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Ground-Water Contamination by Volatile Organic Compounds: Site Characterization, Spatial and Temporal Variability

by

H. Allen Wehrmann
Office of Ground-Water Quality

Michael J. Barcelona
University of Michigan

Mark D. Varljen
Applied Hydrogeologic Research, Inc.

Gary Blinkiewicz
Western Michigan University

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U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
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By:

H. Allen Wehrmann, Illinois State Water Survey
Michael J. Barcelona, University or Michigan
Mark D. Varljen, Applied Hydrogeologic Research, Inc.
Gary Blinkiewicz, Western Michigan University

Prepared for:

USEPA Environmental Monitoring Systems Laboratory
Advanced Monitoring Systems Division
Aquatic & Subsurface Monitoring Branch
Las Vegas, Nevada

Larry Eccles, Project Officer
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GROUND-WATER CONTAMINATION BY VOLATILE ORGANIC COMPOUNDS: SITE CHARACTERIZATION AND SPATIAL AND TEMPORAL VARIABILITY

SUMMARY

Ground-water quality monitoring procedures and methodologies have been the subject of substantial research in the last fifteen years, and the Illinois State Water Survey (ISWS) has been at the forefront of several milestone projects. Work conducted at the ISWS in the early 1980s focused on the errors introduced to chemical results from improper well construction practices and well sampling procedures (Gibb *et al.*, 1981; Barcelona *et al*, 1983; Barcelona *et al*, 1985). By the late 1980s, the ISWS was examining the contribution of sampling, analytical, and natural (or source) variability to the overall variability of sample analytical results (Barcelona *et al.*, 1989ab). All of this early work involved examination of the major inorganic compounds and surrogate organic (e.g., TOC, TOX) ground-water quality parameters. Most recently, however, national focus has been on organic contaminants in ground water, particularly the class of contaminants called volatile organic compounds (VOCs). These compounds have been particularly vexing because of their extremely frequent occurrence as ground-water contaminants and also because of the inherent difficulties involved with sampling and analysis of volatile compounds dissolved in water.

This latest research project concentrated on improving the reliability of site characterization methods for VOC-contaminated ground water. The work emphasized the use of advanced geostatistical and hydrologic monitoring techniques to aid in the interpretation of data on VOCs in ground water.

Since the beginning of the project in 1989, more than 40 monitoring wells ranging in depth from 45 to 100 feet were constructed in and around a large VOC plume in southeast Rockford. Thirty-two of these wells were sampled quarterly from May 1991 to September 1992 to provide data on spatial and temporal trends on VOC concentrations in the ground water. Total VOC concentrations in the wells range from below detection limits to more than 1000 micrograms per liter (μg/L). Principal contaminants include a number of widely used industrial solvents and related compounds: 1,1,1-trichloroethane, trichloroethene, 1,1-dichloroethane, cis-1,2-dichloroethene, and 1,1-dichloroethene. Drinking water standards for those 5 compounds are 20, 5, 5, 70, and 7 μg/L, respectively.

VOC concentration data from these wells were used to: 1) examine monitoring well network design to detect spatial and temporal trends in VOC ground-water quality, 2) establish a documented "history" of VOC concentrations in the wells for comparison with other ground-water sampling techniques such as the *in-situ* sampler called the Hydropunch®, and 3) perform short time-series/purging experiments for 13 wells to examine use of surrogate inorganic and easily interpreted field data (e.g., dissolved oxygen, O_2, and specific conductance, Ω^{-1}) to determine when a well is properly purged for VOC sampling.

Quarterly sampling of 15 monitoring wells was initiated upon their completion in November 1990 and continued in February 1991. With the completion or an additional 18 wells in May 1991, 33 wells were sampled in May, August, and November 1991 and again in March and September 1992 (samples were not collected in May 1992).

Use of geostatistics (i.e., kriging) on our quarterly monitoring well sampling results provided valuable insight on the nature of the spatial and temporal variability of this VOC plume. Often, monitoring well networks rely on a few "key" well locations that are sampled as often as monthly. Our results suggest that contaminant distributions might be better resolved by using more sampling points and fewer sampling events. New techniques, including ground-water sampling without wells, provide a means to collect samples at a variety of locations and depths without being "tied in" to a permanent set of immovable wells.

Contaminant site characterization approaches are generally based on traditional drilling, subsurface sampling, and monitoring well construction techniques. Samples of potentially contaminated ground water are collected from monitoring wells after development and purging to determine the magnitude and extent of contamination. Within the last five years, more rapid sampling and analysis techniques nave been developed to supplement monitoring well-based data collection methods. One of the most well-known new techniques in "rapid" ground-water sampling is the *in-situ* sampler called the Hydropunch®. The Hydropunch® provides an alternative to ground-water sample collection without the need for construction of a permanent well installation. Ground-water sampling in this manner greatly reduces the time needed to extract a sample from the ground for chemical analysis, potentially saving valuable time and money to devote to areas found to be most contaminated.

In order to establish the reliability of the Hydropunch® tool for sampling VOCs relative to monitoring well samples, field experiments were performed to compare statistical differences in VOC concentrations in ground-water samples collected from the Hydropunch® and from monitoring wells. To do this, we collected two Hydropunch® samples within 3 to 5 feet horizontally and at depths adjacent to the screened sections of completed monitoring wells with well-established records of VOC contamination. Thirteen monitoring well-Hydropunch® comparisons were conducted. In addition, aquifer core (solids) samples were collected at the time the Hydropunch® samples were collected.

Our results found only small differences in the VOC concentrations collected from Hydropunch® and conventional well samples. This means that the Hydropunch® is an excellent tool for reconnaissance work to identify the vertical and horizontal extent of VOC plumes and VOC contaminant source locations. Therefore, results from use of the Hydropunch® tool provide a cost-effective means to guide the placement of more expensive "permanent" monitoring installations (i.e., wells).

Analysis of aquifer solids samples collected opposite well-screen intervals showed significantly higher volume-averaged concentrations of VOCs than did well water samples. Therefore, our results show that more or the contaminant is attached to the solid aquifer material than is present in the water. This has great implications, particularly tor ground-water remediation. If most of the contaminant is attached to the solid matrix and must desorb from the solid to the liquid phase, conventional "pump-and-treat" ground-water remediation technologies are doomed to extremely lengthy periods of operation for potentially marginal improvements in ground-water quality. More efforts, then, should he devoted to source removal, enhanced desorption technologies, and *in-situ* treatments.

Research devoted to procedures for sampling monitoring wells for VOCs through time-series sampling for VOCs and inorganic field parameters (O_2 and Ω^{-1}) indicates that representative VOC samples can he collected reproducibly by purging at low flow rates (about 1 liter per minute) with dedicated "bladder-type" pumping devices. Such methods provide reliable, consistent sampling which have been shown to be less time-consuming and to generate less volume of potentially contaminated purge water than conventional high rate purging and/or hailing techniques. Our results show that representative aquifer water can he achieved within about 1 well volume as opposed to 3 or more well volumes typically purged from wells prior to sampling.

Our results show: 1) that an alternative to traditional monitoring well construction and sampling, in particular, the HydroPunch®, is a viable approach to contaminant site investigations even when VOCs are involved, and especially for reconnaissance investigations; 2) that low-flow-rate purging of monitoring wells accompanied by observation of surrogate inorganic parameters during purging can provide a reliable, consistent method for sampling monitoring wells for VOCs; 3) that VOC contaminant concentrations observed dissolved in ground water may be only a fraction of the total contaminant mass contained in a ground-water "plume"; and 4) that the temporal and spatial variability of a VOC contaminant plume is such that better characterizations should rely on less frequent sampling of more locations.

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NOTICE

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ABBREVIATIONS FOR COMPOUND NAMES

Abbreviation	Full Name
DCE	1,1-dichloroethene
MC	methylene chloride
DCE12T	trans-1,2-dichloroethene
DCA	1,1 -dichloroethane
cl2DCE	cis-1,2-dichloroethene
CF	chloroform
BCM	bromochloromethane
TCA	1,1,1-trichloroethane
CT	carbon tetrachloride
DCA12	1,2-dichloroethane
BZN	benzene
TCE	trichloroethylene
DCPA12	1,2-dichloropropane
BDCM	bromodichloromethane
DCPE13C	cis-l,3-dichloropropene
TOL	toluene
DCPE13T	trans-1,3-dichloropropene
B2C1PA	2-bromo-1-chloropropane
TCA112	1,1,2-trichloroethane
PCE	tetrachloroethene
DBCA	dibromochloroethane
CBZN	chlorobenzene
PCA1112	1,1,1,2-tetrachloroethane
EBZN	ethylbenzene
BF	bromoform
DCB14	1,4-dichlorobutane
PCA1122	1,1,2,2-tetrachloroethane
DCBZN13	1,3-dichlorobenzene
DCBZN14	1,4-dichlorobenzene
DCBZN12	1,2-dichlorobenzene
BM	Bromomethane
CA	chloroethane
CM	chloromethane
TCFM	trichlorofluoromethane
TFT	trifluorotoluene

GROUND-WATER CONTAMINATION BY VOLATILE ORGANIC COMPOUNDS: SITE CHARACTERIZATION AND SPATIAL AND TEMPORAL VARIABILITY

INTRODUCTION

This study was designed to provide an evaluation of the strength and weaknesses of various site characterization techniques employed to determine the nature and extent of subsurface contamination by volatile organic compounds (VOCs). Conventional designs for VOC detection monitoring and contamination assessment efforts generally include the use of: surface or subsurface geophysics to determine lithologic detail; soil gas, aquifer solid or soil borings to both detect contaminant compounds and provide samples for aquifer property determinations; and wells, piezometers, or other water sampling and aquifer testing installations to collect data linked to water flow and contaminant transport. There exists a need to investigate the spatial and temporal variability or VOC contamination in large urban industrialized areas with various site characterization techniques and to develop a field test methodology for site characterization which could be used under other hydrogeologic conditions. These large areas often have been affected by multiple contributing sources of contamination over relatively long time periods. The emphasis of this work was to evaluate the performance of various conventional and emerging techniques for site characterization efforts. The Agency could then develop proven guidance or recommendations for these efforts which would improve the efficiency and value of these programs.

The specific objectives of the project focus on the determination of regional hydrogeology and contaminant distributions as the basis for the detailed monitoring of spatial and temporal variability in VOC concentrations at selected sites within an urban region. Specifically:

1. The hydrologic properties and areal extent of the shallow sand and gravel aquifer must be determined with specific attention to the uncertainty associated with using point data to describe regional aquifer characteristics that exhibit spatial variability. Focused data collection and geostatistical analysis of the discrete point data will be used to develop fields for both hydraulic conductivity and head and to estimate the uncertainty (or confidence) associated with the fields. Attention was paid to the maintenance of a high level of confidence in the data as a function of the sample size and the spatial arrangement or sampling locations.

2. Ground-water flow gradients and directions were to be determined using hydraulic head measurements in constructed monitoring wells. These data were used to determine the temporal variability of gradient on the spatial and temporal variability of VOC concentrations in ground water.

3. Preliminary sampling for chemical analysis was conducted at existing wells and piezometers which were constructed to estimate the magnitude and extent of contamination in the study region. Using these data and those from other sources, the uncertainty in the contaminant distributions may be assessed by geostatistical techniques to identify sites of persistent contamination and to distinguish sampling and analytical variability from natural variability due to geologic, hydrologic, or source influences.

4. Candidate sites within the region were selected for detailed investigation of spatial and temporal variability in contaminant concentrations and to determine the range of short-term temporal (i.e., purging and pumping) correlation as well as short-range spatial distribution of contaminants. Time-series sampling was conducted at an array of pumping wells and monitoring well nests at the site to estimate levels of temporal variability. The principal effort was focused on variability in concentrations of the principal contaminant (i.e., trichloroethane) and selected water quality constituents.

5. An intercalibration experiment was run at contaminated sites to compare the reliability of Hydropunch® sampling with the results of samples from conventionally screened monitoring wells. The experiment should disclose the usefulness of soil gas measurements as indicators of shallow ground-water contaminant distributions and the extent to which Hydropunch® samples to either substitute for or supplement similar results from discrete monitoring wells.

The subsurface environment of ground water has commanded substantial legislative, regulatory and scientific attention in the past two decades. Valuable information has been obtained on the hydrogeochemical characteristics of these systems via monitoring and sampling efforts. These efforts have been directed largely towards investigation of contaminated conditions. Hydrogeochemical observations have provided a perspective on the complexity of the subsurface and tempered our expectations for remedial action and cleanup programs (Freeze and Cherry, 1989) . It is important to maintain a balanced perspective on the complexities of the environment and apply what has been learned to future studies (Bach, 1989).

The subsurface environment is a dynamic hydrogeochemical and microbial habitat which cannot be fully understood by cataloging concentrations of natural and anthropogenic chemical compounds. The components of a responsive, cost-effective monitoring design must include careful consideration of background conditions, geologic, microbial and hydrologic influences on system geochemistry, contaminant transport and fate. Sampling protocols must be developed in a progressive manner to permit identification of source type and composition, biological and chemical transformations and potential remedial action alternatives. In most cases, site-specific sampling protocols will be driven by the goals of the monitoring program and the need for error control. This overall objective of this study was to provide a scientific basis for site characterization which serve reliable, long-term data collection needs.

GROUND-WATER QUALITY, VARIABILITY, AND SITE CHARACTERIZATION
A REVIEW

Environmental Sampling

Geochemical conditions in the subsurface at either contaminated or uncontaminated sites are influenced by climatic, meteorologic, and hydrogeologic variables which are dynamic in a global sense (USEPA & UNEP, 1986; NAS, 1989). The time frames and scales of site investigations must be matched to the variability and trends in these factors if environmental monitoring efforts are to yield data of enduring value. The principles of environmental sampling have been reviewed recently with an emphasis on long-term, responsive monitoring network designs (Keith, 1988). Highlighted in the review was the need to develop simple, accurate sampling protocols which recognize both the dynamics of environmental systems and the practical limits which systematic sampling errors represent in data interpretation (Barcelona, 1988).

Sampling the aqueous, solid or hydrogeologic characteristics of the subsurface should be conducted with care to minimize sample disturbance so that subsequent analytical data are representative of actual conditions. These goals can be met most effectively if the monitoring design is based on sound hydrogeologic information and major sources of systematic error, (i.e., bias) are avoided. Sampling protocols are written documents incorporating all procedures and methods used in the establishment of sampling points, selection of analytes, sampling and sample handling operations. Protocols should be prepared with the goal of minimizing error.

Ground-water sampling protocols are often more involved than those which may be needed for surface water, waste stream or air sampling since access to the subsurface involves disturbance of environment. In large part, the results and the conclusions drawn from a sampling and analysis effort will depend on the procedures used in providing a representative sampling point and in sample collection. These procedures should be based on both the level of resolution necessary for the purposes of the program and on hydrogeologic factors which characterize the subsurface environment. The overall goals of the sampling effort in monitoring programs should be to provide representative, unbiased results referenced to a written protocol. The written protocol should also be developed so as to permit reproducible measurements over time.

The elements of a generalized sampling protocol are included in Table 1 with reference to specific criteria common to many types of monitoring programs. Though this approach emphasizes the use of wells as sampling points, parallel protocols can be developed applicable to sampling gas on solid matrices. It should be evident from the table that the preparation of the sampling protocol includes hydrogeologic understanding of the site in question, identification of the purpose and duration of the program and the actual sampling operations. Therefore, the development of the protocol demands active participation from program management, geologists, hydrologists, chemists, engineers and the

Table 1. Elements of a Generalized Sampling Protocol

Element	Procedure/Methods	Principal Design Criteria
Sampling Location	Candidate points located in flow field established by piezometer network and at resolution equal to hydrogeologic complexity.	Upgradient and downgradient locations in three dimensions which are representative of the site and in accord with program purposes.
Sampling Frequency	Attention to compliance requirements, trend identification, and program duration.	Frequencies sufficient to maximize information return with minimum of sampling points and effort.
Analyte Selection	Subsurface geochemical indicators, water quality indicators, potential contaminants.	Chemical and geochemical characterization of background and potentially contaminated conditions which permit analysis of chemical fate and transport.
Sampling Points	Screen design, well construction and grouting, well development, aquifer testing.	Minimum disturbance of subsurface conditions and samples; points will be durable and representative over long periods of time.
Sampling Device Selection	Dedicated purging/ sampling pumps.	Retrieval of minimally-disturbed samples minimizing both systematic and operator-dependent errors in well purging and sample collection at all locations.
Sample Collection	In-line filtration, field measurements of sensitive parameters, sample preservation, ana QA/QC control samples.	Collection of minimally-disturbed samples: minimizing sample handling and potential sources of systematic and operator-dependent errors.

staff involved in sampling and analysis. Error identification and control measures incorporated into the written protocol extend well beyond the routine application of traditional laboratory-based quality assurance and quality control measures.

Error Types, Recognition and Control

Representativeness, Accuracy and Systematic Error

Sampling for chemical analysis assumes that one is able to collect a minimally disturbed, relatively small portion of the medium (e.g., water, solid, etc.) which is representative of the environment under investigation. Therefore it is important that criteria for representativeness include some knowledge of the characteristics of the population to be sampled. For ground-water or subsurface solid sampling, establishing criteria for representativeness entails knowledge of the flow field and the hydrogeochemical characteristics of subsurface media. In this sense, representativeness relates to the hydrogeochemical environment which must be characterized to some extent before one undertakes sampling towards the goals of the monitoring program.

For example, if a program seeks to identify potential health risks due to exposure to chemical compounds or pathogenic organisms via drinking water from wells in a regional aquifer, the hydrogeology of the aquifer provides the basis for water sample representativeness. Regional hydrology, potential sources, geochemical distributions and their relation to the capture zones of drinking water wells provide additional criteria.

Accuracy and representativeness are often confused in discussions of ground-water monitoring or sampling efforts. Accuracy, in environmental sampling, is a measure of the correspondence between a sample result (e.g., a water level or pH measurement) and the average or mean result for a particular value at a known location and time. One can estimate the accuracy of an individual result by the repeated use of unbiased sampling and analysis techniques at the known location. Using the example above, it would be possible to obtain accurate measurements of water levels in a monitoring well in the regional aquifer if one properly used a calibrated steel tape and referenced the measurement to a surveyed elevation. An accurate measurement would be representative provided that the screened interval of the monitoring well was located in the flow field of the regional aquifer intersecting the capture zone of the drinking water well. Therefore, the hydrogeology of a particular site with respect to a potential receptor provides the basis for judging representativeness and subsequent interpretation of the results.

Accuracy may only be improved by repetitive measurements with better technology (i.e., presumably less biased and more precise methods). Accuracy is most often expressed as percent bias or recovery relative to the "true" or mean value of repetitive measurements using the equation:

$$\text{Accuracy (\% bias)} = (\text{Sample Value}/\text{True Value}) \times 100\%$$

Continuing with the water level example, one would expect that a stretched, flexible tape for water level measurements would yield consistently shallower values for water levels than would a comparably calibrated steel tape. In this instance, the positively biased values would result from systematic (i.e., determinate) error in the tape calibration. Common systematic errors in ground-water investigations include negatively biased determinations of volatile organic compounds due to degassing and loss of volatiles in sample collection or handling and positively biased pH values due to the loss of CO_2 from water samples handled open to the atmosphere. Minimal sample handling, the proper choice of sample devices and in-line, closed cell measurement systems can avoid these sources of bias or inaccuracy. Gross determinate errors may result from inaccurate sampling locations, inadequate purging of stagnant water from wells prior to sampling, and poor sample preservation or storage techniques. Careful adherence to the elements of a written sampling protocol provide a basis for accurate, representative sampling efforts.

Precision ana Random Error

Precision is a measure of the spread or range of a value from the mean of repetitive values from the same sample portion. Precision is normally expressed in terms of the standard deviation (σ) of the sample set (where N = the number of samples) from the mean value. When it is expressed as a percentage (e.g. ±20%) this refers to the relative standard deviation or standard error of the mean via the equation.

$$\text{Precision (\%)} = (\sigma/\text{Mean Value}) \times 100\%$$

Precision is primarily influenced by random or indeterminate errors which arise from inconsistent applications of measurement methods, multiple operators and the random distribution of values from dynamic systems. Increasing the number of repetitive values will generally improve the precision of a dataset if unbiased methods are used in a consistent fashion. Complicated sampling methods will often lead to large variations in measurement precision if multiple personnel are involved in an investigation over time.

Error Recognition and Control

Systematic and random errors are the two major types of error involved in ground-water investigations. Systematic error impacts directly on accuracy while random errors influence the precision of a measurement. Either type of error can arise during the sampling and analysis steps in a monitoring program. It is important to note that the recognition and control of error must begin with the design of the overall monitoring program. Therefore, quality assurance and quality control measures should be applied to the decision-making associated with: the review of site and regional hydrogeochemical data, field reconnaissance techniques, analyte and sampling location selection, purging procedures, sampling device and handling precautions among others. All of these decisions should be addressed in the sampling protocol.

Types of Samples

There are a variety of samples, control standards and blanks which should be introduced into the sampling and analytical protocols for the identification and control of errors. These controls apply to the constituent loss or contamination errors which attend sample handling, storage, transport and sampling matrix effects on analytical errors and constitute normal quality assurance and quality control (QA/QC) measures (Kirchmer, 1983).

It should be noted that errors which occur prior to sample retrieval at the land surface can neither be identified nor controlled by the use of QA/QC samples. Complete documentation of the details of sampling point location, design/construction, well purging and sample retrieval (e.g., pumping, etc.) operations can aid in the identification and control of errors which precede sample handling. Control samples which are useful in error identification, beginning with sample handling, include the following types.

Field blanks are samples of freshly distilled or deionized water taken from the laboratory into the field, poured into sample vessels at the site, closed, and returned to the lab with each set of samples. The constituent levels in field blanks establish the zero analyte signal for determining the limit of detection and are also useful in detecting sample contamination during handling, storage and transport.

Rinsing or cleaning blanks are samples of the final rinse of a sampling device before it is placed in a monitoring well. These samples are used primarily to evaluate whether cross-contamination of samples may have occurred due to carry-over from previous sampling operations.

Ground-water samples are actual samples collected in the field as "representative" of conditions at the site and analyzed in the laboratory for constituents of interest. If sampling points or locations are unrepresentative, or biased well purging or sampling procedures are used, no subsequent QA/QC measures can he expected to improve the quality of analytical results.

Duplicate ground-water samples are collected to be pooled for the selection of a sample pair (i.e. unspiked vs. spiked with analyte standards) for the estimation of sampling precision and accuracy.

Split samples are field samples that are split between two storage vessels in the field. One sample may be analyzed by one laboratory and the other subsample may be archived or submitted to another laboratory.

Spiked samples are ground-water samples from the pool of split sample duplicates with one aliquot receiving a spike volume of a reference standard to estimate the recovery of the analyte in the laboratory. Spiked samples allow estimates of accuracy and detect possible matrix interference problems.

Other types or QA/QC samples which pertain to analytical accuracy and precision include:

Laboratory blanks are similar to field blanks, except that the freshly distilled or deionized water used in the laboratory at the time each batch or samples is received and analyzed in the same manner as other samples. These samples aid in the detection or contamination which may occur in the laboratory.

Laboratory standards are normally prepared in the laboratory with freshly distilled or deionized water to provide daily control over lab instrumentation or procedural error and to permit the determination or the limit or quantitation for specific analytes.

External reference samples have been analyzed previously by outside laboratories and are available from commercial sources, the National Institute of Standards and Technology or U.S. EPA to detect either instrument calibration error or the use of inappropriate laboratory analytical methods (Kirchmer, 1983).

Limits of Detection and Quantitation

In order to faithfully document the results of ground-water sampling and analytical efforts, it is important to include assessments of accuracy and precision as well as the limits of detection and quantitation for the analysis. Since constituent concentrations and sample matrix properties vary from sample to sample and between successive sampling efforts, these assessments should be reported with each dataset (Keith *et al.*, 1983). In general, analytical limits of detection (LOD) and quantitation (LOQ) vary substantially between procedures employed for selected classes of chemical constituents. Instrumental detection limits apply to the determination of the lowest reproducible concentration of a particular analyte may which be detected in freshly distilled or deionized water. Practically, the effects of sample matrix and actual instrumental sensitivity and linearity on the limits of detection and quantitation must be determined based on the analytical conditions which apply to a particular set of samples. Therefore, the use of field blanks and laboratory standards at concentrations near the instrumental detection limit on each day of analysis are most often used to determine the LOD and LOQ for individual ground-water constituents. These measures are important components of sampling and analytical protocols.

The American Chemical Society Committee on Environmental Improvement has recommended a convention for the determination of the LOD and LOQ based on the controls noted above (ACS, 1980). Simply stated, the average field blank signal for a particular constituent establishes the zero concentration level and the LOD and LOQ represent concentrations three and ten standard deviations above the zero level respectively. The standard deviation estimated from replicate analytical determinations on the lowest laboratory standard for the constituent is used in these calculations.

For example, if the analytical signal for a benzene in the field blank was zero and the standard deviation for a 5 ppb standard was 1 ppb, the LOD would be 3 ppb and the LOQ would be 10 ppb for the dataset. Concentrations of benzene below the zero level should be reported as negative concentrations, assuming calibration linearity, to avoid censoring of the data (ASTM, 1983; Gilliom *et al.*, 1984). Concentrations between zero ppb and 10 ppb would be reported as trace levels with a cautionary note concerning the levels of detection.

Subsurface Conditions

Geologic formations and the introduction of water and gases via hydrologic processes provide the framework for distributions of the chemical and biological constiuents in the subsurface. Water use, irrigation, infiltration and recharge processes are dominant effects on these systems through advection, diffusion, dispersion and mixing. Hydraulic head and formation pressures which drive bulk water movement, lead one to expect stronger vertical than horizontal gradients in chemical constituent concentrations in undisturbed aquifers. Though this has often been observed to be true, it must be recognized that the introduction of contaminants from a variety of sources have led to significant gradients in chemical and biological variables at disturbed sites. The scales of the gradients in subsurface properties range widely due both to natural and anthropogenic effects.

Physical, Biological and Chemical Gradients

Table 2 contains examples of ranges of physical, biological and chemical variables of concern in monitoring efforts at both relatively undisturbed and disturbed sites. Disturbed conditions encompass far wider ranges of critical variables, such as: temperature, pressure, flow, pH and oxidation-reduction (redox) potential than those observed at undisturbed sites. Also, vertical gradients in both physical and chemical variables are generally greater than horizontal gradients due to limited vertical mixing and the highly stratified nature of the hydrogeologic properties of aquifers (Sudicky, 1986). Strong vertical gradients in dissolved gas concentrations (Rose and Long, 1988) and redox-sensitive constituents (Barcelona *et al.*, 1989a; Back and Barnes, 1965) may *be* expected to be persistent features of subsurface environments which impact on the speciation, mobility, transport and fate of contaminants. The implications for ground-water sampling efforts are that extensive vertical arrays of discrete sampling points may be needed to estimate both the characteristics and extent of subsurface contamination, and to aid in the prediction of contaminant transport and fate. In this respect, the use of an extensive network of piezometers for the determination of water levels hydraulic head distributions, and aquifer properties together with ground-water flow models are recommended before extensive vertical arrays of chemical sampling points are constructed.

Table 2. Ranges of Geochemically Significant Physical, Biological and Chemical Values of Natural ana Disturbed Near-Surface Ground Water

Variable	Effects	Natural	Disturbed
Physical Variables			
Temperature	Mixing, reaction path and rates, solubility	3°-20°C (Δ10-15°C)	3°-35°C (Δ10-25°C)
Pressure	Gas solubility	1-10 bar	1-1000 bar
Velocity	Bulk Flow/Movement:		
	From pumping	< 1-10 m/day	< 1-100 m/day
	Mixing from rapid infiltration	< 1-1000 m/day	< 1-1000 m/day
Biological Variables			
Biomass	Catalytic or transformation potential	10^1-10^8 cells/g	10^4-10^8 cells/g
Activity	Turnover rates	0.1 µg/L.hour	
V_{max} Glucose (Specific activity)	Metabolic status	0.03-0.06 x 10^{-9} µg glucose/hr/cell	
Chemical Variables			
pH	Gas/Fluid Equilibria, Fluid/Solid Equilibria	5.5 to 9.5	3 to 12
Conductance	Indicator of salinity	100 to 5000+	100 to 10000+
Eb(mV)	Redox status	+600 to -100	+600 to -250
Dissolved Oxygen (mg/L)	Redox status	<0.3 to 10	<0.3 to >10
Alkalinity (mg/L $CaCO_3$)	Buffer capacity	100 to 1000	< 100 to > 1000

Scale and Equilibrium Considerations

The scale or hydrogeologic and geochemical variability in aquifer systems ranges from the regional-level (i.e., tens to hundreds of km) to the local or site level (i.e. less than 1 km to 10 km) of importance in many contaminant monitoring efforts. At the regional scale, the impact of hydrogeochemical facies (Bach and Barnes, 1965; Back and Hanshaw, 1971), recharge zones and ground-water basins may be expected to dominate geochemical distributions. The extent to which chemical equilibrium control is evidenced in geochemical distributions depends on the homogeneity of the hydrogeochemical facies involved and the ground-water residence time.

At the regional scale, exquisite examples of equilibrium geochemistry have been reported which have great value to the characterization of background water quality conditions (Back and Hanshaw, 1971; Thorstenson *et al,* 1979). Particular attention should be paid to the delineation of recharge and discharge areas at the regional scale particularly for oxidation-reduction sensitive water quality constituents (Edmunds, 1973).

At the site scale, land disturbance, local recharge/discharge and zones of contaminant releases and transport directly impact the extent to which chemical equilibria control effect contaminant behavior. Contamination from atmospheric or large "point" sources (e.g. smelters, and fills, agricultural activities, impoundments, etc.) may extend from hundreds of meters to kilometers (Starks *et al,* 1986; Reinhard *et al,* 1984; Jackson and Patterson, 1989; Nicholson *et al,* 1983). Zones of contamination from point sources (e.g. underground tanks, spills, etc.) often range from 10's to 100's of meters in both horizontal and vertical directions (Gillham and Rao, 1990; Spayd, 1985). There are a number of excellent examples of coupled transport-chemical equilibrium investigations which are useful in estimating the scale and extent of contamination (Nicholson *et al.,* 1983; Schwartz *et al.,* Anderson and Pankow, 1986; Mackay *et al.,* 1985; Sudicky and Cherry, 1983; Sudicky *et al.,* 1985). The work of Mackay *et al,* (1985), Sudicky *et al,* (1983, 1985), and the review by Gillham and Rao (1990) should be consulted with regard to the use of transport model inputs derived from data collected at the lab, slug-test or full-scale pump-test scales. The application of conditional or steady-state constants for sorption, desorption or complexation reactions in coupled transport-reaction models remains an active area or research. The current literature should be read carefully for trace organic or inorganic constituent equilibria with aquifer solids (Mimides and Lloyd, 1987) and colloidal materials (Penrose *et al,* 1990; Melchior and Bassett, 1990). A promising direction for the determination of in-situ geochemical transport parameters has been developed by Gillham *et al,* (1990, ab) which should improve the quality of model input parameters.

Monitoring Network Design and Site Characterization Strategy

Purpose and Approach

The design and operation or ground-water monitoring networks has improved substantially in the last decade. In large part, the improvements in network design nave been made in response to more active regulatory and compliance efforts as a result or environmental legislation. Regardless or the purposes or the monitoring program or the quantitative basis for network design, the integrity of monitoring operations and the quality of the data reside in the integration or hydrogeologic and chemical knowledge to the site under investigation. Each monitoring site has unique characteristics which require thorough review and consideration prior to the collection or samples for chemical analysis. Peer review of site reconnaissance, hydrogeologic monitoring and preliminary sampling protocols can pay significant dividends in data quality and reduced sampling and analysis costs for site investigations. The primary objective of monitoring network design efforts should be the cost-effective collection of high quality hydrogeologic, chemical and biological information which meets the purposes of the program.

The purposes for ground-water monitoring are manifold including; detection monitoring, where the goals are characterization of site hydrogeology, background water quality and the detection of contaminated conditions; assessment monitoring which builds on the results of a detection effort to assess the type, magnitude and extent of contamination as well as to identify potential remedial action options; and performance monitoring which has the primary goal of monitoring the effectiveness of remedial action operations. The distinction between these general categories of monitoring programs is somewhat arbitrary since regulatory, legal and research requirements may combine or preclude earlier stages of contaminant investigations. For example, emergency actions at newly-discovered contaminated sites (e.g. pipeline failures, spills, etc.) may skip the detection phase and go directly into assessment or performance activities. Nonetheless, characterization of background conditions, identification of likely contaminants and reviews of previous site operations or monitoring investigations are common steps in all monitoring network designs. These general aspects of network design have been treated in a number of publications which should be considered for applications at specific sites (Everett *et al*, 1976; USEPA, 1986; Sanders *et ah*, 1983; Barton and Redwine, 1985; USEPA, 1983; Gillham *et al.*, 1983; Barcelona *et al.*, 1985; Nielsen, 1991).

It has become increasingly obvious from recent reviews of the status of monitoring practices at known sites of contamination that fundamental design problems exist which have major consequences on the success of the monitoring investigations (Plumb, 1987; Feld *et al.*, 1987). Many of the design problems stem from inadequate characterization of hydrogeology, geochemical transport parameters or imprecise well purging and sample collection procedures. These problems can be detected and remedied via peer review or additional effort to improve sampling protocols. However, problems related to the number and placement of piezometers and sampling wells, the number and frequency of samples for both hydrogeologic and geochemical characterization, and interpolation of aquifer property values and chemical constituent concentrations demand a more rigorous design approach.

Encouraging solutions to these problems nave been identified in the recent literature. Among these approaches are the combination or flow and transport models with optimization or decision-analysis frameworks for sample siting and other design factors (Loaciga, 1989; Freeze *et al.,* 1990; Meyer and Brill, 1988) and the use of geostatistical techniques to deal with spatial variability and uncertainty (Spruill and Candela, 1990; Journel, 1988; Flatman *et al.,* 1988) for a variety of analyses. The power of these tools resides in the use of formal framework for network design which permit the expertise of experienced hydrogeologists and engineers to applied in an efficient, documented fashion. Monitoring network development and operation costs can then be kept to a minimum while maintaining the required levels of information return and confidence.

Evolutionary Network Design

Generalized steps in the design of a monitoring network can be formulated which apply to a variety of program purposes. These steps may be grouped in several phases which lend themselves to progressive refinement as information is gathered and the purposes for monitoring change. Briefly, the phases include, site reconnaissance, a preliminary monitoring network design, and a refined (or working) network design.

