*, timing and descriptions).	Constrain interpretations of contaminant migration and historical trends in observed contaminant concentrations.
Constituents that were released, those that are currently present, and toxic transformation products.	Identify potentially dominant transport and fate processes based on chemical properties. Identify monitoring constituents.

geologic features (Mercer and Cohen, 1990; Cohen and Mercer, 1993). Careful evaluation of the extent of NAPL infiltration and migration is needed because NAPL may have migrated both vertically and horizontally far from the original site of the release. Source materials may greatly affect MNA remedy performance with respect to attainment of contaminant reduction goals, the geometry of the associated dissolved plume, and design of the performance monitoring program. It is expected that source control will be a fundamental component of any MNA remedy (U.S. EPA, 1999a).

Detailed definition of contaminant distribution throughout the three-dimensional boundaries of the contaminated aquifer provides data that can be correlated with the hydrogeologic characterization data to determine the effects of the hydrogeologic controls on contaminant migration. The data generally should be sufficient to define the zones of greatest contamination, rapid contaminant migration and greatest risk to possible receptors in addition to defining the plume boundaries in order to target these zones during the performance monitoring program.

The effects of the dominant attenuation processes may be evaluated and field-scale attenuation rates estimated (U.S. EPA, 1998a; Wiedemeier et al., 1999; U.S. EPA, 2002b) in order to identify and monitor the controls on plume stability and project progress toward remedial action objectives of reduction in contaminant concentrations to target levels. Several processes may control the fate of the dissolved plume (*e.g.,* the processes that are the components of the attenuation rate: dispersion, dilution, sorption processes, volatilization, and chemical and biological degradation). The need for determining the contribution of each component of the attenuation rate will vary depending on remedial goals. For instance, only chemical and biological degradation actually destroy contaminant mass; the other processes that only lower contaminant concentration, retard contaminant migration, or move contaminants to other media may not produce acceptable remedial results at all sites.

The controls on each process and the potential for continuation of the processes at current rates throughout the remediation time frame typically should be considered because the effectiveness of some of the processes may vary over time, invalidating predictions of future effectiveness based on historical rates. For example, continued biodegradation of chlorinated solvent contamination may be contingent on the continued supply of readily degradable organic carbon compounds to serve as electron donors in the biotransformation processes (Wiedemeier *et al.,* 1999; Leahy and Shreve, 2000).

Data on the shape and dynamic behavior of the dissolved contaminant plume collected over a period of several years are helpful in order to evaluate natural attenuation processes and develop the monitoring plan. Three to five years of periodic monitoring (during the site characterization and remediation effort) may, in many cases, be sufficient to form a conceptual model of plume behavior adequate for developing the performance monitoring plan. However, more complex or highly variable sites may require longer-term characterization to adequately evaluate the range of plume behavior due to variations in factors such as ground-water flow and biological activity (Barcelona *et al.*, 1989). For the purposes of performance monitoring plan development, these data are used to determine whether significant temporal (*e.g.,* seasonal) fluctuations in plume boundaries are occurring. This information is needed to site wells to monitor long-term plume stability and to trigger implementation of contingency remedies based on observed plume migration. The data may also indicate portions of the plume where the progress toward contaminant reduction goals may be slow and enhanced monitoring may be warranted to determine the cause and any necessary remedy modifications. It is important to note that a few years of site characterization monitoring data are not reasonably sufficient to accurately predict plume behavior (and performance monitoring needs) for decades. However, such data can appropriately be used to refine a conceptual model sufficient for initial design of a performance monitoring program. The monitoring program in operation can then provide data for continual refinement of the conceptual model and, subsequently, of the monitoring program itself.

2.4.3 *Geochemistry*

Characterization of subsurface geochemical environments and their variability provides important insights into the types of biotic and abiotic processes that may be affecting plume behavior. Many of the processes driving plume behavior cannot be measured directly (*e.g.,* biological transformation of contaminants). However, the processes may cause changes in geochemical parameters, leaving an observable geochemical "footprint" that can be related qualitatively and quantitatively to the biotic and abiotic processes (National Research Council, 2000).

In general, fuels serve as electron donors during microbial degradation of the fuels (*i.e.*, the fuels are oxidized during microbial metabolism). More oxidizing redox conditions and greater availability of electron acceptors at a site lead to more efficient biodegradation processes for fuel degradation (Ludwig *et al*., 2000). In contrast, chlorinated solvents may serve as electron acceptors in microbial metabolism (*i.e.*, the solvents can be reduced during microbial metabolism), and more reducing redox conditions lead to more efficient biodegradation (Chapelle, 1996). Note that some chlorinated solvents such as trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC) can also act as electron donors, and degrade under more oxidizing conditions.

Because the degradation of fuels and solvents is influenced by redox conditions, assessment of ambient redox conditions is an important component of any monitoring program for monitored natural attenuation of fuels or solvents (U.S. EPA, 2000b). The nature of this assessment may be as simple as delineating the distribution of oxic/anoxic ground water, or it may be more in depth requiring the delineation of oxic, iron(III)–reducing, sulfate-reducing, and methanogenic zones at the site (Chapelle *et al*., 2000). The role of Eh measurements in redox assessments is subject to numerous uncertainties (Barker, 2000), but Eh measurements are qualitative indicators of redox conditions (Westall, 2000). The list of redox parameters given by Wilson (2000) can be used to develop a site-specific monitoring program for redox parameters. The appropriate level of monitoring can only be determined on a site-by-site basis (Wilson, 2000).

Detailed discussions of biogeochemical reactions pertinent to fuel and chlorinated solvent contamination in ground water and the geochemical patterns associated with these processes may be found in Azadpour-Keeley *et al.* (1999), Azadpour-Keeley *et al.* (2001), National Research Council (2000), U.S. EPA (1998a), and Wiedemeier *et al.* (1999).

Geochemistry can provide the following kinds of information:

- Whether ambient redox conditions and processes favor the natural attenuation of the contaminants of concern, as well as identifying the dominant degradation processes and long-term monitoring parameters indicative of the continuing effectiveness of those processes,

- Whether stoichiometric relationships between electron acceptor (oxygen, nitrate, sulfate, etc.) utilization and contaminant degradation are observable,

- Whether redox conditions or other geochemical conditions could enhance the mobility of certain contaminants of concern (e.g., manganese or arsenic), or

- Identify zones beyond the current plume boundaries where soluble electron acceptors or donors are depleted or nonhazardous reaction products are enriched with respect to ambient ground water but contaminants are not detected. The water in these zones has been called "treated water" (i.e., water that once was contaminated but has been remediated by natural attenuation). Because the plume would travel into these zones if it expands, such zones can serve as target zones for monitoring plume stability.

Geochemical parameters and trends that are often useful indicators of biotransformation processes at sites with fuel and chlorinated solvent contamination are discussed in U.S. EPA (1998), Wiedemeier *et al.* (1999), and Wiedemeier and Haas (2002). The individual parameters diagnostic of dominant processes and most useful in a performance monitoring program depend on site-specific conditions. Parameters to be measured are chosen with regard to their potential to affect site-related decisions (*i.e.*, it would not be useful to measure a given parameter if the information would not be used to change site-related decisions).

2.4.4 *Receptor Locations*

For the purpose of specifying performance monitoring locations, identification of human and ecological receptors that may be affected by the contaminant plume under current and reasonably anticipated future conditions is a critical element. In addition to possible receptors within the areas that are currently contaminated, locations outside of the plume that may be subject to impact during the remedy performance period should be identified. Such receptor locations may include, but are not limited to, water supply wells, buildings, aquifers, wetlands, sediments, and surface-water bodies. In many instances, this list may include aquifers that are below zones of shallow contamination. The vapor intrusion to indoor air pathway is also of considerable importance (U.S. EPA, 2002c). This document focuses on monitoring the saturated zone, but site characterization and monitoring for any remedy should include appropriate monitoring of all significant pathways by which contaminants may migrate and impact receptors. Sources of additional information concerning receptor identification include U.S. EPA (1997c) and U.S. EPA (1998b).

Information on receptors and possible pathways for impact is used to identify appropriate locations for monitoring points between the plume and the possible receptor as well as locations where impact may occur. Monitoring at these locations provides confidence that no unacceptable impacts occur.

2.5 Monitoring Network Design

2.5.1 *Introduction*

The media of primary concern and, therefore, the focus of the monitoring network design, will be ground water at many sites. However, monitoring of other media (*e.g.*, indoor air, soil gas, soils, surface water, and sediments) may be necessary to determine possible impacts to receptors and other measures of remedy effectiveness. Guidance regarding the assessment of the indoor air exposure pathway is provided in U.S. EPA (2002c). Recent discussion of the assessment of the interactions of ground water and surface water useful in formulating effective monitoring networks may be found in U.S. EPA (2000e). At many sites, the assessment of such cross-media transfers of contaminants is essential to adequate performance monitoring for MNA remedies. The focus of the following discussion is primarily on the monitoring of ground water as this is often an exposure pathway of significant concern. Performance monitoring is extended to other media as warranted by site conditions.

A monitoring system designed for evaluating the performance of an MNA remedy with respect to specific remedial action objectives may be very different from the network established during earlier phases of site characterization, feasibility studies, or interim actions. Existing wells were often incrementally installed for different purposes, such as defining the extent of contamination during the remedial investigation or evaluating an engineered remedy during a feasibility study. The location and number of these wells may not be well suited for MNA performance monitoring. Specification of a monitoring network design should be based on consideration of all available information concerning the processes and factors expected to control contaminant distribution. The network is designed to provide data to demonstrate attainment of all the remedial action objectives for an MNA remedy.

A plume is a dynamic, three-dimensional distribution of contaminants in ground water, that generally necessitates three-dimensional monitoring. Plume shape is influenced by many factors, including original source distribution, geology, hydrology, and biologic processes. The resulting spatial and temporal variability significantly impact choice of monitoring locations and frequencies and necessitate continual reevaluation of the performance monitoring network. Appendix A provides a brief discussion of some issues regarding variability.

The density of sampling points in a monitoring network will depend on the geology and hydrology, the spatial scales at which contaminant distribution varies horizontally, vertically and temporally, and the desired level of confidence in the evaluation. Plumes often vary significantly in concentration in transverse and vertical cross sections (*e.g.,* Cherry, 1996) making evaluation of contaminant distribution and remedy performance difficult. In these cases, a dense network of monitoring points will often be needed to support many of the performance monitoring evaluations described below.

One approach to this problem is to define and monitor the plume using clustered monitoring points positioned in transects across and through the plume, perpendicular to the direction of ground-water flow (Figures 4, 5 and 6). The horizontal and vertical spacings of the monitoring points in each transect are determined by the hydrogeologic conditions that control contaminant migration and the dimensions and spatial heterogeneity of the resulting contaminant distribution. The horizontal distance between transects is generally based on changes in contaminant concentration along the plume, and the location of the source and distal portions of the plume. For example, transects may be placed:

- Immediately upgradient of the source area to monitor contaminant and electron acceptor flux into the plume,
- Immediately downgradient of the source area to monitor contaminant flux to ground water,
- Near the downgradient and sidegradient plume boundaries to monitor contaminant concentration increases indicating possible plume expansion,
- Immediately downgradient of the plume or other compliance boundary to monitor for plume expansion, and
- Along the plume to provide information on plume configuration and contaminant attenuation. Horizontal spacing of the transects for determination of contaminant attenuation may be based on the number of locations needed for attenuation rate calculations, and changes in contaminant concentration along the plume (*e.g.*, spacing conforming to order-of-magnitude decreases in contaminant concentration).

The elevations of sampling intervals are generally based on stratigraphy (*i.e.*, sampling the different stratigraphic intervals), the vertical component of hydraulic gradients, and contaminant distribution (*i.e.*, sampling the top, bottom, and "core" of the plume, and, possibly, above and below the plume to vertically bound it).

The use of a transect-based approach to monitoring may greatly reduce the uncertainty in performance monitoring evaluations at many sites by improving the definition of contaminant distribution and its variability. The transect approach helps to locate ground-water flow lines and contaminant migration paths. Transects also provide a better definition of contaminant distribution under conditions of changing hydraulic gradients. A detailed example of the use of a transect-based approach in the evaluation of natural attenuation processes at a site where petroleum products were released may be found in Kao and Wang (2001).

2.5.2 *Monitoring Locations*

Generally, each distinct zone of contaminant migration and geochemical regime is monitored to assess its impact on remediation. For instance, if part of a plume of tetrachloroethene is anaerobic with high levels of electron donors available and another part of the plume is aerobic with few electron donors available, degradation of the tetrachloroethene may be very active in the anaerobic zone but nonexistent in the aerobic zone. For each zone with distinctly different conditions or

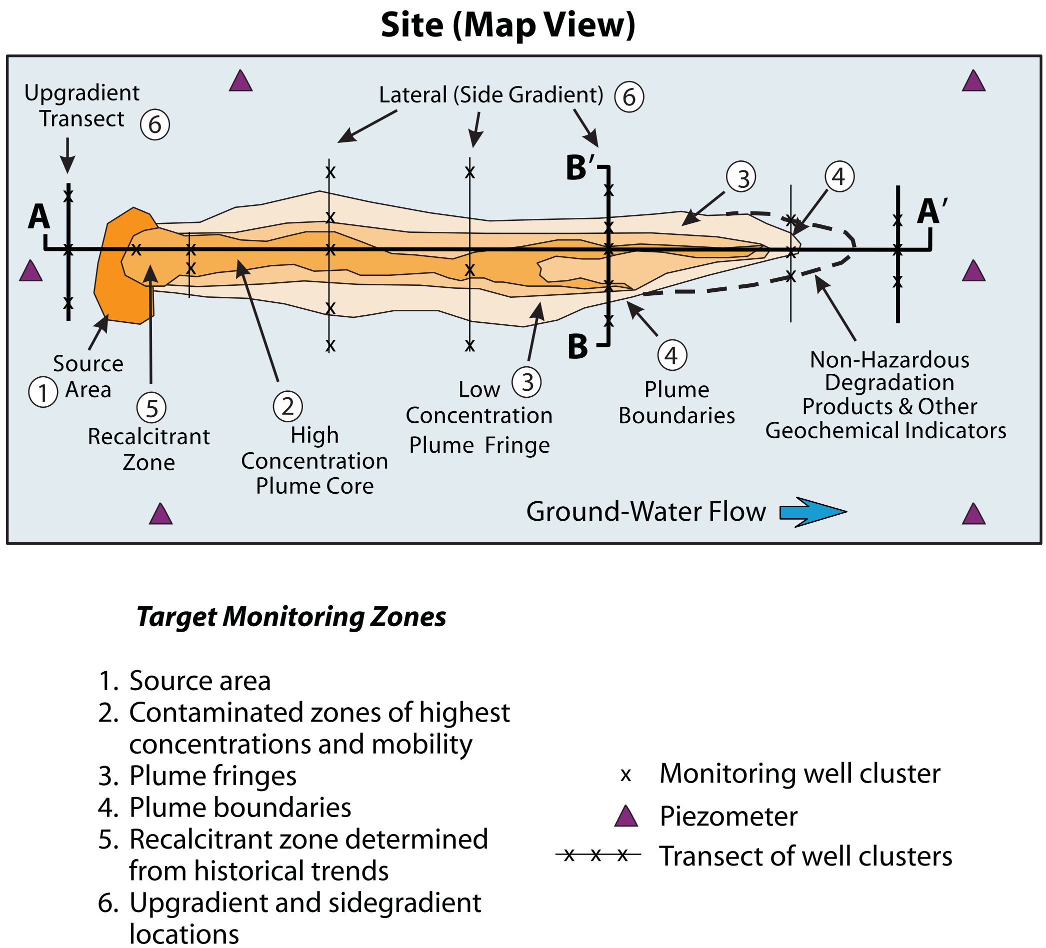


Figure 4. Example of a network design for performance monitoring, including target zones for monitoring effectiveness with respect to specific remedial objectives. In this example, monitoring network design is based on transects of wells oriented perpendicular to the ground-water flow direction. Sampling locations for target monitoring zones were chosen based on site characterization. Piezometers provide additional data for evaluation of changes in potential ground-water flow direction.

controls on contaminant migration and fate, the following locations would be monitored: areas hydraulically upgradient and sidegradient to the plume, source area, main body of the plume, and distal portions and boundaries of the plume.

2.5.2.1 Typical Target Zones

Typical target zones for monitoring a contaminant plume (Figures 4, 5 and 6) include:

- *Source areas - within and immediately downgradient of remediated source areas*

  The monitoring objectives are to determine and demonstrate whether any further contaminant releases to ground water occur and to estimate contaminant reduction over time. In situations where the source is contained, increased contamination or new contaminants could be indicative of such conditions as cap failure, buried drums that

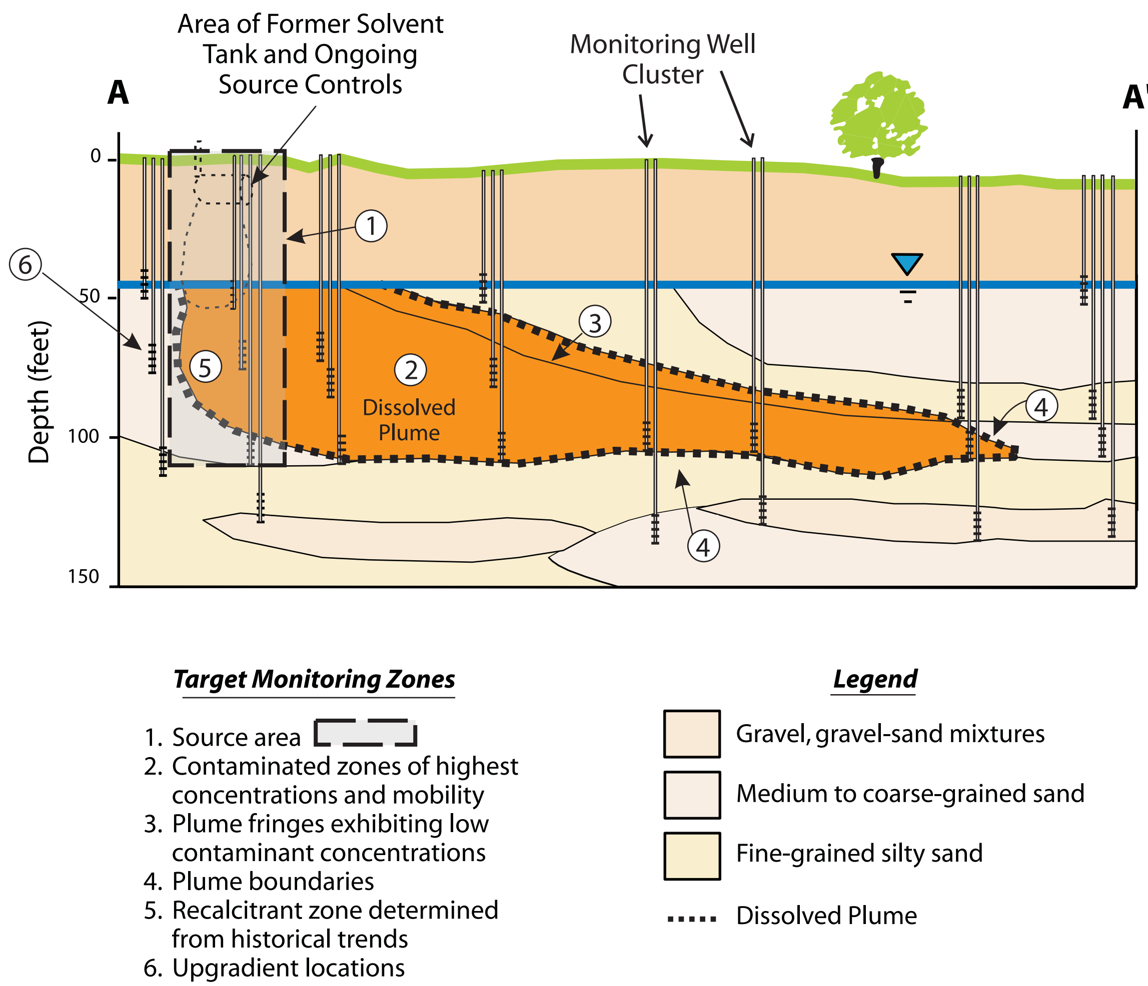


Figure 5. Cross section A-A' through monitoring network in general direction of ground-water flow. Placement of monitoring points within target zones is based on geologic controls and contaminant distribution characterized prior to remedy selection and is periodically modified, as warranted, based on evaluation of performance monitoring data. In this scenario, detailed site characterization data would be used to define the limits of the source area, the distribution of any NAPL and aqueous-phase contaminants, and the effectiveness of source removal and control actions. Source control activities and monitoring associated with the release from the former solvent tank are not pictured.

rupture, a rise in the water table transferring additional contaminants from the vadose zone, or slurry wall failure. These new contaminant releases could be greater than the capacity of the subsurface to attenuate concentrations without significant plume expansion or could include contaminants not effectively remediated by MNA.