During the site reconnaissance phase, land-use, topography and site-operations history, as well as available hydrogeologic and chemical data are reviewed and some exploratory sampling may be conducted. Based on this information, a preliminary network design is prepared consisting of an initial piezometer network, selected aquifer property determinations and soil gas or geophysical investigations. Soil or water sampling may also be conducted during this phase to supplement existing information and to identify likely water quality or contaminant indicator constituents and their approximate concentration ranges. Conceptual models of the geologic and hydrogeologic conditions at the site should then be developed towards the optimization of sampling well locations, sampling frequency, QA/QC and sampling procedures within a sampling protocol. These models and the sampling protocol should incorporate treatments of uncertainty in hydrogeologic and geochemical variables and specific goals for the scope, duration and confidence levels required in the data collection effort.

Ideally, the preliminary network design phase should allow time and resources for optimization and experimentation to refine the conceptual model and sampling protocol for the site specific to program purposes. Examples of such experiments would be: model simulations verified by sampling, limited spatially intense sampling, extended pump testing, time-series sampling (Keely, 1982; Keely and Wolf, 1983) or other exploratory exercises. In the final working network design phase the models should be further refined but the sampling protocol should be kept constant to permit meaningful comparisons of spatial and temporal trends in monitoring data and reasonable approaches to remedial action and risk assessment.

The investment of time and resources in the preliminary network design phase has rarely been made given the regulatory processes and deadlines governing site investigations. The result has often been inconsistent data collection efforts, questionable verification of model results, limited assessments of both contaminant distributions and the effectiveness of remedial actions. Experimental, evolutionary approaches to network design problems can actually reduce the cost and maximize the long-term information return from monitoring efforts. In this fashion, future workers will be able to reference prevailing hydrogeologic and geochemical conditions to those documented in previous investigations at research or regulatory sites. Since current approaches to ground water contamination cleanups and aquifer remediation schemes have met with limited success one can only hope that improved remediation methods will exist in the future (USEPA, 1989). The application of improved techniques will be enabled by well-documented monitoring network operations.

Sampling Protocols for Chemical Analysis

The core of effective monitoring designs must be the geologic and hydrogeologic framework of the site under investigation. The geology of a particular site is unlikely to change significantly over the course of a monitoring program. The local hydrogeological characteristics may change somewhat due to: disturbance, removal or capping of upper soil zones, vertical borings and well completions, differential pumping exercised for plume management or remediation efforts or other measures. Geologic or hydrogeologic changes in site conditions should be minimal in comparison to geochemical or biological variability over time. Indeed, the basis for the interpretation of all geochemical or contaminant distributions at a site will be the geologic and hydrogeologic framework established in the reconnaissance and preliminary network design phases of a monitoring program. It is critical, therefore, that sampling protocols are based on hydrogeologic conditions and that the protocols remain consistent over the course of an investigation. Consistent, simple sampling protocols control both critical variables associated with the representativeness of sampling points and major sources of error unique to the location, construction, development and purging of sampling points which are not amenable to laboratory-based QA/QC measures.

In this section, the elements of the sampling protocol are discussed emphasizing consistency, simplicity, error identification and control so that water sampling and analysis results can be interpreted within the hydrogeologic framework of a network design. One must recognize that future developments in subsurface geochemistry and contaminant hydrogeology will clear up many current areas of confusion or limited understanding in chemical transport, reactivity and fate. The value of ongoing investi-gations of subsurface processes will be more fully realized if monitoring results are well documented and sources of systematic error are controlled. Determinations of water quality and contaminant related species represented by oxidation-reduction sensitive constituents and volatile organic compounds respectively, are among the most common and error-prone determinations in ground water. It may be expected that reliable sampling protocols developed for these species will be sufficient for most monitoring purposes. Given that a number of valuable general references on ground-water sampling and analysis are available (Everett *et al.*, 1976; Sanders *et al.*, 1983;

USEPA, 1983; Gillham *et al.*, 1983; Barcelona *et al.*, 1985; Nielsen, 1991), the following discussion emphasizes simplicity, consistency, and attention to error identification and control.

Sampling Location

The basis for interpretation or sampling and analytical results is the hydrogeologic framework established for a site. It is preferable, therefore, to nave the benefit of an extensive network of piezometers, boring logs and geologic samples as well as thorough geophysical reconnaissance at a site prior to locating wells for chemical sampling. Piezometers will often permit sampling for a limited suite of indicator parameters (e.g., specific conductance, chloride, dissolved organic carbon, pH, dissolved oxygen, etc.). These parameters provide general water quality data at minimum effort and cost for preliminary flow and transport modeling efforts. The model outputs should guide the location of additional piezometers to provide the necessary level of resolution for contaminant transport modeling and the selection of locations for sampling wells. Sampling wells should then be located within the principal geologic formations at selected upgradient and downgradient locations from the potential source zone.

Initially, sampling locations should be selected which are most likely to intercept the path of vertical and lateral transport of chemical constituents from the source zone. An effort should be made to avoid initial well construction activities in areas of unsaturated zone contamination as indicated by shallow soil gas or geophysical results. This will minimize the potential for cross-contamination and enhanced vertical migration of contaminants via bore holes. It will also serve to delimit the potentially contaminated portion of the subsurface as well as to avoid redundant sampling well placement in locations which are likely to be contaminated and add little new information towards the goals of the program.

Once the initial hydrogeologic framework has been established and initial geochemical or contaminant results have been collected from a limited number of wells, statistical, decision-analysis and geostatistical design tools should be employed to aid in the refinement of the site models and monitoring network. Areas of concern or where high levels of confidence in the hydrogeologic and chemical data are needed can then be addressed by additional sampling locations. Standard statistical techniques can be used to provide estimates of the means and precision in aquifer property determinations, ground-water level measurements and water quality constituent concentrations. Then one can derive appropriate confidence levels for the models, estimate data reliability and variability, as well as to identify potential excursions above regulatory threshold (Gibbons, 1990; Nelson and Ward, 1981; Montgomery *et al.,* 1987). The application of standard parametric and non-parametric techniques provides a basic picture of site conditions, water suitability and areas in need of additional attention. Refinements in the network design should ideally be guided by more advanced techniques which can handle spatially variable data and reduce the number of sampling locations and samples necessary to meet program goals (Freeze *et al,* 1990; Meyer and Brill, 1988; Spruill and Candela, 1990; Journel, 1988; Flatman *et al.,* 1988; Gilbert and Simpson, 1985; Warrick and Meyers, 1987). Spruill and Candela (1990) have recently provided an example of the staged application of classical statistical and geostatistical techniques to the characterization of water quality data in a deep confined aquifer. These workers were able to demonstrate that data reliability could he maintained at acceptable levels after reducing the number of sampling locations by nearly 18%. Since there are significant liabilities and costs involved in operating large monitoring networks over time, the advantage of this staged approach to sampling locations should he obvious. Software is currently available to facilitate statistical design and interpretation of monitoring data which is highly recommended to the reader (USEPA, 1989b).

Sampling Frequency, Statistical ana Hydrogeologic Factors

Temporal variability in ground-water quality at a site can be addressed with a sequence of samples in time. The variability may be random or related to periods of recharge, contaminant releases, discharge and the chemical evolution of ground-water interacting with geologic materials. To some extent results from adjacent wells along a flow path provide an indication of temporal variability in water quality since the inter-sampling location distance can be related to an average travel time. The number of samples collected over time from established sampling locations is one of the major cost multipliers in a monitoring network design. Therefore, the decision on how frequently samples are to be taken, bears on the level of temporal variability one may observe and on the costs of operation. Optimizing sampling frequency can improve information return and reduce network operation costs.

One may be constrained to accept a mandated minimum sampling frequency for regulatory compliance monitoring, but this practice assumes a number of statistical properties of the sample population (i.e., normality, independent observations, no serial correlation) which may not be justified. Also, the duration of the monitoring program must be extended over a period at least ten times the time period of periodic (or recurring) variability if the variability is to be observed. It should be recognized that if time series data are highly correlated that more frequent sampling may lead to redundant information collection.

Assuming that the purposes of the monitoring effort include: the violation of water quality standards, the detection of trends in or determination of means in water quality, the quantitative estimation of sampling frequency requires some knowledge of the sample population (i.e., mean, variance, etc.)(Sanders *et al.*, 1983). One can expect that sampling frequencies will differ for individual locations and constituents, therefore, a compromise (or average) frequency may have to be accepted when many chemical constituents are involved. Sanders *et al.*, (1983) have presented a thorough review of methods for estimating sampling frequency for water quality variables with an emphasis on surface water monitoring. They stress the need for the use of representative data in the collection of sampling frequencies for selected variables when the mean variances and acceptable confidence levels for program needs have been identified. Often, assumptions must be made concerning the nature of the distribution of the water quality variability, the independence of the observations, and the levels of expected variability. Clearly, if an extensive database is available for the quantitative estimate of sampling frequency (i.e. the existence of accurate means and estimates for population variance) the more reliable (i.e. higher confidence) the network will be in detecting temporal trends in the data. The discussion of sampling frequency by Sanders *et ah,* (1983) should be consulted for additional background on calculating sampling frequency with available data with network operation and cost limitations.

In the absence of an extensive database for chemical constituent concentrations, several other approaches can be used to estimate sampling frequencies. It is possible to make some assumptions concerning the nature of ground-water flow and the spatial distributions of aquifer properties to arrive at sampling frequencies as a function of distance along a ground-water flow path. The use of a nomograph relating hydraulic conductivity, hydraulic gradient and effective porosity to the sampling interval in days (i.e., equivalent to a distance of flow path) has been suggested (Barcelona *et ah,* 1985). The hydraulically-based sampling interval in days may be calculated from the relation:

$$F = (D \cdot n)/(864 \cdot K \cdot i)$$

where F = the sampling frequency in days, D = the distance (m) along the flow path in which variability is expected, K = the hydraulic conductivity in cm/sec, i = the hydraulic gradient (dimensionless), and n = the effective porosity (dimensionless). This hydraulically-based estimation procedure for sampling frequency assumes some knowledge of the time period of temporal variability. It also neglects differing types of variability and serial correlation among chemical constituents. It would be quite useful to have a sampling frequency estimation procedure which incorporated both hydrologic and geochemical sources of temporal variability.

In a recent study, intensive (i.e., biweekly) sampling of ground-water from 12 wells at two sites within a shallow sand and gravel aquifer was conducted to explore the nature of ground-water quality data time-series properties and to assess the effects of variability on estimates of sampling frequency (Barcelona *et at.,* 1989b). The sites included four wells located in a pristine state forest (Sand Ridge), and two upgradient and six downgradient wells at a site of a leaking anaerobic treatment impoundment (Beardstown). The pristine site was unaffected by sources of contamination while the upgradient contaminated site was influenced by regional effects of irrigated agriculture. Two year, biweekly-frequency datasets were collected for 26 major ions, water quality indicators and geochemical constituents. Sampling and analytical errors (i.e. variance) were controlled at average levels below 10% of the total variance through the use of precise sampling systems, (e.g. dedicated bladder pumps), consistent well-purging procedures and careful QA/QC oversight. Control over sampling and analytical errors permitted the observation of natural or source-related temporal variability and examination of its effect on sampling frequency.

The datasets clearly showed that ground-water chemical data are neither normally distributed nor independent and time series data showed evidence of high levels of autocorrelation. The effects of autocorrelation and temporal trends on the minimum sampling frequency for each chemical constituent at each sampling site was estimated by modeling the time series by a lag one Markov process. The average lag one correlation was used as an indicator of relative serial dependence in the data while the sampling frequency was calculated for selected ratios of effective independent sample size to total sample size (n_{eff}/n). These ratios correspond to the loss of information due to autocorrelation in the data (i.e. causing redundant data collection particularly at high sampling frequencies), defining information in terms of the variance of the mean (Var (x) = σ^2/n) where x = the sample mean, n = the sample size and σ^2 is the variance of the data (Matalas and Langhein, 1962). The reciprocal of the variance of the mean is a measure of the information content of the data. If the σ^2 is large, or the sample size is small, the information content is low. While this definition of information applies to the mean, the power of trend detection (in space or time) is related to the variance of the mean as well.

In this study, seasonality effects were identified subjectively for ground-water temperature (T°C), specific conductance (Ω^{-1}), alkalinity, and calcium levels at all three sites. Autocorrelation effects were generally lowest for pH and redox-sensitive constituents (e.g. NO_2^-, O_2, Fe^{2+}, $S^=$, Eh, NO_3^-, NH_3) and highest for major ionic constituents (e.g. Ca, Mg, Na, K) and general water quality indicators (e.g. Temp., TOC, Ω^{-1}, alkalinity) particularly at the contaminated site. The estimated ranges of sampling frequency (in months) calculated at an n_{eff}/n ratio of 0.9 correspond to a relative loss of information due to autocorrelation in the data of 10% are shown in Table 3. At the pristine site, sampling results for a majority of the variables at a sampling interval of 2 months or more would entail approximately 10% information loss. At the contaminated site, where levels of autocorrelation and long-term trends were greater, information losses between 10 and 20% might he anticipated for some variables at sampling intervals exceeding one year. The observations clearly show the compromise involved in attempting to determine temporal trends in autocorrelated variables by frequent sampling. High-frequency sampling (i.e. in excess of bimonthly) is probably unlikely to provide information return in proportion to the effort, cost or what could he learned by sampling less frequently for a longer duration to observe temporal trends.

The results of the study indicate that sampling frequencies in excess of bimonthly are likely to he inefficient for water quality data collection at similar sites. The practical implication of this for monitoring programs is that relatively long time horizons (e.g., on the order of ten years) may be required to obtain sufficient information for monitoring purposes, given that high frequency sampling will not yield much increase in information.

Bell and DeLong (1988) provided similar insights into the effects of autocorrelation and temporal variability based on the analysis of eight years of ground-water sampling data for tetrachloroethylene. They reported virtually no evidence of seasonality or normality in the first three years of monthly sampling. However, extending the sampling period through years four through eight enabled the identification of a seasonal component of variability. Monthly sampling frequency in this case undoubtedly resulted in redundant data collection though it could not have been predicted beforehand. Their observations and those in the study noted above argue for long-term monitoring program durations at initially quarterly sampling frequencies as being realistic guidelines for monitoring network design.

Table 3. Estimated Ranges of Sampling Frequency (in months) to Maintain Information Loss at <10% for Selected Types of Chemical Parameters

Type of Parameter	Pristine Background Conditions	Contaminated Conditions Upgradient	Contaminated Conditions Downgradient
Water Quality			
Trace constituents ($<1.0\ mg \bullet L^{-1}$)	2 to 7	l to 2	2 to 10
Major constituents	2 to 7	2 to 38	2 to 10
Geochemical			
Trace constituents ($<1.0\ mg \bullet L^{-1}$)	l to 2	2	1 to 5
Major constituents	l to 2	7 to 14	1 to 5
Contaminant Indicator			
TOC	2	3	3
TOX	6 to 7	24	7
Conductivity	6 to 7	24	7
pH	2	2	1

The statistical studies of sampling frequencies based on empirical ground-water datasets nave disclosed the highly autocorrelated, non-normal and serially dependant nature of time series observations of water quality (Montgomery *et al.*, 1987; Barcelona *et al.*, 1989b; Bell and DeLong, 1988).

With good control over sampling and analytical errors a quarterly sampling frequency will be a good starting point for trend or seasonality identification monitoring for many common chemical constituents. The extent to which the results of these studies can he generalized to other sites requires a consideration of the hydrogeologic setting.

Analyte Selection

The selection of soluble chemical parameters and species determined in ground-water investigations is dependent on the specific objectives of the program (Battista and Connelly, 1989; Spruill, 1988). For completeness sake, it is important that the suite of analytes provide information for hydrogeologic and geochemical modeling efforts as well as potential contaminant species (Plumb, 1987, 1991) and transformation products. Suggested analytes for several monitoring objectives are shown in Table 4.

Depending on the purposes and goals of the ground-water sampling program, the suite of target analytes may vary substantially. In many cases, the analytes may be stipulated by regulatory guidelines. However, it is essential that consideration be given to the inputs required for flow, transport and geochemical modeling so that the background or regional hydrogeochemical conditions can be integrated into interpretations of site-related data. Plumb (1991) reviewed the data from 479 disposal site investigations emphasizing the need to select potential contaminants with high detection frequencies in selected compound cases. The value of background water chemistry to predictions of contaminant mobility, stability and treatment efficiencies should be anticipated early in the design of monitoring programs.

It should also be recognized that the subsurface environment is largely composed of solid materials. The solids act as both the substrates for microbial attachment and as reservoirs of carbon, redox-active species and the ambient media for flow, transport and solute-solid interactions. Geochemical and biological analyses of the solids should be given equal consideration to the determination of aquifer hydraulic properties, grain-size, etc.(Boulding and Barcelona, 1991).

Sampling Point Design Considerations

The location, design and construction of sampling points (i.e. monitoring wells, multilevel devices, in-situ samplers, etc.) are critical to the resolution of chemical constituent distributions in the subsurface. The level of three-dimensional data resolution required for hydrogeologic data should be used as a guide for the installation of chemical sampling points. Due to the costs involved in the sampling and analysis of chemical constituents, particular care should be given to the choice of sample numbers and frequency at various site locations. In this respect, there are numerous sampling designs which may be adopted depending on the goals of the program and available data Boulding and Barcelona, 1991).

This discussion focuses on the use of monitoring wells for sampling points. This approach has been taken mainly due to the ease with which the integration of hydrologic and geochemical data can be achieved with monitoring well data. However, many of the design considerations and potential sampling designs apply equally well to the use of multi-level samplers, samples taken during drilling or various in-situ devices.

Table 5 summarizes major types of sampling designs and when they may be used for characterizing subsurface geochemistry. In general, haphazard water-quality or solid sampling is not an appropriate approach to designing networks for subsurface geochemical characterization, even though professional judgment alone, is probably the most frequently used method for siting ground-water monitoring wells. The trends or patterns that commonly exist in subsurface contamination mean that simple

Table 4. Overview of Chemical Parameters and Analytes for Monitoring Networks

Hydrogeologic Modeling Inputs	
"Conservative" Constituents	Cl^-, Br^-
Geochemical Modeling Inputs	
Master Variables	pH, Eh, ionic strength, alkalinity/acidity, temperature, specific conductance
Major Cations/Anions	Na^+, K^+, Ca^+, Mg^+, NH_4^+ , NO_3 , SO_4 , Silicate, $PO_4^{\equiv}$
Minor Cations/Anions	Fe, Mn, NO_2^-, $S^=$, HS^-, Ba, Cu, Pb, Cd, Cr, other trace elements
Other (Redox Indicators)	Dissolved O_2, $Fe^{(II)}$, $Fe^{(III)}$
Potential Contaminants	(Examples, ref. 65)
Volatile Organic Compounds	Benzene, Toluene, Methylene Chloride, Trichloroethylene, Vinyl Chloride
Base-Neutral Compounds	Naphthalene, Fluorene, Phenanthrene
Acid-Extractible Compounds	Phenol, Pentachlorophenol, Nitrophenol
Pesticides	Lindane, Endrin, Silvex, Dieldrin
Other	PCB-1242, PCB-1254

random sampling will not give as accurate an estimate of population characteristics as stratified random and grid sampling designs.

Conceptual hydrogeologic characterization should preceed the physical installation of monitoring wells. The characterization should begin using surface geophysical techniques followed by piezometer installation and preliminary well tests to estimate the distribution of hydrogeologic parameters. Good vertical resolution is essential in sampling to characterize distributions of oxidized and reduced species, contaminants, and microbiota. Achieving this resolution requires more discrete well completions with short screens. In many cases, 1.5 meter (i.e., 5 foot) well screens should give adequate vertical resolution.

Table 5. Summary of Sampling Designs ana Conditions tor Use

Type of Sampling Design	Conditions When the Sampling Design is Useful
Haphazard sampling	A homogeneous population over time and space is essential if unbiased estimates of population parameters are needed. This method of selection is not recommended due to difficulty in verifying this assumption.
Judgment sampling	The target population should be clearly defined by preliminary sampling experiments to be homogeneous, and completely assessable so that sample selection bias is not a problem. Specific environmental samples may be selected for their unique value and interest rather than for making inferences to a wider population.
Probability sampling	
Simple random	The simplest random sampling design. Other designs below will frequently give more accurate estimates of means in the population contains trends or patterns of contamination.
Stratified random	Useful when a heterogeneous population can be broken down into parts that are internally homogeneous.
Multistage	Needed when measurement are made on subsamples or aliquots of the field sample.
Cluster	Useful when sample population units cluster together (schools of fish, clumps of plants, etc.) and every unit in randomly selected cluster can be measured. Soil and ground-water contamination rarely, if ever, exhibit this characteristic.
Systematic	Usually the method of choice when estimating trends or patterns of contamination over space. Also useful for estimating the mean when trends and patterns in concentrations are not present or they are known a priori or when strictly random methods are impractical.
Double	Useful when there is a strong linear relationship between the variable of interest and a less expensive or more easily measured variable.
Search Sampling	Useful when historical information, site knowledge, or prior samples indicate where the object of the search may be found.

Source: (Adapted from Gilbert, 1987)

The spatial distribution of contamination is a major concern with sampling solids. The intensity and number or samples depends on the nonsampling variance, which is the concentration variability that is unrelated to sampling procedures. Spatial structure determines the distance between samples that nave essentially the same concentration, called the range or correlation, to avoid redundant sampling.

There are two broad designs for solid sampling: (1) grids in which samples are taken from a matrix of squares or quadrants at a site, and (2) transects in which samples are taken at specified intervals along a line. Grids presume an aerial or dispersed source of some kind, and transects presume a preferential source. For example, Starks *et al.* (1986) established sampling transects where the length was proportional to the frequency with which wind blew in a particular direction to characterize metal contamination from a smelter near Palmerton, Pennsylvania. Grids can be used to estimate short-range correlation. Transects along the path of ground-water or contaminant movement provide the best way to look at long-range correlation. The combination of the two strategies coupled with the initial analysis of selected solid samples at alternate grid or transect locations can be quite effective.

The combined strategy also can avoid the potential collection of redundant information. Using geostatistical analysis techniques of successive analytical subsets minimizes the number of samples actually analyzed. Transects could be both parallel and perpendicular to the axis of ground-water movement, along with some random samples from a grid. Analysis of samples from four equally spaced locations on a transect or grid within the area of influence is a good starting point to estimate the distance of short-range correlation. For soils, at least 5 percent of sampling points should be duplicated to help determine the sampling variability, so it can be analyzed with geostatistical techniques. At least 5 percent of the samples should be split as well. Flatman (1988, 1986) has described the use of geostatistics for determining sampling intensity.

Preliminary efforts that can help guide the location of initial wells for ground-water sampling include 1) surface or borehole geophysical techniques for mapping the extent of contaminant plumes (Keys & MacCary, 1971; Voytek, 1982; Noel *et al.*, 1983), and 2) soil gas sampling techniques (Kerfoot and Soderberg, 1988; Kerfoot and Barrows, 1987; Marrin and Kerfoot, 1988), 3) Hydropunch® sampling (Edge and Cordry, 1989), and 4) selective sampling of piezometers for simple constituents such as pH, conductance, TOC, and possibly iron or dissolved oxygen concentrations.

Soil gas monitoring and Hydropunch® ground-water sampling probably give the best picture of short-range chemical variability in three dimensions. Sampling from monitoring wells usually provides integrated chemical results depending on the relative width or thickness of the hydrogeologic formation of interest and the length of the screen (Barcelona and Helfrich, 1991). Disadvantages of soil gas concentration determinations include (1) lack of the ability to directly calibrate, because all values are relative and difficult to reproduce, (2) decontamination, and (3) short circuiting of air from the surface, which can distort results.

It is essential to have the objectives for data use and interpretation clearly identified and linked to statistical design criteria (Steel, 1986; Summers *et al.*, 1985; Summers and Gherini, 1987) for the sampling efforts.

Well Design, Construction and Development

The details of well design, construction and development for monitoring purposes have been reviewed by Aller *et al.*, (1989) and Nielsen (1991). In most cases, the hydrogeologic setting and the statistical design criteria of the program will provide the basis for locating sampling points. Chemical considerations which hear on these issues include the integrity of the well seals and construction materials which have the potential to introduce mas into chemical results. Faulty *well* seals may permit water to enter wells via the borehole which may he quite different in composition from water accessed by the screened interval. Also, the long-term durability of the screened section and casing materials under potentially contaminated subsurface conditions should he incorporated into the design criteria (Barcelona and Helfrich, 1986). The durability of the materials is more critical than their sorptive or leaching properties for several reasons.

Casing or screen failure and screen slot fouling may affect water level and hydraulic conductivity measurements which could bias predictions of flow and chemical transport. The purging or stagnant water from monitoring wells prior to sampling should minimize sorptive removal of dissolved constituents or leaching of previously sorbed or casing material constituents (Barcelona and Helfrich, 1991, 1986; Barcelona *et al.*, 1983). A number of reviews of materials' performance under laboratory and field conditions should he consulted carefully in the selection of materials for well components (Aller *et al.*, 1989; Barcelona *et al.*, 1988; Gibb *et al.*, 1981; Barcelona and Helfrich, 1988; Robin and Gillham, 1987; Unwin and Maltby, 1988; Gibs & Imbrigiotta, 1990; Smith *et al.*, 1988; Parker, 1991; Riegel *et al.*, 1991).

Well development procedures involve active pumping or surging of the completed well to remove fines created during drilling for the sand or gravel pack surrounding the screen and to develop the pack-borehole-formation contact (Driscoll, 1986). Development methods vary widely depending on well design, diameter, subsurface geologic and aquifer properties and regulatory guidelines (Aller *et al.*, 1989). Thorough initial well development, periodic re-development, and well maintenance are important to both minimize turbidity in water samples and to make field determinations of hydraulic conductivity more meaningful.

Well Purging

The stagnant water in the well casing, and to some extent in the screened interval, must he removed or isolated from formation water accessed by the screen prior to sampling. This is because the stored water may not be representative of in-situ water quality and would otherwise bias water sampling results. Pressure, temperature, degassing, chemical reactions and microbial interactions can exert major changes in solution composition (Barcelona and Helfrich, 1991, 1986, 1988; Barcelona *et al.*, 1988; Parker, 1991). A number of groups have reported order of magnitude variations in volatile organic compounds concentrations (Barcelona and Helfrich, 1986; Parker, 1991; Riegel *et al,* 1991; Panko and Barth, 1988) and redox-sensitive constituents (Barcelona & Helfrich, 1986) as a function or the number of stored volumes pumped prior to sampling (Rehm *et al,* 1985; Maltby and Unwin, 1991).

A review of trends in chemical constituent concentrations or indicator parameter (i.e. pH, conductance, temperature, etc.) values is shown in Table 6. Increasing, constant and decreasing trends in these species' concentrations as a function of volume pumped are clearly evident. The impact of purge-pumping rates, screened interval length and the nature of the concentration distributions in the screened formation exert major influences on the observed trends. The recent work of Robbins *et al,* (1989, 1991) and Robbins and Martin-Hayden (1991) clearly demonstrates the sensitivity of purge pumping trends to the screen design, pumping mechanism and pumping rate employed prior to sampling. Their work may lead to a hydraulic basis for the development of purging requirements.

Regulatory guidelines usually call for the removal of 3 to 5 stored volumes prior to sampling for chemical analysis (USEPA, 1986). In the purging studies noted above, relatively stable indicator parameter values or chemical concentrations have been achieved within 3 to 5 volumes when the rate of purge pumping was in the one to ten liter per minute range. Purge-pumping rates in excess of this range, particularly those approaching well-development pumping rates, should probably be avoided. Excessive high-rate pumping of monitoring wells is likely to cause further development or well damage (Driscoll, 1986) as well as biased dissolved or suspended (i.e. colloidal) constituent concentrations (Puls and Powell, 1991; Puls and Eychaner, 1990; Puls and Barcelona, 1989).

In the absence of a quantitative basis for the development of a purging strategy, it is recommended to consistently purge monitoring wells by pumping at low flow rates (i.e., ≤ 10L/min) to minimize drawdown while measuring indicator parameters with a closed flow-cell at the land surface (Barcelona *et al,* 1985; Garske and Schock, 1986; Walton-Day *et al,* 1990). A purging strategy such as this will provide documentation of purging conditions and a consistent database of the behavior of the well during pumping conditions. Alternative arrangements, employing packers to isolate the water stored in the casing from the screened interval, may also improve the purging and sampling operations. It is suggested that the pumps and packer apparatus be dedicated to the well.

Purging of slow recovery wells represents a special case which must be approached on a case-by-case basis. the low flow rate purge-pumping strategy may lend itself to use in these situations. However, the time between purging and sampling and the exposure of the screen due to drawdown should be minimized.

Table 6. Observed Trends in Chemical Parameters During Purge Pumping of Stored Water From Monitoring Veils

References Indicating Trend in Measured Concentration with Volume Pumped

Parameter	Increasing	Constant	Decreasing
Arsenic	2		
Alkalinity	10	1	1
Ammonium			3
Bicarbonate	5	1,3,5	1,3,5
Boron		2,3	
Cadmium		2	
Calcium		1,2,3,5	
Carbonate			3,5
Chloride		1,3,5	7
Chromium		5	
Copper			2,5
DOC	3		
Hardness		1	1
Iron	10	2	2
Fluoride		3,5	
Magnesium	2	1,2,3,5	
Manganese		2	5
Nitrate	1,6,7	1	4,6
pH	9,11	1,3	1,5,9,11,12
Potassium		2,3,5	
Selenium	2		
Sodium		1,2,3,5	
Specific Conductance	7,9	1,3	1,3,4,6,9,11,12
Sulfate		1,2,5	5
TDS		1,3	1
Temperature	7,9,11		9,12
Zinc			2,5
Trichloroethylene	8		
Volatile Organic Compounds	10,12	10,12	10

References:

1. Chapin(96)
2. Gibb *et al.,* (84)
3. Slawson *et al.,* (100)
4. Schmidt (98)
5. Marsh and Lloyd (97)
6. Nightingale and Bianchi (99)
7. Keith *et al.,* (101)
8. Smith *et al.,* (102)
9. Panko and Barth (93)
10. Barcelona and Helfrich (81)
11. Maltby and Unwin (95)
12. Gibs and Imbrigiotta (88)

Source: Adapted from Rehm *et al.* (94).

Sampling Device Selection

The selection and operation of ground-water sampling devices are important steps in the sampling protocol since they involve the initial handling or the samples. Errors at this stage cannot be accounted for by analytical quality control measures (Rehm *et al.*, 1985; Barcelona *et al.*, 1985). The principal objective in sampling therefore is to preserve, in so far as possible, the in-situ condition of the sample. The sampling device and subsequent handling techniques should minimize agitation, exposure to the atmosphere or potentially sorbing or leaching materials and the number of transfers of samples prior to analysis.

Following on from well purging steps, the sampling device should also function reproducibly, regardless of the lift, head, surface conditions or operator. Devices which provide a flowing stream of sample for flow-cell measurements of purging indicator parameters and for sample filtration are clearly preferred. Sampling devices which meet these criteria have been shown to maintain levels of error comparable to those involved in sample analysis (Barcelona *et al.*, 1989b). Additional benefits accrue from the use of devices which permit both purging and sampling can be dedicated to each well. In this way, the liabilities of cross-contamination between wells and the need for field cleaning can be avoided.

There are a number of sampling devices which are in use for ground-water sampling. A description of representative devices and commonly-used materials of construction is provided in Table 7. Applying the criteria discussed above (i.e., capability to purge and sample reproducibly, minimize sample disturbance and handling, and permit in-line measurements of purging indicators and filtration). The most generally useful devices in Table 7 may be ranked as follows:

Bladder pumps
Gas Drive (no gas contact), Centrifugal
Gear Drive, Helical-Rotor Pumps
Syringe Samplers, Pneumatic Devices
Bailers

The less generally useful devices (i.e. peristaltic pumps, gas drive (gas contact) and gas lift devices) have limited purging capabilities and subject samples for volatile, gaseous or redox-sensitive constituents to unacceptable bias. The choice of an appropriate sampling device for specific applications is relatively limited based on the criteria discussed above.

There have been a number of comparisons of the performance of sampling devices (Barcelona *et al.*, 1984; Pohlman and Hess, 1988; Tai *et al.*, 1991; Stolzenburg and Nichols, 1985). These studies have generally been limited to low lift (i.e., <25', 8m) laboratory controlled conditions or variable geochemical conditions in the field. This literature should be reviewed critically with consideration of long-term reproducibility, freedom from operator error and the need to keep the sampling protocol

Table 7. Description of Ground-Water Sampling Devices and Materials of Construction

Sample Device	Description
Bailer	A cylindrical device on a tether cord used to manually extract water available with bottom and frequently also top check valves. Fabricated in a wide range of rigid materials.
Point-source bailer	Contains a check valve at both top and bottom of the cylindrical sampler wall. Valves are opened by cable operated from ground surface. Available in a wide range of materials.
Syringe sampler	Sample container is pressurized or evacuated and lowered into sampling installation. Opening the container and/or releasing the pressure allows sample to enter the device. Materials may include stainless steel, Teflon , polyethylene, glass.
Bladder pump	A flexible bladder within a rigid cylindrical body which has check valves at each end. Gas pressure from ground surface is cycled between bladder and sampler wall, forcing sample to enter bladder and then be driven up the discharge line. Gas does not contact sample. Materials may include stainless steel, Teflon^{R}, Viton^{R}, polyvinyl chloride (PVC), silicone, Neoprene^{R}, polycarbonate, Delrin^{R}.
Gear-drive pump	Electric motor rotates a set of Teflon gears, which drives the sample up the discharge line. Constructed of stainless steel 304, Teflon^{R}, and Viton^{R}.
Helical-rotor pump	The water sample is forced up discharge line by electrically driven rotor-stator assembly. Materials may include stainless steel, ethylene propylene rubber (EPDM), Teflon^{R}, Viton^{R}, acrylic, polyethylene.
Centrifugal pump	An electrically driven rotating impeller accelerates water within the pump body, building up pressure and forcing the sample up discharge line. Commonly constructed of stainless steel, rubber, and brass.
Peristaltic pump	A self priming vacuum pump is operated at the ground surface and is attached to tubing, which is lowered to the desired sampling depth. Sample is subjected to vacuum. Materials may include Tygon^{R}, silicone, Viton^{R}, Neoprene^{R}, rubber, Teflon^{R}.
Gas-lift devices	Gas emitted from gas line at desired depth forces sample to surface through sampling installation or discharge tube. Another method utilizes gas to reduce effective specific gravity of water, causing it to rise. Wide variety of materials available for tubing.
Foot-valve devices	A single rigid riser pipe or tubing arrangement with a foot-valve at the sampling depth. It is alternately lowered mechanically to open the valve and admit water, then raised to close the valve drawing the sample up to the surface. A variety of rigid or flexible materials may be used.
Gas-drive devices	A positive gas pressure applied to water within device's sample chamber forces sample to surface. Materials may include polyethylene, brass, nylon, aluminum oxide, PVC, polypropylene.
Pneumatic devices	An in-situ device which generally utilizes the same operating principles as syringe samplers: a pressurized or evacuated sample container is lowered to the sampling port and opened, allowing the sample to enter. Materials may include PVC, stainless steel, polypropylene, Teflon .

(Adapted from Pohlman and Hess, 1988)

as simple as possible. Materials of construction of the devices should be chosen carefully as one would select sample storage vessels. In most cases, the flexible materials which may contact the sample (e.g. tubing, gaskets and seals) have the highest potential for sorption or leaching bias effects (Barcelona and Helfrich, 1988; Barcelona *et al.*, 1985b). Polyvinylcholoride (i.e., Tygon), silicone and low-density polyethylene tubing may be suitable for general water quality and inorganic constituent sampling. They have high sorptive capacities for organic compounds and should not be used for critical applications.

It should be noted that sampling for free petroleum product layers or non-aqueous dense solvents present significant challenges which entail both innovative well design and cautious purging and sampling.

Sample Collection

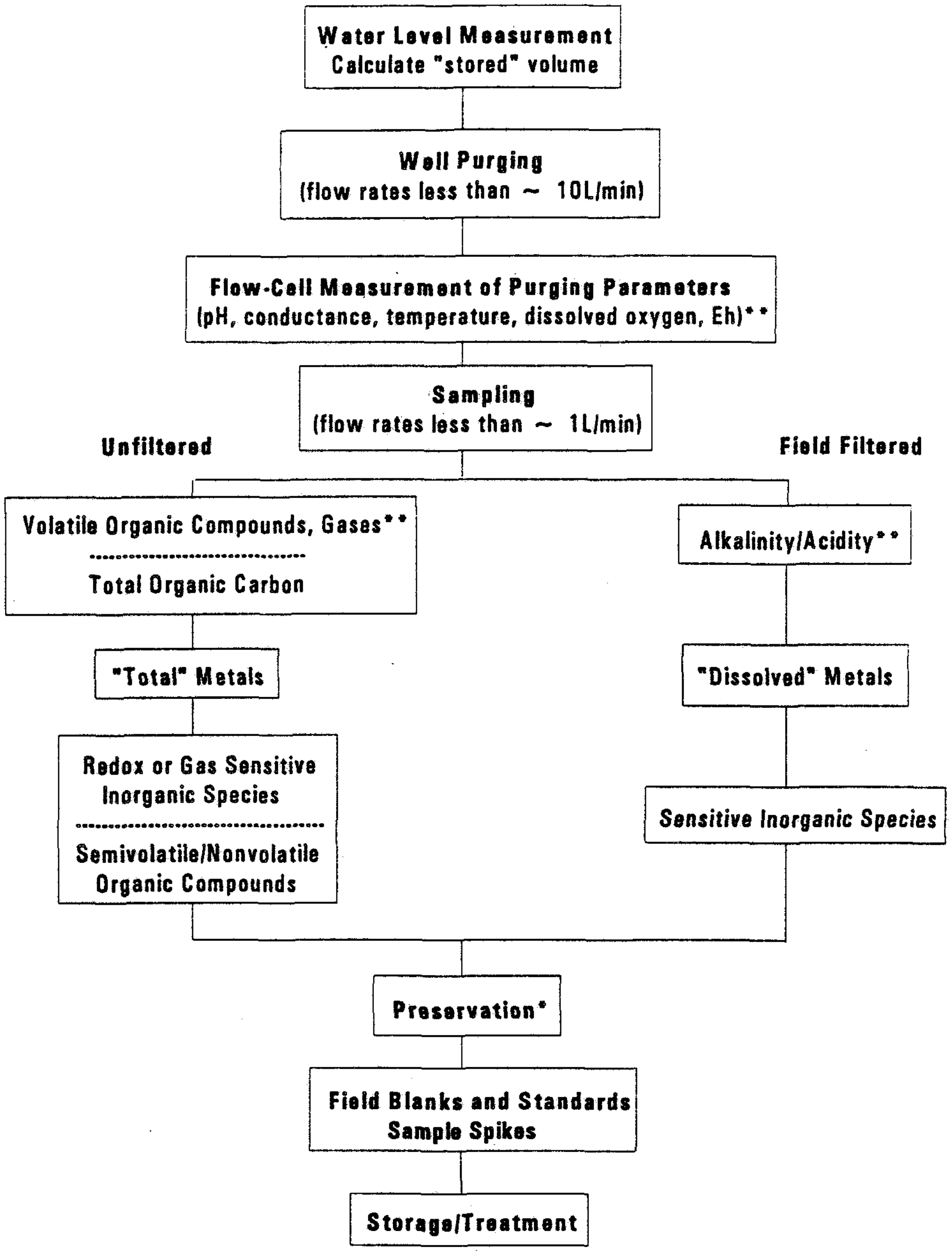
The sample collection and field determination steps in the protocol should be the most satisfying of all the elements of the sampling program. A written sampling protocol detailing purging, sample collection, QA/QC procedures etc., has been drafted and discussed with all program staff. The hydrogeologic interpretation well design and construction and analyte selection decisions have been made and the stage is set for collecting useful hydrogeochemical data.

As usual, in the earth and environmental sciences, the actual conditions of sampling in the field present exciting challenges to informed professional judgement. It is imperative that the sample collection and field determination methods are simple and robust under potentially adverse conditions. These precautions should insure the safety of field staff and permit consistent, accurate data collection.

The following discussion is general and hopefully applicable to the numerous design purposes of monitoring and sampling programs. The schematic diagram in Figure 1 is provided as a framework for field operations. This framework covers the major sampling steps for a range of parameters, though radionuclide and microbial samples may call for special treatment.

Field Determinations

Hydrogeochemical data collection begins with the water level, measurement and calculation of the "stored" volume. The "stored" volume includes water in the casing and screened interval as well as that in the sand or gravel pack (Robbins, 1989; Robbins *et al.,* 1991; Robbins and Martin-Hayden, 1991). At this point, a stable purge pumping rate should be established. Then the outputs from the precalibrated electrode sensors in the flow cell should be monitored as purging progresses. Though criteria vary, it is reasonable to assume that when pH, Temperature, Conductance and Dissolved O_2 stabilize to within ± 0.1 pH unit, ± 0.1 C°, ± 5 μS and ± 0.1 mg/L O_2, respectively, that the well has been purged of stagnant water. It is not unusual for the purging parameters to show significant van ability (i.e. ± 20% of the stable value) in the initial "stored" volumes pumped. One should not



* In-line/Pressure Filtration

** Parameters should be determined in field

Figure 1. General framework for sampling ground water.

expect that stabilization of the indicator parameters verifies reproducible and representative sampling for other constituents (Gits and Imbrigiotta, 1990).

Sample representativeness is largely determined by the hydraulics of the monitoring point relative to the distribution of chemical species in the formations of interest. The purging indicator parameters include master variables for geochemical modeling. They provide a reasonable basis for calculating equilibrium solution composition of specific water types. However, disequilibrium conditions exist in many ground-water systems (Barcelona *et al.*, 1988a; Spayd, 1985; Sudicky *et al.*, 1985) and the mixing of water types and contaminant gradients adjacent to screened intervals (particularly "long" screened intervals, i.e. > ≈ 10'; 3m) complicate the situation (Robbins, 1989, 1991; Ronen *et al.*, 1987; Smith *et al.*, 1991).

Filtration

Once stabilization of the purging indicator parameters has been achieved, the initial field determinations have been completed. The remaining parameters should be done immediately after filtration (e.g. alkalinity, acidity, etc.) or, if unaltered, as soon as possible on sample collection. Table 8 contains recommendations for water sample handling and preservation steps.

Important issues must be addressed with respect to water sample filtration. They are the use of the analytical results to either estimate the solution chemical speciation via equilibrium modeling or to determine the total amounts of a chemical constituent in transport (Puls and Barcelona, 1989). In the first case, the operational definition of "dissolved species" has historically been on $0.45 \mu m$ filtered solution. This definition is important in comparisons of model results on water samples. Water samples may contain suspended acid-neutralizing (e.g. carbonate) particles which would otherwise bias calculations of carbonate equilibria based on unfiltered alkalinity determinations.

The second issue is related to the first in that suspended or colloidal materials have been demonstrated to be present in water from sand and gravel aquifers (Puls and Eychaner 1990; Puls and Powell, 1991; Gschwend & Reynolds, 1987). In this instance, a significant amount of a chemical constituent may be associated with a mobile colloid fraction which could be removed from the water sample by filtration.

There are many potential sources of artifact particles or colloids in monitoring wells, these include: drilling fines, precipitation or casing corrosion products, microbial slimes, etc. If these artifacts could be demonstrated not to be present at a particular well, the obvious choice would be to purge and sample at very low (i.e. < 100 mL/min) flow rates and analyze unfiltered samples (Puls and Barcelona, 1989). Puls and Eychauer (1990) have demonstrated the effects of pumping rates and well disturbance during insertion of sampling devices which cause the population of suspended material to vary be orders of magnitude.'[1] It is reasonable to conclude presently that samples for geochemical modeling should be filtered. Those samples collected unfiltered to estimate total species in transport in porous media must be preserved, analyzed and interpreted very carefully.

Table 8. Recommended Water Sample Handling and Preservation Procedures

Parameters (Type)	Volume Required(mL) 1 Sample[a]	Containers (Material)	Preservation Method	Maximum Holding Period
Well Purging				
pH (flow-cell)	50	T,S,P,G	None; field det.	< 1 hr[b]
Ω^{-1} (flow-cell)	100	T,S,P,G	None; field det.	< 1 hr[b]
T (flow-cell)	1000	T,S,P,G	None; field det.	None
Eh (flow-cell)	1000	T,S,P,G	None; field det.	None
O_2				
Contamination Indicators				
pH, Ω^{-1}	As above	As above	As above	As above
TOG, Volatile Compounds	40	G,T	Dark, 4°C	24 hr[d]
TOX	500	G,T	Dark, 4°C	5 days
Water Quality				
Dissolved gases (O_2, CH_4, CO_2)	10 mL min.	G,S	Dark, 4°C	< 24 hr
Alkalinity/Acidity	100	T,G,P	4°C/None	< 6 hr[b] < 24 hr
	Filtered under pressure with appropriate media			
(Fe, Mn, Na^+, K^+, Ca^{++}, Mg^{++})	All filtered 1000 mL	T,P	Field acidified to pH < 2 with HNO_3	6 months[c]
($PO_4^{\equiv}$, Cl^-, Silicate	@ 50	(T,P,G glass only)	4°C	24 hr/ 7 days[c]; 7 days
HS^-, $S^=$	100	G	Zinc Acetate/4°C	1-2 days
NO_3^-	100	T,P,G	4°C	24 hr[d]
$SO_4^=$	50	T,P,G	4°C	7 days"
NH_4^+	400	T,P,G	4°C/H_2SO_4 to pH < 2	24 hr/ 7 days

Table 8. (Continued)

Parameters (Type)	Volume Required(mL) 1 Sample[a]	Containers (Material)	Preservation Method	Maximum Holding Period
Phenols	500	T,G	4°C/H_2PO_4 to pH < 4	24 hr
Drinking Water	As above	As above	6 months	
Remaining Inorganic Constituents As, Ba, Cd, Cr, Pb, Hg, Se, Ag	Same as above for water quality cations (Fe, Mn, etc.)			
F^-	Same as chloride above	Same as above	Same as above	7 days
Remaining Organic Parameters	Same as for TOX/TOC, except where analytical method calls for acidification or sample			24 hr

[a] It is assumed that at each site, for each sampling date, replicates, a field blank, spiked samples and standards must be taken at equal volume to those or the samples.

[b] Temperature correction must be made for reliable reporting. Variations greater than ± 10% may result from a longer holding period.

[c] In the event that HNO_3 cannot be used because of skipping restrictions, the sample should be refrigerated to 4°C, skipped immediately, and acidified on receipt at the laboratory. Container should be rinsed with 1:1 HNO_3 and included with sample.

[d] 28-day holding time if samples are preserved (acidified).

Note: T: Teflon; S: stainless steel; P: PVC, polypropylene, polyethylene; G: borosilicate glass.

Source: Adapted from US EPA (1986b) Scalf *et al.,* (1981).

Filtration is, of course, a means of preservation which often must he supplemented by chemical reagent addition. The recommendations in Table 8 are offered as examples of preservation techniques. In some cases, extraordinary means may be necessary to determine or preserve the in-situ ground-water geochemical condition (Ball *et al.*, 1975; Pankow, 1990). Among the specialized sampling techniques are: the collection of water in sealed containers delivered directly to the laboratory and inert gas purging of sampling lines prior to sample collection (Pankow, 1990; Dodge and Francis, 1986). Volatile organic compound samples have been found to be effectively preserved for extended periods (i.e. > 24 hours) by the use of sodium bisulfate (Maskarinec *et at.*, 1990) and by the use of metal foil lined caps (Kovacs *et al.*, 1991).

Recent research results on the stability of soil or aquifer solid samples for volatile organic compound determinations suggest that minimal handling and immersion in methanol provide adequate preservation prior to analysis (Hewitt *et al.*, 1992).

Control Samples, Field Blanks and Standards

The field-sampling activities actually begin the formal sample quality control procedures which are carried through the analytical process. The calibration of the electrode sensors for the purging indicator parameters should be conducted prior to measurement and the results recorded in the field notebook. The calibration procedures should be repeated at the end of the sampling day. As samples are collected it is prudent to collect duplicate samples for sensitive parameters (e.g. volatile organic compounds, ferrous iron, ammonium, sulfide, etc.) so that a pool of parallel samples can be developed. At least one sample for each day of sampling should be selected from the pool for spiking with a known volume of standard solution in the field. The spiked samples for each parameter are control samples used to evaluate analyte recovery (i.e., accuracy or percent bias) and precision in the actual sample matrix. Similarly, field control standards (i.e. distilled water samples spiked with standard solutions) and blanks (i.e. distilled water from the lab poured into sample containers) should be introduced into the sample set to account for losses /contamination in handling, storage, spiking steps. It may also be useful to introduce blind samples, which are actually known standard solutions, into the analytical stream as audit checks on sample tracking, processing and analysis. These may be particularly valuable in situations where the sampling site is remote from the laboratory facilities or where very close control over sample chain of custody is an issue.

Conclusions

Progress in the development of reliable ground-water sampling methods has been accelerated in the past twenty years with the enactment of environmental regulation over a range of chemical and waste streams. Sampling and analysis of samples for major ionic species and a large number of inorganic and organic chemical constituents have become major cost considerations in the design and operation of monitoring networks. Though monitoring purposes vary widely, it is essential that the design of the networks include sampling arrays and protocols which complement the hydrogeologic data collection so that the interpretations of the results can be integrated. In this sense, identification and control over errors in sampling point location, design and construction must largely be done by informed professional judgement. On the basis of preliminary hydrogeologic analysis and sampling results, a comprehensive sampling protocol can be established to insure consistent, representative sampling at the required level of detail. Satisfactory control over sampling and analytical error can be achieved over long periods of time if simple consistent procedures are used in the purging and sampling or monitor wells.

Subsurface geochemical conditions may vary significantly over vertical distances of a few meters and horizontal distances of tens of meters. A number of investigations have identified the need for vertically discrete sampling points (i.e. nested wells with short (i.e. < 2m) screens, multi-level devices and depth-specific sampling with specialized drill-tools, screened-augers, etc.). These methods currently provide the most effective means of obtaining three-dimensional or spatial variability information on chemical distributions. Temporal trends and variability in water chemistry can be approached initially with a quarterly sampling frequency. It may be anticipated that more high-quality, long-term hydrogeochemical datasets will be available in the future to refine the design of both monitoring networks and sampling protocols. A major benefit of these datasets will be improvements in the methods of integrating hydrogeology and species-specific chemical concentration in transport and fate studies.

EXPERIMENTAL DESIGN AND PROCEDURES

A major focus or this project was to improve the overall reliability or site characterization methods, particularly as these methods relate to ground-water contamination by VOCs. Another major focus of the project was the examination or spatial and temporal variability or VOCs in ground water within a "large" setting, i.e., several square miles (as opposed to an individual site covering several square feet to several acres, e.g., Roberts *et al.*, 1990). Work was focused on several areas:

- An examination of low-flow rate purging techniques coupled with typical inorganic purging parameters (e.g., dissolved oxygen, specific conductance) to determine when to collect a sample for VOC determinations.
- A comparison between the concentrations of volatiles found in monitoring well water samples and in water samples collected by hydraulic probe (i.e., Hydropunch®).
- A comparison between preservation techniques for geologic matrix ("solids") samples for VOC analysis.
- An examination of the temporal variability of VOC concentrations through quarterly sampling of ground water.
- An examination of the spatial variability of VOC concentrations by geostatistical analysis of the quarterly sampling data as well as the spatial distribution of hydrogeologic properties (e.g., hydraulic conductivity and hydraulic gradient).

Major concern regards estimating the contribution of sampling, analytical, and natural (or source) variability to the overall variability of samples collected by these methods. Previous work (Barcelona *et al.*, 1989b) demonstrated how this can be done for the major inorganic and surrogate organic (e.g., TOC, TOX) ground-water quality parameters. Work under this cooperative agreement was deliberately focused on volatile organic compounds.

Our objective was to develop practical, field-tested methodologies for several site characterization techniques which can be used by the Agency in similar hydrogeologic settings across the nation. Suck methodologies include the use of hydraulic probe (Hydropunch®) and aquifer solids samples for field geohydrologic/geochemical investigations. Further, our work examined the accuracy and precision with which these techniques can be used for investigations involving several volatile organic compounds.

Field and laboratory data were collected in a phased process to determine the distribution of VOC contamination in space and time. the evolutionary field program was conducted with an array of domestic and monitoring wells and real-time data collection methods to evaluate the short- and long-term temporal variability in contaminant distributions as a function of hydrologic conditions. The primary research objectives in their respective project phases are enumerated below.

Phase 1 — Reconnaissance and Development of Monitoring Network

- A. Hydrogeologic data collection
  - Review or all available information on area hydrogeology
- B. Hydrogeochemical data collection
  - Review or background data on contamination history
  - Synoptic sampling of existing domestic wells
- C. Interpretation or preliminary data
  - Conceptual modeling of study area hydrogeology
  - Phase 1 construction of monitoring well network

Phase 2 — Design of Intensive Characterization Studies

- A. Geohydrologic data collection
  - Phase 2 construction of monitoring well network
  - Slug testing of existing monitoring wells
  - Potentiometric surface mapping
- B. Hydrogeochemical data collection
  - Initial quarterly sampling of monitoring well network
  - Initial intercalibration experiments between Hydropunch® tool and monitoring well data
  - Execution of purging experiments
- C. Data interpretation
  - Use or domestic well and early quarterly monitoring well data for locating additional wells for geostatistical analysis
  - Analysis of purging experiments for subsequent VOC sampling

Phase 3 — Final Intercalibration Experiments and Examination of Spatial and Temporal Variability

- A. Geohydrologic data collection
  - Phase 3 (final) construction of monitoring well network
  - Slug testing of remaining monitoring wells
  - Potentiometric surface mapping
  - Hydraulic gradient analysis
- B. Hydrogeochemical data collection
  - Continued quarterly sampling of monitoring well network
  - Final intercalibration experiments between Hydropunch® tool and monitoring well data
  - Collection of aquifer solids samples for preservation techniques investigations
- C. Interpretation of data
  - Analysis of monitoring well - Hydropunch® comparison
  - Analysis of solids samples preservation tekniques
  - Analysis of temporal variability of VOC plume
  - Analysis of spatial variability of VOC plume
  - Analysis of spatial variability of hydraulic conductivity and gradient

Methods of site characterization and procedures to evaluate spatial and temporal variations in contaminant concentrations were the principal means by which the research was to be conducted. In the following sections, the experimental methods and overall designs for the work are described. Foremost among the design criteria for the work was the control or errors in sampling and analysis for VOCs which are particularly error-prone chemical constituents. It was recognized that sampling and analysis methods which permitted accurate and reproducible determinations of VOCs in water and aquifer solids would lend themselves easily to application for most other contaminants of concern as well.

Description of Field Site

Contaminant History

Regional water quality has been a concern in the Rockford, IL area since the early 1970s. Nearly 100 percent of the potable water use is supported by ground water and the resources are plentiful. Kirk *et al.* (1985) estimated that for 1984, nearly 47 million gallons per day were withdrawn for public, industrial and commercial uses in Winnebago County. Shallow sand and gravel (i.e., <100m), deep sand and gravel, and bedrock wells in the area have been found to be contaminated by a number of previous investigators (Dept. of Environmental Health, 1984; Gibb *et al.*, 1984; Shuster, 1976; Wehrmann, 1984). VOCs were the major contaminants determined by these studies.

The documented contamination of public water supply wells led to the realization that widespread shallow sand and gravel wells used for private water supplies were also vulnerable. Colten and Breen (1986) found that land disposal of industrial wastes was common in southeast Rockford for most of the last 100 years. Both Wehrmann *et al.*, (1988) and Clarke and Cobb (1988) reviewed incidents of well water contamination identifying TCA, DCE, cl2DCE and PCE as common contaminants in the southeast Rockford area.

As information on the ground-water quality of this area accumulated, an approximate two square mile area of mixed residential and commercial/industrial development in southeast Rockford was proposed for inclusion on the Natural Priority List (NPL) in June 1988 (Camp, Dresser and McKee, 1990). It was added to the NPL in March of 1989 as a state-lead, federally funded Superfund site. In June of 1990, under a USEPA removal action, water main extensions and hookups to city water were initiated for area residences with private wells which were contaminated with VOCs at levels greater than 25 percent of the Removal Action Limit. The areal extent and the presence of predominantly organochlorine solvent contaminants across the area provided an opportunity to pursue the goals of this study and, therefore, the southeast area of Rockford, Illinois was chosen for our field investigations (figure 2).

Land surface topography within the study area varies from over 850 feet (MSL) on the eastern edge of the study area to approximately 710 feet along the Rock River on the west (figure 3). The land

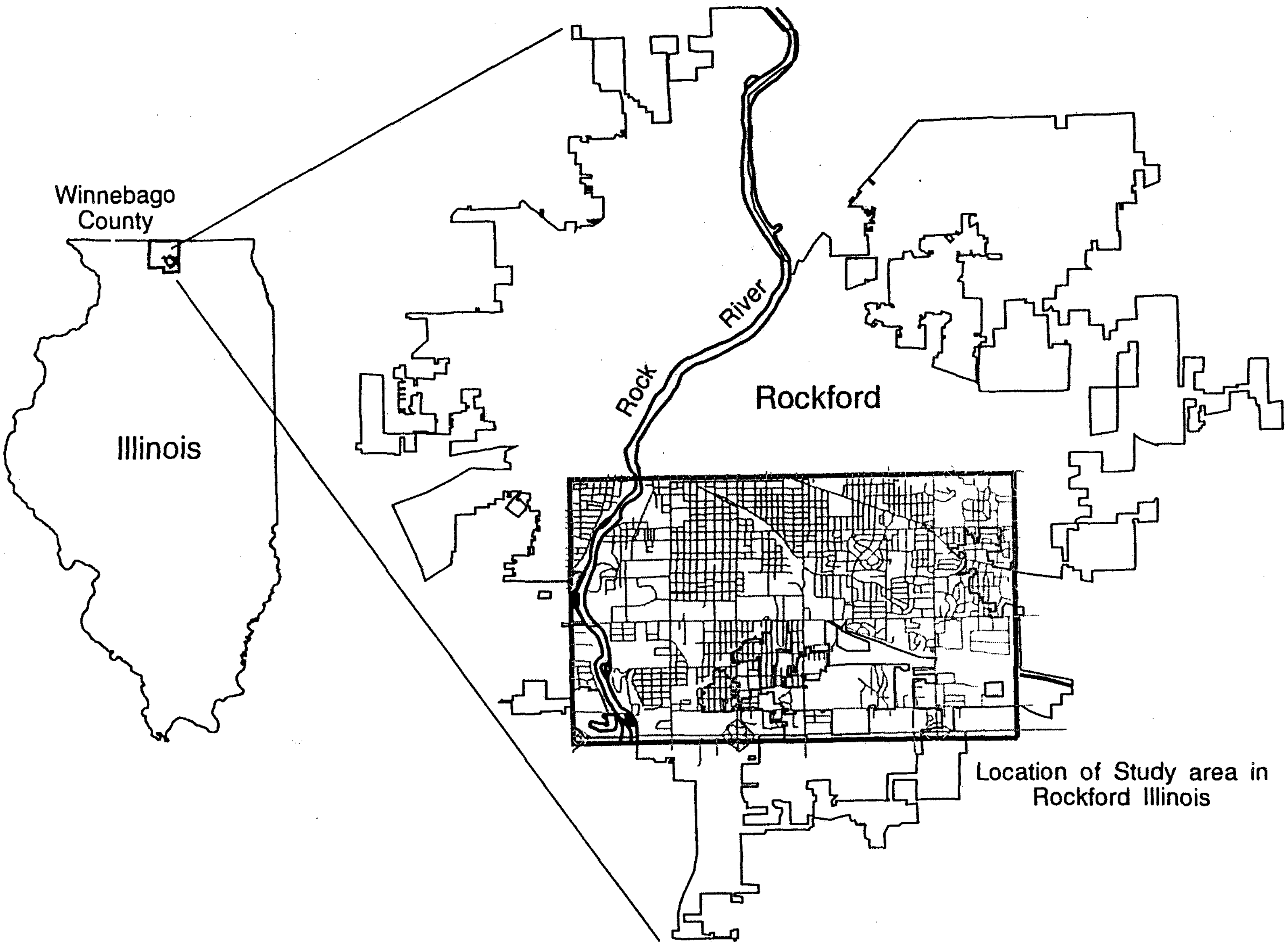


Figure 2. Location or southeast Rockford, Illinois study area.

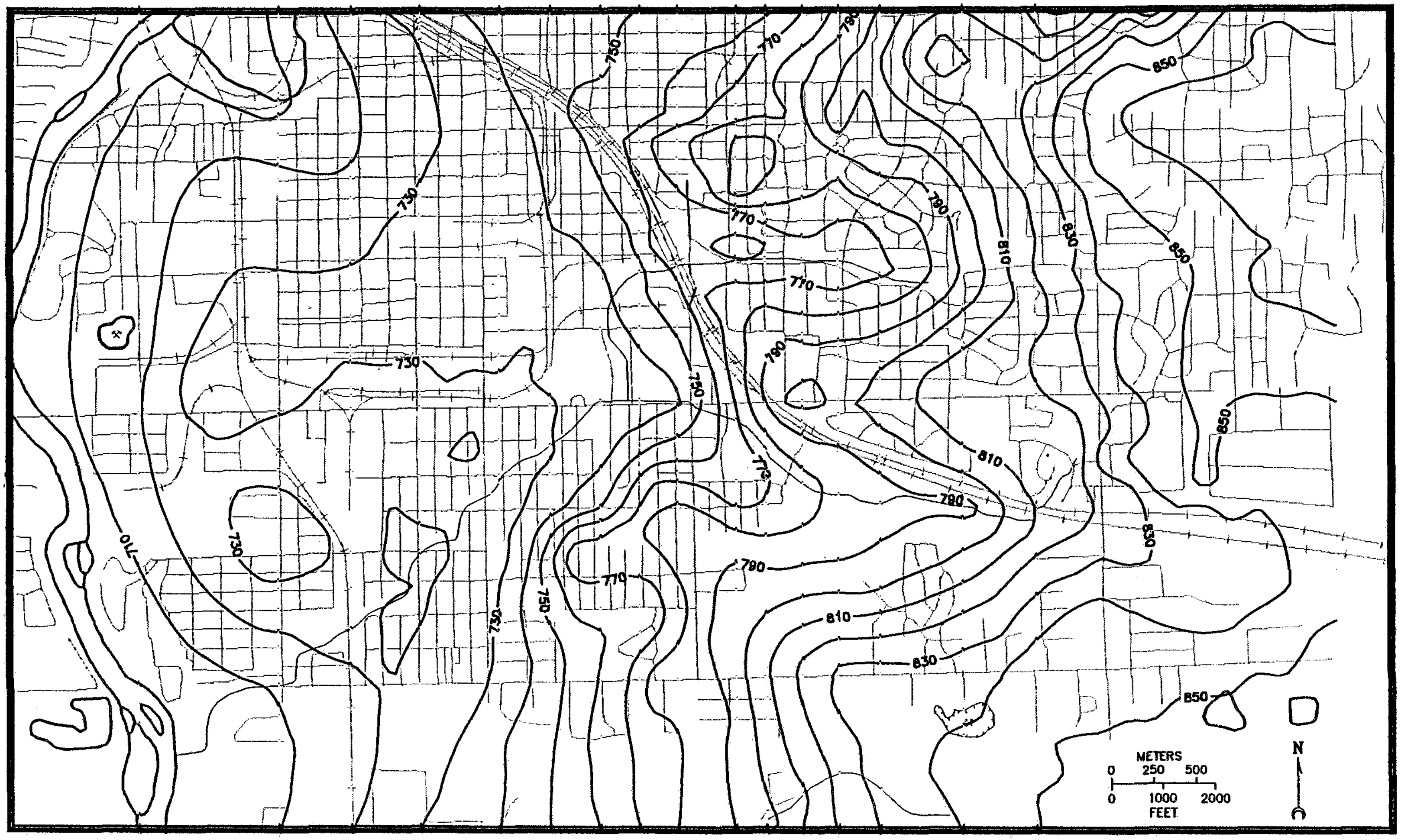


Figure 3. Land surface topography of the southeast Rockford study area *(contour interval = 20 feet).*

surface falls abruptly, in some locales as much as 50 feet, from topographic uplands to the floodplain of the Rock River. The edge of the floodplain falls on a north-south line generally down the center of figure 3. Small east-west trending tributary valleys can be observed entering the broad north-south oriented Rock River valley. These valleys also can be seen on the bedrock surface (figure 4). The eastern one-third of the study area is characterized as bedrock upland — depth to bedrock (Silurian dolomite) is often less than 50 feet (figure 5). Domestic wells in this area often use the highly fractured dolomite as a source of water. When greater supplies are needed such as for municipal or industrial supplies, wells are completed in Cambrian and Ordovician aquifers; immediately underlying the dolomite is an often tapped resource, the St. Peter sandstone. As the Rock River is approached, the bedrock surface declines sharply from over 700 feet to 450 feet (figure 4). In this area the drift thickness increases to over 250 feet and is predominantly composed of outwash sand and gravel. As the bedrock surface falls, the Silurian dolomite pinches out and the underlying St. Peter sandstone subcrops. Both bedrock units are in direct hydraulic connection with the overlying sand and gravel materials. An east-west cross section across the river valley through the study area is shown in figure 6.

The detailed hydrogeologic and chemical data collection activities (i.e., quarterly sampling, monitoring well - Hydropunch® comparisons) that comprised our investigations were concentrated in an approximate two square mile area, roughly coincident with the Southeast Rockford NPL boundary, located in the southern portion of the larger study area. Figure 7 depicts the area of intensive study along with the locations of monitoring wells described in later sections.

Preliminary Sampling

The initial development of the intensive study area monitoring network was done on the basis or available data from prior surveys. Datasets which were used in evaluating the approximate extent of the contaminated zone included results from previous Illinois State Water Survey (ISWS) projects in the area (Wehrmann *et al.*, 1988), selected files from the Rockford Water Department, the Winnebago County Public Health Department (WCPHD), and the Illinois Department of Public Health (IDPH) files, and preliminary sampling of five existing ISWS monitoring wells in April or 1990. These data were visually checked for consistency and major errors. Historical laboratory standards data from the ISWS and IDPH labs provided confidence in each lab's results; these are summarized in Appendix A.