- *Transmissive zones with highest contaminant concentrations or hydraulic conductivity*

  A change in conditions in these zones, such as an increase in contaminant mass from source areas or increased ground-water velocity, may lead to a relatively rapid impact to a downgradient receptor.

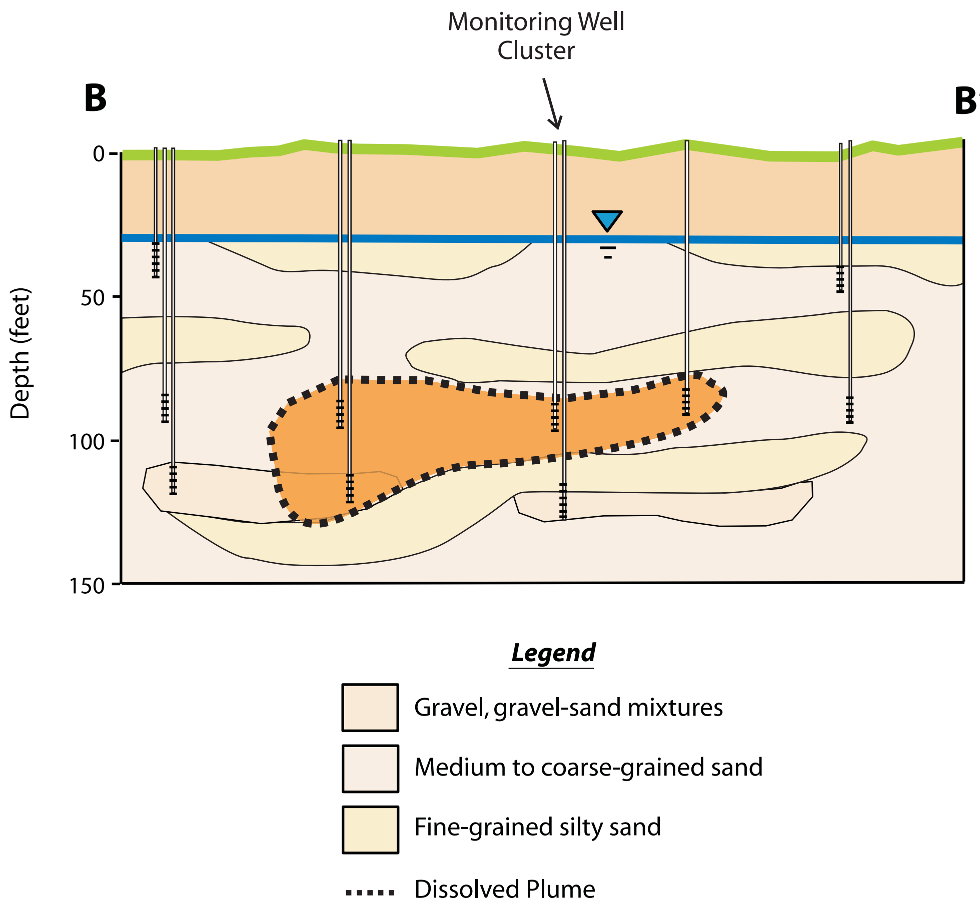


Figure 6. Cross section B-B′ through monitoring network perpendicular to ground-water flow. Monitoring points are placed to define the plume horizontally and vertically, as well as monitor contaminant concentration zones and geochemical zones.

- *Distal or fringe portions of the plume*

  These are areas where reduction of contaminant concentrations to levels required by remedial action objectives may be attained most rapidly or where plume expansion may be observed.

- *Plume boundaries and other compliance boundaries*

  Multilevel monitoring points typically would be placed at the sidegradient, downgradient, and vertical plume boundaries, and between these boundaries and possible receptors. Multilevel monitoring generally should also be performed at any other compliance boundaries specified in remedy decision documents. Results from these monitoring locations may directly demonstrate unacceptable plume expansion and changes in ground-water flow directions.

- *Zones in which contaminant reduction rates appear to be lower than required to meet remediation goals (i.e., recalcitrant zone)*

  These are the areas where attaining cleanup standards within accepted time frames may be impeded due to site conditions (*e.g.,* presence of previously undetected source materials or low flux of electron acceptors). Such areas, if present, will be delineated through evaluation of data obtained throughout the performance monitoring period. These areas may require additional characterization to determine if additional remedial actions are necessary to reduce contaminant concentrations to desired levels.

- *Areas representative of contaminated and uncontaminated geochemical settings*

  Sampling locations for monitoring the geochemical setting include monitoring points that are hydraulically upgradient and sidegradient with respect to the plume. Because assumptions concerning the geochemical setting and naturally occurring changes in geochemical parameters affect interpretation of data from the plume, such assumptions should be tested and evaluated like other parts of the conceptual site model. Therefore, multiple monitoring points generally should be used to determine the variability of geochemical conditions outside the plume. Data concerning the movement of electron acceptors, donors, and any contaminants into the plume aid in understanding and interpreting data from the plume. These geochemical data are used to determine whether the observed differences in geochemical parameter concentrations within the plume are due to contaminant transformation processes rather than natural variations in the background geochemical conditions. The locations sidegradient to the plume help to evaluate changes in plume geochemistry with time as ground water migrates through uncontaminated aquifer materials. Changes in geochemistry within the plume may not be directly related to attenuation of the contaminants, so geochemical changes outside the plume generally should be assessed and compared to geochemical changes taking place within the plume. If upgradient and lateral monitoring points show geochemical changes similar to changes in the plume, such changes may not be attributed solely to contaminant-related processes (*i.e.,* degradation), and, therefore, may not serve as supporting evidence for degradation processes.

- *Areas supporting the monitoring of site hydrology*

  At some sites, monitoring of ground-water elevations at locations additional to those used for the monitoring of chemical parameters may be needed to determine hydraulic gradients. At such sites, appropriate locations for placing piezometers will often include positions that are upgradient and sidegradient to the contaminant plume, as well as in zones above and below the plume. Piezometers are usually spaced across the site so that ground-water elevation measurement errors are relatively small compared to the difference in ground-water elevations between piezometers.

2.5.2.2 Screen Lengths

The screen length for a given well constitutes an important part of the three-dimensional monitoring location. The screen is sized to sample the interval of interest. The interval may be defined by stratigraphy, contaminant loadings, or geochemistry, based on the site characterization data. Factors to consider in determining screen length include the following:

- Well screens can be matched to stratigraphic intervals if the intervals are relatively small, and the geochemical and contaminant values are similar throughout the vertical extent of the interval intersected by the well screen. For instance, a five-foot thick sand layer within which contaminated water migrates could be sampled with a five-foot screen to intersect the entire interval. Any interval of significantly different conductivity could be targeted by a specific screen length. Well clusters can be used to provide coverage of the entire contaminated unit, as needed.

- Monitoring wells typically should screen comparable intervals. For example, well screen lengths can be matched to contaminant loadings. Suppose that dissolved petroleum contaminants (*e.g.*, benzene, toluene, ethylbenzene, and xylenes) were transported primarily within a 5 ft to 10 ft thick interval of a 30-ft thick sandy unit. In this situation, a monitoring well screen could be sized to sample the most contaminated part of the unit to help determine attenuation of the contaminants in that interval. The use of longer screens may result in artificially lower measured containment concentrations, or even lack of detections, due to the mixing of water with different chemical compositions. Calculated attenuation rates or estimated plume boundaries may reflect variations in screen length and placement rather than actual attenuation if monitoring well screen intervals are not matched to contaminant distribution in the contaminated stratigraphic interval.

- Well screen lengths can be matched to geochemistry, to sample a zone where a particular geochemistry prevails. Because attenuation of some contaminants is highly sensitive to the geochemical environment, it is often desirable to be able to accurately identify and discretely sample locations in the plume where a particular geochemistry prevails.

2.5.3 *Monitoring Parameters*

The primary classes of parameters to be monitored during these evaluations generally will be the contaminants of concern (COCs), geochemical indicators of transformation processes, and hydrogeologic parameters. Contaminants of concern are those chemicals identified during site investigations that are required to be addressed by the response action proposed in the remedy decision documents.

Contaminants of concern may be identified from:

- Ground-water and soil monitoring data,

- Contaminant source histories, and

- Evaluation of contaminants that potentially may be formed or mobilized as a result of biotransformation processes or changes in the geochemical environment. For example, toxic products such as dichloroethene and vinyl chloride would be measured at sites contaminated with chlorinated solvents where they might be expected to be present.

At some sites, it may be necessary to identify and include chemicals that have only been tentatively identified in previous sampling (*e.g.,* Tentatively Identified Compounds (TICs)).

Because the effectiveness of natural attenuation processes varies markedly for different contaminants, it is often inappropriate to assume that other components of the plume will be adequately remediated along with the primary contaminants of concern during MNA. Potentially hazardous plume components should be positively identified, evaluated to determine if they will be sufficiently mitigated by MNA, and monitored, as appropriate, if they are a threat to human or environmental health. For instance, MTBE (commonly found in gasoline-sourced plumes), was overlooked at most sites for many years because sampling and analysis at most such sites emphasized BTEX. However, at many such sites, BTEX components may be attenuated to meet standards before MTBE, so monitoring only BTEX may result in a mistaken interpretation of the effectiveness of MNA. Another example of an overlooked contaminant is 1,4-dioxane, which may be associated with certain plumes of volatile organic contaminants. Recent advances in analytical methods allow detections in ground-water samples at much lower concentrations (*e.g.*, 1.5 µg/L) than previously possible. 1,4-Dioxane has been used as a solvent stabilizer in 1,1,1-trichloroethane at concentrations of 2% to 8% by volume (Mohr, 2001) and is a class II-B probable carcinogen. This contaminant is highly soluble in and mobile in ground water. At sites where this contaminant is present, it may be expected to migrate further than the associated plume of chlorinated solvent compounds (Fetter, 1994). At such sites, a monitoring program that does not include 1,4-dioxane would likely result in a mistaken interpretation of the effectiveness of MNA.

At a well-characterized site, the DQO process can be used to choose parameters and monitoring frequencies for each monitoring location based on the value of the data to monitoring MNA, as an alternative to the measurement of all parameters at all locations. For example, if several years of monitoring indicate that the geochemistry in the central portion of a BTEX plume is stable, it may not be necessary or useful to continue to analyze samples from these locations for all of the geochemical parameters at each sampling event. However, all contaminants normally would be measured in all samples on a periodic basis to verify the conceptual site model. The most important monitoring parameters are derived from a thorough understanding of site history, ambient geochemistry, contaminant sources, and geochemical changes induced by contaminant degradation.

The purposes for long-term monitoring of geochemical parameters in addition to ground-water contaminants include:

- Confirmation of dominant biotransformation processes,
- Evaluation of the potential for continued transformation, and
- Identification of the zones of contaminant migration (*e.g.*, where geochemistry indicates contaminant degradation has taken place).

These purposes are discussed in Azadpour-Keeley *et al.* (1999), Azadpour-Keeley *et al.* (2001), U.S. EPA (1998a), Wiedemeier *et al.* (1999), and Wiedemeier and Haas (2002).

The specific parameters useful at a given site depend on site contaminants, natural geochemical settings, and dominant biotransformation processes. In most cases, a select group of parameters that indicate the geochemical environment (*e.g.,* oxidation-reduction potential, dissolved oxygen, pH), identify geochemical regimes affecting contaminant degradation (*e.g.*, nitrate, iron (II), sulfate, methane), or are products of contaminant degradation (*e.g.,* ethane, ethene) will be measured in most samples. In addition to the measurement of geochemical parameters in ground-water samples, periodic monitoring of solid-phase electron acceptors, such as bioavailable iron, in aquifer materials may be useful at some sites to evaluate the supply of such materials relative to the mass of contaminants to be degraded (Huling *et al*., 2002). The geochemical parameters measured generally should be chosen based on the utility of the data for affecting site-related decisions (*i.e.*, if no decisions would be changed based on the data, then the data need not be collected).

The primary hydrologic parameter of interest is the elevation of ground water in monitoring wells and piezometers. Estimates of hydraulic gradients and changes in the elevation of the water table with respect to locations of residual source materials (*i.e.*, any source materials that remain after all appropriate source control actions have been completed in accordance with OSWER Directive 9200.4-17P (U.S. EPA, 1999a)) are fundamental to all evaluations conducted during performance monitoring. The wells and piezometers used in these evaluations should be discretely screened in individual hydrogeologic units within and adjacent to the contaminant plume. Additional data that are often essential in assessing ground-water flow include surface-water elevations, local rates and schedules of irrigation, local precipitation data, and pumping rates and schedules for nearby wells. The evaluations should be three-dimensional in nature, including both horizontal and vertical components of hydraulic gradients that control three-dimensional contaminant migration. In many cases, the vertical component of the hydraulic gradient may be larger and may display more variability than the horizontal component. Depending on the anisotropy in the hydraulic conductivity of aquifer materials and the magnitude, direction, and duration of the hydraulic gradients, vertical movement of ground water and contaminants may be significant and fluctuations in both the horizontal and vertical components of ground-water flow may exist.

2.5.4 *Monitoring Frequency*

Monitoring frequency affects the ability of the performance monitoring program to:

- Provide timely warning of impact to receptors,
- Detect contaminant releases to ground water that warn of possible plume expansion,
- Detect changes in plume size/concentration,
- Determine temporal variability of data,
- Detect changes in geochemistry that warn of changes in attenuation, and
- Yield data necessary to reliably evaluate progress toward contaminant reduction objectives.

The most appropriate frequency for ground-water sampling depends on the rate with which contaminant concentrations change due to ground-water flow and natural attenuation processes, the degree to which the causes of this variability are known, the types of evaluations to be performed, the location(s) of possible receptors, and the RAOs for the site. Based, in part, on previous studies (*e.g.*, Barcelona *et al*., 1989), quarterly monitoring will often be an appropriate frequency to establish baseline conditions over a period of time sufficient to observe seasonal trends, responses to recharge, and to estimate attenuation rates for key contaminants. Quarterly monitoring for several years provides baseline data to determine trends at new monitoring points and test key hypotheses of the conceptual site model. In situations where hydrologic, geochemical and contaminant trends are stable and the conceptual site model is verified by measured site data, reductions in sampling frequency may be warranted. In situations where variability is high, increases in monitoring frequency and additional investigations to determine the source of the variability may be warranted. More frequent monitoring may be appropriate under circumstances where ground-water flow is rapid and/or contaminant travel time to receptors is short.

More frequent monitoring of ground-water elevations may be warranted, particularly during the establishment of baseline conditions, to improve the characterization of ground-water flow patterns. In addition, more frequent monitoring may be needed to observe changes in ground-water flow patterns in response to other site activities, such as the start or cessation of ground-water extraction, source control activities, and other significant changes in the hydrologic system. In some cases, monitoring of this parameter on a very frequent basis using automated recording equipment may be needed to determine the effects of variability in recharge and discharge rates or locations on ground-water flow patterns. This will aid in specification of appropriate long-term monitoring frequencies and locations for evaluating fluctuations in hydraulic gradients and trends in chemical parameters. Based on the results of such assessments, initial monitoring frequencies may be adjusted to adequately capture the fundamental features of the trends. In situations where temporal trends in hydraulic gradients are absent or well characterized, monitoring of ground-water elevations at a frequency no less than that of the chemical parameters is generally appropriate.

Several years of monitoring data are typically necessary for estimation of the site variability and expected rates of change in ground-water flow, contaminant concentrations, and geochemistry (Barcelona *et al.*, 1989). Once site characterization and initial performance monitoring activities have provided these data, reevaluation of the monitoring frequency may be warranted if trends are established and the remedy is progressing as expected. Increases and decreases in monitoring frequency may occur several times over the life of the remedy in response to changes in site conditions and monitoring needs (Figure 7). For example, note in Figure 7 that monitoring frequency was decreased in response to stable contaminant concentration declines, increased in response to a sudden increase in contaminant concentration, decreased again based on the reestablishment of stable contaminant concentration declines, and increased yet again with the implementation of the verification monitoring program.

Specifically, monitoring frequency generally should be related to detecting changes in site parameters that indicate ability of the MNA remedy to achieve site-related remedial action objectives, and to provide early warning of possible impact to receptors. The monitoring frequency may be adjusted to capture information regarding trends of interest while eliminating unnecessary redundancy. However, monitoring frequency determinations should take into account that apparently stable site parameters may sometimes change due to natural or anthropogenic causes. For example, contaminant releases or remediation activities on adjacent properties may cause chemical or hydrologic changes in plume properties at the site. Increased rainfall can change recharge rates, ground-water extraction can cause changes in ground-water flow, and air sparging for volatiles stripping or hydrogen peroxide injection for contaminant oxidation could change the geochemical regime possibly changing biodegradation rates. Water-table variations and changes in velocity are common in flood plains, particularly near large rivers that have major changes in the stage of the river. In some climates, most of the recharge to aquifers due to precipitation occurs in only a few months of the year. In some settings, water extracted by trees from shallow water table aquifers can influence the direction of ground-water flow. Irrigation or municipal water supply wells that pump intermittently can change ground-water flow in an irregular manner.