Domestic Well Sampling

Initial concern was raised by local public health officials after the discovery of a number of VOCs m several SE Rockford domestic wells by the county health department in 1984; however, little attention was paid by the community at-large. Subsequent domestic well sampling in the area by the ISWS (Wehrmann *et al.*, 1988) confirmed the presence of VOCs in shallow SE Rockford ground water. The first "mass" sampling of over 200 domestic wells in southeast Rockford was undertaken

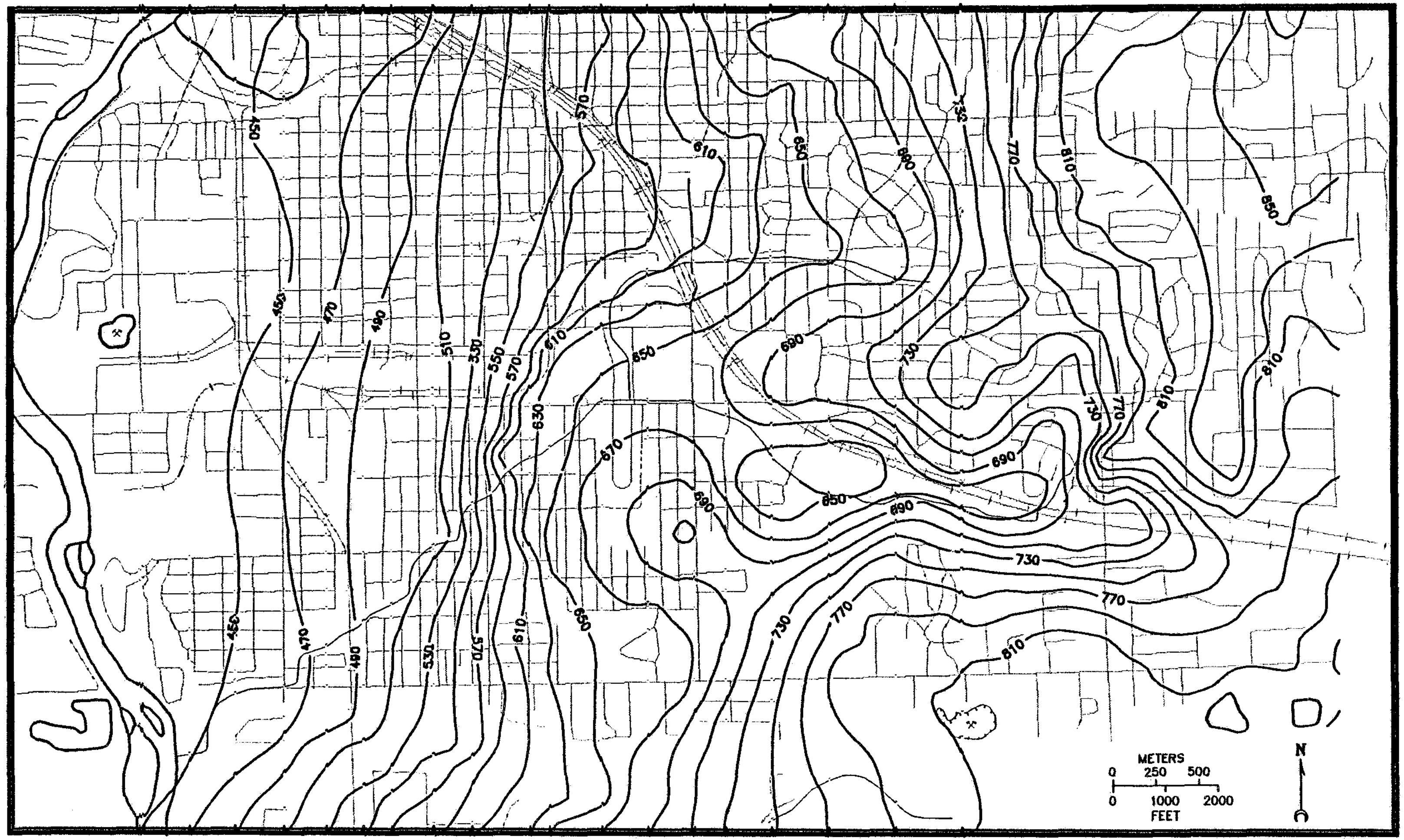


Figure 4. Bedrock surface topography of the southeast Rockford study area *(contour interval — 20 feet).*

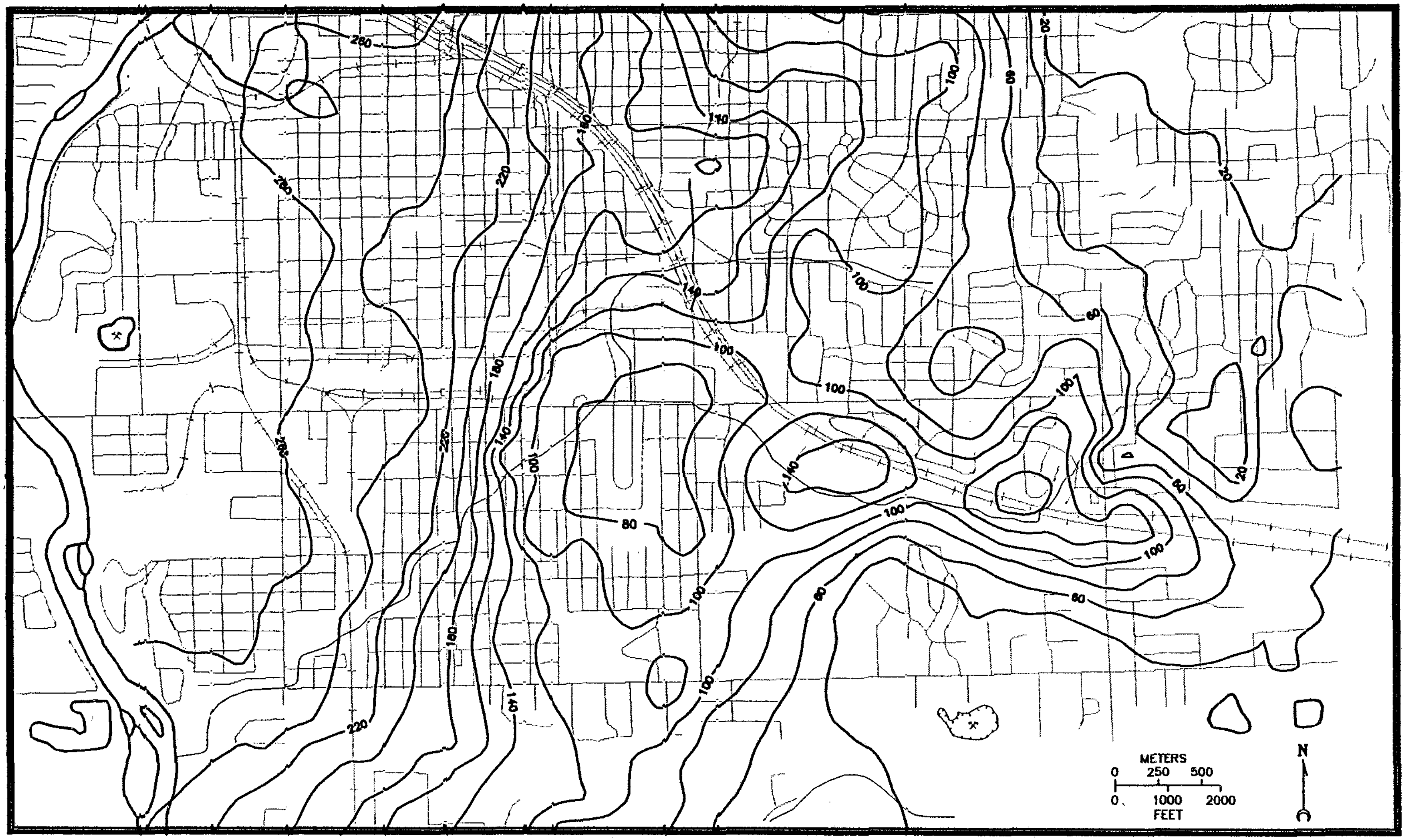


Figure 5. Glacial drift thickness of the southeast Rockford study area *(contour interval = 20 feet).*

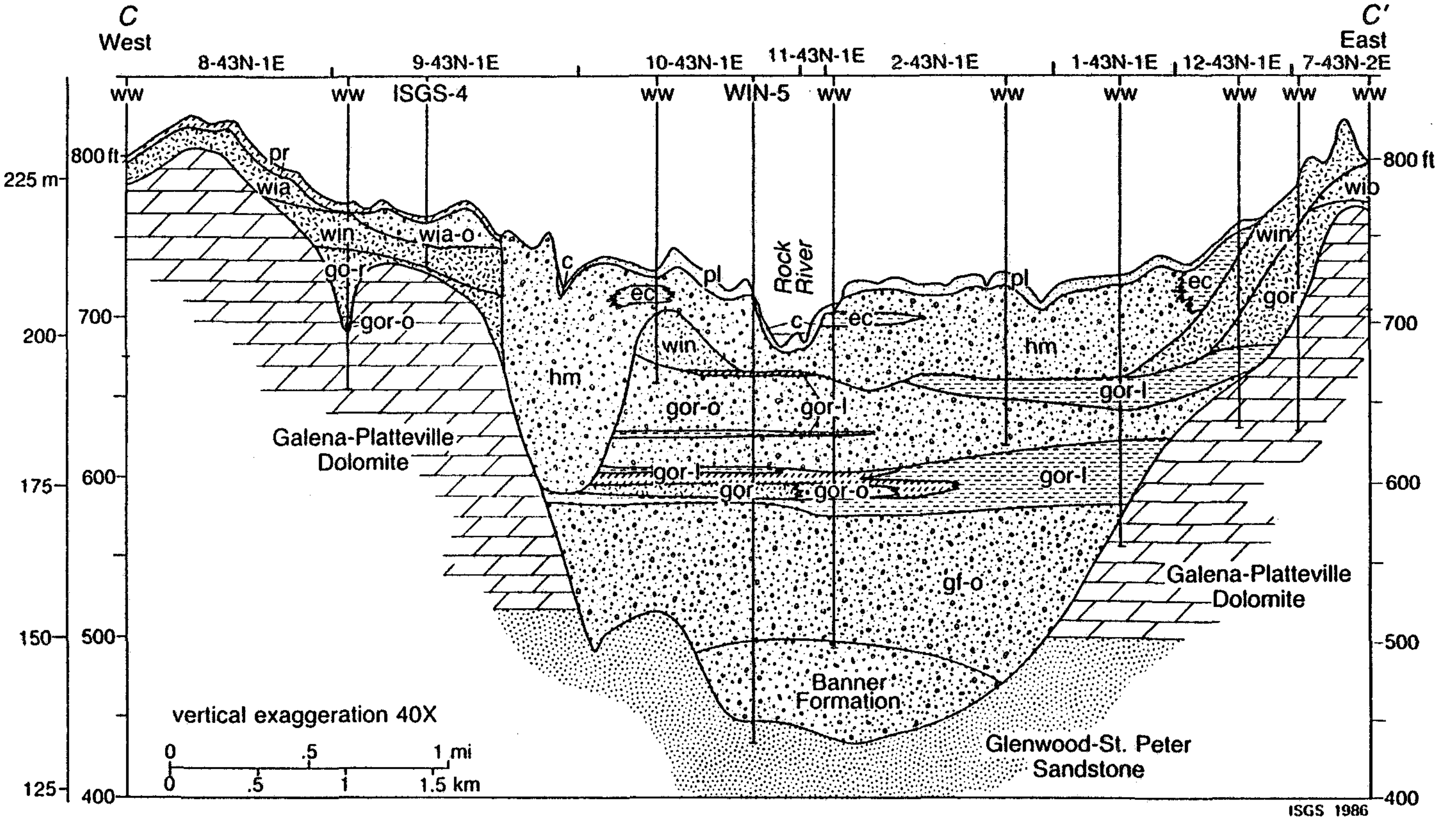


Figure 6. East-west geologic cross section through the southeast Rockford study area.

by the IDPH in collaboration with the WCPHD in late fall, 1989. Results of this sampling provided an alarming look at a VOC plume that extended over one mile in length and affected the drinking supplies of hundreds of homes.

By July of 1990, USEPA Region V Emergency Response had become involved. Activities in southeast Rockford had progressed to the point that contaminated residential wells in the zone of highest contamination were being slated to be abandoned with the extension of city water to the residences. In an effort to assemble more data that would give us additional data on the spatial and temporal variability of the VOC distribution, our research team in cooperation with the USEPA and IDPH undertook a mass sampling of residential wells just prior to well abandonment. This sampling effort was planned to supplement June 1990 sampling of wells on the fringe of the abandonment zone by the Illinois EPA's RI/FS subcontractor Camp Dresser & McKee (IEPA-CDM). Sampled wells included previously sampled wells in areas of known contamination and additional wells for which previous results were not available.

Sampling personnel were mobilized on July 24, 1990 to conduct outside-tap sampling of the target domestic wells. Sampling was conducted jointly by personnel of the IDPH, the WCPHD, and our research team from Western Michigan University - Water Quality Laboratory (WQL). Outside residence taps were run at five to ten liters per minute until it was estimated that the pressure tank had been cleared and that the temperature stabilized to ±0.1°C with a hand-held thermometer. Samples were collected by reducing the flow to ~100 mL/min and then filling 40 mL vials by directing the flow down the side of the vial. Duplicate zero-headspace samples were collected at each residence. the samples were refrigerated on the day of collection and split samples were shared with IDPH staff to evaluate inter-laboratory analytical performance. A total of 97 samples (from 80 wells) was collected. the locationsof those domestic wells within the intensive study area are shown in figure 8. the sample numbers, addresses and analytical results for Fall 1989 and Summer 1990 domestic well samplings are contained in Appendix B. Domestic well locations were digitized, coupled with VOC results, and analyzed by geostatistical techniques (e.g., kriging) for comparison with subsequent monitoring well sampling results.

Domestic Well Sample Analysis

Domestic well samples were analyzed by purge and trap gas chromatography (GC) with flame ionization detection (FID) on a coupled Tekmar LS2 purge & trap unit - HP 5890 GC - HP 3393A Integration system. This system represented a compromise in analytical resolution and compound specificity as a result of project funding difficulties which delayed installation of the preferred analysis system (i.e., automated static-headspace capillary GC with electrolytic conductivity and photoionization detection). [NOTE: This analytical deficiency was overcome with the delivery and installation of the optimized system in November of 1990.]

The analytical performance achieved in the summer of 1990 was acceptable, within the limits of the available instrumentation, judging from the results of sample duplicate determinations and of split

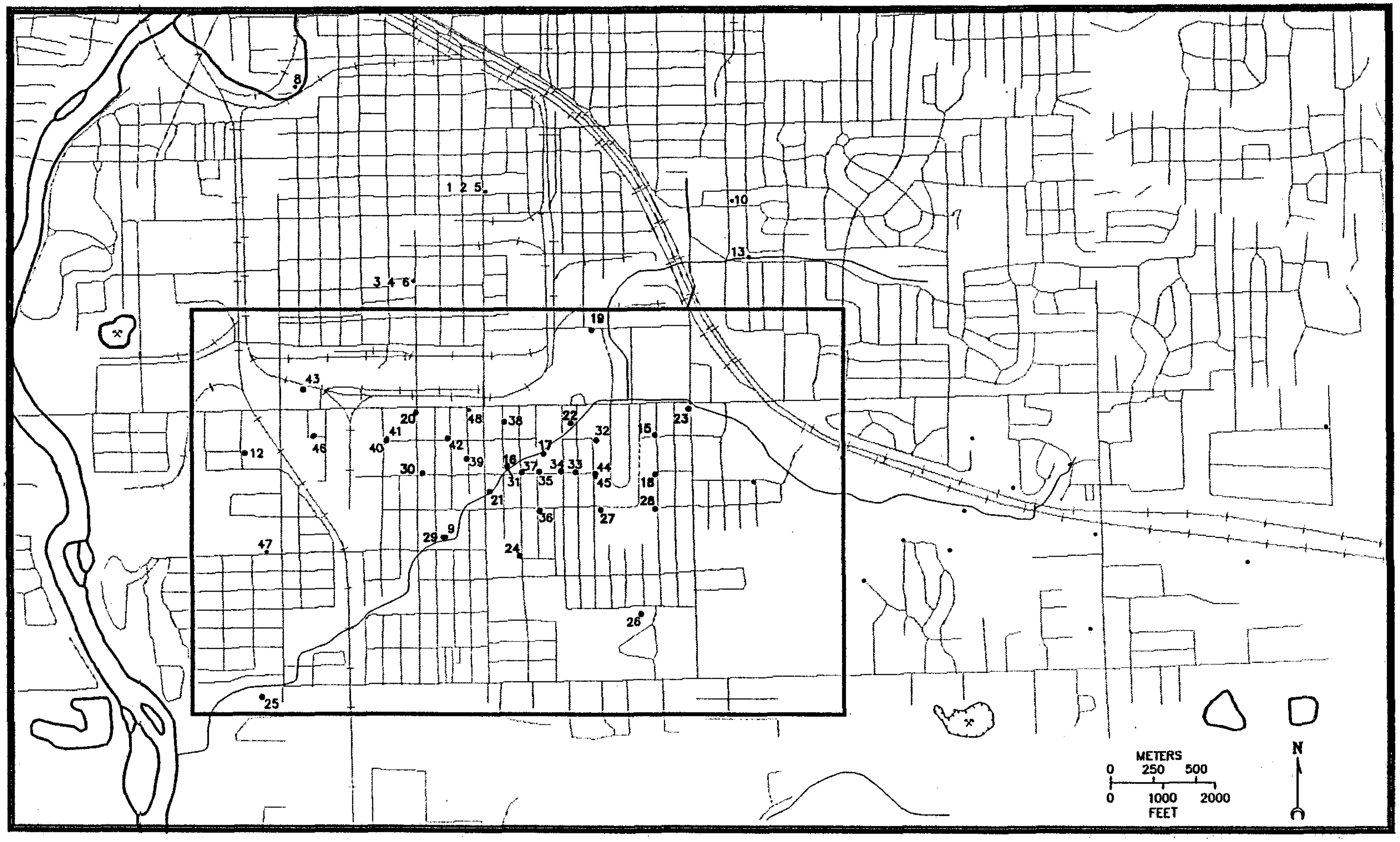


Figure 7. Location of the intensive study area within SE Rockford (numbered dots represent locations of ISWS monitoring wells).

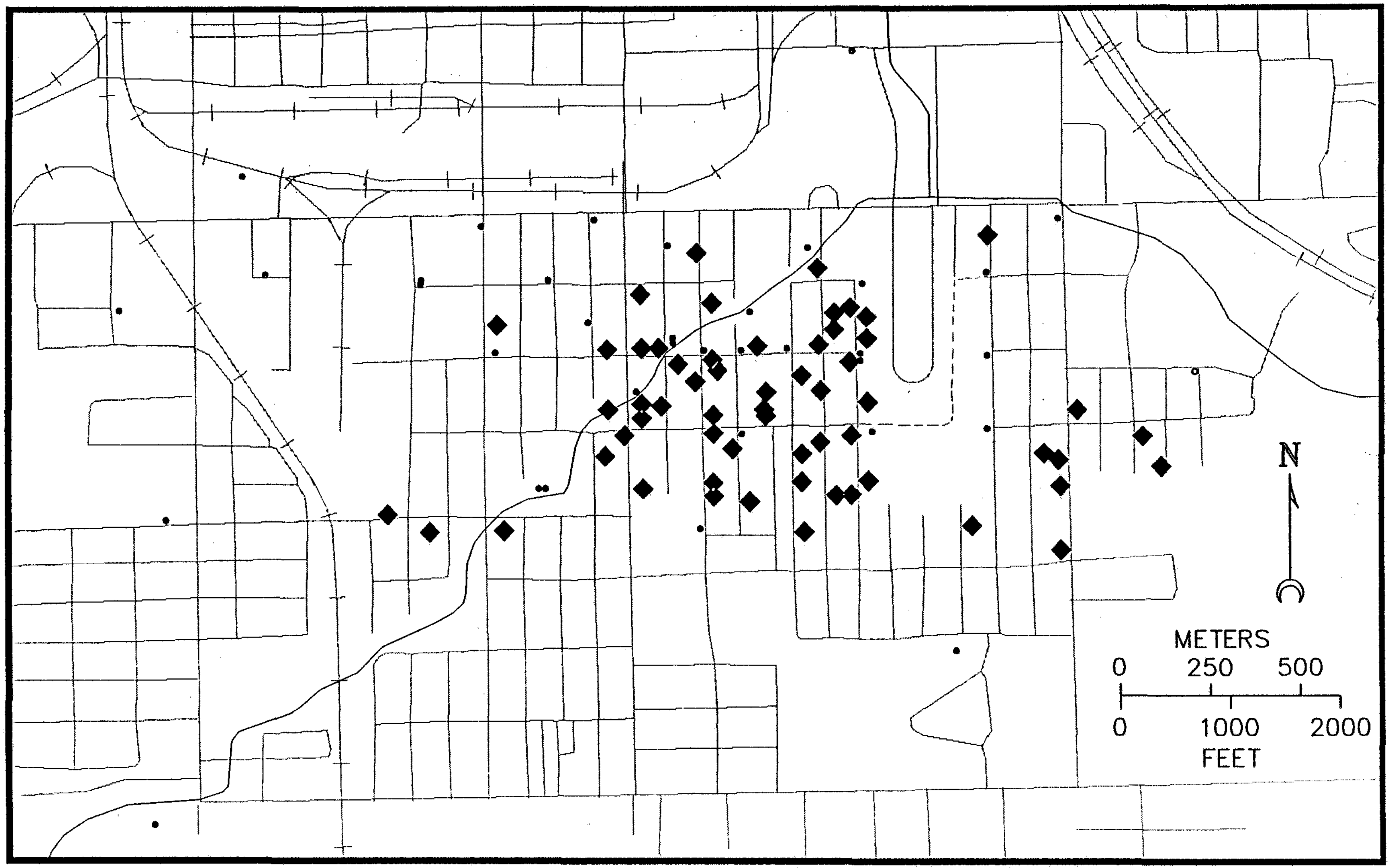


Figure 8. Locations of domestic wells (diamonds) sampled in July 1990 within the intensive study area.

sample determinations from IDPH. The average accuracy and precision results for the major volatile contaminants (i.e., DCE, DCA, cl2DCE, TCA, and TCE) and the surrogate standard compounds (i.e., bromochloromethane, 2-bromo-l-chloropropane, and 1,4-dichlorobutane) are shown in Table 9. Average WQL precision for the analysis of field duplicate samples was consistently in the 7% relative standard deviation range with the exception of DCE which averaged 20% due to problems in chromatographic resolution. This compound eluted in the early portion of the chromatogram and frequently overlapped with the peak for methylene chloride. The accuracy results for the spiked surrogate standard compounds showed a consistently high average bias relative to laboratory standards which can, in part, be attributed to poor chromatographic resolution for the samples containing 20-35 individual organic compounds. The complexity of the actual ground-water sample contaminant mixture was not anticipated when the project was conceived. This was due to the fact that previous studies did not report the large number of halogenated and aromatic compounds as contaminants in the SE Rockford region which we observed. We confirmed with the new analytical system that the high bias can be brought under control with the use of: a capillary column with higher resolution, dual ECD and PID detection systems and the inclusion of additional external reference and certified analytical standards. Therefore, the improved procedures were sufficiently robust to maintain analytical accuracy and precision for the principal contaminants to within ±20% of compound recovery.

There were a total of six sample pairs which were successfully analyzed by both WQL and IDPH. Both laboratories had difficulties (i.e., sample breakage, analytical problems) which resulted in the loss of two additional sample pair results. The intercomparison of the average results for the principal contaminants is shown in Table 9. The relative differences between IDPH and WQL results based on the WQL results average d -42% (i.e., the IDPH results were low relative to WQL results). These differences are significant relative to the levels of accuracy required in volatile organic compound analysis and may be attributed to either relatively high bias in WQL results or low bias in the IDPH results.

It should be recognized that both labs used different chromatographic and standardization practices and compensating errors could be expected to yield closer comparisons which masked true bias. It would have been preferable to share an external reference standard between the labs, with the samples, to evaluate these apparent differences in analytical accuracy. External reference standards supplied by the USEPA or commercial source were analyzed in duplicate with each subsequent set of samples collected in the project. These results were helpful in determining the analytical precautions necessary in sharing split samples with other laboratories.

Construction of Monitoring Wells

With the pending connection of all the domestic wells in southeast Rockford to city water and subsequent abandonment of those wells, monitoring wells for sampling the VOC plume were needed. Construction of the wells took place in three phases over a period of 18 months between October

Table 9. Precision ana Accuracy of July 1990 Private Well VOC Sampling and Analysis, and Inter-Laboratory Comparison of Analytical Results for the Major Contaminant Compounds

Statistics	Contaminant Compound					Surrogate Compound		
	DCE	DCA	cl2DCE	TCA	TCE	BCM	B2C1PA	DCB14
WQL Analysis								
Relative Standard Deviation[a]	20.0%	6.7%	6.7%	6.4%	7.2%	-	-	-
Relative Bias	-	-	-	-	-	63.0%	6.3%	67.0%
IDPH Analysis Relative Bias[c]	-36.2%	-56.7%	-60.9%	-38.9%	-17.5%	-	-	-

a. Relative Standard Deviation (RSD) was estimated from the Range (R) and the Mean (M) of the reported concentration for field duplicate samples, assuming a formula of RSD = 0.886*R/M. Averaged results on 6 pairs of samples;

b. Average results on 7 field surrogate samples;

c. From WQL results; Averaged results on 6 sets of samples split between IDPH and WQL.

1989 and May 1991. A phased approach to monitoring well placement was chosen to allow an examination or VOC quality from the monitoring wells constructed in each phase. This allowed tor better selection or monitoring well locations within (and adjacent to) the VOC plume.

The information provided by the domestic well sampling gave us with some basic geostatistical information about the VOC concentration distribution (e.g., spatial correlation distances). To make up for the loss of those wells, new monitoring wells were drilled to replace them. The advantages of monitoring wells over the use of domestic wells (which were no longer available anyway) were many: 1) well construction details were more certain, 2) sampling procedures were more uniform, 3) locations were more ideally situated, 4) access to the well for sampling or other experiments was certain, and 5) the wells could be used for a variety of purposes including water level measurements and hydraulic conductivity testing, as well as sampling. The major drawback to not having the domestic wells available for sampling was in sheer numbers; reducing the number of available sampling points from over 200 to less than 50 created more uncertainty in geostatistical evaluations of spatial variability.

Forty-eight (48) monitoring wells were constructed for this project in the greater SE Rockford area. Thirty-two of the wells were either within the zone of VOC contamination or in close enough proximity to the contaminated area to help define the areal extent of the contamination (locations of wells within the intensive study area are shown on figure 7). Three well sites in the intensive study area also contained two nested wells at each site (Wells 44 & 45, Wells 16 & 31, Wells 40 & 41). The deeper wells 41 and 45 contain 10-foot screens — all other wells contain 5-foot screens. The deeper wells allowed some examination of three-dimensional water quality; however, our budget did not allow for a complete examination of the plume in all three dimensions. In addition, "duplicate" wells were constructed within 5 to 10 feet and immediately downgradient of wells 16, 17, 21, and 35. These wells were emplaced in boreholes created during our monitoring well - Hydropunch® comparisons. The wells were constructed exactly as their counterpart wells and were named with an "A" suffix (i.e., 16A, 17A, 21A, and 35A).

A brief summary of the construction details of each well is given in Table 10; a typical well is shown in figure 9. Complete geologic descriptions and construction notes for each well are located in Appendix C. All wells were drilled with a Mobile B-57 hollow stem auger (4.25-inch inside diameter augers). After drilling to the desired depth, the well casing and screen were placed down-hole inside the hollow augers. The augers were then pulled back and the natural aquifer materials were allowed to collapse around the well screen. Collapse of aquifer materials occurred up to the height of the water table (approximately 25 to 30 feet below land surface). A 2- to 4-foot thick bentonite plug was placed in the annulus atop the collapsed hole after which the hole was backfilled with sand cuttings. All wells were constructed of 2-inch diameter casing and screen. All wells were constructed with stainless steel screen unless otherwise noted; stainless steel casing was used up to a point above the water table after which polyvinyl chloride (PVC) casing was used. A surface seal of bentonite was

Table 10. SE Rockford Monitoring Well Construction Details

Well No.	Lambert E	Lambert N	Depth (feet)	Date Drilled	Screen Length, ft*
1	796480	2035051	87.5	11/87	5 SS
2	796480	*2035051*	52.5	11/87	5 SS
3	795088	2033348	92.5	11/87	5 SS
4	795088	2033348	52.5	11/87	5 SS
5	796480	2035051	125	11/87	5 SS
6	795088	2033348	125	11/87	5 SS
7	794967	2038610	62.6	10/89	5 SS
8	792798	2037052	32.6	10/89	5 SS
9	795693	2028467	50	10/89	5 PTFE
10	801215	2034859	22.3	10/89	2.5 SS
11	806574	2029396	25.4	10/89	5 SS
12	791830	2030071	57.6	10/89	5 SS
13	801536	2033798	96.1	7/90	5 PVC
14	803710	2027629	25	7/90	5 SS
15	799728	2030420	51.5	7/90	5 SS
16	796862	2029806	47.8	7/90	5 SS
17	797586	2030063	45.2	7/90	5 SS
18	799728	2029670	73.9	7/90	5 SS
19	798506	2032425	49.5	7/90	5 SS
20	795130	2030838	53.6	7/90	5 SS
21	796539	2029346	46.7	10/90	5 SS
22	798104	2030629	45.5	10/90	5 SS
23	800378	2030902	60.4	10/90	5 SS
24	797122	2028090	42.9	10/90	5 SS
25	792145	2025425	40.2	10/90	5 PVC
26	799441	2027008	72.3	10/90	5 PVC
27	798677	2028982	61.9	10/90	5 SS
28	799723	2029000	99.3	10/90	5 SS
29	795675	2028463	36.9	10/90	5 SS
30	795238	2029682	50.3	10/90	5 SS
31	796862	2029806	60	5/91	5 SS
32	798601	2030321	50	5/91	5 SS
33	798183	2029714	46	5/91	5 SS
34	797914	2029724	44.6	5/91	5 SS
35	797487	2029714	44.8	5/91	5 SS
36	797506	2028958	50	5/91	5 SS
37	797158	2029714	44.2	5/91	5 SS
38	796830	2030660	48.9	5/91	5 SS
39	796103	2029963	51	5/91	5 SS
40	794560	2030311	65.5	5/91	5 SS
41	794560	2030311	85.4	5/91	10 SS
42	795745	2030351	53.8	5/91	5 SS
43	792947	2031287	81.4	5/91	5 SS
44	798581	2029674	52.4	5/91	5 SS
45	798581	2029674	72.4	5/91	10 SS
46	793157	2030401	75.1	5/91	5 SS
47	792261	2028182	54.9	5/91	5 SS
48	796163	2030899	50.4	5/91	5 SS

* SS: stainless steel, PTFE:polytetraflouroethylene (teflon®), PVC: polyvinylchloride

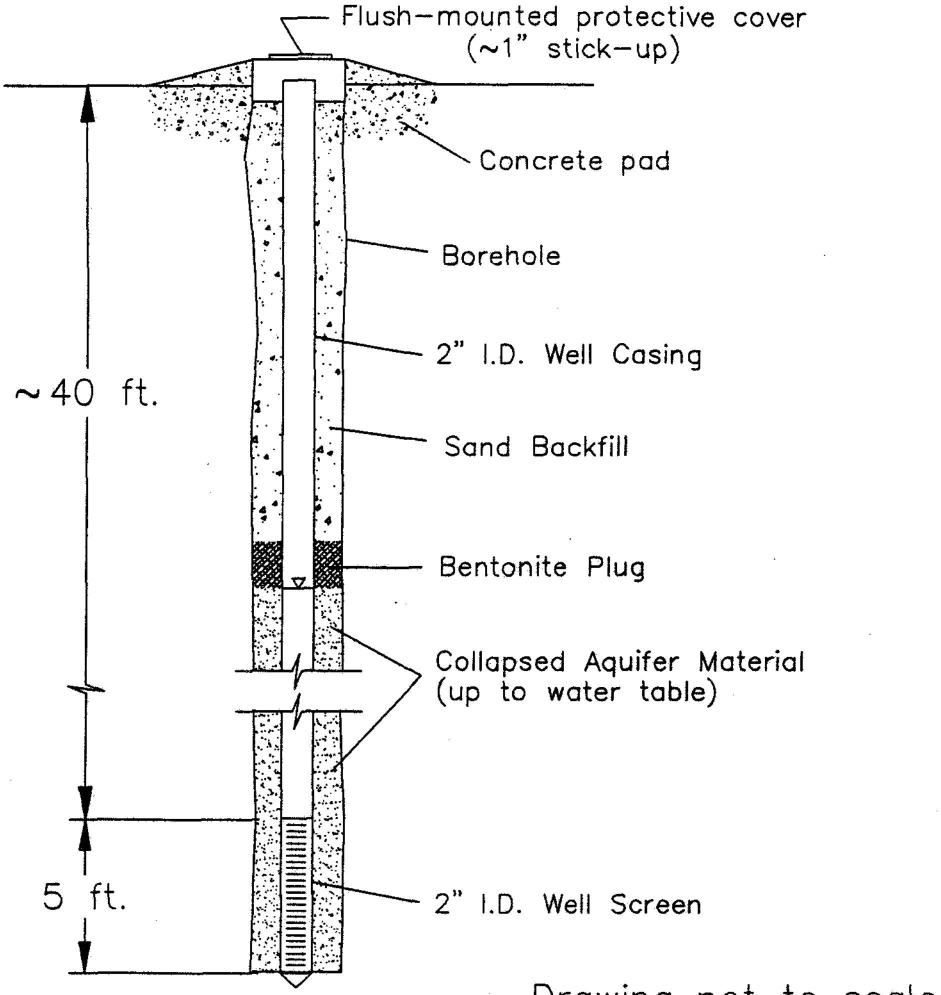


Figure 9. Cross section of typical monitoring well in SE Rockford.

used atop the backfill. This was followed by either a 6-inch diameter steel protector with locking cap or a flush-mounted, lockable, water-tight protector.

Hydrologic Monitoring

Water Level Monitoring

Water level measurements (depth-to-water readings) were taken in all monitoring wells on a regular basis throughout the term of the project, in some wells from September 1990 through May 1993. Traditional optical surveying techniques (level circuits) were conducted to determine top-of-casing and land surface elevations for all wells. Depth-to-water measurements were subtracted from top-of-casing elevations to calculate ground-water surface elevations. Ground-water surface elevations coupled with Rock River elevation data were subsequently used to create potentiometric surface maps for the shallow sand and gravel aquifer, particularly for quarterly sampling periods. Simple interpolation techniques in the popular Surfer® (Golden Software, Inc.) contouring package were used to create the potentiometric surface contours.

Water level information was also used to develop hydrographs to examine seasonal changes in water levels as well as to examine the water levels for long term trends. Daily precipitation records from the Rockford Municipal Airport located less than one mile south of the study area were obtained to examine water level response to precipitation events.

Hydraulic Conductivity Analyses

Slug tests were performed on 47 of the 48 monitoring wells in the network to determine the spatial distribution of aquifer hydraulic conductivity. Hydraulic conductivities were determined by analysis of water level response to slug tests performed through a casing pressurization technique similar to that described by Prosser (1981) and modified by Kelly (1990). The casing pressurization technique was used because the highly conductive outwash sands at this site allow very rapid water level response to induced head changes (e.g., often less than 10 seconds for 7 to 8 feet of water level displacement). A micro-computer based data acquisition system developed at the Illinois State Water Survey was used to collect water level response data (Kelly 1990).

Each well was tested in triplicate and, when possible, the resulting data were analyzed by methods described by Bouwer and Rice (1976). Of the 47 wells, 34 were amenable to analysis by the Bouwer and Rice methodology. This technique is applicable to wells in unconfined aquifers with a water level response that forms a straight line on a semilogarithmic graph (with time on the linear x-axis and water level displacement on the logarithmic y-axis). An example of such a response is shown in figure 10. Water level responses such as this are called "overdamped" because frictional forces exerted on the water column in the well are greater than the momentum effects of the water column as it moves up the well casing.

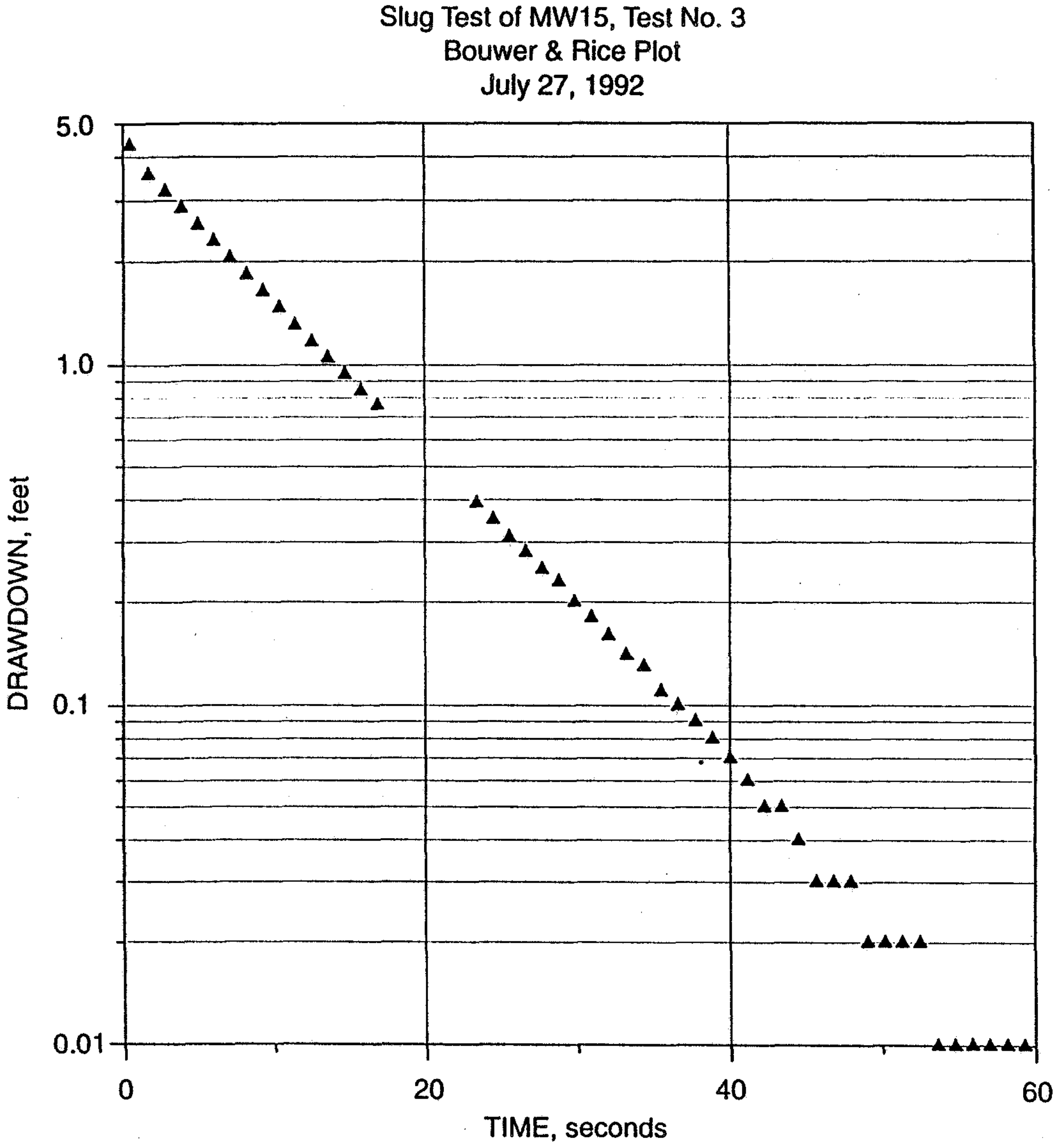


Figure 10. Typical overdamped slug test water-level response.

When momentum or inertial effects are greater than frictional forces, the displaced water responds in an oscillatory fashion, initially rebounding above original static level. This response is called "underdamped" and appears to be the type or response seen in at least six or our monitoring wells. An example or this type or response is shown in figure 11. Until recently, analysis of this type of response could not be easily done. However, Springer (1991), in bis Master's thesis at MIT, provided such a solution.

Basically, when underdamped conditions are present, inertia! effects cause the observed water level to not be equal to the head within the well screen. Springer used the momentum equation for a pipe system to provide a relation between observed water levels and bead, thus allowing for analysis of hydraulic conductivity. The solution is also valid for the underdamped conditions present in the Bouwer and Rice solution. In fact, because Bouwer and Rice do not account for momentum effects, the Bouwer and Rice solution may overestimate the hydraulic conductivity (K) for larger values of K. A Springer-type analysis was performed on all wells where the Bouwer and Rice method was used. A comparison of the results or the two methods was possible and implications for the range of hydraulic conductivities (K) where the Bouwer and Rice method may overestimate K was made.

Springer's analysis requires a) computation of a term be called L_e, the effective water column length, equal to the water column length from the static water level to the midpoint of the screen, b) transformation of the raw time data into dimensionless time, t-hat, by dividing time by the square root of the quantity of (L_e/g), c) transforming the water level data into dimensionless water level displacement by dividing the water level displacement by the total displacement, d) converting the dimensionless water level data into all positive values by squaring all dimensionless displacement values (figure 12), and e) matching a straight line drawn through the data maxima to a family of type curves (figures 13 and 14).

Several wells appeared to respond in a "critically damped" manner, being neither overdamped or underdamped. The data from these wells could not be satisfactorily analyzed with either Bouwer and Rice's method or Springer's method. An estimate of the hydraulic conductivity was made using the Bouwer and Rice method.

Finally, a contour map of hydraulic conductivity for the field site was created. Values of hydraulic conductivity were log-transformed for input into GEO-EAS 2.1 for kriging. A contour map or the expected error in the hydraulic conductivity field was also created.

Hydraulic Gradient Analyses

In order to examine changes that might affect the temporal and spatial variability of the VOC plume, we sought to examine changes in the hydraulic gradient that occurred over the study period. Series of three-well groupings were selected from the monitoring well network as shown in figure 15. For purposes of this discussion, a three-well group was called a triplet. Using the water elevation information collected during our investigations, gradients (magnitude and direction) were calculated

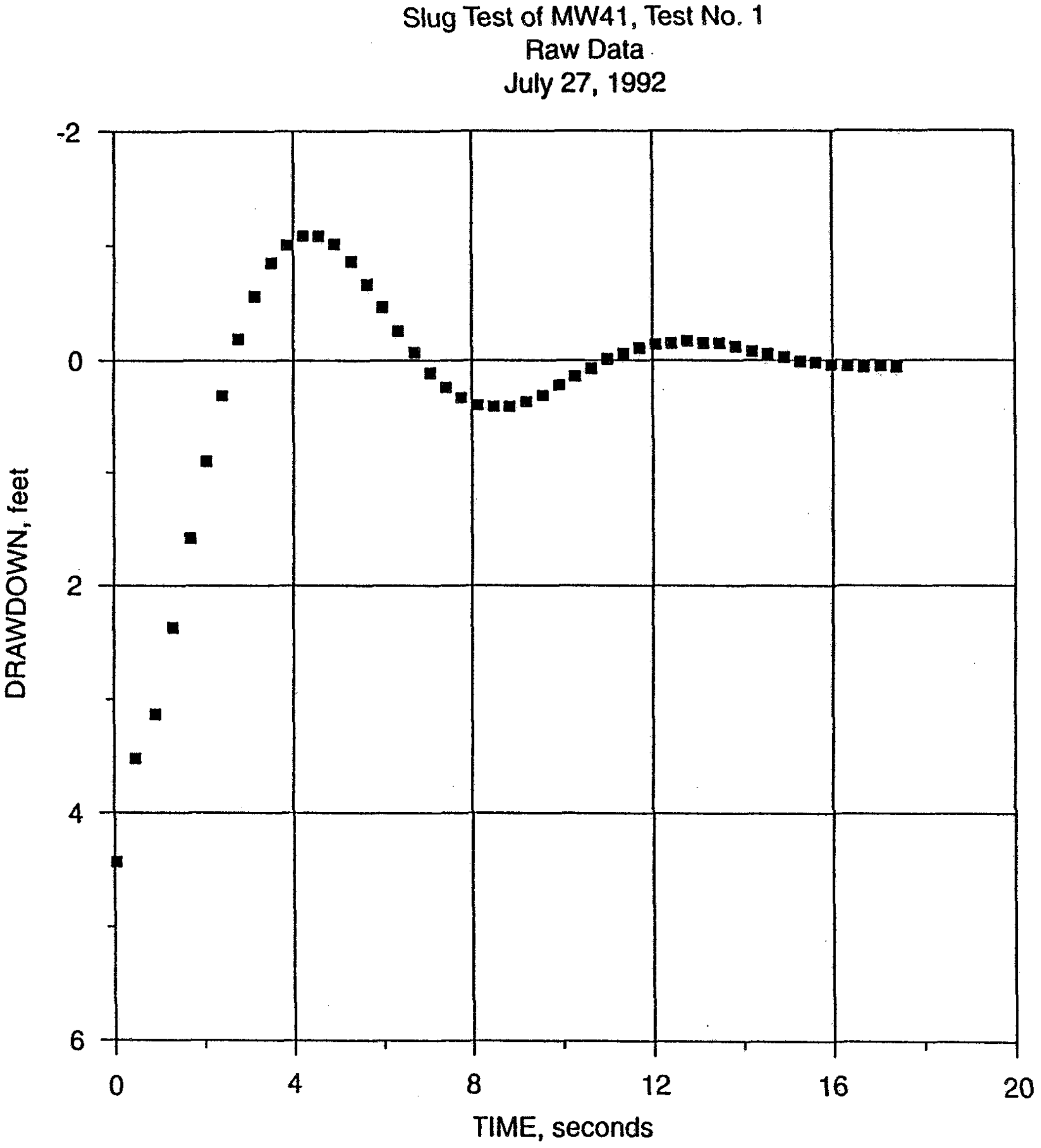


Figure 11. Underdamped water level response during slug test at monitoring well 41.

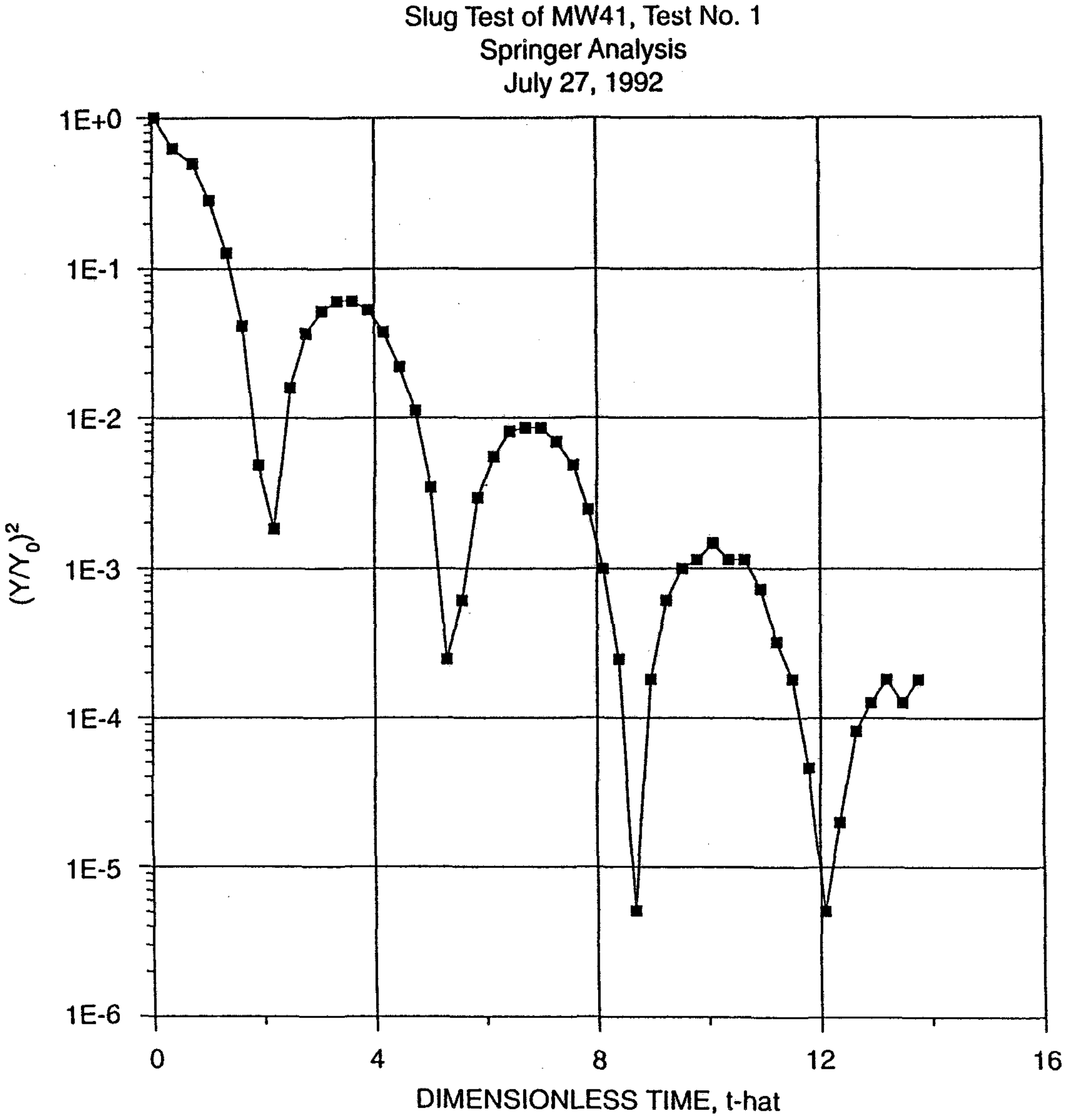


Figure 12. Springer (1991) analysis for underdamped slug test response at monitoring well 41.

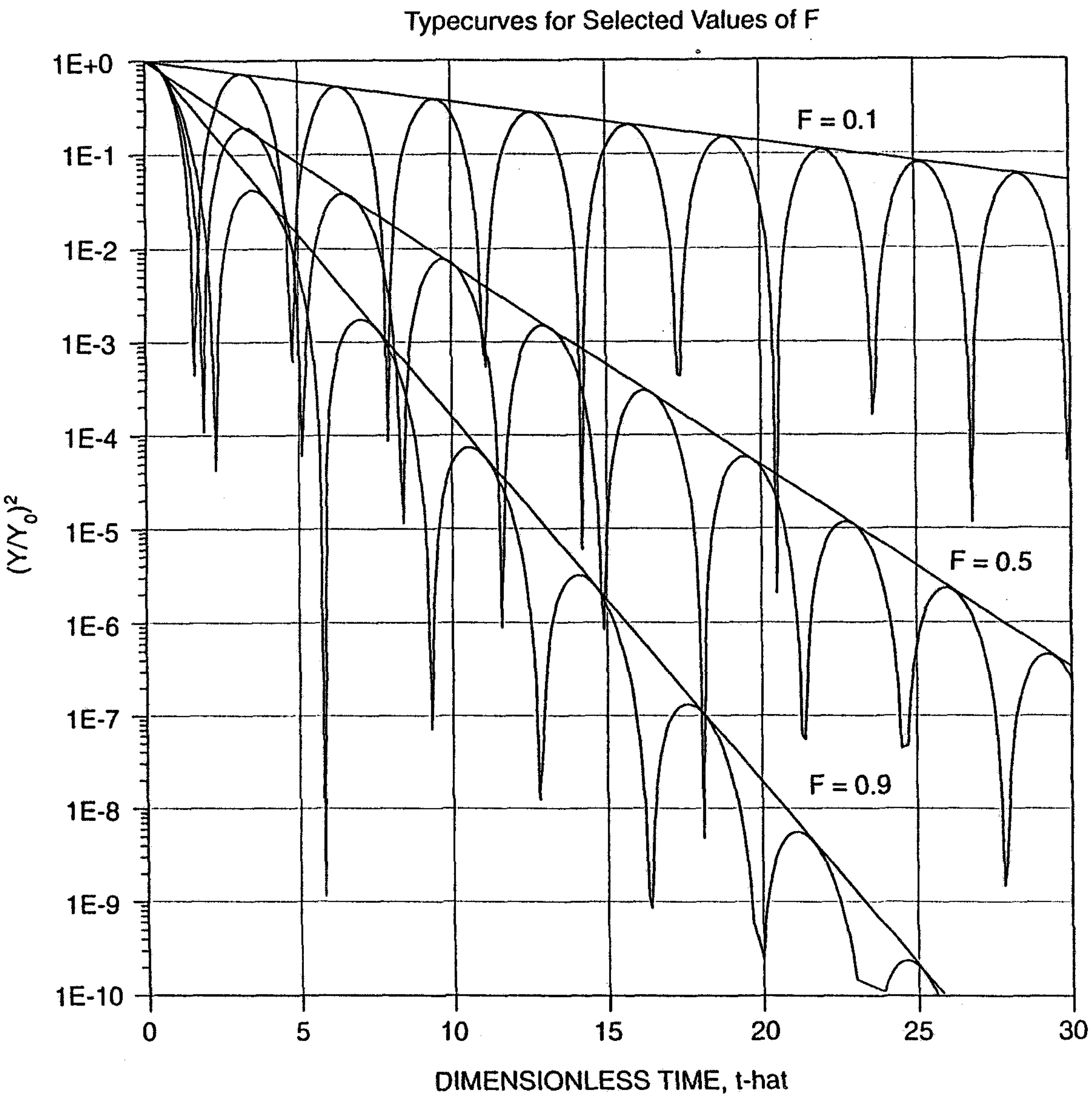


Figure 13. Family of friction parameter (F) type-curves for underdamped slug test analysis (after Springer, 1991).

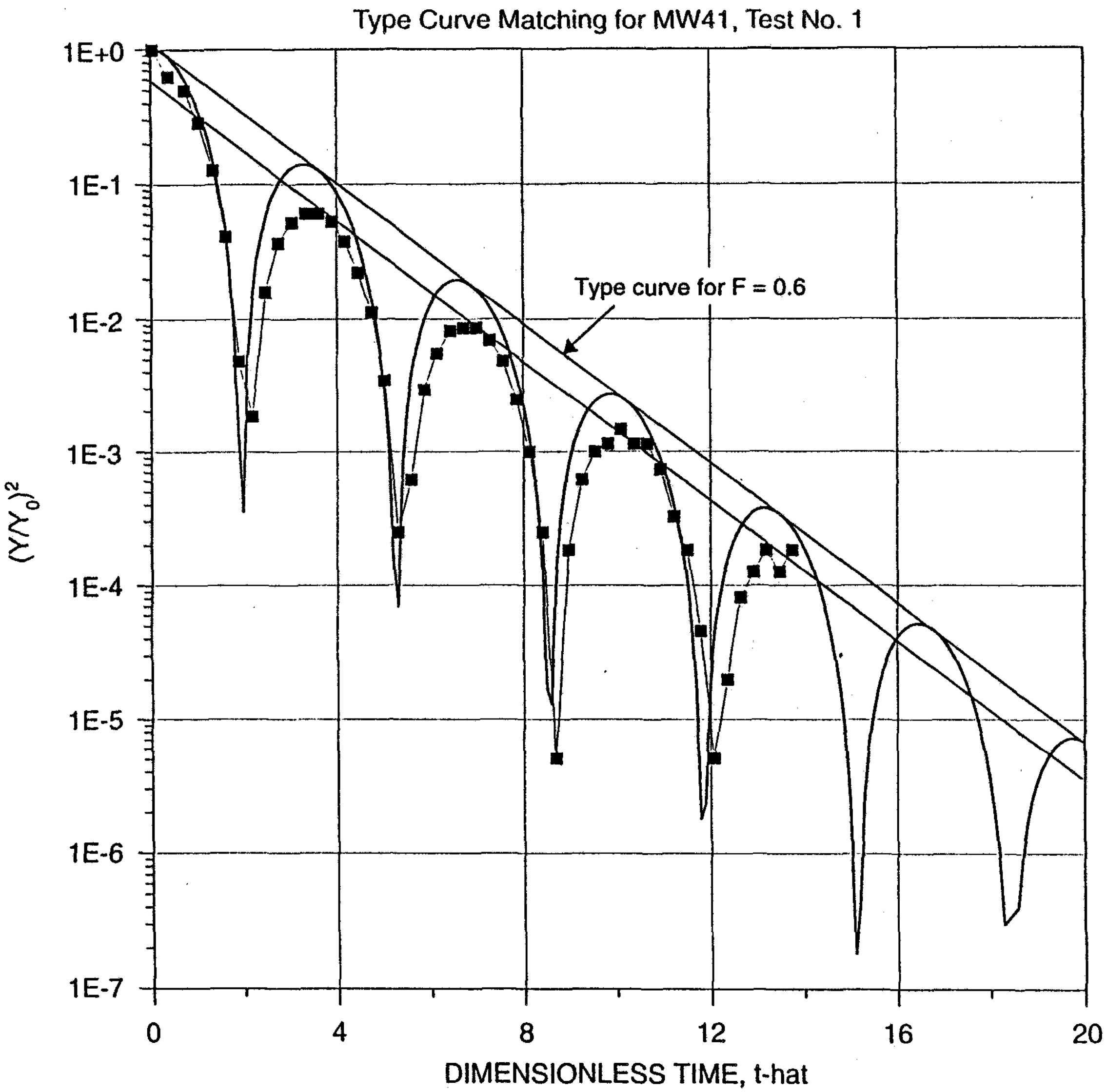


Figure 14. Type-curve matching for slug test analysis at monitoring well 41 (note parallel lines through data and type curve peaks).

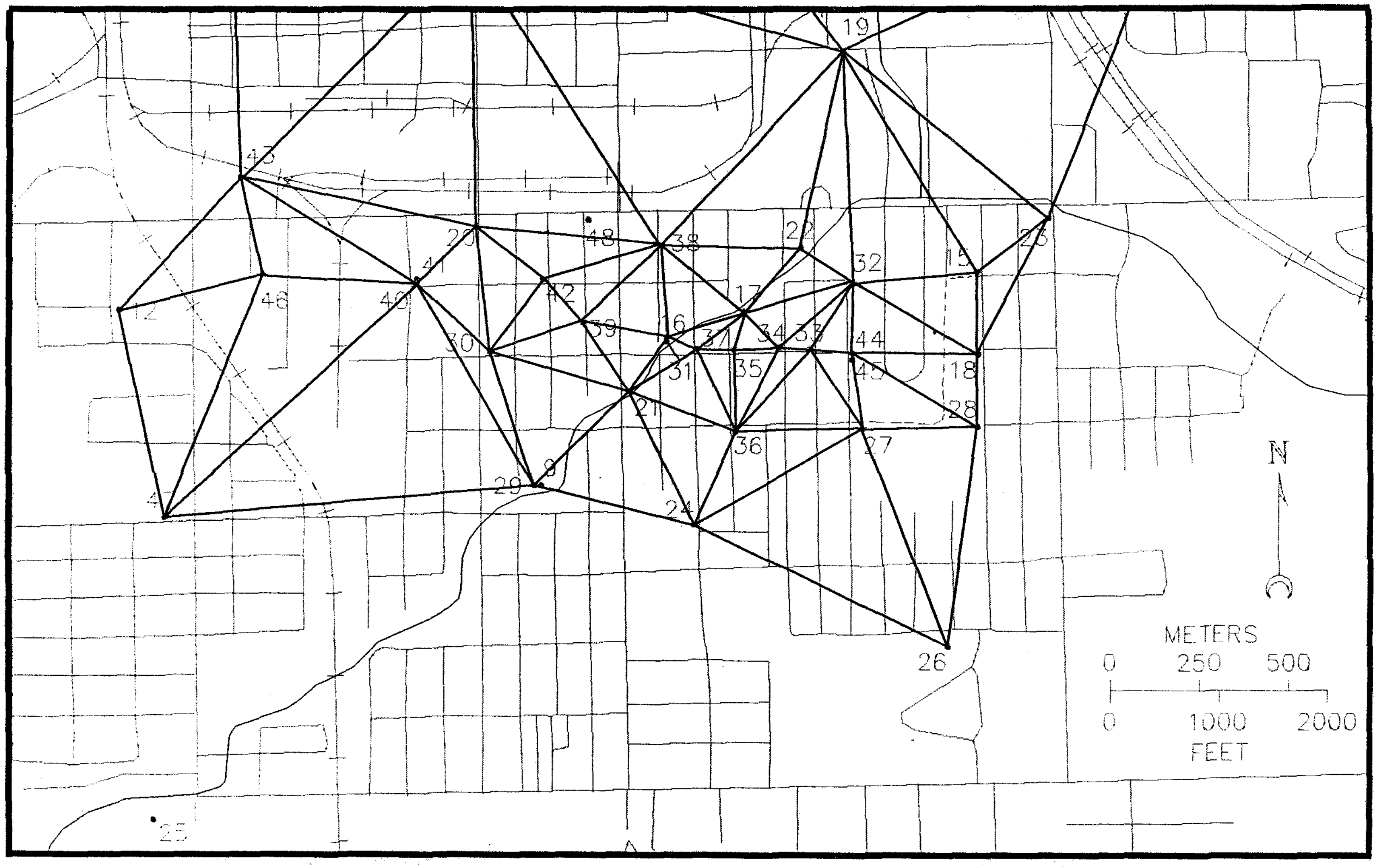


Figure 15. Three-well groupings (triplets) for hydraulic gradient analysis.

for each triplet for each measurement date. Mean gradient magnitudes and directions were subsequently calculated for each of the triplets. A unique map of the mean direction (and magnitude) and also including the standard deviation of the magnitude and direction was prepared.

Chemical Monitoring of Water ana Aquifer Solids

Monitoring Well Sampling

The basis for this portion of the work was established in previous investigations by Barcelona *et al.* (1985) and Barcelona *et al.* (1989a,b). Monitoring well sampling was conducted as part of three separate, yet related investigations: 1) low-flow purging experiments to examine traditional inorganic purging parameters and simultaneous VOC concentrations, 2) comparisons between traditional monitoring well samples and water samples collected by hydraulic probe (Hydropunch®), and 3) quarterly sampling to examine spatial and temporal trends in VOC concentrations in ground water. The protocols were kept simple and direct with an emphasis on consistency over time, regardless or the operator or technician.

Briefly, each well was unlocked and measurements were taken of water level and in-situ temperature (using a thermistor probe, Omega Instruments). Sample tubing connections were made and pumping was started. All of the monitoring wells were outfitted with dedicated polytetrafluoroethylene (PTFE) bladder pumps (Well Wizard®, QED, Inc.) with the intakes set at midscreen. Fluoroethylene polymer (FEP) discharge tubing (l/2"o.d.) from the bladder pump was directed to a three-way stainless steel valve which led to either: a) an FEP sampling tube, b) a discharge line to waste or, c) a flow-cell (Garske and Schock, 1986) equipped with dissolved oxygen, pH, temperature, and specific conductance sensors. The flow rate was maintained at 1.0± 0.1 L/min. and the cumulative volume pumped was measured and recorded. At least one sample was spiked with a combined standard solution to evaluate storage and analysis error for each sampling trip. Pumping and sampling were continued until all of the indicator parameters stabilized to within ±0.2 mg O_2/L, ±0.10 pH units, ±0.1 C° and ±10.0 μS/cm over a successive bore volume. A bore volume was taken to be the water included in the sand pack, screen and casing of the well.

Well Purging Experiments. Well purging experiments were conducted in February 1991 to examine the efficacy of low-flow purging (i.e., ~1 L/min) of small-diameter (2 inch) monitoring wells with short screened intervals for VOC sampling. For this particular investigation, a subset of fourteen wells was selected. Well volumes (i.e., borehole volume, screen, and sandpack volumes) were calculated for each well under the water level conditions at the time they were sampled. Wells were selected to cover a range of VOC concentrations and hydraulic conductivities. The wells selected were: 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 27, 28, 29, and 30 (figure 16). The well purging experiments were conducted as part of the February 1991 quarterly sampling event.

Triplicate VOC samples (i.e., 8 to 10 per well) were collected at intervals of ~1 to 3L by diverting a portion of the monitoring well pump discharge to an FEP sampling line at flow rates of ~100

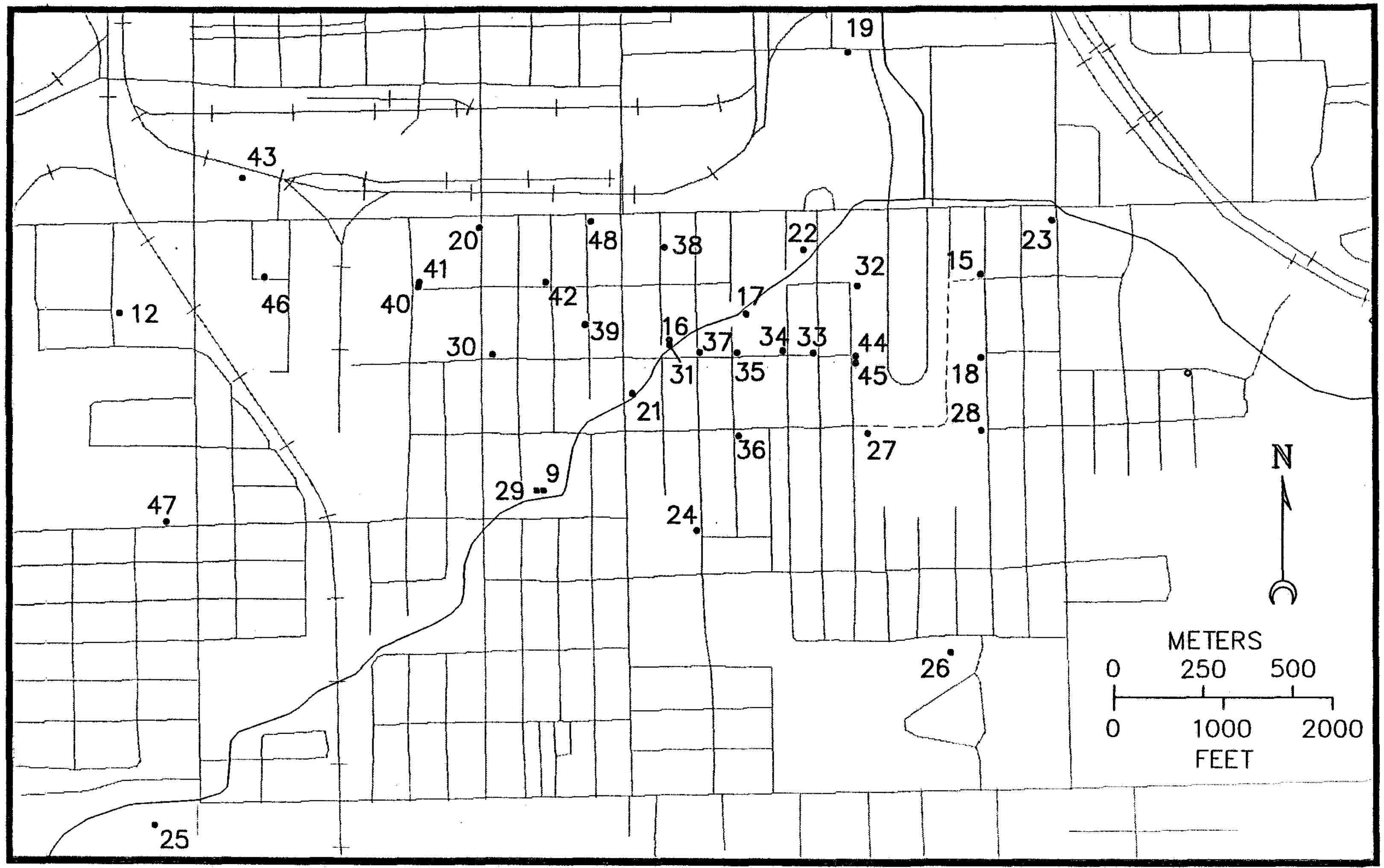


Figure 16. Locations of monitoring wells in the intensive study area (enlarged view of figure 7).

mL/min. Readings of indicator parameters (dissolved oxygen, specific conductance, pH, and temperature) from flow-through cell probes were recorded regularly as the well was purged. Pumping was frequently continued beyond three bore volumes to document complete stabilization. It was rarely necessary to pump the wells beyond two bore volumes at ~1 L/min (entrance velocity ~0.2 ft/min; 6 cm/min) to achieve indicator parameter stabilization. Due to the steady discharge/recharge cycling of the bladder pumps it was possible to achieve control over flow rates within ±0.1 L/min. Indicator parameter readings were taken (i.e., 12 to 20 per well) from the meters connected to the electrodes in the flow cell during the middle to end of the bladder pump discharge period. In selected cases, the water levels in the wells were monitored during pumping with either an electric drop-line or a down-hole transducer linked to a lap-top computer. An example of water level response during pumping is shown in figure 17. The bladder pump action caused cycling of water levels of ~0.2 to 0.3 ft (0.06-0.09m) during pumping but no significant net drawdown was observed in any of the wells at the conclusion of sampling operations.

Quartery Sampling. The quarterly sampling and well purging experiments (February, 1991) were designed to evaluate the utility of a quarterly sampling frequency for long-term temporal VOC concentration trend evaluation and the purging procedures which had been established by previous work on inorganic constituents (Barcelona *et al.*, 1989b) Preliminary sampling in November 1990 provided us with basic design parameters.

Quarterly sampling began in November 1990 with the sampling of 17 wells (wells 9, 11, 12, 15 - 24, and 27 - 30). Quarterly sampling in February 1991 was pared down to 15 wells located within the smaller "intensive" study area containing the primary *VOC* plume; this included wells 12, 15 - 24, and 27 - 30. After the construction of wells 31 - 48 in April and May 1991, the May 1991 sampling event was the first essentially complete sampling of the final network of 33 wells (11, 12, 15 - 24, 27 - 46, and 48). This was followed by sampling events in August 1991, December 1991, March 1992, and finally September 1992 (May 1992 sampling was not conducted due to EPA funding difficulties). Well 11 was dropped from the sampling after May 1991. Wells 16A, 17A, and 21A were sampled in August 1991 (for a 35 well total); those three wells plus well 35A were sampled in March 1992 (36 well total for that quarter). Well 48 was abandoned due to street construction during the summer of 1992 and was not available in September 1992.

Hydropunch® - Monitoring Well Comparisons

This intercalibration experiment had as its goal the intercomparison of total VOC results from conventional monitoring wells and adjacent Hydropunch® samples. An additional aspect of the experiment was the inclusion of aquifer solid analyses for VOCs from split-spoon samples collected following Hydropunch® casts (see following section).