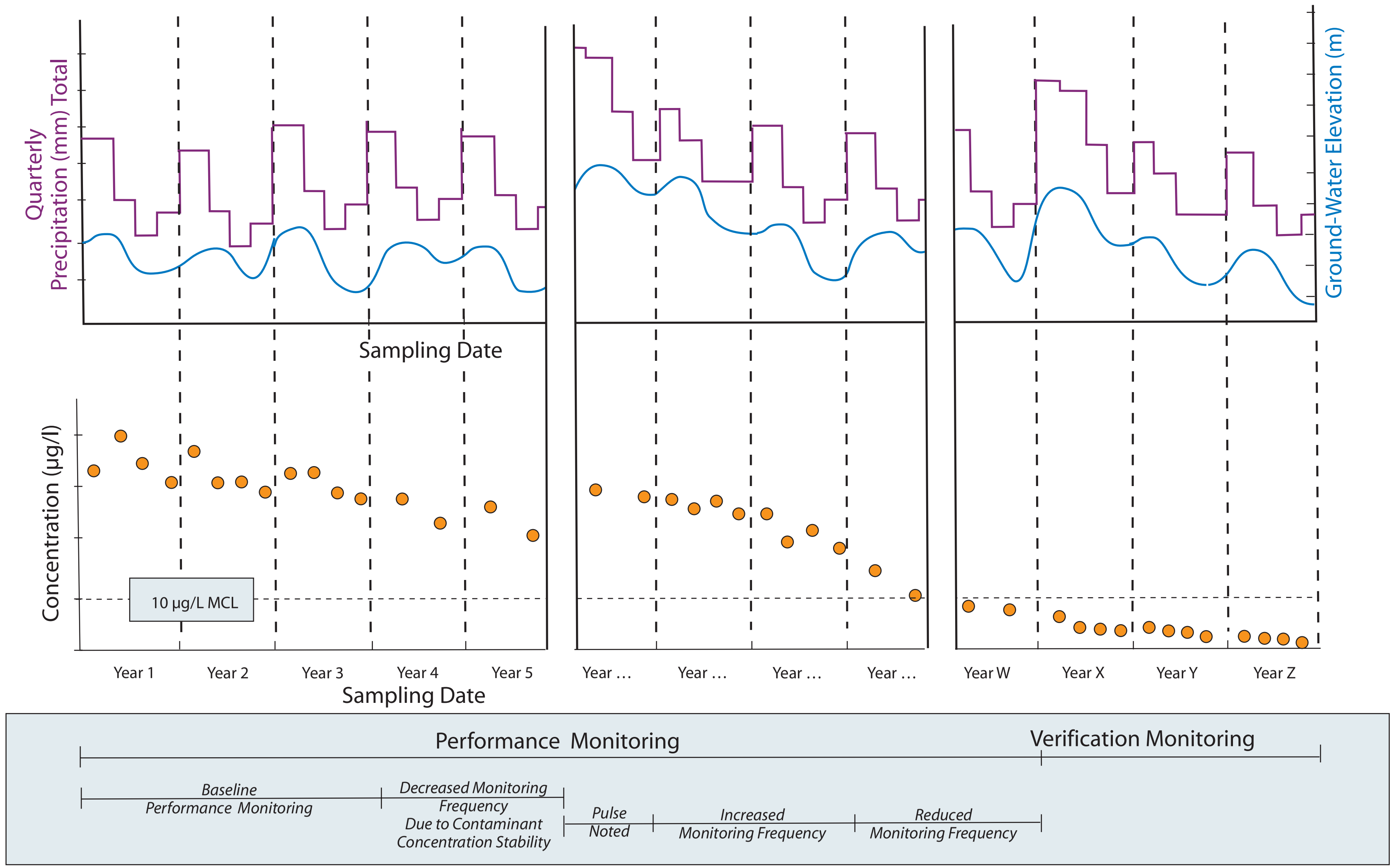


Figure 7. Examples of possible changes in monitoring frequency over the monitoring life cycle.

Examples of factors influencing specification of the monitoring frequency are provided below. Each example considers only the point under discussion. The actual monitoring frequency selected would be based on consideration of all the factors bearing on the given parameter and monitoring location.

- *Monitoring Frequency Determination Based on Possible Contaminant Travel Time to Receptors*

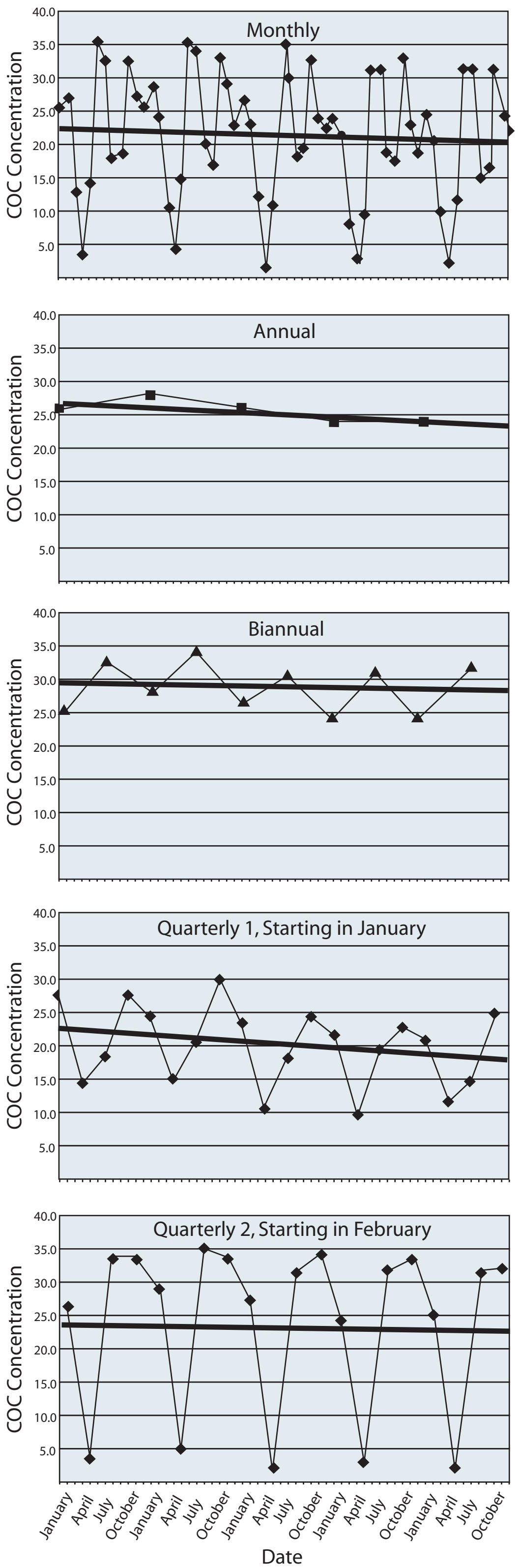
  Consider a site with the following conditions: the travel time for ground water from the downgradient plume boundary to a receptor was expected to be two years, based on analysis of the ground-water flow field. The time required to design, construct and bring an alternative remedy online to intercept the contaminant and protect the receptor would be added to the ground-water travel time. In this hypothetical situation, monitoring contaminant concentrations at wells placed downgradient of the current plume boundary to detect plume expansion would be conducted at least annually, and, in most cases, more frequently (*e.g.,* quarterly) to allow time for confirmation of detections and other contingencies. Monitoring may be more frequent for wells near and downgradient of the plume boundary or other compliance boundaries than for interior wells. In this example, the travel time for a conservative constituent was used in the calculations to allow a more conservative estimate of the minimum contaminant migration time than that obtained through use of an estimated transport velocity for a contaminant that may undergo sorption or biotransformation reactions.

- *Monitoring Frequency Determination Based on Evaluation of a Cyclic Change*

  Some sites, such as sites where the climate produces a pronounced wet season/dry season with associated changes in recharge rates and ground-water flow characteristics, may display pronounced cyclical trends in contaminant concentrations and plume boundaries. For example, seasonal changes may involve seasonal inputs of contaminant from the vadose zone, and may require more frequent monitoring or changes in monitoring timing relative to cyclical changes (*i.e.*, the particular dates when samples are taken) (Figure 8). By reviewing the historical variability in water levels for the site and recorded climatic variability (*i.e.*, drought frequencies, periods of above-average rainfall), a plan for specifying the monitoring frequency may be established. The objective of such a plan is to increase monitoring frequency sufficiently to prevent unmonitored expansion of the plume while avoiding collection of unnecessary data. Typically, data gathered over several years are necessary to evaluate seasonal trends and determine what frequency and time of monitoring are appropriate to capture changes related to seasonal trends (Barcelona *et al.*, 1989). Examination of prevailing annual weather patterns (available from National Weather Service historical data) may be helpful for determining appropriate sampling frequencies.

- *Monitoring Frequency Determination Based on Relevance of Parameters*

  If a parameter is not expected to significantly influence evaluations of remedy performance at a site, then monitoring frequency for that parameter could be greatly reduced or eliminated. If information gained from frequent sampling for a given parameter would not be reasonably expected to change site-related decisions, sampling for that parameter could be reduced in frequency. However, absent specific reasons for excluding a parameter,



EFFECTS OF MONITORING FREQUENCY

The following example is used to illustrate the effect of different monitoring frequencies and timing on monitoring data and data interpretation.

Site Characteristics

The site had a leaking underground storage tank that contained gasoline. The tank has been removed and source control actions implemented, but some undetected petroleum product remains at residual saturation in the vadose zone and saturated zone extending downgradient of the source area. The water table varies about four feet in elevation throughout the year.

This example is focused on one monitoring well from the multi-well performance monitoring network. The well is constructed with a ten-foot screen and located 100 feet downgradient from the LNAPL release area. Travel time for contamination to move from the release area to the monitoring well varies, but averages about five months. The top of the well screen is located at 20 feet below ground surface (bgs) (*i.e.*, about one foot above the highest observed water table elevation). The bottom of the well screen is at 30 feet bgs and is terminated at a regionally extensive, uniform clay layer.

The ground water is contaminated from the water table to a depth of about 28 feet bgs. There is an uncontaminated zone about two feet thick over the clay confining layer, so that some clean water is intercepted by the lower part of the well screen.

During the rainy season in the fall (November-December) and spring (March-May), the water table reaches its "maximum" elevation at about 22 feet bgs, which is about two feet below the top of the well screen. The higher water table intercepts more of the previously undetected residual LNAPL and sorbed contaminants in the vadose zone in the release area, causing a pulse of contaminants to enter the ground water.

From December to March and May to June, the water table declines to its "average" elevation, at about 24 feet bgs. During July, a nearby irrigation well comes online, and continues pumping until sometime in September, causing the water table to decline to elevations as low as 26 feet bgs, its "minimum" elevation. Also, ground-water flow is shifted so that the monitoring well is not directly downgradient of the source zone.

During periods of high water table elevations, flushing and interception of contaminated vadose zone by infiltration and the elevated water table cause pulses of contaminant to move toward the monitoring well, arriving several months after the rain. During periods of low water table elevations, less residual NAPL is intercepted by the ground water, so water with lower contaminant concentrations moves toward the monitoring well. Also, the shift in ground-water flow direction caused by the irrigation well causes the monitoring well to intercept the fringe of the plume, rather than the more central, highly contaminated volume of the plume.

Results

The concentrations of a contaminant of concern (COC) from the monitoring well are shown in the adjacent panels. The trend line in each graph shows the estimated linear trend of contaminant concentration based on the data in the chart. It can be seen that at sites where conditions cause significant changes in the contaminant concentration throughout the year, the frequency of sampling and the timing of the sampling cycle relative to the contaminant concentration cycle can strongly affect the data obtained and the interpretation of the data. These data highlight the importance of site characterization in choosing monitoring frequency and, in this example, identifying the need for additional source controls for effective remediation.

Figure 8. Monitoring frequency effects on sampling data collection and interpretation. The relationship of monitoring frequency and timing to cyclical changes in contaminants may significantly affect data collection and interpretation.

it generally would be expected that the entire suite of geochemical parameters relevant to the site, as well as contaminants and hydrogeological parameters, would be measured at all monitoring points on a set schedule. This allows an evaluation of continued stability in the geochemical setting and the potential for changes in biotransformation processes and attenuation rates to be performed.

- *Monitoring Frequency Determination Based on Information Redundancy*

  If, over a period of several years, data trends are stable, a reduction in monitoring frequency may be warranted (Figure 7). Also, if two or more wells sampling the same zone are located close together, and consistently produce similar data, changes in the monitoring frequency of one or more of the wells may be considered. For example, if the geochemical indicators at a given monitoring location are stable over a long period (*e.g.,* within a range indicating suitable conditions for degradation of the contaminants), then monitoring for these geochemical indicators could be reduced in frequency, to the point of being measured annually, biennially, or at even greater intervals. However, the possibility of a rapid change in a previously stable pattern may affect determination of the monitoring frequency. For instance, nitrate concentrations, that can 1) change quickly due to anthropogenic inputs and 2) strongly inhibit reductive dechlorination of the chlorinated solvent compounds, generally should continue to be monitored frequently at sites where reductive dechlorination is an important component of the MNA remedy.

  Contrastingly, for example, if a sudden change in contaminant concentrations were noted (Figure 7), an increase in monitoring frequency may be warranted to provide information to facilitate understanding of the change and provide earlier warning of further change.

2.6 Demonstrating MNA Effectiveness with Respect to Remedial Objectives

Representative techniques for demonstrating the effectiveness of MNA, with respect to the remedial objectives provided in Table 1, are discussed below. The discussions are intended to provide general suggestions on the types of assessments, monitoring network designs, parameters, and evaluation frequencies. However, specific study designs depend on site conditions and the site-specific limits on decision errors. For additional information concerning remedial objectives, refer to current program-specific guidance.

2.6.1 *#1 - Demonstrate that Natural Attenuation is Occurring According to Expectations*

Although remedial expectations and, consequently, appropriate performance monitoring analyses are site specific in nature, reduction in contaminant concentrations to specified levels is a general expectation for most selected remedies. Other common goals, such as the prevention of additional contaminant migration, are discussed in the following sections. Data analyses useful in evaluating progress toward contaminant reduction objectives include evaluation of temporal trends in contaminant concentrations or mass, comparisons of observed contaminant distributions with predictions or required milestones, and, in some cases, comparison of calculated attenuation rates with the range of rates required to meet remedial objectives within the required time frame. Evaluations of adequate progress toward restoration objectives are difficult due, in large measure, to subsurface variability and to a lesser extent, measurement variability (Appendix A). This will often necessitate use of multiple lines of evidence (*e.g.,* temporal trends and estimates of contaminant mass loss, as discussed in the following sections) and relatively dense monitoring networks to reduce uncertainty to acceptable levels.

2.6.1.1 Temporal Trends in Individual Wells

Temporal trends in the concentrations of all contaminants of concern measured in ground-water samples are essential indicators of plume stability and progress toward contaminant reduction objectives. Temporal trends in an individual well can sometimes be used to estimate the potential lifetime of the plume at that location (U.S. EPA, 2002b). However, contaminant trends at monitoring points located throughout the plume will be needed to adequately interpret progress toward most contaminant reduction goals.

Wells used for analysis of temporal trends generally should be screened in portions of the plume representative of areas where different processes may be dominant (*e.g.,* different biotransformation processes or processes that mobilize naturally occurring toxic metals) and representative of the range of contaminant concentrations observed at the site. Such areas (Figures 4, 5, and 6) include:

- In and immediately downgradient of suspected or former source areas,
- In the most contaminated zones downgradient of these areas,
- In areas (recalcitrant zones) where contaminants may be attenuating at rates too low to meet remediation goals due to differences in geochemistry or other factors,
- In fringe areas of the plume,
- In locations surrounding the plume or other compliance boundaries,
- In contaminated zones with the highest ground-water flow or contaminant migration rates that may serve as pathways for rapid migration.

Statistical techniques, such as those described in Gibbons (1994), Gilbert (1987), Helsel (1995), and U.S. EPA (2000c), may be used to objectively determine whether contaminant concentrations are increasing or declining with time, and to compare trends between wells. A trend may be assessed to determine if the trend would be sufficient to meet remedial goals in the desired time frame.

Temporal trends observed in wells may result from processes such as biotransformation that reduce contaminant mass or concentrations. However, temporal trends may be the result of contaminant release history and effects of source control actions. Trends may also result from processes such as changes in ground-water elevations (Figure 8) or ground-water flow directions (Figure 9) that merely change the shape of the plume or retard its movement, rather than degrading contaminants. For instance, changes in ground-water flow patterns may cause a change in plume shape, perhaps causing some wells to have lower contaminant concentrations, and other wells to have higher concentrations. Ground-water flow patterns vary in response to temporal differences in the rates and locations of recharge (*e.g.*, precipitation or irrigation) and discharge (*e.g.*, pumping of potable or agricultural wells or operation of drainage systems) at many sites. Variations in ground-water flow directions and rates may occur on scales of hours to years and may influence contaminant concentration trends in individual wells.

Variations in recharge may cause pulses of contaminants to be released from poorly controlled sources, or may provide pulses of relatively uncontaminated ground water. For instance, rain

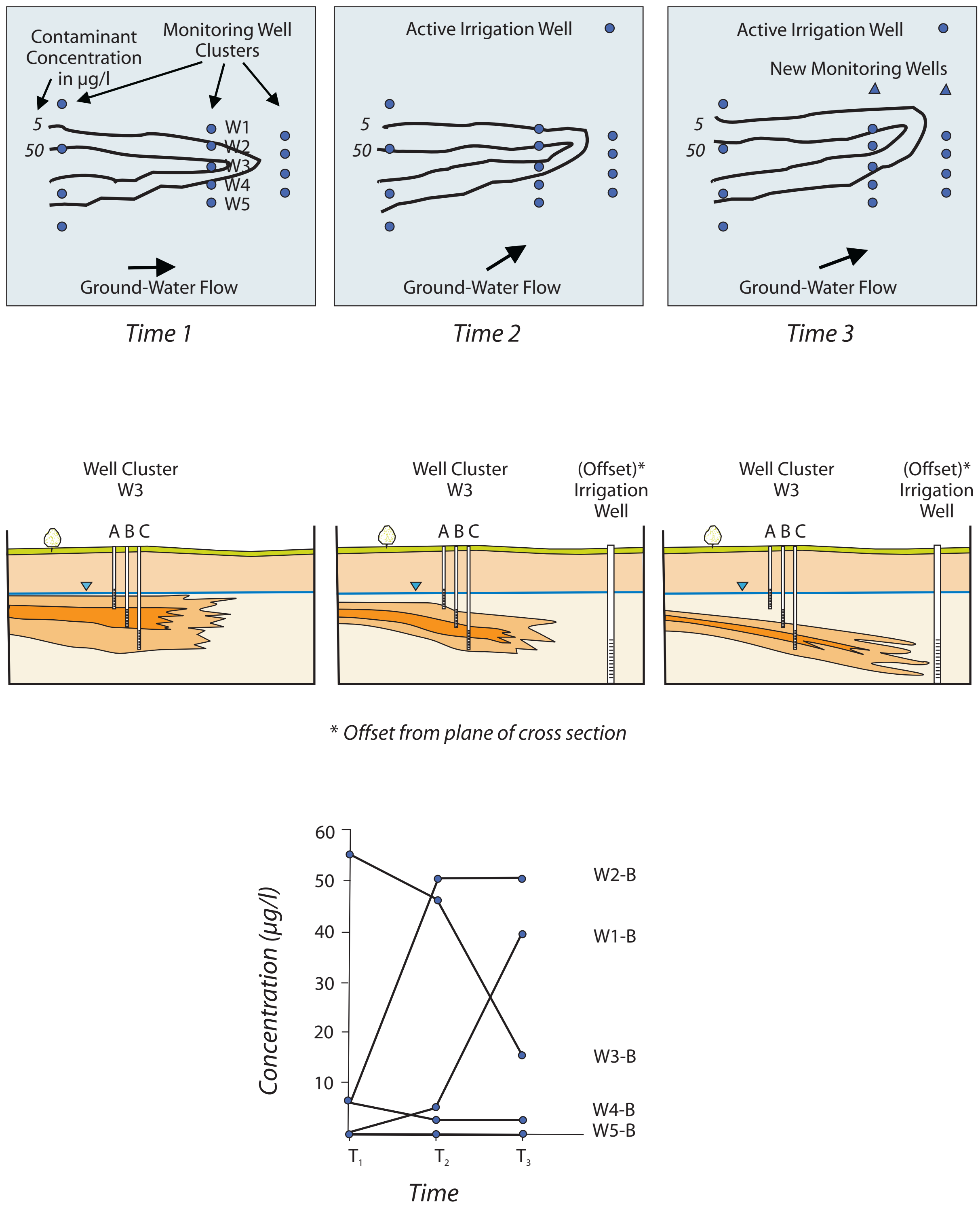


Figure 9. Potential effects of changes in ground-water flow direction on temporal trends in contaminant concentrations.

may infiltrate through a vadose zone source, or higher water tables may intercept vadose zone contamination, causing increased contaminant concentrations in ground water. As pulses of contaminants or uncontaminated ground water move downgradient, contaminant concentrations in monitoring wells may increase or decrease temporarily, perhaps leading to false inferences about contaminant attenuation.