Ground-water contaminant site characterization approaches are generally based on traditional drilling, subsurface solid sampling, and monitoring well construction techniques. Samples of potentially contaminated ground water are collected from monitoring wells after development and

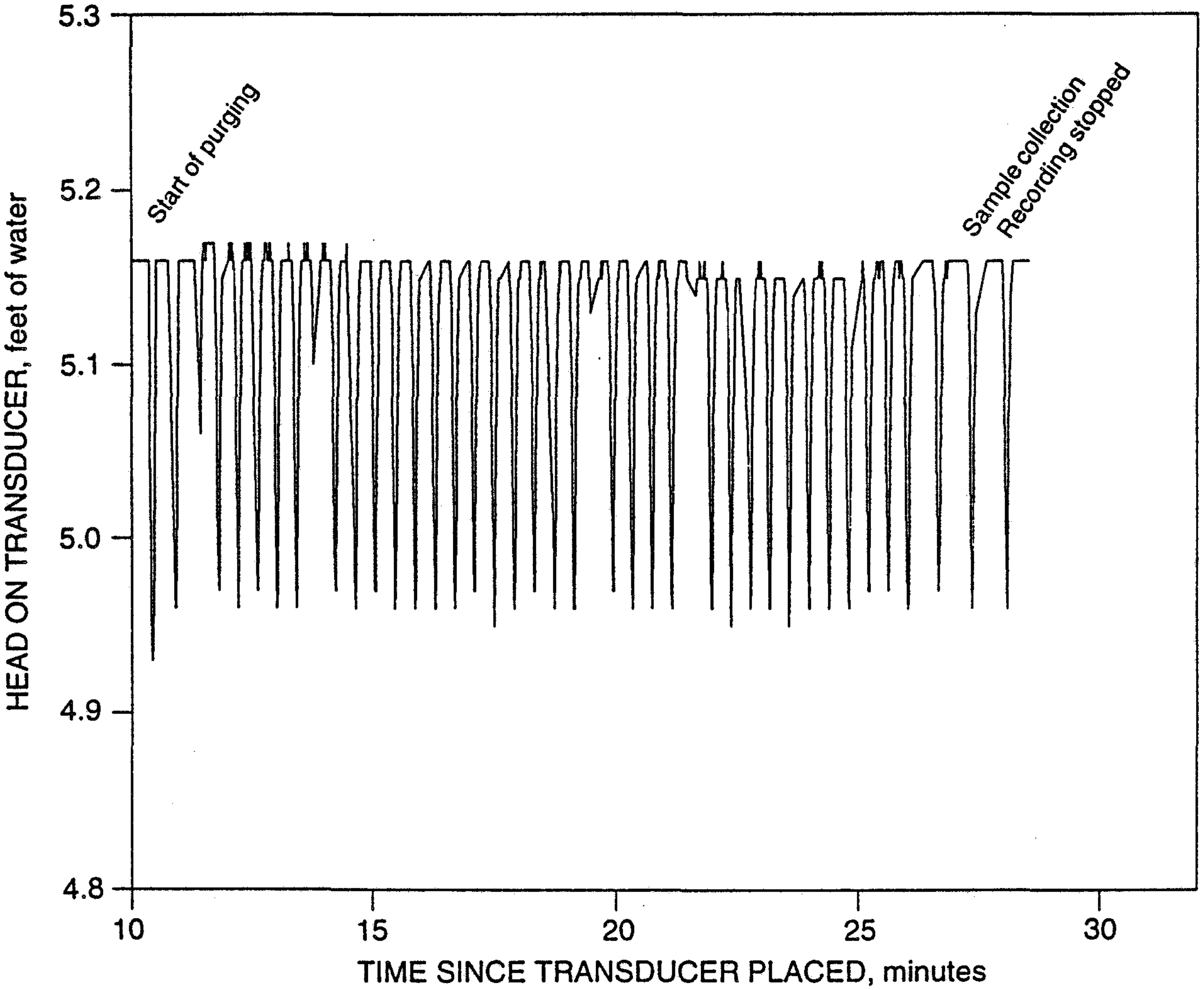


Figure 17. Typical ground-water level response to bladder pump operation in SE Rockford monitoring well.

purging to determine the magnitude and extent of contamination. The expense and time requirements involved in this approach nave substantial drawbacks, particularly in the reconnaissance phase of site characterization efforts. Within the last five years, more rapid field sampling and analysis techniques nave been developed to supplement monitoring well-based data collection methods. One of the most well known new techniques in "rapid" ground-water sampling is the *in-situ* sampler called the Hydropunch$^{®}$.

The Hydropunch$^{®}$ is a small diameter "tool" often used with drilling machines or cone penetrometer rigs that is capable of collecting a ground-water sample without the installation of a monitoring well (figure 18a). To collect a sample, the Hydropunch$^{®}$ is attached to standard AW drive rod and is driven or pushed to just below the desired sampling depth. As the Hydropunch$^{®}$ is advanced, the sampling chamber is not exposed and is incapable of collecting a water sample. Once the desired sampling depth is reached, the sampling chamber within the tool is exposed or "opened" by pulling back on the drive rods (about 0.5m is sufficient). The drive cone on the end of the tool is held in place by soil friction, thus exposing the bottom end of the sampling chamber and allowing ground water to enter the chamber by hydrostatic pressure (figure 18b). A small screen inside the chamber prevents most collapsible materials (e.g., sand) from entering; the device can hold as much as 1250 mL. Once the device is full, the drill rods are retracted and the Hydropunch$^{®}$ is retrieved. Check valves on both ends of the sampling chamber prevent the sampled water from escaping while also preventing external water from entering the chamber. At the surface, the drive rods are disconnected from the Hydropunch$^{®}$ and a sampling valve and tube are connected to the top. The device is inverted and the water sample can be transferred to suitable containers.

For our operation, Hydropunch$^{®}$ samples were collected ahead of the augers during drilling by driving the tool with the drill rig hammer at least 0.5m beyond the bottom of the borehole. The tool was then pulled hack approximately 15 to 20 cm to drop the drive head and permit water to enter the tool. The tool was allowed to fill for a minimum of fifteen minutes, at which point the drill string was pulled from the hole. The tool was retrieved at the surface and maintained in an upright position until it could be dismantled at the top to attach the sampling tap. The tool was then inverted and sample was transferred to 40 mL VOC vials. The vials were filled from the bottom and allowed to overflow, retracting the tube to leave a meniscus, and capped. At least two vials were filled from each Hydropunch$^{®}$ cast, volume permitting, and they were immediately stored on ice. The tool was then completely dismantled, cleaned in detergent solution (Alkonox) and rinsed thoroughly with distilled water to prepare it for reuse. In many cases, the stainless-steel inlet screen was replaced between casts because of mechanical damage to it due to sand heaving.

Hydropunch/monitoring well samples were collected over two one-week periods in August 1991 and August 1992. Comparison sampling was conducted at the locations of wells 15, 16, 17, 20, 21, 24, 31, 32, 35, 37, 39, and 42. Sites were chosen to provide a range of hydraulic conductivities and VOC concentrations. At each site, the comparison experiment was conducted in the following manner.

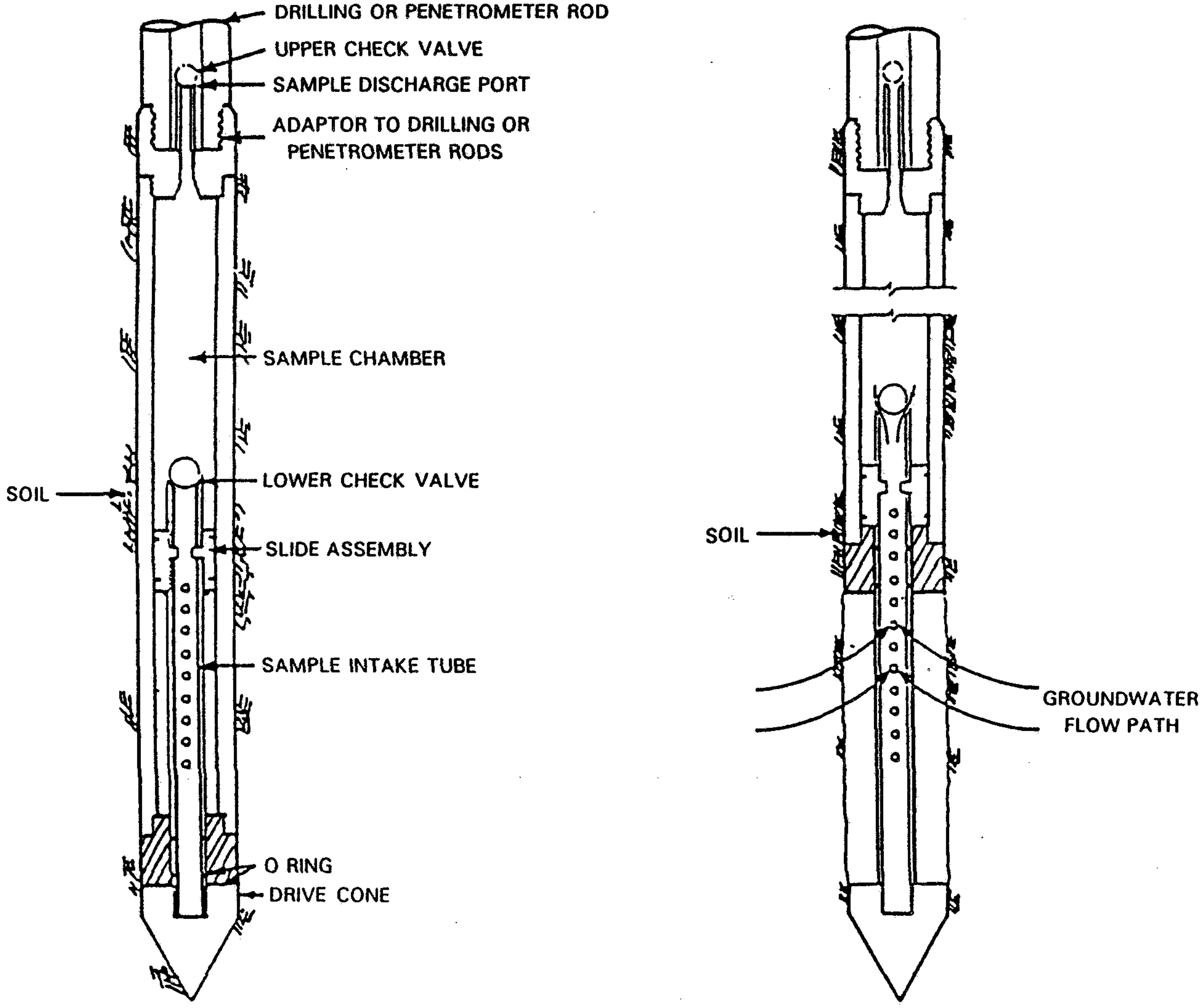


Figure 18. a) Schematic drawing of Hydropunch ground-water sampling tool, b) Ground-water movement into the Hydropunch after deployment (from Edge & Cordry, 1989).

First, a borehole was drilled by hollow stem auger within approximately 5 to 10 feet laterally of well. The borehole was drilled to a depth just above the top of the adjacent well's screen. The Hydropunch® was lowered to the bottom of the augers and driven out the bottom of the lead auger to a depth opposite approximately the midpoint of the well screen (see figure 19). The Hydropunch® was pulled back to open the sample chamber and was allowed to fill. The Hydropunch® was retrieved and a water sample was collected in duplicate 40 mL VOC vials. The augers then were retrieved and the borehole abandoned. A second borehole was drilled on the opposite side of the monitoring well and another Hydropunch® sample was collected in similar fashion as just described for the first sample. As the second borehole was abandoned, a monitoring well sample (again, duplicate 40 mL VOC vials) was collected.

Due to field time constraints, a second Hydropunch® sample was not collected at monitoring well 21. A single Hydropunch® sample was also only collected at well 24. In this case, the sample was accidentally collected at a depth of 60.5 feet, far below the screened well interval (42 - 47 feet). The data produced from analysis of these samples were excluded from well - Hydropunch® comparison.

At each well location, then, three ground-water samples were collected: one Hydropunch® sample from each of two boreholes at depths approximately opposite the midpoint of the adjacent well's screen and one sample from the monitoring well. A summary of the sample collection details is shown in Table 11. For the purposes of these comparisons, only the five principal VOC contaminants found in southeast Rockford were analyzed (TCA, TCE, DCA, DCE, and c12DCE). Subsequent examination of these data provided an ability to not only compare Hydropunch samples with well samples, but also Hydropunch® samples with each other. This gave us some insight on the repeatability, or reliability, of the Hydropunch device.

Analysis of Data

The resulting VOC concentration data were scrutinized principally in two ways. Three simple scatter plots were made for each of the five compounds: monitoring well vs. Hydropunch® 1, monitoring well vs. Hydropunch® 2, and Hydropunch® 1 vs. Hydropunch® 2. These were inspected visually and linear regressions were performed to examine the best straight-line fit to the data and to compute the linear coefficients of correlation (i.e, R^2).

The data were also examined to determine if differences in sampling technique were statistically significant. With only 12 data pairs maximum available for comparison (as well-site 24 was not used), it was sometimes difficult to determine if the data were normally distributed; however, for most cases, histograms of the data clearly revealed the data were not normally distributed. For this reason, a nonparametric test, the Wilcoxon Signed-Rank test, was used. Again, the data were paired (i.e., monitoring well and Hydropunch® 1, monitoring well and Hydropunch® 2, and Hydropunch® 1 and Hydropunch® 2) only in this case, the differences between sample results were used (e.g., monitoring well result - Hydropunch® 1) The Wilcoxon test was used to check the null hypothesis that there was no difference between sampling techniques.

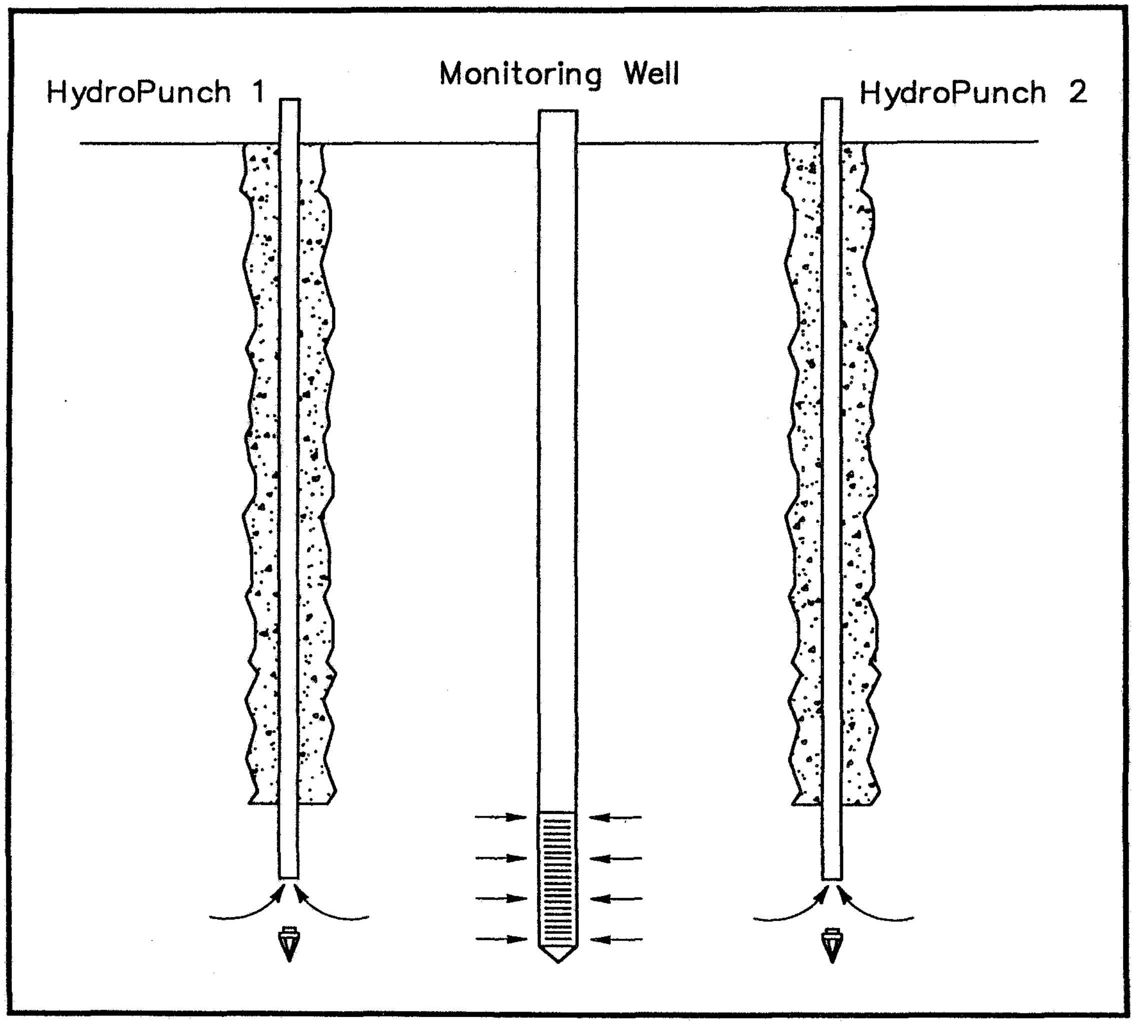


Figure 19. Schematic of monitoring well - Hydropunch comparison field setup.

Table 11. Monitoring Well - Hydropunch® Sampling Details

Sample Location	Date	Sample Deptk (ft.)*	Depth to Water (ft.)
MW15	8/92	45-50	41
HP15-1		45.5	
HP15-2		45.5	
MW16	8/91	40-45	26
HP16-1		40.5	
HP16-2		40.5	
MW17	8/91	40-45	26
HP17-1		41	
HP17-2		41	
MW20	8/91	50-55	30
HP20-1		49.5	
HP20-2		49.5	
MW21	8/91	40-45	27
HP21-1		40.5	
MW24	8/92	42-47	31
HP24-1		60.5	
MW30	8/92	46-51	34
HP30-1		47.5	
HP30-2		47.5	
MW31	8/92	55-60	29
HP31-1		58	
HP31-2		56.5	
MW32	8/92	45-50	33
HP32-1		46.5	
HP32-2		45.5	
MW35	8/91	40-45	28
HP35-1		41	
HP35-2		41	
MW37	8/92	40-45	26
HP37-1		41.5	
HP37-2		41.5	
MW39	8/92	46-51	35
HP39-1		47.5	
HP39-2		47.5	
MW42	8/92	50-55	34
HP42-1		51.5	
HP42-2		51	

* Sample depths tor monitoring wells are given as screened intervals.

For our data, the following procedures were used to compute information for the Wilcoxon test. First, for each of the five principal VOC compounds, the differences between analytical results for each well site were computed. For example, for TCE, the differences between monitoring well results and Hydropunch 1 results were computed for each well site. The resultants were then ranked from lowest value to highest without regard to sign (that is, by the absolute value or the magnitude of the difference). Next, the value of the ranks of all the positive values were added and likewise for the values of the ranks of all the negative values. If the differences in values were random, we would expect the sum of the positive ranks to be about the same as the sum of all the negative ranks, which is the null hypothesis, H_O. A statistical table of critical values of W (using an $\alpha = 0.05$) for the number of ranked pairs was used to determine statistical significance. For an $\alpha = 0.05$, a rejection value for Z of 1.96 was found; Z values greater than 1.96 signify rejection of the null hypothesis. If the water sampling data did not indicate that significant differences existed between the two sampling techniques, the null hypothesis could not be rejected and the techniques were accepted as insignificantly different.

Aquifer Solids Sampling

VOCs pose problems to environmental characterization efforts, particularly when they are present with contaminated solids (Mackay *et al.*, 1985). Characterization approaches have often been focused on VOC presence in soil gas and water to *estimate* the spatial extent of VOC contaminant *influences* on the subsurface. However, in order to identify the *VOC source* distributions (i.e., the long-term problem), it is essential to focus on the free product and sorbed VOC phases which through dissolution and desorption will continue to yield mobile contaminant for decades (Gillham and Rao, 1990; Ball *et al*, 1992).

To date, most sampling and analytical methods which minimize sample transfer, handling, and VOC losses have focused on soil gas and water sample screening. More attention should be placed on contaminated solids since the bulk of the contaminant mass may often reside in the solid and free product phases (Ball *et al.*, 1992; Siegrist and Jenssen, 1990). The need is particularly acute for the field preservation of solid samples after screening for more quantitative, complete laboratory determinations of contaminant breakdown product mixtures.

One of the major emerging research directions deals with immediate preservation of VOC samples with the extraction solvent used for more detailed laboratory analysis. Bone (1988) published an application of this type of method (methanol preservation of solids samples) which essentially begins the analytical process in the field. This approach affords the possibility of more meaningful VOC analyses on heterogeneous materials. His work included sampling, field preservation, and analyses of thirteen chlorinated and nonchlorinated VOCs in soils. For 12 of 13 compounds, the methanol-preserved samples consistently showed several orders of magnitude greater concentration than bulk samples held for subsequent purge and trap analyses. These observations have been supported by the work of a number of other groups (Maskarinec and Moody, 1988; USEPA *et al.*, 1993).

For this study, split-spoon core samples were collected in boreholes adjacent to the mid-points of four of our monitoring wells. The selected well locations were wells 15, 31, 32, and 37. The work was conducted simultaneously to our investigations on monitoring well - Hydropunch® comparisons (see previous section). Duplicate samples were preserved by two different methods: a) field preservation in a bulk sampling jar with ~75% (v/v) methanol and b) placement in a similar bulk sampling jar (with no methanol) and refrigeration at 4°C (Hewitt *et al.*, 1992). Samples were transported back to the laboratory for subsequent analysis.

Analytical Procedures

VOC analytical protocols following the preliminary November 1990 sampling date were those described in Barcelona *et al.*, (1993). The principal difference between the protocols for the first sampling date versus those which followed for two years was that flame-ionization detection (FID) was used for gas chromatography. Thereafter (i.e., 1/91-9/92), simultaneous photoionization (PID) and Hall electrolytic conductivity (HECD) detectors were used for the VOCs. In all sampling events, laboratory calibration standards, field spiked sample duplicates, lab, and field blanks were analyzed along with the samples. All samples, field-spikes and blanks were analyzed in duplicate. Each standard blank or split-sample, prepared for gas chromatography analysis, was spiked with an internal standard before being sealed in the static headspace (Tekmar 7600) vials. After every ninth sample, a lab standard was run to check for detector sensitivity or retention time drift over the course of the analytical process. Retention time, peak identification, and quantitation of individual compounds was done with the Varian Star Chromatography Data System. Participation of the Western Michigan Water Quality Lab (WQL) was maintained in the USEPA Water Pollution Performance Studies coordinated by the Development and Evaluation Branch, Quality Assurance Research Division - Environmental Monitoring System Laboratory - Cincinnati, Ohio.

Field analytical determinations of pH, temperature, specific conductance, and dissolved oxygen were done with a prototype Purge-Mizer® (QED, Inc.) flow cell equipped with a multifunction probe. The probe was calibrated for each day of sampling activities with appropriate standards in the field. Wet chemistry colorimetric and titrimetric determinations of geochemical parameters (e.g., O_2, Fe^{2+}, $PO_4^{\equiv}$, NH_3, NO_3^-, NO_2^-, alkalinity, silicate) were done in the field with a Chemetrics field laboratory kit.

Spatial and Temporal Variability

Analyses of spatial and temporal trends in the quarterly sampling results were designed to evaluate various available statistical techniques and their sensitivity to the density of sampling points and the accuracy/precision of the data. An emphasis on the use of statistical packages which were relatively user-friendly and provided confidence levels on spatial mass or concentration estimates was identified at the outset. The overall objective was to indicate cost-effective strategies for the design of site characterization efforts of practical application by professionals.

Natural Variability and Error Control

The basis for spatial analysis of the VOC contaminant distributions in groundwater relied on an overall evaluation of the errors involved in sampling and analysis relative to natural variability in contaminant concentrations. These sources of variability were assumed to be physically independent so that their corresponding normalized variances could be used to determine individual contributions to the total variability in samples. This method had been employed in previous investigations of temporal variability (Barcelona *et al.*, 1989b). the source of variance equation is:

$$\sigma^2 \text{ TOTAL} = \sigma^2 \text{ SAMPLING} + \sigma^2 \text{ ANALYSIS} + \sigma^2 \text{ NATURAL}$$

where the contribution of analytical error was evaluated from the precision of laboratory calibration standards in the concentration range of interest. the sampling (or field) error was determined by subtracting the analytical error from the variance calculated from split-samples which has been spiked with known amounts of VOCs. Natural variance contribution was determined by subtracting sampling and analytical errors from the total observed in actual samples over time. This excercise was expected to provide confidence that controllable sources of error could be held constant and provide confidence in subsequent temporal and and spatial concentration analyses.

Temporal Variability Analyses

VOC analyses for the five principal compounds were graphed for each well for all quarters sampled. This allowed us to make general observations regarding temporal changes and possible trends.

Geochemical (Ω^{-1}, pH, temperature, and O_2) and VOC (TCE, TCA, DCA, DCE, cl2DCE) data also were evaluated for temporal change using the Wilcoxon Signed-Rank test on the seven quarterly sampling periods (November 1990, February 1991, May 1991, August 1991, December 1991, March 1992, and September 1992). the test was applied to each of the chemical constituents twice, once for all wells sampled (9 - 48) and again for only those wells completed within the depth range of 15 to 18 meters. This latter set excluded wells 10, 11, 13, 14, 18, 25, 26, 28, 29, 40, 41, 43, 45, and 46.

The Wilcoxon test was also used to compare data collected approximately one year apart. Several sets of data were used for this analysis: November 1990 to December 1991, February 1991 to December 1991, and August 1991 to September 1992. Analyses of the significance of differences were calculated for the geochemical parameters Ω^{-1}, O_2, and pH and the five principal VOCs.

Spatial Variability Analyses

Investigations of spatial variability were performed principally through structural (variogram) analyses of the quarterly TCA sampling data. TCA lent itself to suck analysis because it was present in nearly all the wells sampled and it was present in concentrations well above the detection limit for most wells, thus allowing for enough data points in our analysis. As expected, exploratory data analysis (histogram and probability plots) indicated the TCA data from each sampling period were lognormally distributed. A natural log transformation was found to adequately normalize the TCA distributions. All subsequent analyses were conducted with the natural log-transformed data. For "non-detect" samples, a value of 1 μg/L was substituted because zero cannot be log-transformed.

Structural analyses of the natural-log transformed data were difficult due to the small sample size (in geostatistical terms) and the amount of noise in the data set (which is typical and expected with VOCs). Another complicating factor was that the correlation scale appeared to be around 1000 feet and most of the monitoring wells are separated by a greater distance than this. This means that there is little information available to define the sample semivariogram within the correlation scale. While it may be viewed that the experimental semivariograms have no spatial correlation, we feel that the slight deflections that appear in our experimental semivariograms are in fact showing spatial correlation. This correlation was readily supported in the domestic well data where there were many wells that were spaced less than 1000 feet apart.

To conduct interpolation via kriging, the spatial correlation was characterized, or fit by a theoretical model to our experimental data. In general, an exponential model was assumed for each quarter. Kriging was performed (with the natural-log transformed data) on a 38 x 20 grid (250ft centers). After interpolation, the block-by-block concentration values were back-transformed prior to contouring. This process produced five contour maps for the quarterly data May 1991, August 1991, December 1991, May 1992, and September 1992. The kriging standard deviation was also contoured; however, the values were reported in natural log space due to the complexities of back-transforming variances.

Temporal Variability in Spatial Variability

To examine temporal variability in the plume more rigorously than visual inspection of the contour maps, two approaches were taken. First, the time series (across the five sampling periods) of interpolated values at each of the 38 x 20 blocks were analyzed. A contour map of the standard deviation of interpolated concentration at each block was subsequently produced. This provided a map of the locations where the most variability was encountered.

Second, the jackknife approach was used to estimate confidence limits on the quarterly TCA sample semivariograms. Detection of temporal changes in the spatial correlation of ground-water quality through direct comparison of experimental semivariograms is difficult due to the uncertaintly in sample semivariograms constructed from field data. Using the jackknife approach to estimate the confidence limits, examination of the "spread" of those confidence limits about the semivariograms can provide insight on temporal variations in spatial variability.

Shafer *et al.*, (1989) discussed the jackknife technique for developing confidence limits on a sample variogram of shallow ground-water nitrate data. The computational aspects of the technique were described in more detail by Shafer and Varljen (1990). In our study, we applied the jackknife technique to the quarterly TCA data as well as to the TCA data compiled from the two domestic well samplings of over 200 wells in December 1989 and July 1990. The number of wells in those two sampling periods were pared down to the 59 wells that were common to both samplings.

RESULTS AND DISCUSSION

Hydrogeologic Investigations

Ground-Water Levels and Precipitation

Hydrographs or wells 12, 16, and 18 located in the west, central, and eastern sections of the intensive study area, respectively, are shown in figure 20. Appendix D contains water level data and hydrographs for all the SE Rockford monitoring wells. These hydrographs reveal a very gentle reaction to precipitation patterns (figure 21) and a very close relationship to one another (i.e., a rise in one well is mimiced by rises in other wells). This was generally true across the study area and is revealed most particularly by contour maps of the potentiometric surface. Figures 22 - 27 present potentiometric (water table) surfaces of the shallow sand and gravel aquifer for May 1991, August 1991, October 1991, March 1992, May 1992, and September 1992, respectively. These maps clearly show the east to west movement of ground water beneath the study area; the influence of the Rock River as a regional ground-water discharge zone just off the western edge of these figures is evident. Ground-water elevations generally fall about 18 feet, from 710 feet (MSL) on the east to 692 feet on the west, for all measurement periods. As shown by the hydrographs and as would be expected for this wide-spread sand and gravel system, water levels rise and fall in unison creating only minor changes in the pattern of ground-water movement.

Hydraulic Gradients

Figures 22-27 show a flattening of the water table surface as the land surface topography falls from the uplands to the river floodplain. Hydraulic gradients generally decrease from approximately 0.0041 ft/ft (as ground-water elevations fall from 710 to 702 feet) to 0.0010 ft/ft (as ground-water elevations fall from 698 to 692 feet).

To obtain a better quantitative appraisal of changes which occurred in the hydraulic gradients over the study period, a unique map of the mean hydraulic gradients and standard deviations of those gradients was created (figure 28). This map was created by calculating means and standard deviations of hydraulic gradients (magnitudes and directions) for the triplets (three-well groupings) shown in figure 15. Three lines were drawn emanating from the center of gravity of each triplet. The center line represents the mean magnitude and direction of the hydraulic gradient for that triplet computed from all the mass water level measurements taken over the study period. The two outside lines represent the values of the standard deviations (in magnitude and direction). The lengths of the lines represent the mean plus one standard deviation and the mean minus one standard deviation. The angle of the outer two lines represent the spread in the mean direction by one standard deviations.

Several things become apparent in examining this summary hydraulic gradient map (figure 28). First, the direction of the gradients is generally west-northwesterly and, for most of the triplets, changes in direction and magnitude are very small (i.e., each three-line grouping is very narrow and

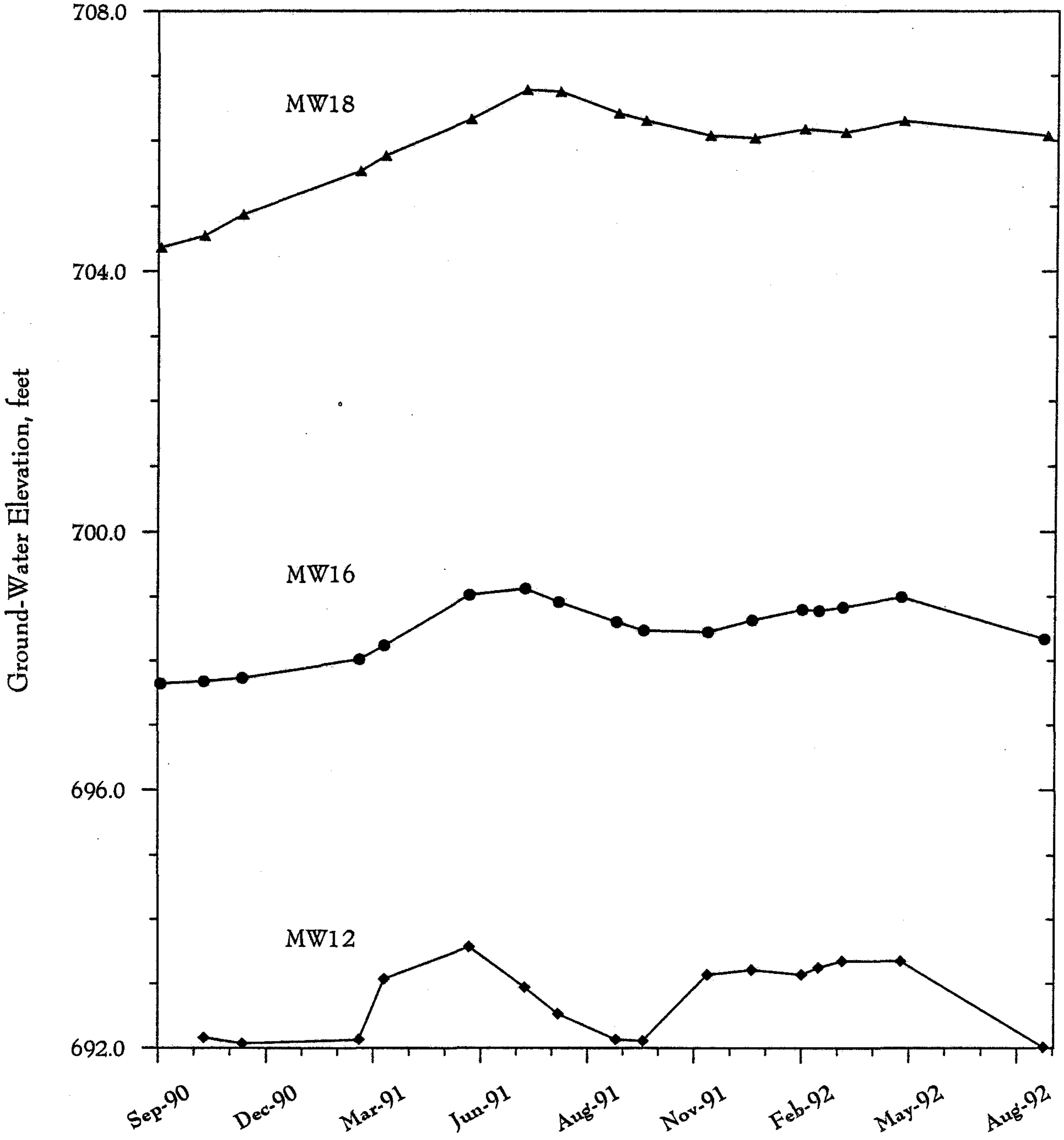


Figure 20. Ground-water hydrographs for monitoring wells 12, 16, and 18, September 1990 - September 1992.