Trends in contaminant concentrations may also result from measurement variability. For example, changes in sample collection and analysis procedures and personnel can introduce variability into contaminant data. Consideration of these sources of variability may be helpful for interpretation of patterns in the data, especially when abrupt changes in established patterns are noted.

Due to the variety of possible causes, it may be difficult to isolate or identify specific causes of contaminant concentration trends either in individual wells or groups of wells. The range of viable hypotheses that may explain observed trends generally should be incorporated into the conceptual site model and consistently used for evaluating site data in order to obtain accurate interpretations of the data. Contaminant concentration changes in wells ordinarily should be evaluated in the context of the conceptual site model and sampling history before they are attributed to natural attenuation processes or other possible causes.

A site-wide trend cannot be satisfactorily elucidated from monitoring one sampling location, or one target monitoring zone within a plume. Significant reductions in contaminant concentrations from all or most sampling locations may indicate decreases in contaminant mass and imply progress toward restoration. Mixed trends in different portions of the aquifer (Figure 9) may imply temporal changes in plume migration and an inadequate conceptual site model rather than contaminant mass loss.

2.6.1.2 Estimation of Contaminant Mass Reduction

Estimation of the reduction in total contaminant mass is another tool that may be used to evaluate progress toward achieving contamination reduction objectives. The production of daughter products from parent contaminants is generally primary evidence of biotransformation processes, particularly at chlorinated solvent sites. However, certain compounds that can be daughter products (*e.g.,* trichloroethene) may be or have been present as a substantial portion of the source materials at many sites. Thus, source characterization information is needed to ensure their appearance is not incorrectly attributed to natural attenuation processes.

Qualitatively, simple comparisons of the stoichiometric ratios of parent contaminants to daughter products in different parts of the plume provide important evidence of the effects of degradation processes with migration distance and should be considered during evaluations of contaminant mass reduction. However, data for quantitative assessments of contaminant mass reduction would consist of the concentrations of all contaminants of concern in samples obtained throughout the contaminated aquifer. As with all methods used to evaluate subsurface remediation performance, the most appropriate spacing of monitoring points for evaluation of mass reduction depends on the variability in contaminant distribution. Uncertainties in these methods normally result from use of sparse data sets relative to in-situ variability. Application of transect-based approaches with monitoring at multiple depths may be needed to provide adequate data for evaluation of mass reduction. Given a sufficient density of monitoring points, evaluation of contaminant mass reduction may provide a more consistent indication of MNA effectiveness than analysis of temporal contaminant concentrations trends in individual monitoring wells.

Cohen *et al.* (1994) describe methods for estimating total contaminant mass in the aquifer if no NAPL or other source material is present. Although the authors describe this methodology for evaluation of pump-and-treat performance, the techniques would be identical for estimating total contaminant mass within the plume during MNA performance evaluations. Depending on site conditions and contaminant properties, periodic sampling of both ground water and aquifer materials may be needed to better determine total contaminant (dissolved and sorbed phase) mass trends.

Data from transects of clustered sampling points, placed perpendicular to the longitudinal axis of the plume, may also be used to estimate contaminant flux within the plume, and, therefore, mass loss along the plume axis (Weaver *et al.*, 1996). Such transects provide two-dimensional cross sections of contaminant distribution. Use of multiple transects can provide a three-dimensional view of the plume. If used with hydrogeologic data, contaminant mass flux through each cross section can be calculated. Contaminant mass loss and, consequently, attenuation rates may be estimated using the differences in the fluxes between transects. Sampling density and frequency for transects generally should be based on the factors identified in Sections 2.5.2 Monitoring Locations and 2.5.4 Monitoring Frequency.

As noted in other sections, evaluations of cross-media transfers of contaminants are important elements of performance monitoring for MNA. Subsurface contaminant mass within one medium may be reduced due to contaminant migration into other media, so the potential for such loss should be evaluated in order to provide a comprehensive assessment of contaminant mass reduction (*e.g.*, evaluate the potential for cross-media transfer into soil gas). Contaminant mass in all physical phases (*e.g.*, NAPL, aqueous phase, vapor phase, sorbed) should be assessed within each medium to estimate the actual contaminant mass reduction.

2.6.1.3 Comparisons of Observed Contaminant Distributions with Predictions and Required Milestones

Contaminant distribution data obtained during performance monitoring may periodically be compared with previous predictions or specified milestones (*e.g.,* at least 50 % contaminant reduction at all monitoring points within a specified number of years) to ensure that suitable progress toward contaminant reduction goals is achieved. Quantitative models may be used to help set or evaluate the milestones. For example, models may be used to estimate the range of time frames for achieving remedial objectives (*e.g.*, contaminant concentrations below Maximum Contaminant Levels (MCLs) in all wells within 20 years) and set intermediate milestones (*e.g.*, concentrations in all wells at the current plume periphery below MCLs in five years). Although these comparisons may be as simple as visual comparisons of contoured maps or comparisons of predicted and observed total contaminant mass estimates, the use of statistical methods provides a more objective basis for evaluation. Types of data comparisons for such evaluations are discussed in Chapter 3.

The goal of these comparisons is to identify any significant deviations from predictions or other progress requirements that may signify flaws in the conceptualization of site conditions. For instance, a gradual long-term trend of increasing water levels may cause increased dissolution of inadequately removed or contained vadose zone contaminants, causing increased ground-water contaminant concentrations in the source area and, potentially, resulting in plume expansion. Comparison of the observed contaminant concentrations with predicted concentrations or milestones would highlight the change and trigger reevaluation of the conceptual site model. If the potential impact on the remedy is negligible, revision of the conceptual site model may be the only outcome of such evaluations. However, if the potential impact is significant, implementation of alternative remedies may be triggered or, at a minimum, additional characterization to better define the factors limiting contaminant reduction and determine methods for mitigating the magnitude of their impact on the remedy would be warranted.

Monitoring parameters for these periodic comparisons may include all contaminants of concern but, at some sites, may be limited to the most mobile, toxic, or recalcitrant compounds as indicators of the behavior of other site contaminants. The most appropriate frequency for performing this type of evaluation depends on the expected rate of change in contaminant concentrations and the ability of the monitoring network to reliably measure significant changes (Section 2.5.4.). It is likely that performance of such evaluations at a frequency coincident with major, comprehensive site reviews (*e.g.,* every few years) may be appropriate for most sites.

2.6.1.4 Comparison of Field-Scale Attenuation Rates

Information obtained during periodic performance monitoring may also be used to estimate field-scale attenuation rates and compare these estimates with the range of rates determined to be necessary to meet remediation objectives within specified time frames. Methods that have been used to estimate attenuation rates and the biodegradation component of the attenuation rate are described in U.S. EPA (1998a), Wiedemeier *et al.* (1999), and U.S. EPA (2002b). However, commonly used calculation methods (*e.g.*, Buscheck and Alcantar, 1995) often suffer from significant uncertainty regarding the applicability of assumptions required in the calculations as well as the limited data available from many sites (McNab and Dooher, 1998). Careful evaluation of site conditions and the assumptions inherent in the method of analysis is required to produce useful results. Due to the increased uncertainties inherent in the estimation of attenuation rates, it is anticipated that periodic evaluation of such rates during performance monitoring often may have few advantages over the direct comparisons of contaminant distributions described above.

2.6.2 ***#2 - Detect Changes in Environmental Conditions that May Reduce the Efficacy of Any of the Natural Attenuation Processes***

Changes in hydrogeological and geochemical conditions may affect microbiological populations, the transformation processes that result in contaminant destruction, and rates or directions of ground-water flow and contaminant migration. Reductions in the effective rates of contaminant transformation, sustained increases in hydraulic gradients, or, in some cases, exceedence of sorptive capacity may lead to plume expansion. Sustained changes in ground-water flow directions may result in risk to receptors that were not originally identified at the time of remedy selection. The monitoring network should be designed to detect changes in such parameters to allow determination of their effects on remedy performance.

It is particularly important to monitor and evaluate the effects of other remedial actions that may be taking place on or near the site. Many remedial actions (*e.g.*, capping of the site, pump and treat, air sparging, chemical oxidation) would be expected to change hydrogeologic and/or geochemical conditions, potentially adversely affecting the MNA remedy. For instance, a site cap could reduce the flux of oxygen to a shallow aquifer, potentially slowing degradation of petroleum hydrocarbons, or a pump and treat remedy could alter the flow of ground water at the site, and potentially change the geochemical environment. In addition, the potential effect of planned remedial actions should be taken into account when predicting the efficacy of MNA during the remedy selection phase, and designing and implementing the performance monitoring system.

Routine monitoring parameters for these determinations are primarily geochemical indicators of the contaminant transformation reactions that may occur within the aquifer, and ground-water elevations in wells and piezometers that are used to estimate hydraulic gradients in each hydrogeologic zone.

2.6.2.1 Geochemical Parameters

The values and patterns of geochemical parameters other than ground-water contaminants provide evidence of the potential for continued biotransformation. The usefulness of geochemistry for performance monitoring comes from these factors:

- Degradation of some contaminants (*e.g.,* some highly chlorinated ethenes, highly chlorinated methanes, and highly chlorinated chlorobenzenes) appears to occur only under fairly specific geochemical conditions, and

- Degradation of contaminants causes specific geochemical changes that may be, at least qualitatively, correlated with microbial activity and contaminant degradation.

Though rates may differ, some contaminants (*e.g.,* BTEX) can be degraded under a variety of geochemical conditions, but others (*e.g.,* tetrachloroethene (PCE)) may require a more narrow range of conditions (Wiedemeier *et al.,* 1999). The controls on biotransformation processes at chlorinated solvent sites are very complex and not as well understood as at sites contaminated solely by more readily degradable hydrocarbons such as the aromatic components of fuels (*i.e.,* BTEX). Appreciable amounts of a biodegradable carbon compound can produce appropriate geochemical conditions for reductive dechlorination (Wiedemeier *et al.,* 1999; Leahy and Shreve, 2000). Therefore, depletion of the carbon source may limit the extent of biotransformation of chlorinated ethenes if reductive dechlorination is a significant biodegradation process. Biotransformation of some contaminants, such as MTBE and other ethers that may be present in fuel contamination, is not well understood and is the subject of continuing research (National Research Council, 2000).

Most of the geochemical signatures seen at sites of chlorinated solvent contamination are reflections of biological processes utilizing various carbon sources and often are not directly caused by biotransformation of the chlorinated solvent contaminants. However, these data have value as continuing indicators of appropriate geochemical environments for biotransformations of contaminants in many situations. The analyses provide evidence regarding the continued effectiveness of MNA and the adequacy of the conceptual site model. If biotransformation is a major natural attenuation mechanism, then the geochemistry generally should be monitored to determine that biotransformation continues. If a strong correlation exists between changes in geochemical indicators, decreasing contaminant levels, and the products of known biological transformation processes in a particular portion of the plume, this may be considered supporting evidence for continued microbial destruction of contaminants. However, in areas of decreasing contaminant concentration that do not bear a strong geochemical signature, other processes typically should be considered. The relationship between geochemical patterns and degradation of organic carbon other than the contaminants of concern should also be considered.

Geochemical parameters generally should be measured throughout the plume in order to establish a correlation between reductions in contaminant concentrations and microbial activity (U.S. EPA, 1998a; Wiedemeier *et al.,* 1999). In addition, geochemical samples generally should be obtained upgradient and sidegradient of the plume (Figure 4) to determine the range and variation in ambient conditions, in order to differentiate changes in geochemistry related to microbial metabolism of contaminants from unrelated processes. The specific parameters useful at a given site include:

- Parameters displaying correlations with contaminant distribution that are indicative of dominant biotransformation processes,

- Parameters showing conditions that are necessary for contaminant degradation, and

- Parameters whose appearance may indicate changes detrimental to continued biotransformation.

Discussion of these parameters and the interpretation of geochemical data is found in U.S. EPA (1998a) and Wiedemeier *et al.* (1999).

At sites where the total available supply of electron acceptors utilized in contaminant biotransformation is predominantly composed of solid phase material (*e.g.*, bioavailable iron species), periodic monitoring of bioavailable electron acceptors in soil samples may provide information concerning their rates of depletion (Huling *et al.*, 2002) and the potential for renewed plume migration. This type of monitoring may be useful where a large mass of biodegradable contaminant relative to the total electron acceptor supply is present. Where warranted, it is anticipated that this type of assessment would be performed on a relatively infrequent basis determined by the possible time frames over which significant changes are expected to occur.

2.6.2.2 Hydrogeologic Parameters

Long-term changes in ground-water flow directions due to sustained changes in recharge or discharge locations or rates may result in risks to receptors that were not originally identified at the time of remedy selection. In addition, increases in ground-water flow rates may result in expansion of the plume. Such changes may result from many factors including land use changes (*e.g.,* irrigation of adjacent areas), installation of new pumping wells or increase in pumping rates of existing wells, and installation of drainage systems, as well as climatic patterns.

Monitoring of ground-water and surface-water elevations should be performed at a frequency sufficient to determine significant variations in hydraulic gradients. The frequency would usually be no less than the monitoring frequency for the chemical parameters. Other hydrologic data such as rates of local ground-water pumping, irrigation, and precipitation may also be needed at some sites. As previously noted, the evaluations generally should be three-dimensional in nature, monitoring horizontal and vertical components of hydraulic gradients. The monitoring network should be dense enough to accurately estimate spatial variations in gradients. The number of monitoring points needed at any given site depends in large measure on the sources of aquifer recharge and discharge in the vicinity of the site and the degree of geologic heterogeneity.

2.6.3 *#3 - Identify Any Potentially Toxic and/or Mobile Transformation Products*

Contaminant transformation processes may result in the formation of new chemicals that may be more toxic or more mobile than their “parent” compounds. Transformation products may appear sequentially along the direction of ground-water flow and all possible products may not be present throughout the plume. Potentially toxic daughter products should be evaluated based on information regarding contaminant transformation pathways and monitoring data. All such products typically should be included as contaminants of concern in the monitoring program and monitored at the same frequency as other contaminants of concern. Mobile but nontoxic transformation products may be monitored as an aid to determining flowpaths and demonstrate continued biotransformation processes, as discussed in Sections 2.6.1, Demonstrate that Natural Attenuation is Occurring According to Expectations, and 2.6.2, Detect Changes in Environmental Conditions that May Reduce the Efficacy of Any of the Natural Attenuation Processes.

Minerals in the aquifer matrix have specific chemical compositions and crystalline structure and are in dynamic equilibrium with surrounding pore water. Large changes in oxidation-reduction potential caused by biological processes within the contaminant plume may result in transformation of some naturally occurring mineral species into more soluble and mobile forms that pose risks to human health or the environment (Brady *et al.,*1999, U.S. EPA, 1998a, Wiedemeier *et al.*, 1999). Mobilization of arsenic and manganese species has been observed at some sites. Where such mobilization is possible, these species generally should be monitored as potential contaminants, and also for interpretation of their possible use as electron acceptors. Metals that are possible contaminants of concern due to human health or surface-water quality criteria should be included in the ground-water monitoring program at the same frequency as other contaminants. Removal of these constituents from the monitoring program may be warranted if data demonstrate lack of appropriate mineral species or that such mobilization does not occur under site conditions.

2.6.4 #4 - Verify that the Plume is Not Expanding Downgradient, Laterally, or Vertically

Plume expansion may result in a plume extending to areas that were previously uncontaminated, migrating beyond established compliance boundaries, degrading additional ground-water resources, and potentially increasing risk to receptors. Previous site characterization and performance monitoring data obtained using a three-dimensional monitoring network will likely be needed to assess hydrogeological changes, temporal variability in the lateral and vertical extent of the plume, and to determine the effective boundary for demonstrating compliance with the nonexpansion objective. Assessment of plume expansion is complicated because ground-water flow systems, like all natural systems, are temporally dynamic. For example, precipitation may vary seasonally and/or over longer time frames. This may result in changes in water table elevations and possible changes in hydraulic gradients and contaminant inputs to a plume. Anthropogenic effects (*e.g.,* variations in ground-water extraction rates or loss of water from distribution systems) also can be a source of changes in subsurface conditions. Such changes may result in three-dimensional changes in plume geometry, causing the plume boundary to be in continual flux. This constant variation in plume geometry means that, in some cases, it may require several years of monitoring to definitively determine if a plume is not expanding. In such cases, particularly where receptors are immediately susceptible to impact, implementation of alternative remedies may be more appropriate than waiting to verify a lack of plume expansion.

Plume expansion may be caused by many geochemical and biologic processes as well as variability in site hydrology. Examples of these processes include:

- Increases in contaminant inputs to the plume that exceed the capacity of transformation and hydrologic processes to attenuate the concentrations within the current plume boundaries, and

- Changes in oxidation-reduction potential due to factors such as the depletion of electron donors or acceptors that reduce the effective rates of transformation processes. For example, depletion of a degradable carbon source prior to complete biotransformation of tetrachloroethene to lesser chlorinated products may result in additional tetrachloroethene migration.

A three-dimensional performance monitoring network (Figures 4, 5 and 6) will often be necessary to meet this objective. Monitoring of points throughout the plume, including locations in or near existing or suspected source areas and in the zones of highest contaminant concentrations, generally will be needed to evaluate changes that may lead to plume expansion. Monitoring points of the most immediate concern will often be those points located near the horizontal and vertical plume boundaries and any other compliance boundaries specified in the remedy decision. Trends of increasing contaminant concentrations in these wells will often be direct evidence of plume expansion. In addition, evaluations of temporal trends in individual monitoring points and comparisons with trends observed in different areas of the site may aid in confirming the roles of the dominant processes (*e.g.,* advection, dispersion, and transformation) controlling contaminant migration. The appropriate number and locations of monitoring points will be dependent on such factors as the size of the plume, ground-water velocity, proximity to receptors, and presence of preferential pathways for contaminant migration.

In practice, wells located at the plume and other compliance boundaries, and between the boundaries and receptors, may often be used to detect contaminant increases and trigger the implementation of contingency or alternative remedies to prevent impact to receptors. Such wells would be located sufficiently upgradient of receptors to allow adequate time for implementation of the contingency remedy and demonstration of its effectiveness given the ground-water velocity within the most transmissive contaminated zones. Monitoring at the receptor point generally should also be included in all settings. For example, monitoring of public and private water supply wells that would be at risk if the plume expanded should be incorporated into the performance monitoring program, as warranted. Wells chosen for sampling should be based on evaluations of the capture zone for each well. In similar fashion, monitoring at locations of possible impact to ecological or other receptors should also be included.

At some sites, the geochemical fingerprint of ground water can be established and used to trace water downgradient to distinguish ground water that has never been contaminated from ground water that was previously contaminated (National Research Council 2000, Weidemeier and Haas 2002). Such information may be used to site wells near the current plume boundary in zones where contaminant migration would be expected if plume expansion occurred. Depletion of electron acceptors, and presence of metabolic by-products and nonhazardous daughter products may be used as indicators of appropriate monitoring locations. The most useful parameters for sites with hydrocarbon contamination may include nitrate, sulfate, iron, methane, and dissolved oxygen. The most useful tracers in plumes of chlorinated solvent compounds are often their reduced transformation products, particularly ethane or ethene, but also include the same parameters as for petroleum hydrocarbon plumes. The most appropriate parameters for determining locations for monitoring wells downgradient of a contaminant plume depend on site-specific correlations of contaminants and geochemical indicators.

2.6.5 *#5 - Verify No Unacceptable Impacts to Downgradient Receptors*

Impacts to receptors may result from plume migration to wells used for drinking and other domestic purposes, irrigation or industrial purposes; contaminant migration to indoor air; or discharge of ground water to wetlands or surface-water bodies. Prevention of unacceptable impacts to receptors includes continuing verification of plume stability and the reliability of institutional controls. Adequate demonstration of the lack of unacceptable impact to receptors will often require monitoring of wells located between the plume boundaries and the receptors, in the transmissive zones where contaminants may migrate if plume expansion occurs. In the case of potential impacts to receptors associated with water production wells, it would generally include periodic monitoring of the production wells. The potential for impacts to both human and ecological receptors should be evaluated, and the performance monitoring system designed to verify that no unacceptable impacts occur.

Performance monitoring with respect to this objective also includes monitoring of the cross-media transfer of contaminants. Cross-media transfers of concern include transfers between ground water and soil gas, air, sediments, and surface water. For example, in some situations, particularly where volatile contaminants are found in the vicinity of existing buildings or other structures, the potential may exist for contaminant migration through the vadose zone to indoor air. In such situations, periodic monitoring of soil gas and indoor air may be needed to determine that no impacts occur. Guidance regarding techniques for the monitoring of soil gas may be found in U.S. EPA (1988, 1993b). Fate and migration of volatile contaminants from the subsurface to indoor air is a rapidly evolving area of research and guidance/policy development. The reader is referred to U.S. EPA (2002c) for further information.

Another major cross-media transfer process of concern is movement of contaminants between ground-water and surface water/sediments. The ground-water/surface-water transition zone, where ground water and surface water mix in the saturated sediment beneath and beside surface water, may exert a major influence on input of contaminants to surface water because of the enhanced chemical and biological activity often found in these zones. The hydrologic and geochemical conditions in areas where ground water interacts with surface water often differ markedly from those in the main body of the plume and may require more intensive monitoring to determine the effect on remedial goals (Winter, 2000).

The locations and characteristics of contaminated ground-water discharges generally should be determined. Areas of discharge and interaction may vary rapidly both temporally and spatially. Plume discharge to the surface-water body or wetlands may not be at the immediate shoreline or channel edge, and the discharge may vary spatially through time. In addition, contaminant plumes may also migrate beneath streams and drainage features in some settings. Monitoring generally should occur in the interface between ground water and surface water as well as in the surface-water column (U.S. EPA, 1991b).

Tools to characterize the hydraulic relationships between ground water and surface water (Figure 10) include piezometers, pore water sampling devices, devices for the in situ measurement of ground-water velocity, and certain geophysical techniques. Such tools may be used to define ground-water flow from the plume into the surface-water bodies and to aid in siting monitoring points for determining the impact of the discharging water on the sediments and surface-water quality. It should be noted that mobilized metals may be a primary concern during these investigations due to the relatively low thresholds for unacceptable ecological impact. Multilevel monitoring is generally needed to identify contaminant discharge locations. Once the hydraulic relationships are characterized, water and sediment sampling locations may be specified.

2.6.6 *#6 - Detect New Releases of Contaminants*

Increases in contaminant concentrations or detection of new contaminants at monitoring points located within and immediately downgradient of source areas may be indications of new releases. Releases may result from such causes as the failure of source control measures, increased water infiltration or water table rise into contaminated portions of the vadose zone, or new releases to the environment. In many cases, it may be difficult to determine whether increased contaminant concentrations are due to new sources or other causes. Increases in contaminant mass may be

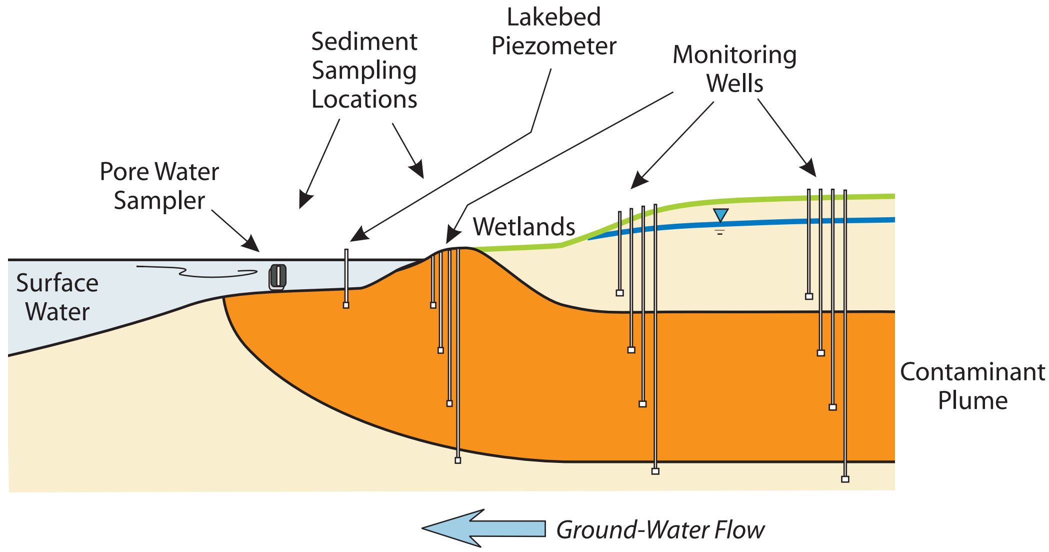


Figure 10. Conceptual monitoring network for verifying lack of impact to surface water from ground-water discharge.

sufficient to result in expansion of the plume and/or extension of time frames required to attain contaminant reduction objectives, warranting implementation of additional source control/ removal measures, other remedy modifications, or alternative remedies.

2.6.7 *#7 - Demonstrate the Efficacy of Institutional Controls*

Institutional controls may be put in place to prevent access to or use of contaminated ground water. These controls are an integral and necessary part of an MNA remedy because they are relied upon to ensure that the remedy is protective to human health and the environment. For this reason they should be monitored with the same degree of thoroughness as other components of the remedy. Institutional controls (U.S. EPA, 2000d) include:

- Governmental controls (*e.g.*, zoning restrictions, ordinances, statutes, building permits),
- Proprietary controls (*e.g.*, easements, covenants),
- Enforcement and permit tools (*e.g.*, administrative orders or consent decrees with institutional control), and
- Informational devices (*e.g.*, state registries, deed notices, hazard advisories).

At a minimum, the following questions should be answered during development of the monitoring plan to allow an initial assessment of the potential efficacy of institutional controls:

1) Are institutional controls in place?

2) What are the criteria for determining that institutional controls are effective and operating as intended?

3) Who is responsible for monitoring and reporting on the integrity and effectiveness of institutional controls for the site?

4) Are institutional controls being monitored regularly and at an appropriate frequency?

5) Are institutional control monitoring results included in either a performance monitoring report or a separate report? Are these reports completed at an appropriate frequency and forwarded to the appropriate regulator?

6) What procedures are in place to report breaches or failures of the institutional controls to the appropriate U.S. EPA and/or state regulator, local or tribal government, and the designated party or entity responsible for reporting?

7) Is the property likely to be transferred in the near future, and if so, who will be responsible for the future monitoring and reporting and enforcement of the institutional controls?

8) Are there provisions in place to notify regulators of any impending property transfer such as in a consent decree or order?

The MNA performance monitoring plan should include a description of activities to initiate and periodically monitor institutional controls, or refer to a separate plan for monitoring institutional controls. The assumptions and uncertainties associated with the site-specific institutional controls should be carefully considered in designing the monitoring plan and determining effectiveness. Compliance monitoring may include field inspection of affected areas, particularly if affected properties have been sold or land use patterns have changed, as well as determinations that the specified controls have been enacted. Each control should be periodically investigated to determine whether the control continues to be implemented as specified.

2.6.8 *#8 - Verify Attainment of Remediation Objectives*

One of the fundamental cleanup objectives for most sites is the reduction of contaminant concentrations in subsurface media (*i.e.,* soil and/or ground water) to specified levels. The remedial action objective of attaining permitted standards throughout the plume should be demonstrated before monitoring is terminated to ensure that the required standards are actually achieved. The techniques for determining compliance with RAOs under a natural attenuation remedy are similar to those used for determining compliance following application of other remediation methods. The demonstration of the attainment of cleanup objectives should include sufficient verification monitoring (*e.g.,* three to five years) once the standards are met to evaluate the effects of natural variations in site conditions, based on objective statistical analyses of the data. Statistical methods useful in these evaluations include analyses of temporal trends in contaminant concentrations and comparisons with the specified concentration standard. Guidance regarding verification of compliance with cleanup objectives is provided in Cohen *et al.* (1994) and U.S. EPA (1992a).

2.7 Monitoring Plan Contents

2.7.1 *Introduction*

The following material has been prepared to provide suggestions regarding appropriate formats and components of performance monitoring plans. Although there is no standard format that is universally accepted, most monitoring plans make extensive use of maps, cross sections, and

Table 4. Elements of a Performance Monitoring Plan

Background and Site Description

The following information typically would be discussed or incorporated by reference:
- ❑ Site setting, history, and characteristics
- ❑ Remedial goals
- ❑ Past and present remedial actions and institutional controls

Conceptual Site Model for Natural Attenuation

The following information typically would be discussed or incorporated by reference:
- ❑ Descriptions and locations of potential receptors (text and maps)
- ❑ Geologic and hydrologic controls on ground-water flow (text, maps, and cross sections)
- ❑ Contaminant sources, distribution, migration, and fate (text, maps, and cross sections)
- ❑ Relationship of geochemistry to attenuation processes

Objectives and Decision Points

- ❑ Remedial Action Objectives (RAOs)
- ❑ Monitoring Objectives
- ❑ Performance Criteria
- ❑ Decisions to be made based on monitoring data (e.g., monitoring network changes, implementation of contingency/alternative remedy, implementation of verification monitoring, terminate performance monitoring) and the criteria for making each decision

Monitoring Network and Schedule

- ❑ Detailed discussion of relationship of conceptual model, supporting data, and analyses to design of the monitoring network
- ❑ List and map of monitoring locations
- ❑ Description and construction details for each monitoring point
- ❑ Monitoring schedule specifying monitoring parameters, analytical methods, sampling frequency
- ❑ Maps, cross sections, and other visual aids to show where, when, and by what methodologies samples are to be taken and analyzed
- ❑ Statistical methods and test designs to be used for data interpretation

Monitoring of Institutional Controls (ICs)

- ❑ Descriptions of ICs and the procedures for their implementation
- ❑ Procedures for verifying establishment of ICs
- ❑ Frequency for monitoring ICs
- ❑ Procedures for routine monitoring of the effectiveness of ICs and parties responsible for the monitoring

Evaluations of Remedy Effectiveness

- ❑ Description of evaluations to be performed to demonstrate effectiveness of natural attenuation with respect to site-specific remedial action objectives
- ❑ Determination of temporal and spatial trends in contaminant concentrations or mass
- ❑ Comparisons of contaminant concentrations with previous predictions or milestones
- ❑ Comparisons of contaminant concentrations in areas outside the previous plume boundaries or other compliance boundaries with specified action levels
- ❑ Frequency (*e.g.,* quarterly, annually) on which each evaluation is to be conducted and the data that are to be used
- ❑ Data presentations to be used (*e.g.,* tables, maps, cross sections, and other figures)

Methodology or Plan for Verifying Attainment of Remedial Objectives and Initiating Termination of Performance Monitoring

Sampling and Analysis Plan

Quality Assurance Project Plan

figures to convey monitoring requirements and approaches. Ideally, monitoring data would be acquired, transmitted, evaluated and presented in an electronic form for ease of transmission and analysis. The format and content of a monitoring plan will vary according to site-specific needs, but most plans would contain or reference the elements listed in Table 4 and briefly discussed in the following sections.

2.7.2 *Background and Site Description*

Background information on the site, including a discussion of the site setting, history, characteristics, remedial goals, past and present remedial actions, and any institutional controls, typically would be provided in abbreviated fashion or incorporated by reference to existing documents. Essential aspects (*e.g.,* hydrogeologic setting, contaminant distribution, remedial goals and actions) generally should be addressed at sufficient length that the technical reviewer can judge the adequacy of the monitoring efforts. The geologic and hydrogeologic controls on ground-water flow at the regional scale and site scale should be discussed in detail with references to the supporting data or provided by reference to specific portions of existing documents.

2.7.3 *Conceptual Site Model for Natural Attenuation*

Essential elements of the conceptual site model for natural attenuation include:

- Descriptions and locations of possible receptors,
- Geologic and hydrologic controls on ground-water flow,
- Contaminant distribution and behavior, and
- Relationship of geochemistry and anthropogenic factors to attenuation processes

The monitoring plan typically would provide a detailed discussion of how the conceptual site model and the supporting data and analyses were used to design the network.

2.7.4 *Objectives and Decision Points*

The monitoring plan typically should specify the RAOs, monitoring objectives, and performance criteria used to guide the performance monitoring plan development and provide decision points for continuing, modifying, or terminating performance monitoring. The decisions to be made should be thoroughly discussed in relation to site objectives, specific decision points, methods of determining attainment of goals, and how site activities would proceed based on decisions made. The criteria upon which each decision is to be based should be explicitly stated.

2.7.5 *Monitoring Network and Schedule*

The plan should include information on the monitoring network including a list and map of monitoring locations; a description of the construction of each monitoring point; and a monitoring schedule specifying monitoring parameters, analytical methods, sampling frequency, and statistics to be used for data interpretation. Information regarding Data Quality Objectives (DQO's) should be provided or incorporated by reference. It is particularly important that maps, cross-sections, and other visual aids be extensively used so that the reviewer can determine exactly where, when, and by what methodologies samples are to be taken and analyzed. In situations where different hydrogeologic units are monitored, separate maps with wells/sampling locations for each major lithologic unit may provide additional clarity in visualization of the network design.

2.7.6 *Monitoring of Institutional Controls*

The monitoring plan should include detailed descriptions of the institutional controls and their implementation procedures. Procedures for verifying that institutional controls are put in place, for monitoring the effectiveness of the controls, and for reporting monitoring results to appropriate government entities should be described. The frequency for monitoring and reporting effectiveness should be specified. The parties responsible for implementing, verifying, and monitoring effectiveness of the institutional controls should be listed, along with complete contact information.

2.7.7 *Evaluations of Remedy Effectiveness*

The monitoring plan should specify the evaluations that will be performed to demonstrate the effectiveness of natural attenuation with respect to the site-specific remedial action objectives. The frequency (*e.g.,* quarterly, annually) on which each evaluation is to be conducted and the data that are to be used would also be specified. The evaluations should be designed to objectively determine performance in relation to specific performance criteria established in remedy decision documents. Pertinent evaluations include:

- Determination of temporal and spatial trends in contaminant concentrations or mass,
- Comparisons of observed contaminant concentrations with previous predictions or established milestones, and
- Comparisons of contaminant concentrations in areas outside of previous plume boundaries with specified action levels (*e.g.,* drinking-water standards)

In addition, the plan should specify the data presentation methods (*e.g.,* tables, maps, cross sections, and other figures). Submission of data in electronic formats should be considered for ease of manipulation and independent analysis.

2.7.8 *Plan for Verifying Attainment of RAOs*

The performance monitoring plan should include discussion of the methodology or plan for verifying attainment of all remedial action objectives and initiating termination of performance monitoring. In general, the plan developed at the initiation of performance monitoring should be flexible and allow for future modifications based on observations of actual remedy performance. The methodology should include:

- Proposed time period for verifying attainment of objectives, considering any observed seasonal or other temporal trends,
- Description of monitoring locations, parameters, and frequency, including discussion of any possible changes that may be warranted, and

- Specification of statistical methods of data analysis to be used in demonstrating attainment.

It is recommended that the plan for the verification of RAOs be reevaluated prior to its implementation to insure that the verification methodology initially proposed is still valid considering the additional data obtained and any changes in the conceptual site model that occurred during the performance monitoring period.

2.7.9 *Sampling and Analysis Plan*

The sampling and analysis plan typically should include a description of:

- Sample collection methods,
- Sample preservation and handling,
- Chain-of-custody procedures,
- Analytical procedures, and
- Field and laboratory quality assurance/quality control.

Guidance regarding the development and specific elements of sampling and analysis plans is found in a variety of sources including U.S. EPA (1986a, 1986b, 1992b, 1993a, 2002a).

2.7.10 *Quality Assurance Project Plan*

The quality assurance project plan (QAPP) documents the manner in which quality assurance and quality control activities will be implemented throughout the performance monitoring program. The QAPP is composed of the following elements:

- Description of project tasks, data quality objectives, and management,
- Description of data acquisition and management,
- Description of assessments, responses, and oversight, and
- Description of data validation, verification, and usability.

Detailed guidance regarding preparation of quality assurance project plans is available in U.S. EPA (1998c).

Chapter 3
ANALYSIS OF PERFORMANCE MONITORING DATA

3.1 Introduction

Data interpretation involves these basic steps of the data quality assessment (DQA) process :

- Placing the data in context of time, location, sampling and analytical methods,
- Preliminary assessment of the data with basic statistical measures (*e.g.*, means and ranges), and graphs, charts, maps, time-series plots, and cross-sections,
- Applying appropriate statistical tests to detect changes, trends, and assess attainment of goals, and
- Making decisions based on the data.

The conceptual site model for MNA and the monitoring program are continually refined as new data are gathered and interpreted. Each new round of data should help develop a better understanding of the site and site processes, including plume shape, location, stability, and dynamics; attenuation rates; geochemical regimes; and site hydrogeology.

The criteria used for site-related decision-making are usually based on either presence of specific contaminant concentrations (*e.g.,* MCLs at a specified group of wells), or spatial and temporal trends in concentrations (*e.g.,* a decreasing trend in contaminant concentrations that indicates progress toward contaminant reduction objectives). Other site-related data (*e.g.,* geochemical and ground-water flow data) are important for corroborating contaminant migration, fate, and attenuation processes. These data may be used to provide evidence for contaminant degradation and the continuation of appropriate conditions for attenuation at acceptable rates.

3.2 The DQA Process

The Data Quality Assessment (DQA) process is an iterative procedure used to evaluate, analyze, and interpret data. Guidance for the DQA process is found in U.S. EPA (2000c). The assessment methods used at each site should be specified in the performance monitoring plan.

Briefly, the DQA process for performance monitoring of an MNA site is as follows:

- Review the Data Quality Objectives (DQOs) and the sampling design to ensure that the design is suited to achieving the DQOs. The data derived from the monitoring should have the proper characteristics for their intended use; that is, data should be of the correct type, quality, and quantity in order to be useful for making site-related decisions.
- Conduct a preliminary review of the data, such as calculating means and other basic statistics, graphing the data, and mapping the data to identify obvious

patterns, relationships, and anomalies, such as possible "outliers". Simple scatter plots, for example, may show relationships between two variables that are not evident using purely numerical methods. Mapping the data in plan view and cross-section is helpful for understanding patterns of contaminant distribution and migration, and for understanding relationships between geochemical zones and contaminant attenuation.