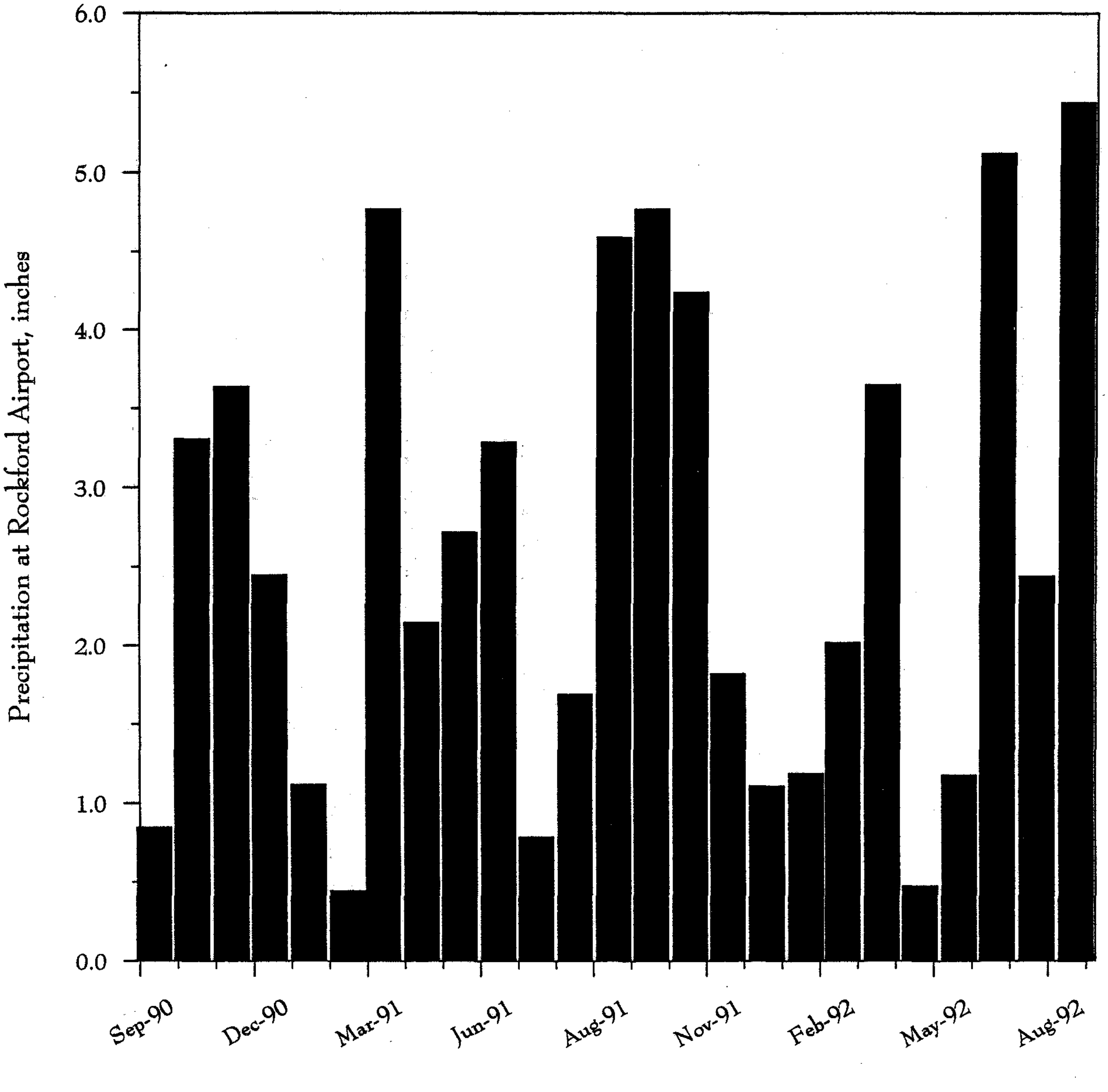


Figure 21. Monthly precipitation at the Rockford Airport, September 1990 - September 1992.

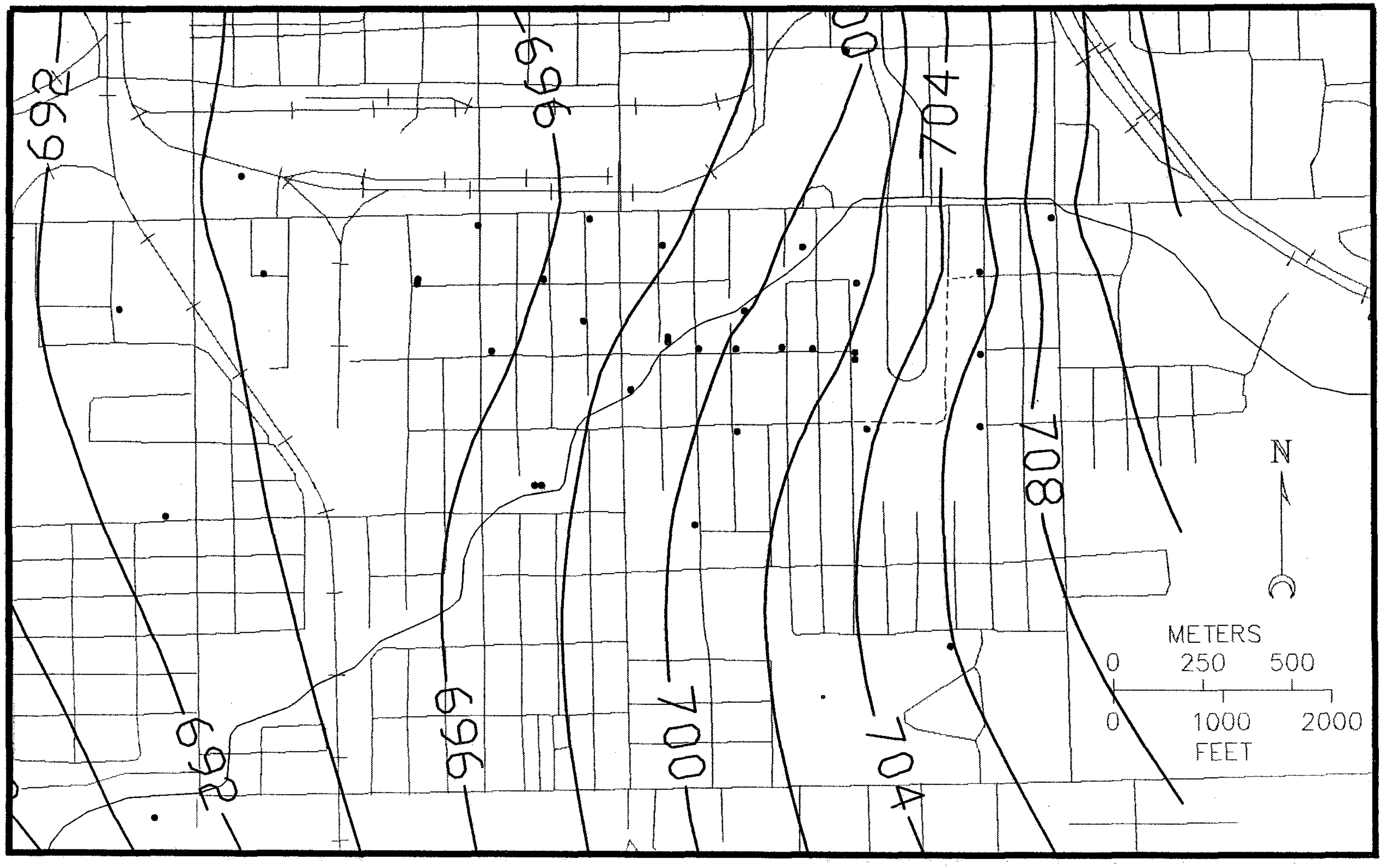


Figure 22. Potentiometric surface for May 1991.

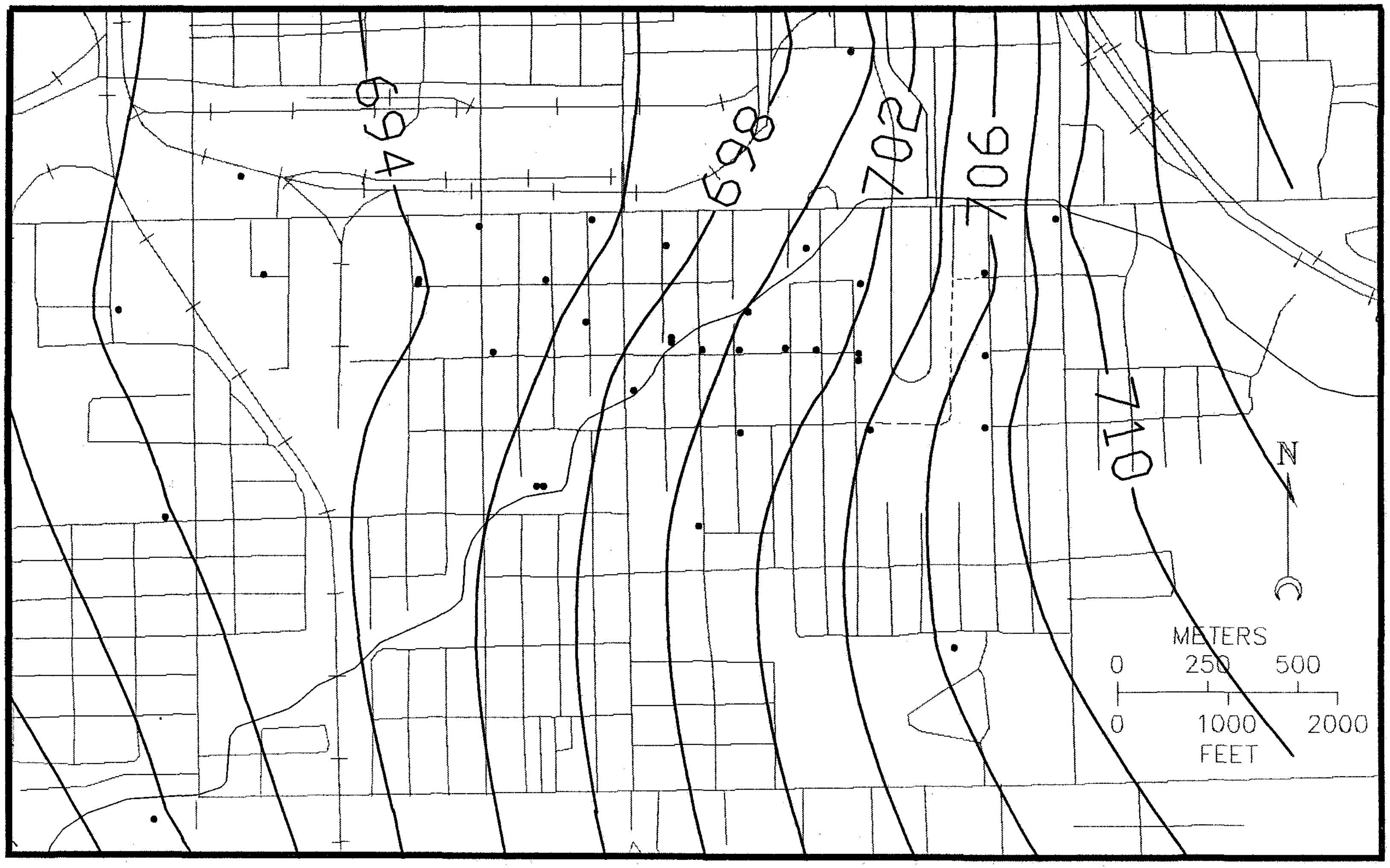


Figure 23. Potentiometric surface for August 1991.

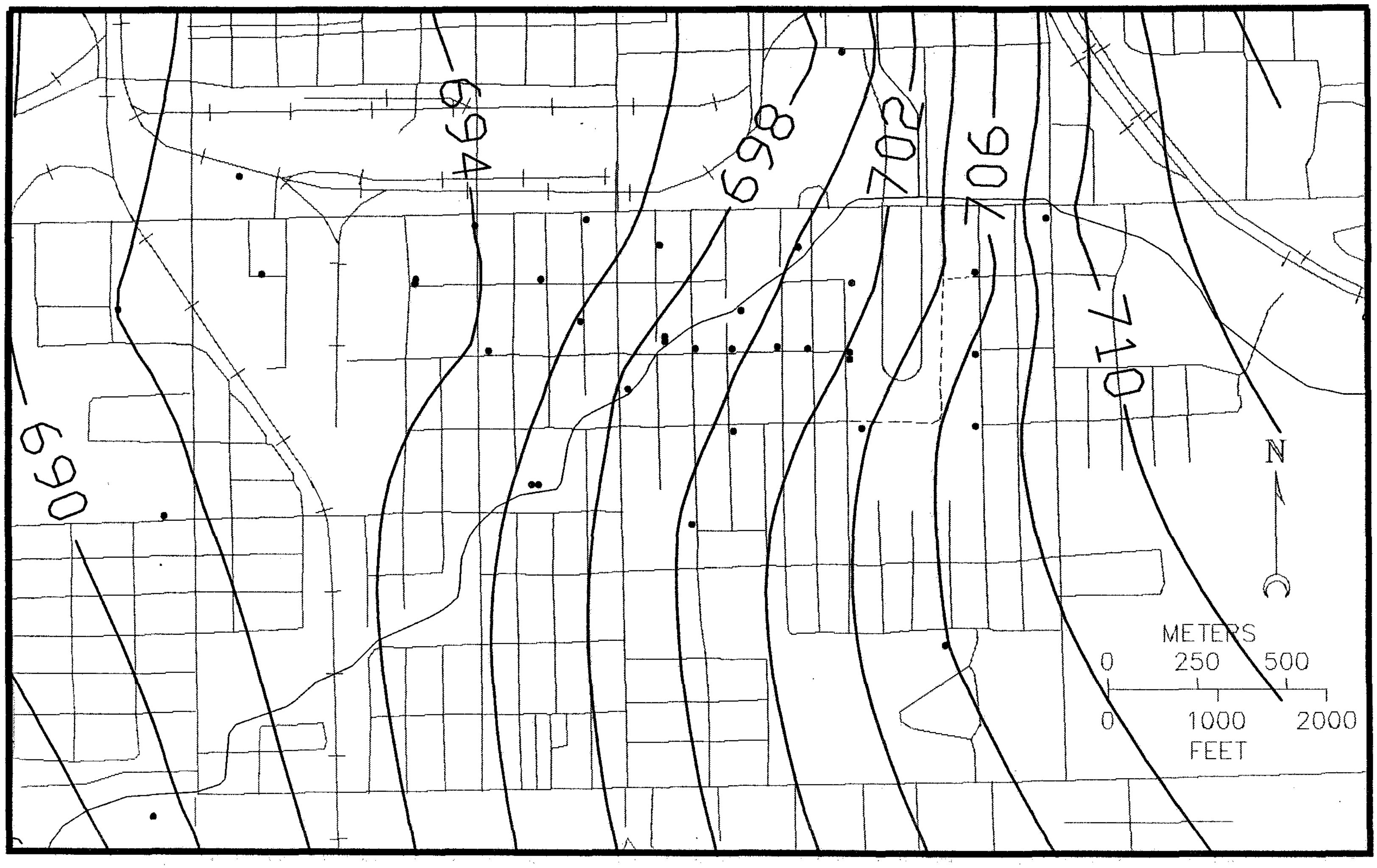


Figure 24. Potentiometric surface for October 1991.

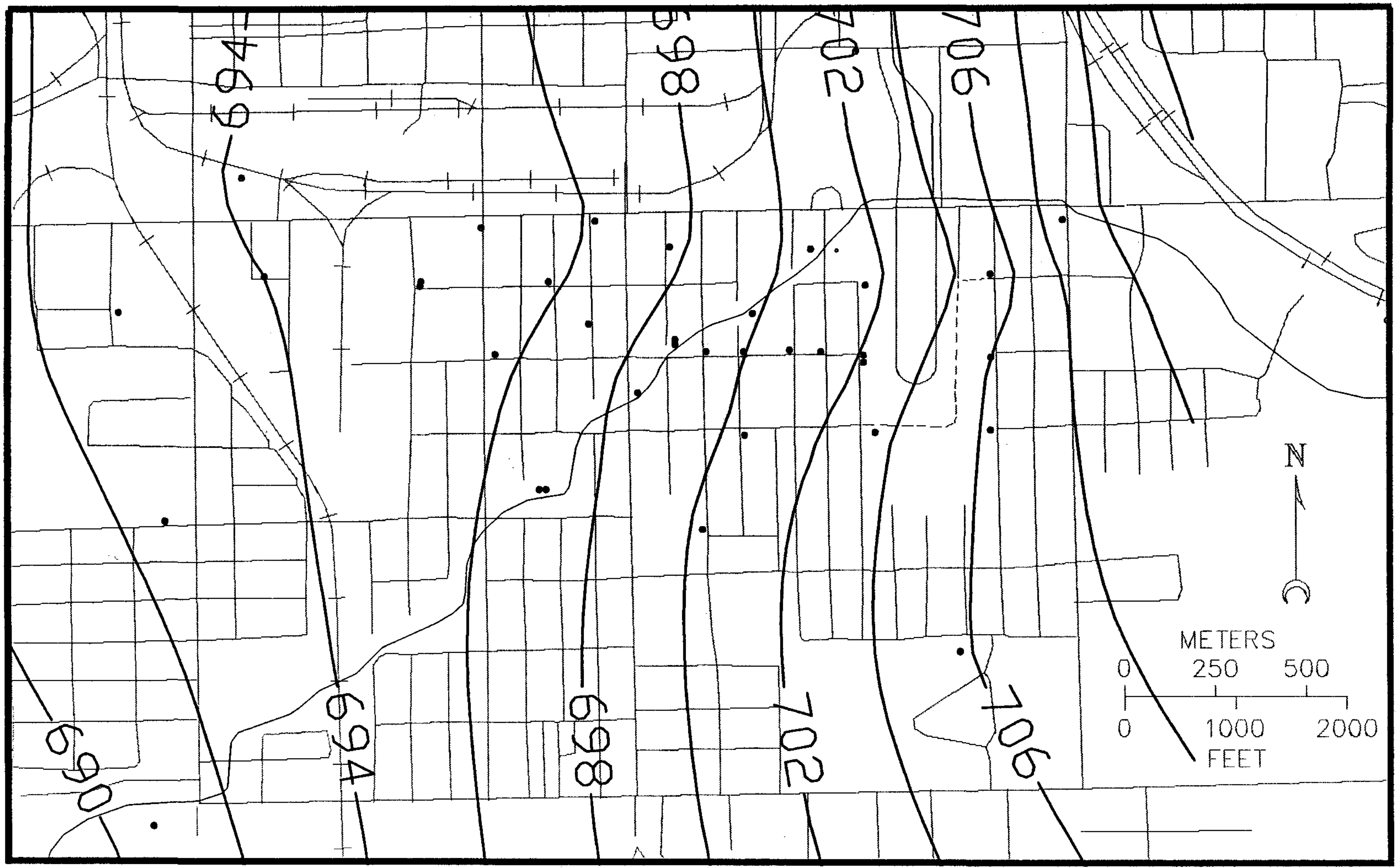


Figure 25. Potentiometric surface for March 1992.

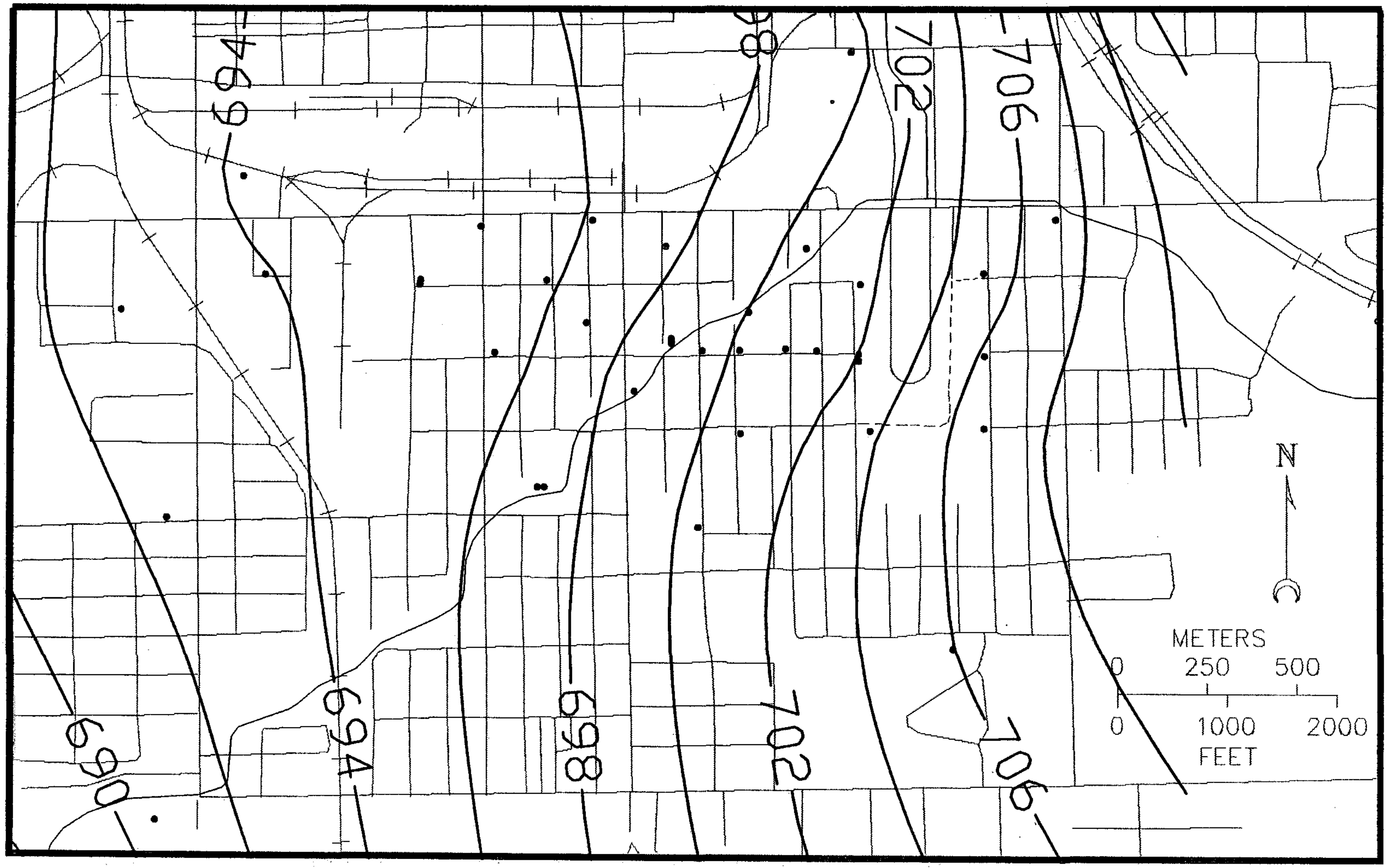


Figure 26. Potentiometric surface for May 1992.

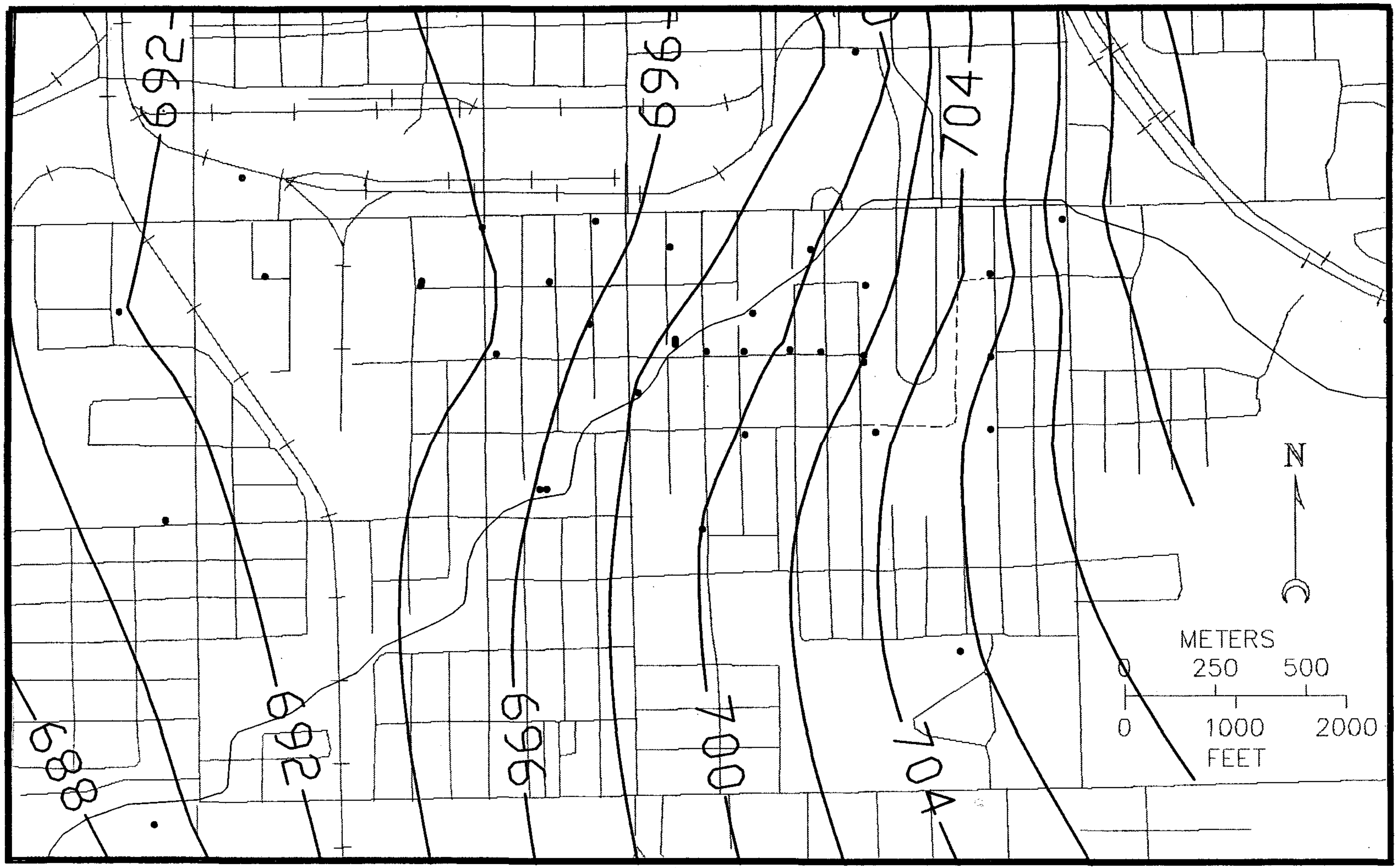


Figure 27. Potentiometric surface for September 1992.

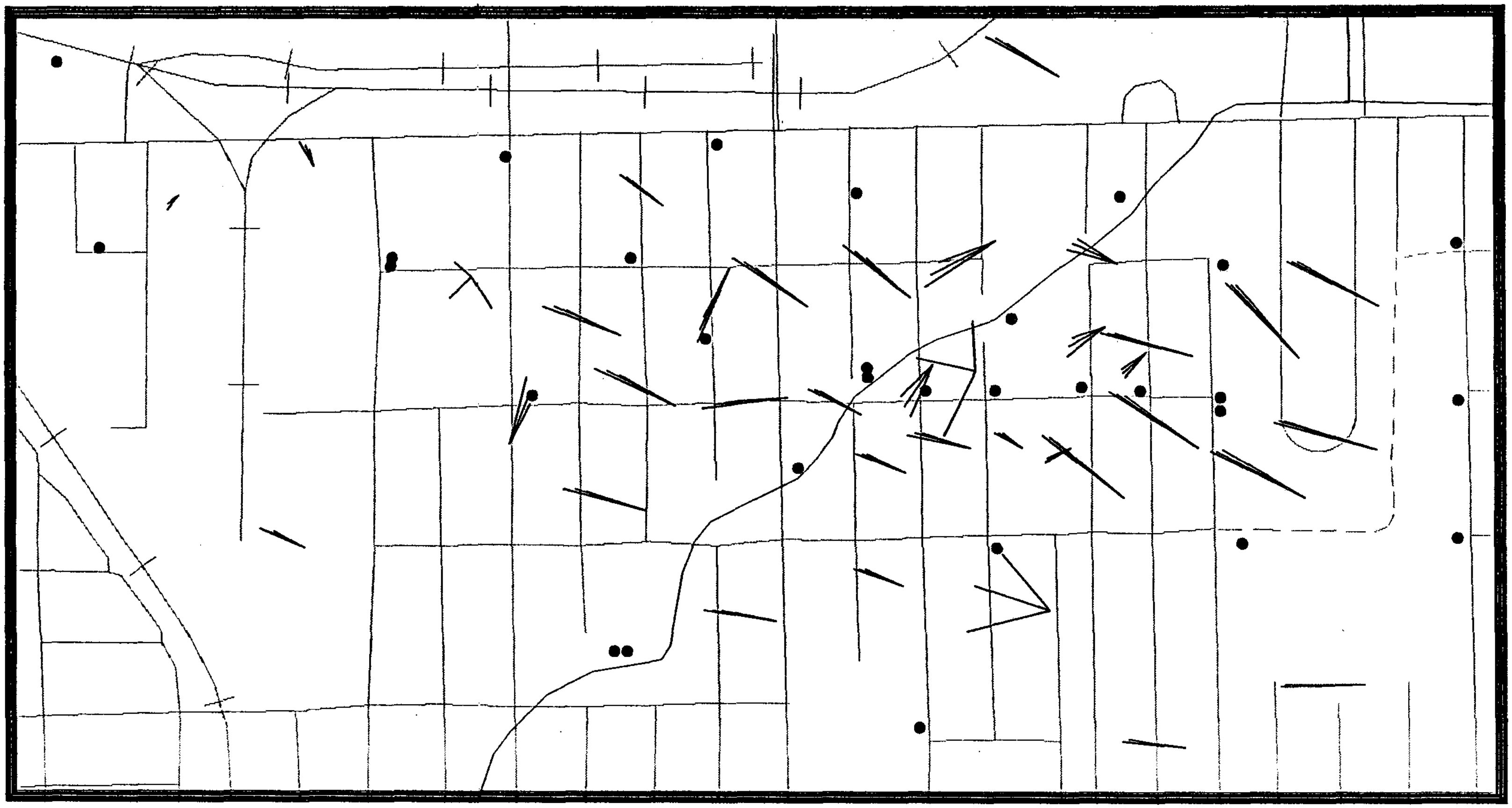


Figure 28. Mean and standard deviation of hydraulic gradients in an enlarged view of the intensive study area.

does not change greatly in length). A few three-line groupings don't make sense in terms of the orientation of their direction; several three-line groupings (using wells 32-33-34; wells 17-32- 34; wells 16-17-37; wells 29-30-40; wells 33-34-36, and wells 38-39-42) were likely to be artifacts of the shape of the triplets. In suck instances, minor perterbations or errors in water level measurement can create large swings in apparent ground-water flow direction. However, large spreads in direction are apparent in triplets 17-35-37, 24-27-36, and 20-30-40. Directional variations in triplet 20-30-40 are readily apparent as the 694' contour migrates back and forth through the triplet. Such directional variations can give rise to temporal and spatial variability in transported contaminants.

Hydraulic Conductivity

Results of hydraulic conductivity analyses are summarized in Table 12. Where possible, comparisons Between slug test solutions by the Bouwer & Rice and Springer methods were made. A graph of the comparison is presented in figure 29. As mentioned previously, because the Bouwer & Rice solution does not account for momentum effects, the solution will tend to overestimate the hydraulic conductivity especially as hydraulic conductivities increase. Ratios of K_{BR} to K_s (see Table 12) range from 0.63 to 1.62 (although the 0.63 ratio was for very small values of K and is probably subject to measurement error). As suggested, the larger ratio values tend to be for greater K-values, in this case, in excess of 1000 gpd/ft^2 (4.72xl0^{-2} cm/sec).

A contour map for the hydraulic conductivity within the intensive study area is shown in figure 30. The map was produced by kriging log-transformed values of K and back-transforming the kriged estimates for mapping. A map of the estimate of the kriged error is presented in figure 31. The K-map shows an area of increasing hydraulic conductivity in the western half of the study area. This is most probably due to a coarsening of the sand and gravel deposits within the deeper portions of the Rock River bedrock valley.

Preliminary Sampling and Error Analysis

Preliminary Sampling

Five existing wells (i.e., 2, 4, 7, 8, and 12) were sampled in April of 1990 to begin the evaluation of sampling and analytical methods to be used in the project and to provide information on general water quality conditions. Tables 13 and 14 present data on the VOCs and selected water quality parameters for the five wells. Although these wells were on the periphery of the intensive study area, all wells showed evidence of TCA contamination. In general, total VOC concentrations were low (i.e., <50 ppb). However, wells 4 and 8 showed slight evidence of gasoline contamination with detections of toluene (~0.2 ppb) and ethylbenzene (~0.23 ppb), which had not been previously reported in the area. The duplicate analyses (well 7) were quite reproducible despite the fact that the analytical instrumentation was not optimized for the chlorinated VOCs. Levels of metals associated with contamination (e.g., Cu, Cd, Pb) were in the low ppb range confirming the results of previous studies by Wehrmann *et al.,* (1988).

Table 12. Results of Hydraulic Conductivity Analyses

Well No.*	Depth (feet)	Date Drilled	Aquifer Type	Date Tested	DTW Tes	Water Height Over Screen	Effective Length	Aquifer Thickness	K(Springer gpd/sq ft)	K Bouwer-Rice (gpd/sq ft)	K *br*/K *s* ratio	Comments'*
1	87.5	11/87	Sand	9/90	39.1	43.4	45.9	146			ERR	C: F=2.05 poor str line
2	52.5	11/87	Sand	9/90	40.3	7.2	9.7	145	590	730	1.24	O:B&R C? 2 tests
3	92.5	11/87	Sand	8/89	45.2	42.3	44.8	195	850		0.00	O:B&R C? 2 tests
4	52.5	11/87	Sand	9/90	44.0	3.5	6	196	690		0.00	O:B&R, 1 test
5	125	11/87	Sand	9/90?	40.6	79.4	81.9	144			ERR	U:S, 4 tests
6	125	11/87	Sand	8/89	45.1	74.9	77.4	195	880	—	—	U: F = 1.3-1.4, 2 tests
7	62.6	10/89	Sand	12/89	40.0	17.6	20.1	260	770	820	1.06	O:B&R, 3 tests
8	32.57	10/89	Sand	12/89	20.2	7.37	9.9	210	220	250	1.14	O:B&R, 3 tests
9	49.88	10/89	Silty Sand	9/90	22.0	22.88	25.4	198	2	1.25	0.63	O:B&R, 1 test
10	22.3	10/89	Till	—	—	—	—		—	—	—	No test performed
11	25.39	10/89	Till	7/91	20.0	0.39		?	22		0.00	O:B&R, 1 test
12	57.55	10/89	Sand	9/90	38.8	13.75	14.7	256	620	650	1.05	O:B&R, 2 tests
13	96.08	7/90	Clay?	9/90	41.2	49.88	52.4	84	17	12	0.71	0:B&R, 1 test
14	25.03	7/90	Till	—	—	—	—	95	—	—	—	No test performed
15	51.48	7/90	Silty Sana	9/90	42.9	3.58	6.1	27	115	170	1.48	O: F=47, 1 test
16	47.78	7/90	Sand	9/90	30.4	12.38	14.9	150	660	660	1.00	O: F=4, 2 tests
16A	47.78		Sand		29.13	13.65	16.15	150	810	855	1.06	O: F = 3.6, 3 tests
17	45.28	7/90	Sand	9/90	28.3	11.98	14.5	97	*580*	650	1.12	O: F=4.3, 2 tests
17A	45.28		Sand		26.63	13.65	16.15	99	860	950	1.10	O: F = 3.4, 3 tests
18	73.9	7/90	Sand	9/90	66.2	2.7	5.2	29	230	365	1.59	O: F=18, 2 tests
19	49.53	7/90	Silty Sand	9/90	36.9	7.63	10.1	198	350	450	1.29	O: F = 9, 2 tests
20	53.6	7/90	Sand	9/90	30.3	18.3	21.6	220	840	910	1.08	C? F=2.07-2.9, 3 tests
21	46.68	10/90	Sand	7/91	27.2	14.48	17.0	148	870	910	1.05	O: F=3.2, 2 tests
21A	46.68		Sand		27.39	14.29	16.79	148	1360	1890	1.39	C? F=2.1, 3 tests
22	45.5	10/90	Sand	7/91	29.5	11	13.5	81	760	840	1.11	O: F=4, 3 tests
23	60.44	10/90	Sand	7/91	35.1	20.34	22.8	40	450	450	1.00	O: F=5., 2 tests
24	42.88	10/90	Sand	7/91	31.0	6.88	9.4	104	250	310	1.24	O: F = 15, 3 tests
25	40.24	10/90	Sand	7/91	19.7	15.54	18.0	240	670	730	1.09	O: F= 3.9, 3 tests
26	72.27	10/90	Sand	7/91	53.5	13.77	16.3	62	440	470	1.07	O: F = 6.3, 2 tests
27	61.88	10/90	Sand	7/91	48.9	7.98	10.5	41	350	410	1.17	O: F= 10.2, 3 tests
28	99.34	10/90	Sand	7/91	72.4	24.44	25.7	48	56	55	0.98	O: F = 58, 2 tests

Table 12 (continued). Results of Hydraulic Conductivity Analyses.