- Verify the selection of the appropriate statistical test(s) (if needed) for analyzing the data, considering the types of decisions that are to be made (*e.g.*, attainment of contaminant reduction objectives) and the sampling design. Identify the assumptions that underlie the chosen statistical test (*e.g.,* normally distributed data). The appropriate statistical tests are identified through the application of the DQO process during monitoring system design, because the design is chosen considering the requirements of the particular tests to be used.

- Verify that the data meet the assumptions of the statistical test, and whether any departures from the assumptions are acceptable. Given the nature of many sites, it is possible that data will not always meet the assumptions of either parametric or nonparametric statistical tests. Ground-water monitoring data typically exhibit extremely high variability and skewed distributions. Although certain assumptions of particular tests may be in question, statistical tests are often still a worthwhile guidance tool for decision-making. Statistical analyses should be considered as a way to bring a measure of objectivity to the decision-making framework.

  As the design of the sampling and analysis plan can minimize or eliminate violations of statistical assumptions, it is recommended that statisticians be included in the performance monitoring planning phase. The data analyst, however, bears the ultimate responsibility of determining if the assumptions of a particular statistical test are violated and how these violations may affect site decisions.

- Interpret and draw conclusions from the data analysis by performing the appropriate statistical tests. The sampling design should be evaluated to determine if any changes are needed to enhance the usability of the data.

- Interpret and draw conclusions from the data in the context of the conceptual site model for MNA and site remediation goals.

In addition to the steps presented here for assuring the quality of the data, it is recommended that a process be implemented to assure the quality of the conceptual site model for MNA. With each new round of sampling, the conceptual site model for MNA should be reevaluated and, if necessary, modified. In particular, the conceptual site model for MNA should be reevaluated from the standpoint of its power to explain observed plume shape, location, stability, and dynamics; ground-water flow patterns; and geochemical regimes.

At many sites, source control and interim remedial activities will occur between the original site characterization process and implementation of performance monitoring. Because these activities are expected to change the site's characteristics and behavior, it is possible that performance monitoring will require development of a conceptual site model for MNA that is substantially different from the MNA conceptual site model that was based on the initial site characterization data. Development and implementation of the new conceptual site model for MNA may require collection of additional data to better depict existing site characteristics and parameter variability. These data are used to determine trends, determine plume characteristics, and assess the likelihood of meeting site remediation goals.

3.3 Interpreting the Data

3.3.1 *Introduction*

Data analysis and interpretation focus on two fundamental aspects: detection of changes or trends in the data, and assessment of the changes or trends in the context of their impact on the potential for MNA to achieve site-related goals. Data can be interpreted with regard to variability so that attenuation-related changes and trends can be distinguished from other sources of variation in the data. In addition, once changes or trends are identified, the importance of the trend should be considered (*i.e.,* Does the trend indicate that MNA will or will not meet site-specific goals?).

Particular changes that are of interest include:

- Changes in ground-water flow rates or directions that indicate contaminants may move farther downgradient, laterally or vertically into previously unimpacted areas,
- Changes in contaminant concentrations within the plume, that may indicate new releases, significant changes in the rate of release from any source materials that remain following implementation of all appropriate source control measures, or changes in the attenuation rate,
- Detections of contaminants outside the known plume or other compliance boundaries, indicating unacceptable plume expansion or additional source areas, and
- Changes in geochemistry that may indicate changes in attenuation rates, such as changes in availability of electron donors and electron acceptors, changes in oxidation-reduction potential, or other primary geochemical indicators; or changes in sorption characteristics (*e.g.*, adsorption, precipitation).

Data interpretation is complicated by data variability (Appendix A). This variability is inherent in the measurement process, in which case it may be evaluated in a carefully designed and implemented sampling and analysis-related QA/QC program, and it is also associated with natural causes. Due to the dynamic nature of natural processes, data typically exhibit fluctuations of various magnitudes. For example, there is an expected degree of natural variability within a plume that may include small-scale expansion and shrinkage in response to changes in ground-water flow rates and biological degradation rates throughout the year. Contaminant concentrations in individual wells may fluctuate with changes in plume configuration caused by oscillations in ground-water flow. Also, changes in ground-water elevations can cause changes in contaminant concentrations measured in monitoring wells if there are vertical differences in water quality or other factors.

Examination of historical and spatial patterns may provide information useful in assessing the source and significance of variability in the measured parameters. For instance, if there are multiple wells in the same hydrogeologic setting that show a consistent trend for a number of monitoring variables across two monitoring events, then one may suspect a natural variation, such as recharge differences, and investigate a correlation of recharge or other external hydrologic factors with concentration as indicative of the likely cause of the change. If, on the other hand, a specific well shows an unusually large change in concentration between monitoring events, relative to nearby monitoring wells, then one may suspect a measurement factor is involved in that localized change and look at the possible influences of sampling technique or other such factors on the concentration change.

Because plume variability should be taken into account when interpreting monitoring data, it is important to have a good estimate of natural variability derived from the site investigation. In addition, it is recommended that performance monitoring data be continually evaluated with respect to variability, so that there is an ever-expanding database for the site that can be used for comparison with the changes in parameters noted between monitoring events as well as for comparison to predicted, acceptable trends.

Statistical procedures are available that allow assessment of site characteristics and trends. If a change in site characteristics or a departure from a predicted trend is found, it can be evaluated to determine what impact the change may have on MNA's ability to achieve site-related goals. Conceptual models for MNA can be used to conduct sensitivity analyses to help determine what changes may be significant in the context of the site-related goals. For instance, sensitivity analyses could be used to determine if a two-fold or three-fold change in attenuation rate will significantly affect attainment of remedial goals. Departures from expected trends may not mean remedy failure, because there may be a range of attenuation rates that will achieve the desired remedial goals in the allotted time.

3.3.2 *Preliminary Presentation and Evaluation of the Data*

The data analyst conducts an initial evaluation and review of the data by calculating means, modes, medians, and ranges, graphing the data, and mapping the data in plan and cross sectional views to identify obvious patterns, relationships, and anomalies. Simple graphical representations include site maps and cross sections with posted and contoured data, plots of data as a function of time, plots of the relationship between two or more variables, and measures of central tendency (*e.g.,* means, modes, medians) and data dispersion (*e.g.,* standard deviations). It is recommended that the data analyst consider as many graphical techniques as possible to maximize the amount of information gained in this step.

As part of this initial evaluation process, it is essential that each data point be interpreted in the context of its derivation in time and space. For instance, monitoring wells produce data that should be interpreted in terms of the three-dimensional location of the well screen with respect to contaminant sources, site stratigraphy, the ground-water flow field, the plume, possible receptors, season of the year, and, potentially, numerous other factors. The sampling methodology should also be considered, due to possible differences in contaminant concentrations derived from different sampling techniques or devices. The analytical methodology may be evaluated in terms of accuracy, precision, and detection limits. This list of data considerations is not exhaustive, but merely emphasizes that a number (*i.e.,* a data point) should be placed in context to be interpreted. The better a data analyst understands the derivation and context of the data, the more likely it is that the data analyst can make the appropriate decision based on the data.

3.3.3 *Data Comparisons*

The following types of data comparisons are commonly useful during performance monitoring evaluations.

3.3.3.1 Comparisons of Concentrations Within and Outside the Plume

Data obtained within the plume are compared to data from monitoring points upgradient of the source area and sidegradient to the plume. Data acquired upgradient of the source area may be used to monitor for contaminants coming from other sources and for electron donors and acceptors migrating into the contaminated area (U.S. EPA, 1998a; Wiedemeier *et al.,* 1999). It often is important to obtain geochemical data from locations sidegradient to the plume because there may be geochemical changes in the ground water as it flows through the aquifer that are unrelated to processes in the plume. The range of values and spatial patterns for the particular parameter should be considered during data interpretation. If the range of values in the geochemical setting surrounding the plume is similar to (or greater than) the range of values for the parameter in the plume, then it may be problematic to attach any particular interpretation to the changes of the parameter in the plume. For instance, suppose sulfate values in uncontaminated ground water adjacent to a plume vary from less than 1 mg/L to 30 mg/L; then a drop in sulfate concentration from 20 mg/L to 5 mg/L within the plume may not necessarily be conclusive evidence that sulfate reduction is important in plume geochemistry.

3.3.3.2 Trend Analyses

Data are compared to determine if temporal and spatial trends exist within the plume and in surrounding areas. Trends of interest include trends in contaminant and daughter product concentrations, electron acceptors and donors, oxidation-reduction potential, and other general geochemical indicators. These comparisons include trend-to-trend comparisons (*e.g.,* a decreasing trend in tetrachloroethene compared to an increasing trend in trichloroethene in the same transmissive zones may indicate degradation of tetrachloroethene to trichloroethene).

Trends at individual sampling points or groups of sampling points may be compared to other sampling points, or to trends in other groups of sampling points. For instance, contaminant concentrations at individual sampling points may show different trends. However, evaluating trends in data from all sampling locations in the plume will determine if the plume exhibits stability or reduction in contaminant concentrations. Similarly, data from a group of sampling points at the downgradient limits of a plume may be compared to data from previous sampling rounds to determine if the plume seems to be stable, shrinking, or expanding.

In some cases, particularly with petroleum hydrocarbons, known stoichiometric relationships between usage of electron acceptors and degradation of contaminants may be used to relate trends in geochemistry qualitatively or semi-quantitatively to degradation of contaminants.

3.3.3.3 Comparisons with Existing Literature and Laboratory Studies

Parameter values from other sites and the literature may be used to determine how ranges of values at a particular site compare to the ranges that have been found through research or experience at other sites or laboratory studies. Typically, these comparisons are made during site characterization, but they may also be useful in the performance monitoring planning phase. For instance, a calculated degradation rate for a contaminant may be compared to values found at other times and places at the same site and to values found at other sites or in laboratory studies. If literature reports indicate that a compound does not degrade under conditions similar to those found at the site under investigation, but data from the site seem to indicate the compound is disappearing at a substantial rate, it would be advisable to carefully reevaluate the monitoring operations before concluding that the compound is indeed degrading. Note that literature values cannot substitute for values determined at the site for evaluating and monitoring MNA.

3.3.3.4 Comparisons with Threshold Values

Contaminant concentrations at the site may be compared to values set by regulation or other factors. For instance, MNA may be required to reduce the concentration of a contaminant to an MCL of 5 mg/L at a particular sampling point. Of particular interest for this comparison is that the threshold value is typically assumed to be a true value, not an estimate of a population parameter; that is, it has no variability associated with it. This affects the statistical procedures used for comparing the values, as discussed in the references given below.

3.3.4 *Statistics*

The previously discussed data comparisons can be conducted by simply comparing measured values, calculated (or graphed) trends, or set values for contaminants or geochemical parameters. However, statistical procedures and models provide a formal, quantitative method for assessing the relationship of sample measurements to characteristics of the sampled system, for using sample data to make decisions, and for predicting future states of the sampled system.

Statistical procedures are often used to evaluate the variability associated with data, and to use estimates of variability to guide decision-making processes. For example, if multiple analyses are performed, statistical procedures can be used to express a measure of the analytical variability associated with a reported contaminant concentration (*e.g.*, 4.9 mg/L +/- 3.2 mg/L, representing the 95% confidence limits on the mean value).

Statistical methods are also available to facilitate analysis and comparison of trends by considering data variability through time. For instance, changes in contaminant concentrations over space or time can be used to calculate attenuation rates, and the variability associated with those rates can be quantified with confidence intervals about the rates. These confidence intervals can be used to determine the likelihood of attaining site-related remedial goals. If all values of the attenuation rate falling within the confidence intervals lead to predictions that site remedial goals will be attained in the desired time frame, then confidence that MNA can attain remedial goals is increased.

Implementing formal methods that compare data by taking into account data variability is especially important for decision-making purposes. Gibbons (1994), Gilbert (1987) and Helsel (1995) contain extensive discussions of the issues concerning use of statistics in environmental and ground-water monitoring. For a detailed discussion of these points, as well as step-by-step guidance on calculations for the various types of comparisons mentioned above, see also U.S. EPA (2000c) and U.S. EPA (1992a).

3.4 Elements of a Performance Monitoring Report

3.4.1 *Introduction*

Compilation and presentation of monitoring data in an easily usable form that facilitates interpretation requires significant effort. As was discussed for the monitoring plan, there is no standard format that is universally acceptable, but, ideally, monitoring data would be acquired, transmitted, evaluated and presented in an electronic form, and the report would make extensive use of maps, cross sections, and figures to convey the results of monitoring efforts.

The following material has been prepared to provide suggestions regarding appropriate components of performance monitoring reports. The format and content of these documents will vary according to site-specific needs but most reports would contain or reference the elements listed in Table 5 and briefly discussed in the following sections.

Elements of a monitoring report (Table 5) include:

- Summary of data interpretations and recommendations,
- Background and site description,
- Monitoring network and schedule description,
- Evaluation of new data and comparisons with previous data and established performance criteria,
- Interpretation of new data with respect to the conceptual site model for natural attenuation, and
- Recommendations for action.

3.4.2 *Summary*

The summary typically would contain a brief description of the site, remedial goals, a narrative summary of new data and their interpretation, and any recommended actions. This portion of the report should be written to convey essential findings to both technical and nontechnical readers.

3.4.3 *Background and Site Description*

Background information on the site, such as a discussion of the site setting, history, characteristics, remedial goals, past and present remedial activities, and any institutional controls, typically would be provided in abbreviated fashion or incorporated by reference to existing documents. The most salient issues (*e.g.,* hydrogeological setting, contaminant distribution, remedial goals and actions) generally should be addressed at sufficient length that the technical reviewer can judge the adequacy of the monitoring efforts. The geologic and hydrogeologic setting of the site, including controls on ground-water flow at the regional scale and site scale, would be illustrated in map and cross-sectional views.

3.4.4 *Monitoring Network and Schedule*

The report typically would include information on the monitoring network including a list and map of monitoring locations; a description of the construction of each monitoring point; and a monitoring schedule specifying monitoring parameters, analytical methods, and sampling frequency. Information regarding Data Quality Objectives (DQOs) may be provided or incorporated by reference. It is particularly important that maps, cross-sections, and other visual aids be extensively used so that the reviewer can determine exactly where, when, and by what methodologies each sample was obtained and analyzed. In situations where different hydrogeologic units are monitored, separate maps with wells/sampling locations for each major lithologic unit may provide additional clarity in visualization of the network design.

Table 5. Elements of a Performance Monitoring Report

Summary of Data Interpretations and Recommendations

- ❑ Brief description of site
- ❑ Remedial goals
- ❑ Narrative summary of new data and their interpretation
- ❑ Recommended actions

Background and Site Description

The following information typically would be discussed or incorporated by reference:

- ❑ Site setting, history, characteristics
- ❑ Remedial goals
- ❑ Past and present remedial activities, and any institutional controls
- ❑ Map and cross-sectional views illustrating geologic and hydrogeologic setting of the site, including controls on ground-water flow at the regional scale and site scale

Monitoring Network and Schedule

- ❑ List and maps of monitoring locations for each sampled medium and each major hydrogeologic unit
- ❑ Description and construction details for each monitoring point
- ❑ Monitoring schedule specifying monitoring parameters, analytical methods, and sampling frequency for each monitoring location
- ❑ Data Quality Objectives (DQOs) to be met

Evaluation of New Data

- ❑ Detailed discussion of new results and evaluations
- ❑ Data in tables and electronic files
- ❑ Potentiometric surface maps for each hydrostratigraphic unit
- ❑ Hydrographs of ground-water elevations for key wells in each hydrostratigraphic unit and surface-water monitoring points
- ❑ Contaminant data posted and contoured on maps for each media and major hydrogeologic unit
- ❑ Hydrochemical cross sections along and perpendicular to ground-water flow directions depicting contaminants, monitoring points, and hydrogeology
- ❑ Geochemical data posted and contoured on maps for each major hydrogeologic unit
- ❑ Cross sections depicting geochemical data, monitoring points, and hydrogeology
- ❑ Comparison of the new data with previous data and established performance criteria
- ❑ Results of statistical comparisons
- ❑ Discussion of trends and the relation of any trends to remedial goals
- ❑ Assessment of measurement variability from analysis of QA/QC data
- ❑ Observed changes in land use

Evaluation of Institutional Controls (ICs)

- ❑ Description of ICs that are in place with appropriate verification
- ❑ Evaluation of the effectiveness of ICs
- ❑ Discussion of any pending changes in property ownership
- ❑ Observed changes in land or resource uses

MNA Conceptual Site Model Evaluation

- ❑ Evaluation of the conceptual site model incorporating any new data and data trends
- ❑ Discussion of consistency of previous conceptual site model with new data
- ❑ Suspected sources for continued ground-water contamination (*e.g.,* number, location(s), characteristics of sources)
- ❑ Trends in contaminant and geochemistry values
- ❑ Discussion of any observed changes in site hydrology (*e.g.*, water elevations, ground-water velocities)
- ❑ Discussion of refinements/modifications to conceptual site model
- ❑ Consistency of current data with previous predictions
- ❑ Discussion of changes in land use and potential effects on the conceptual model

Recommendations (as warranted)

- ❑ Recommended changes in monitoring locations
- ❑ Recommended changes in monitoring frequencies
- ❑ Recommended changes in sampling methods
- ❑ Recommended changes in analyses
- ❑ Discussion of new data in relation to performance criteria previously established to trigger implementation of a contingency remedy
- ❑ Discussion of changes in land use and potential effects on site remedies, and remedy protectiveness for human and ecological receptors
- ❑ Recommended remedy modifications (*e.g.*, additional source removal actions)
- ❑ Recommendations for starting verification monitoring, or terminating performance monitoring
- ❑ Rationale for recommended changes

3.4.5 *Evaluation of New Data*

The evaluation of new data and comparisons with previous data typically should provide a:

- Detailed discussion of new results and evaluations with presentation of data in tables, maps, and figures,
- Comparison of the new data with previous data and established performance criteria,
- Discussion of uncertainty with statistical measures of variability, including discussion of measurement variability assessed through evaluation of QA/QC data, and
- Discussion of trends and the relation of any data trends to the remedial goals.

Tables ordinarily would include hydraulic head data, contaminant data, and geochemical data in both in-well and between-well comparisons. In other words, all data for each sampling point would be tabulated to facilitate assessment of the geochemistry at that location, and a tabulation of data by monitoring parameter would be provided to facilitate comparison of each parameter across all sampling locations. Tables and figures depicting contaminant concentrations and geochemical data for individual wells over time would be included to aid in the evaluation of trends. Maps and cross-sections of the plume would be prepared and compared to previous conditions. Contour maps of the contaminant concentrations and geochemical parameters are helpful for visualizing broad trends. These comparisons aid in the evaluation of temporal changes. They may also serve to identify areas where additional data are needed. Data submission in electronic formats should also be considered.

3.4.6 *Evaluation of Institutional Controls*

The performance monitoring report typically would include a full description of all institutional controls implemented or planned at the site, along with verification of their implementation. The results of the monitoring activities, including an evaluation of the effectiveness of the individual institutional controls, should be discussed at length so that the reviewer can judge whether the controls are likely to continue to meet performance objectives. Any observed or pending changes in land or resource uses or ownership (e.g., property ownership change, housing developments, well installations) should be discussed in view of their current and possible future impact on the effectiveness of the controls and the performance monitoring operations.

3.4.7 *Conceptual Site Model Evaluation*

The report typically would contain an evaluation of the conceptual site model incorporating any new data and data trends. Included in this section would be a discussion of the following questions:

(1) Do the new data fit the previous conceptual site model?

Consider:

- Suspected sources for continued ground-water contamination (*e.g.,* number, location(s), characteristics of sources),
- Trends in contaminant and geochemistry values, and

- Changes in hydrologic factors (*e.g.*, ground-water elevations, hydraulic gradients, velocities)

(2) Should the conceptual site model be refined/modified?

(3) Do current data support previous predictions?

Consider uncertainty in previous predictions and implications for the effectiveness of natural attenuation mechanisms and the current monitoring network.

3.4.8 *Recommendations*

Recommendations for action, based on interpretation and evaluation of the data in reference to RAOs, monitoring objectives and performance criteria should be provided and discussed. Recommendations for action may include changes in monitoring locations, frequencies, methods, and analyses with a rationale for changes. Recommended actions may also include additional source removal or other remedy modifications, implementation of contingency or alternative remedies, advancement to verification monitoring, or termination of performance monitoring based on achievement of site remedial goals.

Chapter 4
APPLICATION OF MONITORING DATA TO REMEDIAL DECISIONS

4.1 Introduction

Following data evaluations, decisions are routinely made regarding the effectiveness of the MNA remedy, the effectiveness of institutional controls, the adequacy of the monitoring program, and the adequacy of the conceptual site model for MNA. Important decisions that may be made include:

- Continue monitoring program without change,
- Modify the monitoring program,
- Modify the institutional controls,
- Implement the contingency or alternative remedy, or
- Verify remedial goals have been met and terminate performance monitoring.

Site-specific criteria should be developed to define conditions that indicate the appropriateness of increased or decreased monitoring, additional characterization, reevaluation of the conceptual site model, modification of institutional controls, implementation of a contingency or alternative remedy, or termination of performance monitoring. The following discussion briefly considers each decision and points relative to why it may be chosen.

4.2 Decision 1 - Continue Monitoring Program Without Change

Evidence leading to this decision would include contaminant concentrations, including toxic transformation products and any mobilized by-products or secondary contaminants (*e.g.*, arsenic, manganese) remaining within the bounds of acceptable trends. Ground-water flow parameters would not have changed outside previously identified acceptable ranges. The geochemistry would not have changed in such a way as to indicate that the contaminant degradation or other natural attenuation processes would be significantly affected. Significant changes in geochemistry include a marked reduction of electron acceptors or donors essential to the important natural attenuation processes identified at the site, an influx of substances such as oxygen or nitrate that could interfere with desired processes, or a change in oxidation-reduction potential bringing the potential into a range not suitable for the identified important natural attenuation processes (Ferrey *et al.*, 2001). Performance monitoring continues until all remedial action objectives have been met.

4.3 Decision 2 - Modify the Monitoring Program

Modification of the monitoring program may be warranted to better reflect changing conditions or increased understanding of natural attenuation processes at the site. Changing conditions, the need to test key assumptions, or providing final confirmation of remedial goal achievement may require new sampling points or increases in monitoring parameters or frequency. Examples include:

- A change in ground-water flow rate and direction caused by installation of an irrigation well may necessitate reevaluation of the monitoring frequency and locations (Figure 9),

- Input of nitrate from fertilizer applications may sufficiently change the geochemistry to inhibit reductive dechlorination. Increased monitoring frequency and locations may be necessary to delineate the effect of nitrate influx,

- Periodic pulses of contaminants from the former source area may be caused by flushing of contaminant from undetected residual material in the vadose zone. Monitoring in the vadose zone as well as the saturated zone may be needed to determine the nature and characteristics of the contaminant pulses and provide data for assessing the appropriate response, and

- Contradictory indications of the potential for plume expansion in some areas or the data may be so highly variable that interpretation is difficult and unacceptably uncertain. High data variability, making interpretation difficult, may be caused by variability inherent in sampling and, in some cases, analysis. In addition, contaminant concentration changes caused by seasonal changes in ground-water flow, degradation rates, contaminant releases from poorly controlled source(s), and influx of electron acceptors can make interpretation difficult unless monitoring is sufficiently frequent to allow delineation of the changes due to seasonal cycling. A determination may be made to collect more data sufficient to interpret trends. However, if the protectiveness of the remedy is in question, implementation of the specified contingency or an alternative remedy will generally be warranted.

In other instances, decreases in monitoring parameters, frequency, or locations may be appropriate. For example, decreases in monitoring frequency for certain parameters may be warranted if the remedy is proceeding according to expectations and trends are stable after evaluation of data from a sufficient number of monitoring periods (*e.g.,* many years). To support such a decision, the available data generally should cover a time period sufficient to allow evaluation of seasonal trends and other long-term cycles and trends. Evidence supporting reduced monitoring includes trends in contaminant concentrations continuing as expected and geochemistry and ground-water flow conditions remaining stable (*i.e.,* in the ranges suitable for continued natural attenuation). Also, the time required for implementation of the contingency remedy after established decision criteria are met would be considered in any decision to reduce monitoring frequency. In any case, performance monitoring should continue until all remedial action objectives have been met (*e.g.*, contaminant concentrations are below levels of concern).

Once performance monitoring data indicate that site remedial goals have been met, a period of verification monitoring may be initiated. Verification monitoring may include different sampling frequencies or additional locations from those used during routine performance monitoring, especially if monitoring locations or frequency had been reduced during the performance monitoring period. For instance, the number of monitoring locations and monitoring frequency may have been reduced if data had indicated that the MNA remedy was proceeding as expected. In such cases, some of the sampling locations or times may have been eliminated from the sampling program as unnecessary. However, it often may be appropriate to include these sampling locations and times during verification sampling in order to increase certainty that goals are met at all locations and times. Once verification monitoring has shown that all MNA remedy goals have been met, then termination of performance monitoring generally would be warranted.

4.4 Decision 3 - Modify Institutional Controls

Some changes in land or ground-water use have the potential to decrease the effectiveness or the protectiveness of the MNA remedy. Such changes could include installation of new pumping wells in the vicinity of the site. New pumping wells could change ground-water flow patterns and increase the potential for plume migration, thereby increasing the risk to receptors. Some changes in land use could affect subsurface geochemical conditions. For example, excessive application of nitrogen-containing fertilizers could cause an influx of nitrate to ground water and possibly inhibit reductive dechlorination. Changes in land or ground-water use should be monitored and evaluated to determine potential impacts to the MNA remedy. If existing institutional controls or procedures for monitoring the controls are not sufficient to maintain the effectiveness or protectiveness of the MNA remedy, the site manager should consider modifying the institutional controls or monitoring procedures. If the changes in land or ground-water use resulted from a breach of the institutional controls established for the site, the procedures used to monitor and enforce the existing institutional controls should be evaluated and modified to prevent future breaches. If the changes in land or ground-water use were allowed by the current institutional controls, the site manager should consider modifying the institutional controls to minimize future adverse impacts to the MNA remedy.

4.5 Decision 4 - Implement a Contingency or Alternative Remedy

Remedies relying upon MNA may have an associated contingency remedy in case the MNA component fails to perform at the desired effectiveness (U.S. EPA, 1999a). In any case, alternative remedies are usually considered during remedy selection and these or other remedies can be considered for use if it is determined that the current remedy has failed. Criteria for determining specific failures and implementing modifications, a contingency, or alternative remedy may be explicitly stated in the remedy decision documents. If not provided in previous documents, it is recommended that objective and quantitative decision criteria for determining remedy failure be developed for use in designing the performance monitoring system and evaluating data from the system.

Development and evaluation of specific criteria to trigger implementation of a contingency or alternative remedy are generally based on and related to the purpose behind site RAOs. That relationship not only provides a rationale for a specific trigger, but also provides context for evaluating the trigger once it occurs, and deciding on the appropriate response. For example, a site RAO may require that the MNA remedy control the plume. Suppose that contaminants were detected in wells outside the previously-known plume boundary in 1) an existing well with a long history of no contamination, or 2) a newly installed well. If the aim of the RAO was that there should be no contaminant beyond a specific point (the previously-known plume boundary), then the response to situation 1) or 2) may be the same. However, if the aim of the RAO was that the plume should not expand, then the response to situations 1) and 2) may differ, because contaminants in the existing well indicate plume expansion, whereas contaminants in the new well may or may not indicate plume expansion (*i.e.*, the contaminants may have been at the new location for many years, but there were no samples previously collected in the new location).

Situations that may warrant implementation of a contingency or other remedy modifications depend on site conditions and include, but are not limited to, the following examples:

- Contaminant concentrations in soil or ground water at specified locations exhibit an increasing trend not originally predicted during remedy selection,
- Near-source wells exhibit large concentration increases indicative of a new or renewed release,
- Contaminants are identified in monitoring wells located outside the original plume boundary or other specified compliance boundary,
- Contaminant concentrations are not decreasing at the rate previously determined to be necessary to meet the remediation objectives,
- Changes in land and/or ground-water use will adversely affect the protectiveness of the MNA remedy, and
- Contaminants are identified in locations posing unacceptable risk to human or ecological receptors.

4.5.1 *Decision Criterion 1: Contaminant Concentrations in Soil or Ground Water at Specified Locations Exhibit an Increasing Trend Not Originally Predicted During Remedy Selection*

This criterion involves the identification and assessment of trends in contaminant concentration data, including toxic transformation products or mobilized inorganic constituents, that indicate plume expansion, lack of progress toward cleanup objectives, or additional contaminant releases. Statistical tests such as those described in the references may be used to objectively identify trends in these data. An example of a criterion based on a trend would be detection of a consistent, increasing trend in contaminant concentrations in wells near the downgradient edge of the plume. Such an event may be evidence of plume expansion, and, if so, may trigger the contingency or alternative remedy based on the previously-established, site-specific guidelines for assessing trends and remedy effectiveness.

For some locations in the plume, a detection of a significant change may not trigger immediate implementation of a contingency or alternative remedy. For instance, a low-level or otherwise limited contaminant concentration increase near the source area does not necessarily mean that remediation time frames will be expanded, or that by the time the pulse moves downgradient to the boundary of the plume there will be a significant plume expansion. Criteria for determining acceptable limits for increases in contaminant concentrations in locations near the source area should be based on site conditions and specified in decision documents. Because the contaminant travel time from the source area to the downgradient edge of the plume may be many years at some sites, there may be time for further monitoring and assessment before a contingency or alternative remedy would have to be implemented. In some cases, if contaminants will not reach receptors for several years, it may be possible to allow verification procedures to continue until the next sampling event (*i.e.,* the next quarterly or semiannual sampling event). In contrast, if a significant trend of increasing contaminant concentration in wells near the downgradient edge of the plume was noted, there may be much less time available to assess the trend if receptors were only a short travel time downgradient. In this case, a contingency or alternative remedy may be triggered immediately.

In some cases, the site characterization may indicate that concentrations in some portions of the plume are expected to increase temporarily, yet MNA would still meet remedial objectives. If so, the temporary increase would not trigger the contingency or alternative remedy as long as the increase conformed to the predictions and MNA remained protective. Specific criteria for determining that a significant change in trend has occurred may be developed to ensure that sampling variability or acceptable seasonal fluctuations do not unnecessarily trigger a contingency or alternative remedy.

4.5.2 *Decision Criterion 2: Near-Source Wells Exhibit Large Concentration Increases Indicative of a New or Renewed Release*

A release may result from such conditions as drum rupture or increased flushing of the source area caused by changes in hydrologic conditions. The expectation is that the new or renewed release may increase the time needed to meet remedial objectives or cause the plume to expand. Contaminant concentration increases beyond those previously predicted and stated in decision documents could trigger a contingency or alternative remedy, or implementation of sampling efforts to determine the causes of the increases and the impact on the remedy. In some cases, detailed characterization and modeling of contaminant fate and migration may indicate that the increased concentrations would be expected to attenuate without causing plume expansion, allowing observation for several years to test model predictions, if time is available. In situations where evaluation shows the observed contaminant concentration increases are expected to unacceptably increase the time for plume restoration, or cause unacceptable plume expansion, triggering the contingency or alternative remedy generally would be warranted.

4.5.3 *Decision Criterion 3: Detection of a Contaminant in Monitoring Wells Located Outside of the Original Plume Boundary or Other Compliance Monitoring Boundaries*

Detections of contaminants outside of the predetermined horizontal or vertical plume boundaries or other compliance boundaries may indicate unacceptable plume expansion. Procedures for verifying contaminant detections typically should be included in the monitoring plan. The choice of procedures depends on many factors including: the locations of the new detections, distance between these monitoring points and receptors, possible contaminant migration rates to receptors, time frames required for implementation of the contingency or alternative remedy, and monitoring procedures. Appropriate verification procedures will often include:

- Verification of the detection, by verifying the analytical procedures showing the detection and identity of the contaminant. This verification would be conducted by the analytical laboratory. It may also be possible for the laboratory to analyze another aliquot of the same sample, if available, and

- Verification by immediately resampling the well. Criteria defining the necessary level of agreement between results may be developed to facilitate evaluations. For example, a conservative decision criterion would be implementation of the contingency remedy if the contaminant concentration measured in the second sample exceeded the action level.

If these are verified, this may indicate remedy failure, depending on the RAO for the site. Verified detections of contaminants in these wells may be used to trigger implementation of an alternative or contingency remedy. Similar criteria may be developed to support decisions regarding other types of compliance boundaries.

4.5.4 *Decision Criterion 4: Contaminant Concentrations Are Not Decreasing at a Sufficiently Rapid Rate to Meet the Remediation Objectives*

This assessment will involve such evaluations as the comparison of current data with predictions used to support the remedy decision and evaluation or projection of temporal trends in contaminant concentrations. There will generally be significant uncertainty in these evaluations due to uncertainty in the projection of future conditions and sampling and measurement variability. Specific, objective criteria and milestones specified in the remedy decision should be reviewed. If specific criteria and milestones are not stated, they may be developed in the performance monitoring plan. Specific milestones (*e.g.*, 50 % contaminant concentration decrease in all wells within a specified number of years) may be developed using such techniques as projection of calculated attenuation rates. Failure to meet specified milestones or criteria could result in triggering of the contingency or alternative remedy.

4.5.5 *Decision Criterion 5: Changes in Land and/or Ground-Water Use that Have the Potential to Reduce the Protectiveness of the MNA Remedy*

This involves reevaluating the conceptual site model for MNA and determining whether there are receptors at higher risk than originally conceptualized or whether the change in land or ground-water use has resulted in hydrologic changes that affect plume stability, or geochemical changes that affect biotransformation processes. Such changes could increase the potential for contaminant migration and increased risk to the receptors as noted in Section 4.4. In such situations where modification of the institution controls is not possible, appropriate, or sufficient to restore the protectiveness of the remedy, triggering of a contingency or alternative remedy may be appropriate.

4.5.6 *Decision Criterion 6: Contaminants Are Identified in Locations Posing or Having the Potential to Pose Unacceptable Risk to Receptors*

In addition to monitoring contaminants in ground water at locations that indicate unacceptable risk to human receptors, cross-media transfer of contaminants from ground water to surface water, to indoor air, or other human or ecological receptors should be monitored based on a site-specific evaluation of the risk posed by the contaminants. Monitoring may include, for example:

- Sampling in the aquifer near the point of discharge to the surface-water body,
- Pore water or sediment samples where ground water moves into the surface water,
- Samples from the surface-water body, and
- Soil gas and indoor air in enclosed areas near plume or source materials.

Decision criteria may be based on contaminant concentrations exceeding action levels in these media. Assessment of this decision criterion would use statistical tests and verification procedures similar to decision criteria 1 and 3.

4.6 Decision 4 - Terminate Performance Monitoring

Specific methods and criteria for demonstrating the attainment of all remedial action objectives should be developed as noted in Sections 2.6.8 and 2.7.7. In general, once a thorough analysis of performance/verification monitoring data shows that all MNA-related site remedial goals have been achieved, termination of performance monitoring would be warranted.

REFERENCES

Azadpour-Keeley, A., H.H. Russell, and G.W. Sewell, 1999. *Microbial Processes Affecting Monitored Natural Attenuation of Contaminants in the Subsurface*, EPA/540/S-99/001. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. http://www.epa.gov/ada/download/issue/microbial.pdf

Azadpour-Keeley, A., J.W. Keeley, H.H. Russell, and G.W. Sewell, 2001. Monitored natural attenuation of contaminants in the subsurface: Processes. *Ground Water Monitoring and Remediation*, 21(2): 97-107.

Barcelona, M.J., H.A. Wehrmann, M.R. Schock, M.E. Sievers, and J.R. Karny, 1989. *Sampling Frequency for Ground-Water Quality Monitoring*, EPA/600/4-89/032. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Barker, J., 2000. Redox processes in petroleum hydrocarbon remediation or Why I never want to measure Eh again. In: *Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary*, Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

Brady, P.V., B.P. Spalding, K.M. Krupka, R.D. Waters, P. Zhang, D.J. Borns, and W.D. Brady, 1999. *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites*. SAND99-0464. US Department of Energy, Sandia National Laboratory, Albuquerque, NM. http://www.sandia.gov/eesector/gs/gc/na/mnatoolbox.pdf

Buscheck, T.E., and C.M. Alcantar, 1995. Regression techniques and analytical solutions to demonstrate intrinsic bioremediation. *Bioremediation*, 3(1):109-116.

Butler, J.J., 1998. *Design, Performance, and Analysis of Slug Tests*. Lewis Publishers, Boca Raton, FL.

Chapelle, F.H., 1996. Identifying redox conditions that favor the natural attenuation of chlorinated ethenes in contaminated ground-water systems. In: *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, Hyatt Regency Dallas, Dallas, TX, September 11-13, 1996, EPA/540/R-97/504. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. http://www.epa.gov/ordntrnt/ORD/WebPubs/natural/natural.pdf

Chapelle, F.H., 2000. Identifying the distribution of terminal electron-accepting processes (TEAPS) in ground-water systems. In: *Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary*, Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

Cherry, J.A., 1996. Conceptual models for chlorinated solvent plumes and their relevance to intrinsic remediation. In: *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, Hyatt Regency Dallas, Dallas, TX, September 11-13, 1996, EPA/540/R-97/504. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.
http://www.epa.gov/ordntrnt/ORD/WebPubs/natural/natural.pdf

Cohen, R.M., and J.W. Mercer, 1993. *DNAPL Site Evaluation*. CRC Press, Boca Raton, FL.

Cohen, R.M., A.H. Vincent, J.W. Mercer, C.R. Faust, and C.P. Spaulding, 1994. *Methods for Monitoring Pump-and-Treat Performance,* EPA/600/R-94/123. U.S. Environmental Protection Agency, Office of Research and Development, Ada, OK. 74820.
http://www.epa.gov/r10earth/offices/oea/gwf/issue20.pdf

Ferrey, M.L., J.B. Lundy, and P. Estuesta, 2001. The effect of groundwater aeration on PCE natural attenuation patterns. *Bioremediation*, 5(3):211-224.

Fetter, C.W., 1994. *Applied Hydrogeology*. Macmillan College Publishing Company, New York.

Galloway, W.E., and J.M. Sharp, Jr., 1998. Characterizing Aquifer Heterogeneity within Terrigenous Clastic Depositional Systems. In: *SEPM Concepts in Hydrogeology and Environmental Geology No. 1: Hydrogeologic Models of Sedimentary Aquifers*. G.S. Fraser and J.M. Davis, eds., Society for Sedimentary Geology, Tulsa, OK.

Gibbons, R.D., 1994. *Statistical Methods for Groundwater Monitoring*. John Wiley & Sons, New York.

Gilbert, R.O., 1987. *Statistical Methods for Environmental Pollution Monitoring.* Van Nostrand Reinhold, New York.

Helsel, D.R., and R.M. Hirsch, 1995. *Statistical Methods in Water Resources.* Elsevier, Amsterdam, The Netherlands.

Huling, S.G., B.E. Pivetz, and R. Stransky, 2002. Terminal electron acceptor mass balance: NAPLS and natural attenuation. *Journal of Environmental Engineering*, 128(3): 246-252.

ITRC (Interstate Technology and Regulatory Cooperation Work Group), 2000. *Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies*.
http://www.itrcweb.org/DNAPL-1.pdf

Kao, C.M., and Y.S. Wang, 2001. Field investigation of the natural attenuation and intrinsic biodegradation rates at an underground storage tank site. *Environmental Geology*, 40(4-5):622-630.

Kruseman, G.P., and N.A. de Ridder, 1989. *Analysis and Evaluation of Pumping Test Data, International Institute for Land Reclamation and Improvement*. Wageningen, The Netherlands.

Leahy, J.G., and G.S. Shreve, 2000. The effect of organic carbon on the sequential reductive dehalogenation of tetrachloroethylene in landfill leachates. *Water Research*, 34(8):2390-2396.

Ludwig, R., M. Barcelona, and K. Piontek, 2000. Redox processes in petroleum hydrocarbon site characterization and remediation. In: *Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary,* Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

McNab, W.W. and B.P. Dooher, 1998. Critique of a steady-state analytical method for estimating contaminant degradation rates. *Ground Water,* 36(6):983-987.

Mercer, J.W., and R.M. Cohen, 1990. A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation. *Journal of Contaminant Hydrology*, 6:107-163.

Mohr, T.K.G., 2001. *Solvent Stabilizers*, white paper, Santa Clara Valley Water District, Santa Clara, CA.

National Research Council, 2000. *Natural Attenuation for Groundwater Remediation*. National Academy Press, Washington, DC. http://books.nap.edu/books/0309069327/html/index.html

Palmer, C.D., and W. Fish, 1992. *Chemical Enhancements to Pump-and-Treat Remediation,* EPA/540/S-92/001. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. http://www.epa.gov/ada/download/issue/chemen.pdf

U.S. EPA, 1986a. *RCRA Ground-Water Monitoring Technical Enforcement Guidance Document*, OSWER-9950.1. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA, 1986b. *Test Methods for Solid Waste, SW-846*. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC. http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm

U.S. EPA, 1988. *Soil Gas Sensing for Detection and Mapping of Volatile Organics*, EPA/600/8-87/036. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV.

U.S. EPA, 1991a. *Seminar Publication: Site Characterization for Subsurface Remediation*, EPA/625/4-91/026. U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH. http://www.epa.gov/swerust1/cat/sitchasu.pdf

U.S. EPA, 1991b. *A Review of Methods for Assessing Nonpoint Source Contaminated Ground-Water Discharge to Surface Water*, EPA/570/9-91/010. U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA, 1992a. *Methods for Evaluating the Attainment of Cleanup Standards, Volume 2: Ground Water*, EPA/230/R-92/014. U.S. Environmental Protection Agency, Office of Policy, Planning, and Evaluation, Environmental Statistics and Information Division, Washington, DC. http://www.epa.gov/superfund/resources/gwdocs/per_eva.htm

U.S. EPA, 1992b. *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance*. U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC.
http://www.epa.gov/epaoswer/hazwaste/ca/resource/guidance/sitechar/gwstats/gritsstat/download/addendum.pdf

U.S. EPA, 1993a. *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide, Volume 1: Solids and Ground Water*, EPA/625/R-93/003a. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

U.S. EPA, 1993b. *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide, Volume 2: The Vadose Zone, Field Screening and Analytical Methods*, EPA/625/R-93/003b. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

U.S. EPA, 1993c. *Seminar on Regional Considerations for Dense Nonaqueous Phase Liquids at Hazardous Waste Sites: Implementation and Enforcement Issues*, EPA/600/K-93/004. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

U.S. EPA, 1994. *DNAPL Site Characterization*, EPA/540/F-94/049. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA, 1997a. *Rules of Thumb for Superfund Remedy Selection,* EPA/540/R/97/013, OSWER 9355.0-69. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA, 1997b. *Expedited Site Assessment Tools for Underground Storage Tank Sites: A Guide for Regulators,* EPA/510/B-97/001. U.S. Environmental Protection Agency, Office of Underground Storage Tanks, Washington, DC.

U.S. EPA, 1997c. *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final*, EPA/540/R-97/006. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC.
http://www.mng-ltd.com/ert/p_ecorisk.htm

U.S. EPA, 1998a. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water,* EPA/600/R-98/128. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH.
http://www.epa.gov/ada/download/reports/protocol.pdf

U.S. EPA, 1998b. *Risk Assessment Guidance for Superfund (RAGS): Volume I Human Health Evaluation Manual, Part D: Standardized Planning, Reporting, and Review of Superfund Risk Assessments*, EPA/540/R-97/033, OSWER 9285.7-01 D-1, PB 97-963305. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/superfund/programs/risk/ragsd/

U.S. EPA, 1998c. *EPA Guidance for Quality Assurance Project Plans,* EPA QA/G-5, EPA/600/R-98/018. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.
http://www.epa.gov/swerust1/cat/epaqag5.pdf

U.S. EPA, 1999a. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17P*. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/swerust1/directiv/d9200417.pdf

U.S. EPA, 1999b. *A Guide to Preparing Superfund Proposed Plans, Records of Decision, and Other Remedy Selection Decision Documents,* EPA/540/R-98/031, OSWER 9200.1-23P, PB98-963241. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/superfund/resources/remedy/rods/

U.S. EPA, 2000a. *Data Quality Objectives Process for Hazardous Waste Site Investigations,* EPA QA/G-4HW, EPA/600/R-00/007. U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC.
http://www.epa.gov/quality1/qa_docs.html

U.S. EPA, 2000b. *Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary*, Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH.
http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

U.S. EPA, 2000c. *Guidance for Data Quality Assessment: Practical Methods for Data Analysis* (EPA QA/G-9), EPA/600/R-96/084. U.S. Environmental Protection Agency, Washington, DC.
http://www.epa.gov/quality/qa_docs.html

U.S. EPA, 2000d. *Institutional Controls: A Site Manager's Guide to Identifying, Evaluating and Selecting Institutional Controls at Superfund and RCRA Corrective Action Cleanups*, OSWER 9355.0-74FS-P, EPA-540-F-00-005. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/superfund/action/ic/guide/guide.pdf

U.S. EPA, 2000e. *Proceedings of the Ground-Water and Surface-Water Interactions Workshop*, EPA/542/R-00/007. U.S. Environmental Protection Agency, Washington, DC.
http://www.epa.gov/tio/pubitech.htm#gwc

U.S. EPA, 2001a. *Using the Triad Approach to Improve the Cost-Effectiveness of Hazardous Waste Site Cleanups. Current Perspectives in Site Remediation and Monitoring*, EPA 542-R-01-016, October 2001. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response (5102G), Washington, DC.
http://www.epa.gov/tio/triad/

U.S. EPA, 2001b. *Current Perspectives in Site Remediation and Monitoring: Clarifying DQO Terminology Usage To Support Modernization of Site Cleanup Practice*, EPA/542/R-01/014. U.S. Environmental Protection Agency, Washington, DC.
http://www.clu-in.org/tiopersp/#curr_pers

U.S. EPA, 2002a. *Site Characterization Library, Volume 1 (Release 2.5)*, NERL-LV-02-030, EPA/600/C-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Las Vegas, NV.

U.S. EPA, 2002b. *Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies*, EPA/540/S-02/500. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. http://www.epa.gov/ada/pubs/issue.html

U.S. EPA, 2002c. *OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*, RCRA-2002-033. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/correctiveaction/eis/vapor.htm

U.S. EPA, 2003a. *MTBE (methyl tertiary-butyl ether) and Underground Storage Tanks*. U.S. Environmental Protection Agency. OSWER/OUST. Washington, DC .
[Online] Available: http://www.epa.gov/swerust1/mtbe/index.htm (April 2, 2004).

U.S. EPA, 2003b. *Using Dynamic Field Activities for On-Site Decision Making: A Guide for Project Managers,* OSWER No. 9200.1-40, EPA/540/R-03/002, May 2003. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/superfund/programs/dfa/guidoc.htm

U.S. EPA, 2003c. *Field Analytic Technologies Encyclopedia (FATE)*. U.S. EPA Technology Innovation Office, Washington, DC.
[Online] Available: http://fate.clu-in.org/ (April 2, 2004).

U.S. EPA, 2004. *Handbook of Groundwater Protection and Cleanup Policies for RCRA Corrective Action*, EPA/530/R-01/015. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
http://www.epa.gov/epaoswer/hazwaste/ca/resource/guidance/gw/gwhandbk/gwhndbk.htm

Weaver, J.W., J.T. Wilson, and D.H. Kampbell, 1996. Extraction of degradation rate constants from the St. Joseph, Michigan, trichloroethene site. In: *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, Hyatt Regency Dallas, Dallas, TX, September 11-13, 1996, EPA/540/R-97/504. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.
http://www.epa.gov/ordntrnt/ORD/WebPubs/natural/natural.pdf

Westall, J.C. 2000. Geochemical equilibrium and the interpretation of Eh. In: *Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary*, Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH.
http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

Wiedemeier, T.H., H.S. Rifai, C.J. Newell, and J.T. Wilson, 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, New York.

Wiedemeier, T.H., P.E. Haas, 2002. Designing monitoring programs to effectively evaluate the performance of natural attenuation. *Ground Water Monitoring & Remediation*, 22(3):124-135.

Wilson, J. 2000. Current state of practice for evaluation of oxidation reduction processes important to the biological and chemical destruction of chlorinated organic compounds in ground water. In: *Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary,* Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH.
http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

Winter, T.C., 2000. Interaction of ground water and surface water. In: *Proceedings of the Ground-Water and Surface-Water Interactions Workshop,* EPA/542/R-00/007. U.S. Environmental Protection Agency, Washington, DC.
http://www.epa.gov/tio/tsp/issue.htm

GLOSSARY

abiotic not relating to living things, not alive.

adsorption process by which molecules collect on and adhere to the surface of an adsorbent solid because of chemical and/or physical forces.

aerobic living, active, or occurring only in the presence of oxygen.

alkalinity the capacity to accept protons (acid) while maintaining the pH above a predetermined value. Ground-water alkalinity may be increased as carbon dioxide emitted during biodegradation causes bicarbonate production.

alluvial relating to material deposited by moving water.

anaerobic living, active, or occurring only in the absence of oxygen.

anthropogenic man-made.

attenuation a lessening in concentration or mass.

biodegradable refers to a material or compound that can be broken down by natural processes of living things such as metabolization by microorganisms.

biodegradation act of breaking down material by natural processes of living things such as metabolization by microorganisms.

contaminants of concern those chemicals identified during site investigations that are required to be addressed by the response action proposed in the remedy decision documents.

daughter product degradation product of a compound. Vinyl chloride is a daughter product of the reductive dechlorination of dichloroethene.

diffusion process by which ionic and molecular species move from a region of higher concentration to a region of lower concentration.

dispersion phenomenon by which a solute in flowing ground water mixes with uncontaminated water, becoming reduced in concentration. Dispersion is due both to differences in water velocity at the pore level and differences in the rate at which water moves through different strata. Also refers to statistical measures of how widely a set of data vary.

dispersivity property that quantifies dispersion in a medium.

electron acceptor a compound capable of accepting electrons during oxidation-reduction (redox) reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as tetrachloroethene, trichloroethene, dichloroethene, and vinyl chloride.

electron donor a compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.

hydraulic conductivity relative ability of soil, sediment, or rock to transmit water; a coefficient of proportionality describing the rate at which water can move through a permeable medium.

hydraulic gradient the change in total hydraulic head with a change in distance in a given direction.

hydraulic head sum of the elevation head, the pressure head, and the velocity head at a given point in an aquifer; also referred to as the total head.

hydrostratigraphic unit in which the geologic materials have similar hydrologic properties.

in situ refers to a technology or treatment process that can be carried out in place at the site of contamination.

metabolic by-product a product of the reaction between an electron donor and an electron acceptor. Metabolic by-products can include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, chloride, carbon dioxide, and water.

oxidation chemical process that results in a net loss of electrons in an element or compound.

porosity the ratio of void volume to total volume of a rock or sediment.

pump and treat treatment method in which contaminated water is pumped out of the contaminated aquifer, then treated.

reduction chemical process that results in a net gain of electrons to the reduced element or compound.

sorb to remove a substance from the aqueous phase to the solid phase.

sorption movement of a substance from the aqueous phase to the solid phase, whether by adsorption, absorption, fixation or precipitation. Sorption may be reversible or irreversible.

substrate substance(s) that provides growth and energy requirements for cells.

tentatively identified compounds (TICs) compounds appearing in a chemical analysis of environmental media from a site that have not been definitely identified.

transmissive zones subsurface units where ground-water flow is constrained or bounded by lower hydraulic conductivity materials (*i.e.*, geologic impediments to flow) or hydrologic barriers (*e.g.*, hydraulic head boundaries). Transmissive zones may be bounded by components as obvious as the water table or units with low hydraulic conductivity, or by conditions as subtle as small differences in grain size, sorting, and packing of seemingly uniform sands.

uncertainty reduction of confidence in a conclusion when more than one estimate is available for a variable.

vadose zone zone between the ground surface and the water table.

Appendix A

VARIABILITY IN MEASURED PARAMETERS AND THE EFFECTS ON PERFORMANCE MONITORING

Appendix A
VARIABILITY IN MEASURED PARAMETERS AND THE EFFECTS ON PERFORMANCE MONITORING

A.1 Introduction

Monitoring data often exhibit significant variability. The variability in the measured values reflects both the inherent spatial and temporal variability in the subsurface as well as variability introduced into the data by the measurement techniques. The variability in the data introduce uncertainty into the decision-making process, increasing the probability of making incorrect decisions. Therefore, it is important to be able to assess the nature of data variability to understand its importance toward achieving remedial goals. Identification and quantitative assessment of data variability may often be more important in remedies that rely solely on natural attenuation processes than for engineered remedies as neither contaminant migration nor attenuation processes are actively controlled.

A.2 Spatial and Temporal Variability

A major source of variability in measured and interpreted contaminant distributions will generally be related to the placement and screening of monitoring points within the spatially and temporally heterogeneous subsurface. Current methods for defining subsurface contaminant distributions rely on techniques that generally sample only a small volume of material immediately surrounding a well or borehole. Therefore, the locations of sample collection often greatly affect the interpretation of natural attenuation processes. For example, a vertical series of ground-water samples collected using short-screened (*e.g.*, 0.5 ft to 1 ft) wells, such as those installed by direct push technologies, may display differences in contaminant concentrations of several orders of magnitude over short vertical distances. In comparison, a nearby conventional monitoring well screened over the same total interval as the series of short-screened wells may yield samples with contaminant concentrations that are essentially a flow-weighted average of the samples taken from the short-screened wells.

The issue of obtaining "representative" samples from heterogeneous media is complex and has been termed sample "support" (U.S. EPA, 2000a). Proper sample support involves ensuring that the sample is representative of the original matrix under investigation (U.S. EPA, 2001b). Sample support and the scale at which remedy performance will be evaluated should be considered during design of the performance monitoring system because it strongly affects monitoring network density and the specification of appropriate data evaluation methods. For instance, as in the example given above, it may be possible to find a narrow zone in the subsurface where contaminant concentrations exceed allowable limits, but ground water at the receptor point (*e.g.*, an irrigation well) may not exceed limits because the receptor derives ground water from a much thicker zone in the subsurface. In such a case, the sample support chosen can determine the remedial decision, because a sample representative of the narrow highly contaminated zone may lead to a decision different than that derived from consideration of a sample representative of the thicker zone with a lower mean contaminant concentration.

Three-dimensional spatial variability in dissolved contaminant concentrations occurs due to such complex factors as the:

- Nonuniform distribution of the original source materials for ground-water contamination,
- Heterogeneity in site geology, and
- Differences in the geochemical environment.

Source materials in various forms such as sorbed materials and NAPL may be non-uniformly distributed throughout the vadose and saturated zone. This variability in source distribution means that source contact with recharge water and ground water (and therefore dissolution of contaminants into the ground water) is significantly different at varying locations in the aquifer. Also, the geochemical environment varies throughout the aquifer due to the interactions of microbial communities with the supply of terminal electron acceptors (TEA) and electron donors carried by ground water from upgradient locations or released locally from the aquifer matrix. Therefore, types and rates of contaminant degradation can vary throughout the plume.

After installation of the performance monitoring network, temporal variations in contaminant distribution may become major influences on observed contaminant trends and data interpretations. Sources of this variability include:

- Changes in contaminant input to ground water,
- Changes in degradation processes,
- Short-term changes due to seasonal factors (*e.g.*, recharge or other physical factors such as temperature), and
- Long-term changes due to substrate or TEA depletion, or changes in site hydrology.

Changes in contaminant input to ground water may result from source control actions, additional releases to the environment, dissolution of vadose zone contamination during infiltration of precipitation, and dissolution during increases in water table elevation. Changes in site hydrology, such as drought, extremely wet periods, and changes in ground-water extraction or recharge due to different land uses may change ground-water flow rates, directions, and, correspondingly, contaminant concentrations at established monitoring points.

A.3 Measurement Variability

Other sources of variability are related to the measurement processes for monitoring parameters and variability in the interpolation and data interpretations. Numerous factors, such as:

- Differences in sample collection methods (*e.g.*, changes in equipment, pumping volumes or rates, or pump intake location within a well screen),
- Differences in sample preparation methods (*e.g.*, sample filtration or lack thereof, sample preservation, and adherence to holding times), and
- Analytical variability (*e.g.*, incorrect instrument calibration, improper operating parameters)

may result in variability in measured contaminant concentrations. The variability from these sources is often much less than the variability due to subsurface heterogeneity and temporal variability. However, measurement variability can be significant, and caution should be exercised in the use of samples taken or analyzed by different methods to assess plume changes (*e.g.*, calculating attenuation rates). Measurement variability is generally more readily definable and controllable than spatial and temporal variability, using proper quality assurance/quality control procedures such as those discussed in U.S. EPA (1998b). Additional discussion of the sources of variability in subsurface investigations of contaminant migration and fate is provided by Barcelona *et al.* (1989).

A.4 Variability in Data Interpretation

In addition to spatial and temporal variability, and variability in measured contaminant concentrations, variability is also introduced during the data interpretation process due to the non-uniqueness of possible explanations of measured site conditions. That is, there may be a variety of configurations of the conceptual site model that could explain the available data (*e.g.*, with regard to source factors, ground-water flow, and components of the attenuation rate). It may be possible to reduce the number of alternative explanations by designing a focused sampling program to fill the data gaps. The alternative explanations may be grouped by their probable impact on attainment of remedial goals, and their likelihood of accurately describing site conditions, in order to assess the desirability of performing additional work to verify or eliminate important alternative explanations.

United States
Environmental Protection
Agency

National Risk Management
Research Laboratory
Cincinnati, OH 45268

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