Well No.*	Depth (feet)	Date Drilled	Aquifer Type	Date Tested	DTW Tes	Water Height Over Screen	Effective Length	Aquifer Thickness	K Springer (gpd/sq ft)	K Bouwer-Rice (gpd/sq ft)	K br/ K s ratio	Comments**
29	36.86	10/90	Sana	7/91	21.2	10.66	13.2	199	900	1100	1.22	O: F=3.5, 3 tests
30	50.32	10/90	Sana	7/91	33.4	11.92	14.4	227	665	770	1.16	O: F=4.4, 3 tests
31	62.48	5/91	Sana	7/91	28.8	28.68	31.2	151	620	560	0.90	O: F=3.1, 2 tests
32	49.98	5/91	Sana	7/91	32.4	12.58	15.1	43	1140	1460	1.28	C? F=2.5, 3 tests
33	46	5/91	Sana	7/91	34.8	6.2	8.7	50	860	1150	1.34	O: F=4.5, 3 tests
34	44.61	5/91	Sana	7/91	33.1	6.51	9	67	660	860	1.30	C? F=2.4, 3 tests
35	44.79	5/91	Sana	7/91	28.0	11.79	14.3	102	1250	1750	1.40	C? F=2.4, 3 tests
35A	45		Sana		28.14	11.86	14.36	102	1110	1290	1.16	C? F=2.85, 3 tests
36	49.84	5/91	Sand	7/91	31.8	13.04	15.5	78	900	1060	1.18	C? F=3.1, 3 tests
37	44.24	5/91	Sana	7/91	25.7	13.54	16.0	139	1150	1620	1.41	C? F=2.4, 3 tests
38	48.9	5/91	Sana	7/91	31.6	12.3	14.8	173	590	630	1.07	O: F=4.9, 3 tests
39	50.97	5/91	Sana	7/91	34.2	11.77	14.3	206	1010	1260	1.25	C? F=2.9, 3 tests
40	65.5	5/91	Sana	7/91	28.3	32.2	34.7	242	1800	—	—	U:S (F = 1.1)
41	85.44	5/91	Sand	7/91	28.4	47.04	52.0	242	1700	—	—	U:S (F=0.6)
42	53.8	5/91	Sana	7/91	33.7	15.1	17.6	220	1200	1940	1.62	C? F=2.2, 3 tests
43	81.42	5/91	Sana	7/91	40.1	36.32	38.8	265	1200	—	…	U:S (F = 1.4)
44	52.38	5/91	Sana	7/91	39.7	7.68	10.2	40	360	435	1.21	O: F=9.9, 3 tests
45	72.4	5/91	Sana	7/91	40.3	22.1	27.1	40	410	625	1.52	C? F = 3.1, 3 tests
46	75.12	5/91	Sana	7/91	31.1	39.02	29.6	264	2200	—	…	U:S (Fave= 0.95)
47	54.94	5/91	Sana	7/91	43.6	6.34	8.8	261	730	980	1.34	O: F= 5.3, 3 tests
48	50.35	5/91	Sana	7/91	33.4	11.95	14.5	217	1900	—	—	U:S(F=1.57)

* All wells have 5-foot long screens except MW10 & MW28 (2.5-foot) and MW41 & MW45 (10-foot).

** U: Underdamped response; O: Overdamped response; C: Critically damped response; B&R: Bouwer and Rice method; S: Springer method

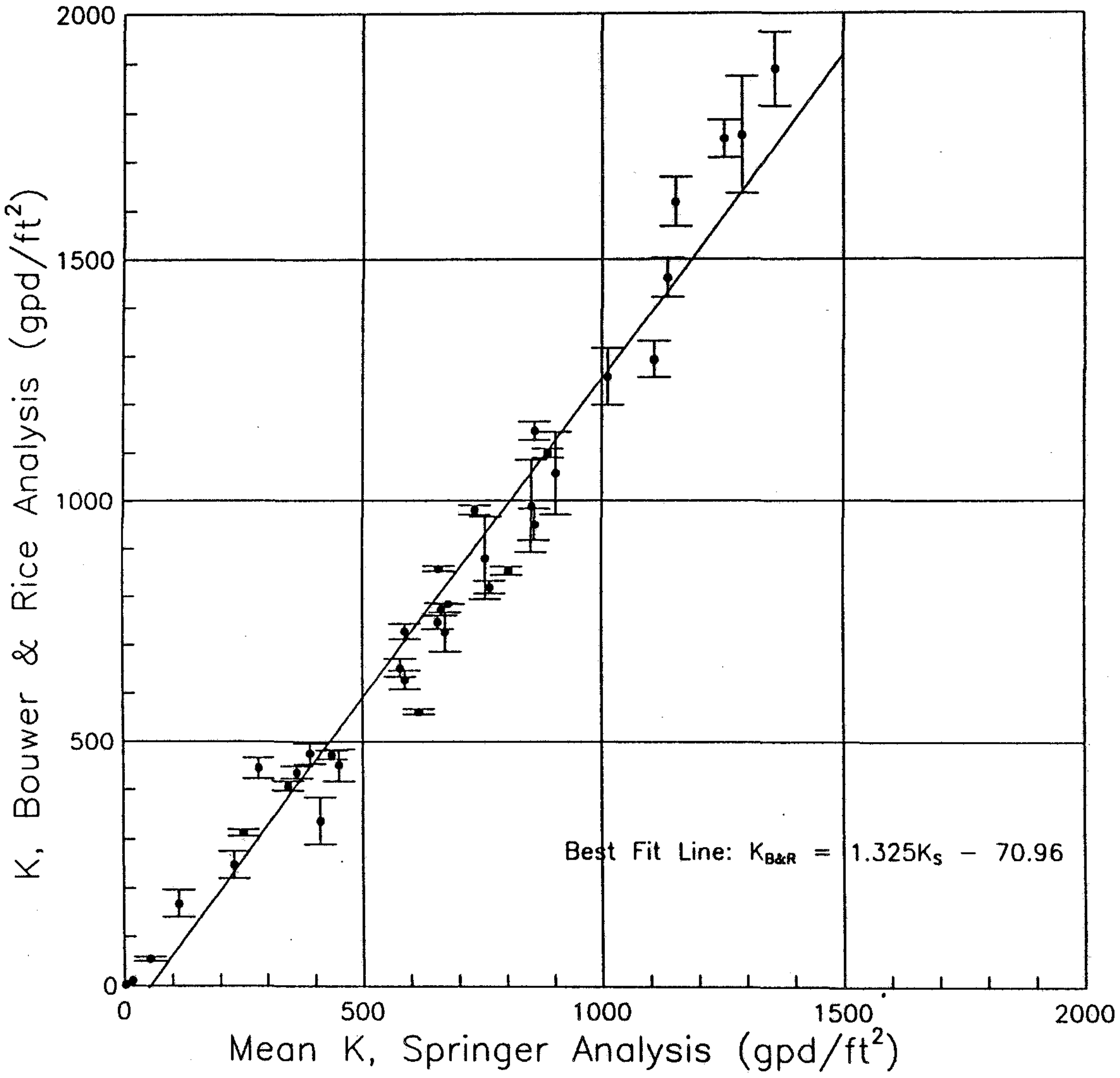


Figure 29. Comparison of hydraulic conductivities determined by Bouwer & Rice (1976) and Springer (1991) solutions. Error bars denote standard deviation of three test results at each well.

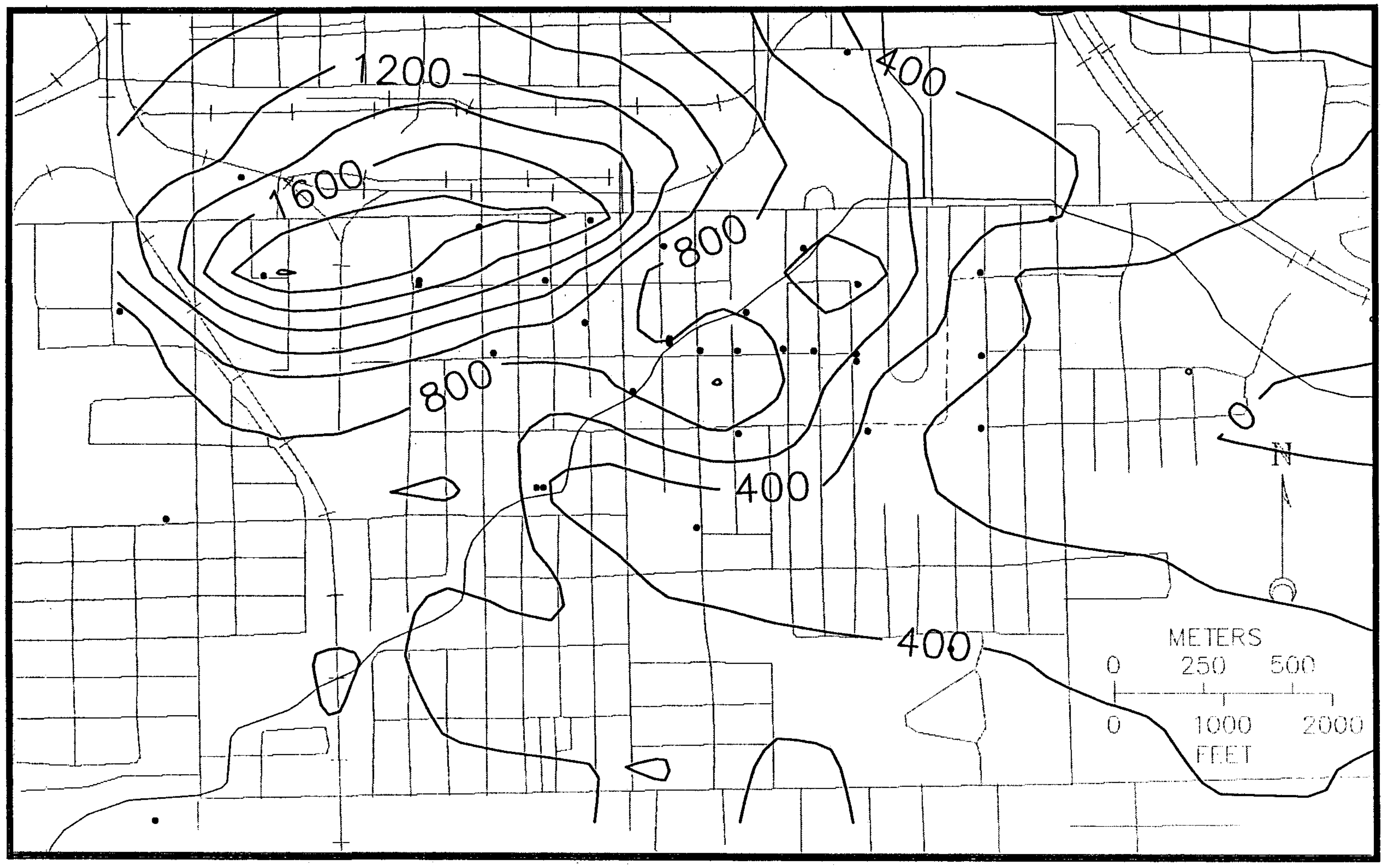


Figure 30. Hydraulic conductivity (in gpd/sq.ft.) in intensive study area.

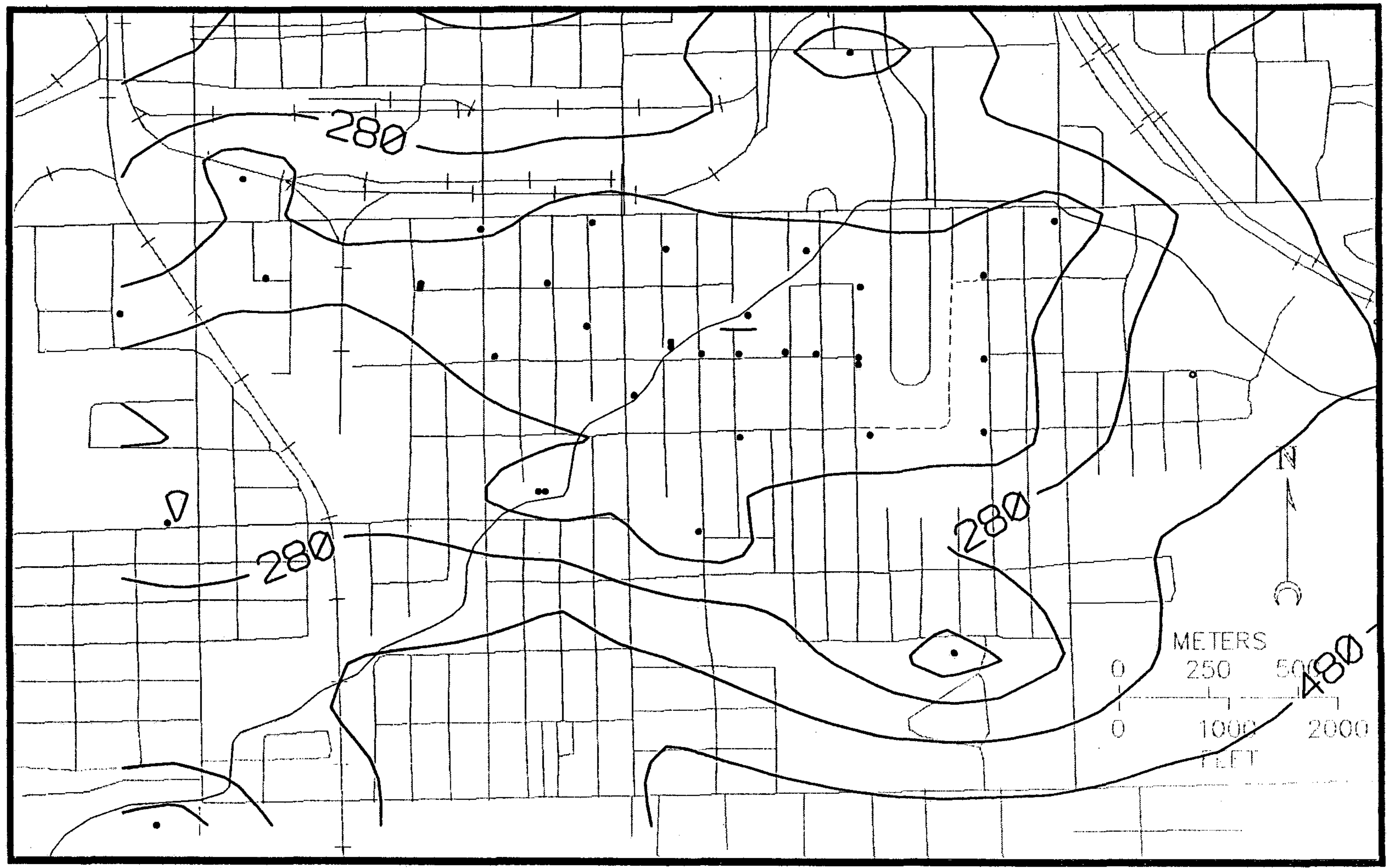


Figure 31. Error (variance) of interpolated (kriged) hydraulic conductivity.

Table 13. Volatile Organic Compounds Detected in Ground Water Sampled on April 17-18, 1990

Well No.	Compound	Concentration µg/L)[a,b]
2	1,1,1 -trichloroethane	15.2
	tetrachloroethene	12.8
	bromodichloromethane	1.82
	dibromochloromethane	21.2
4	1,1,1 -trichloroethane	15.2
	toluene	0.2
7	1,1,1 -trichloroethane	16.2/15.3
	1,3-dichlorobenzene	0.82/0.30
8	1,1,1 -trichloroethane	15.1
	1,1,1,2-tetrachloroethane	0.15
	ethylbenzene	0.23
12	1,1,1 -trichloroethane	14.3

[a] Duplicate concentrations indicate results of duplicate analysis.
[b] Samples were analysed by the Water Quality Laboratory-WMU using a GC-FID method.

Error Analysis

The basis for the interpretation of the spatial and temporal variability in the VOC plume within the intensive study area resides in the control of sampling and analytical error. The quarterly dataset from the study wells together with results for the corresponding analytical standards and duplicate spiked field samples were used to evaluate the percent contributions to error from these sources relative to the overall variability observed in samples. These results are provided in Appendix E for each of the five major VOCs for each well. Table 15 contains an overall summary of percent error contributions for each compound due to analytical, field (i.e., sampling), and natural variability.

Table 14. Metals and Nutrients Determined from Ground Water Sampled on April 17-18, 1990 (concentrations in mg/L)

Well No.	Ca	Mg	Na	K	Mn	Fe	Ba
2	81.2	35.6	26.8	2.38	0.02	0.03	0.04
4	79.1	30.8	28.8	2.96	<0.01	0.01	0.03
7	72.9	45.0	25.2	5.96	0.04	0.04	0.17
8	76.0	35.5	15.6	3.14	0.01	0.01	0.06
12	51.0	17.7	23.2	1.40	0.01	0.53	0.03

Well No.	Cu	Cd	Pb	Zn	Cl	SO_4	NO_3--N
2	0.01	<0.01	0.04	<0.001	50.1	32.1	1.69
4	0.01	<0.01	0.04	0.002	57.2	31.3	8.24
7	0.01	<0.01	0.04	0.003	66.7	44.5	2.42
8	0.01	<0.01	0.04	0.002	23.9	32.9	1.19
12	0.02	<0.01	0.01	<0.001	10.1	9.32	1.07

Well No.	NH_3-N	TDS	Si	TC	IC	TOC
2	0.24	465	7.56	90.9	85.9	5.0
4	0.27	475	8.50	78.6	70.9	7.7
7	0.31	495	6.11	89.5	87.2	2.3
8	0.39	460	9.42	90.5	88.0	2.5
12	0.22	290	6.90	73.6	68.1	*5.5*

TDS: Total Dissolved Solids; TC: Total Carbon; IC: Inorganic Carbon; TOC: Total Organic Carbon

Table 15. Overall Mean, Relative Standard Deviation and Percentage of Total Variance Attributable to Lab or Field (Sampling) Error, and Natural Variability (November 1990-September 1992)

	Overall	Relative	Percent of Total Variability		
VOC (μg/L)	Mean %	(Std. Dev.) %	Lab %	Field %	Natural
TCA	119.5	(36%)	1.29	3.26	95.45
TCE	29.8	(43%)	1.95	12.75	85.30
cl2DCE	45.2	(32%)	1.69	4.72	93.59
DCA	44.3	(28%)	1.02	5.22	93.76
DCE	16.3	(31%)	3.61	4.15	92.24

The data in the table show that overall concentration variability across the intensive study areas for two years was ≤43% over the quarterly datasets. Of this total variability, lab and field error constituted less than ~15% of the error in the final concentration result. These results provide strong evidence that our QA/AC procedures were in control over the study period. Also, they demonstrate that natural variability in VOC contaminant concentrations can be reproducibly observed with the simple sampling protocol used in this work.

Water Quality Conditions

Selected study wells were sampled in December 1991 for VOCs as well as geochemical and water quality parameters (Table 16). Dissolved O_2, pH, temperature (well-°C) and conductance were measured in the field via a flow-cell (QED-Purge Mizer®) while Fe^{2+}, NH_3^+, NO_2^-, NO_3^-, and alkalinity were measured colorimetrically. Metals and other nutrients were determined in the laboratory on field-filtered samples by inductively coupled plasma spectrophotometry and ion-chromatography, respectively.

The results show that general water quality varied substantially across the study site with significant differences in apparent oxidation reduction conditions (e.g., O_2, Fe^{2+} and NH_3) and nitrate levels. However, the nitrate levels were all below water quality standards (e.g., 45 mg/L as NO_3^-). It is worthwhile to note that the shallow wells, finished within 20 ft (6.1m) of the water table, generally showed high dissolved oxygen and low ferrous iron concentrations indicative of oxidizing subsurface conditions. Under these redox conditions, we would not expect that reductive dehalogenation reactions would be favored which would alter the distribution of VOCs. Deeper wells (e.g., 28, 43 and 46) showed much lower O_2 levels and variable Fe^{2+} concentrations which suggest suboxic to

Table 16. Water Quality Results for Geochemical Analytes, December 1991

Well No.	Dissolved O_2	pH	Temp	Spec. Cond	Fe^{2+}	NH_3	NO_2^-	NO_3^-	PO_4^{3-}	SiO_2	Alk.	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe-T	Mn-T
12	5.8	7.51	12.1	483	0	0	0	0	0	0	240								
17	1.4	7.26	1.4	800	0	0	0	4.78	0	13.1	330	36	35.7	93	49.7	22.4	2.56	0.08	0
20	0.28	7.28	13	956	0.05	0.24	0	0	0	21	430	140	5.82	80	43.2	85.2	3.22	0.29	0.36
21	4.2	7.8	11.6	765	0.02	0.61	0.03	7.71	0	16.5	375	21	31.8	90.5	46.7	19.4	1.91	0.014	0
22	0.2	7.24	12.3	781	0	0	0	6.42	0	12.2	350	38	32.8	87.6	43.5	29.4	3.32	0.2	0
28	0.4	7.4	1.1	710	0	0.56	0	2.35	0	11.8	300	16	36.2	88.1	46.1	14.2	1.58	0.005	0
29	4.3	7.36	13.2	724	0	0.27	0	27	0	5.69	310	22	43.8	91.5	44.7	18.7	1.26	0.04	0
30	4.6	7.31	12.1	790	0	0.18	0	6.33	0	12.2	325	40	39.1	92.7	43	25.1	2.21	0.05	0
34	7.8	7.23	11.9	792	0	0	0	4.65	0	15.4	360	28	31.9	92.3	52.4	23.7	1.94	0	0
36	3.6	7.19	11.4	783	0.04	4	0	5.76	0	26	320	20	33.6	90.6	47.6	18.9	1.79	0.18	0
39	3.7	7.36	11.3	762	0	0.39	0	4.08	0	8.6	335	42	32.8	91	46.7	20.8	1.81	0.01	0
41	2.9	7.3	13	835	0.05	0	0	0	0	14.2	400	25	19.7	85.8	52.3	33.7	2.45	0.29	0.4
43	0.4	7.3	12.9	923	0	0.29	0	4.65	0	5.42	300	100	40.4	100.3	46.7	40.7	3.44	0	0
44	2.6	7.27	11.4	743	0	0	0	8.11	0	46	320	26	31.5	89.7	46.6	16.1	1.81	0.11	0
46	0.21	7.14	12.6	992	0	0.39	0	4.16	0	2.42	350	67	73.4	127.7	44.4	24.6	8.12	1	0
48	5	7.22	13	844	0.13	0.21	0.01	26.6	0	4.18	350	43'	31.8	91.4	42.5	41.4	3.52	0.23	0

*Results in mg/L except for pH, temperature (°C), specific conductance (μS) ana alkalinity (mg/L as $CaCO_3$).

mildly reducing conditions. There was no other indication of widespread contamination by other organic compounds or metallic elements.

Purging Experiments

As described in the preceeding Experimental Design section, monitoring wells were purged and sampled by low flow-rate pumping at quarterly intervals. A subset or thirteen wells was selected for detailed purging analysis to examine the use of traditional inorganic purging parameters for VOC sampling.

Indicator Parameters and VOC Stabilization

Dissolved oxygen and specific conductance (Ω^{-1}) readings were found to be the most useful field indicator parameters for stabilization of background water chemistry during purging. The pH and temperature readings achieved stable values almost immediately (i.e., within 1 to 2 L) during purging m all cases. The temperature readings at the flow cell differed from the downhole probe values by 3 to 5 C° due to seasonal changes in air temperature even though the sample discharge line from the well-head to the cell was insulated with foam tubing. An example of well-purging to stabilization is shown in figure 32 for well 18. Identification of the initial volume to stabilization (V_i), for each well and parameter was done by manually extrapolating to the intersection of lines on the stabilization plateau and rising or falling limb of the concentration curve as a function of volume purged.

The median and range of maximum and minimum percent bore volumes to stabilization for the indicator parameters and VOCs for the study wells are shown in figure 33. The box and whisker plots show the median as a vertical line and the limits of the box as the upper and lower quartiles of the distribution. The "whiskers" represent the minimum and maximum stabilization volumes for all study wells. The average stabilization volume of at least four quarterly sampling events for all of the wells was less than one-half of a bore volume. The volume to stabilization for O_2 and conductance exceeded one bore volume in only one instance out of 64 quarterly sampling events.

The average initial concentrations of dissolved O_2 were significantly higher (~6x) and those for Ω^{-1} significantly lower (~0.7x) than the final purged values. The values for the ratio of the initial concentration C_o (unpurged) to the final purged concentrations are shown in Table 17.

These observations are consistent with the exposure of the standing water in the well to oxygen and the loss of CO_2 resulting in oxidation and precipitation of dissolved solutes. These marked differences between pre-purged and purged concentration values for the indicator parameters indicate the need to purge wells prior to sampling. The following discussion treats these observations more quantitatively as well as those regarding purging behavior of the VOCs.

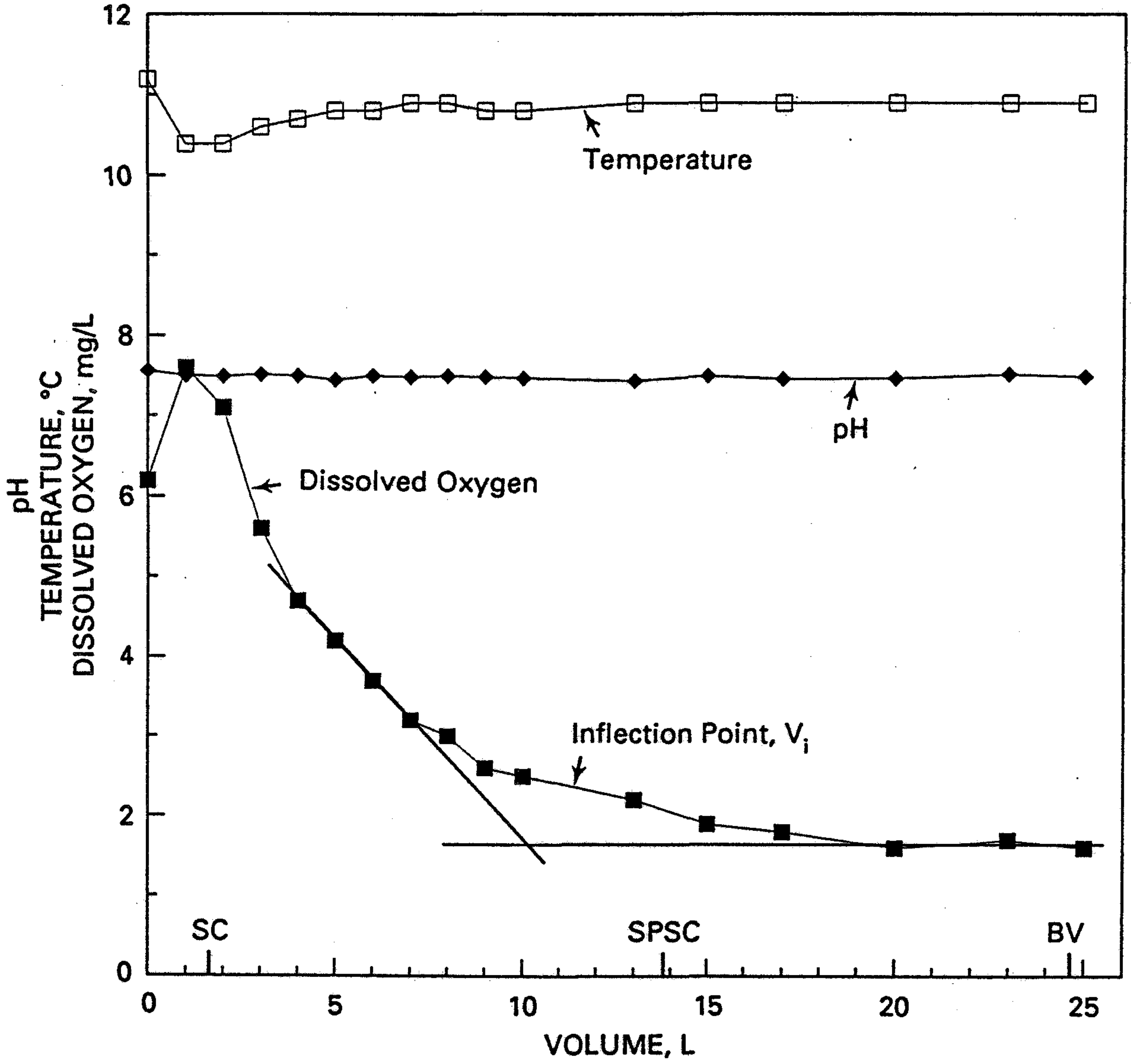


Figure 32. Plot of typical purging behavior of temperature, pH, and dissolved O_2.

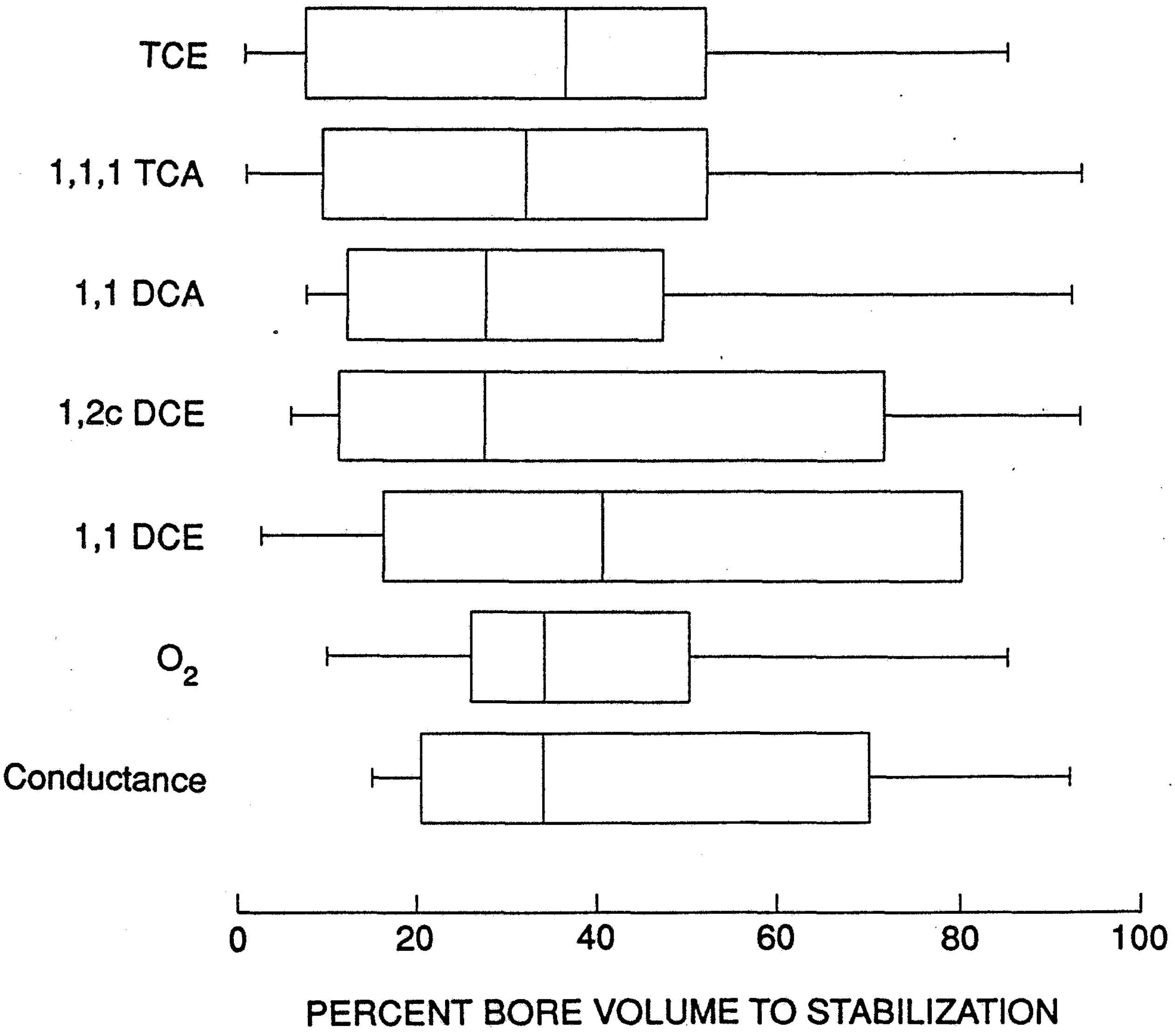


Figure 33. Box and whisker plots of the percent of bore volume purged to react stabilization for the indicator parameters and five principal VOCs.

Table 17. Compilation of Initial to Final Concentration Ratios

A Well	B Oxygen	C Conductance	D 1,1DCE	E 1,1DCA	F l,2cDCE	G 1,1,1TCA	H TCE
15	3.05	0.96	1.00	1.04	0.92	0.80	1.07
16*	N.A.	0.98	0.21	0.25	0.27	0.24	0.27
16	N.A.	N.A.	0.90	1.06	0.83	1.12	0.85
17	1.44	0.77	0.76	0.98	0.65	0.95	0.66
18	3.88	0.33	0.48	0.78	0.64	0.63	0.80
19	1.25	0.69	0.20	-	-	0.53	-
20	49.00	0.43	0.95	0.99	1.06	0.84	-
21	N.A.	0.90	1.23	1.07	1.34	1.20	1.46
22	4.30	0.80	1.40	0.87	0.94	1.10	1.21
23	1.03	0.95	1.10	1.17	1.09	1.22	0.91
24	1.61	0.10	-	-	-	0.41	0.08
27	1.54	0.68	0.72	0.78	0.71	0.77	0.70
28	2.17	1.04	0.50	0.90	0.82	0.70	0.90
29	1.68	0.62	-	-	-	1.07	1.10
30*	N.A.	N.A.	0.02	0.01	0.01	0.78	0.84
30	1.10	0.26	1.35	0.98	0.94	1.14	1.05
AVG	6.00	0.68	0.77	0.84	0.79	0.84	0.85
STDEV	13.58	0.30	0.44	0.34	0.35	0.29	0.36

N.A. = Data Not Available
\- = Compound Not Detected
* = Preliminary Purging Results for 11/90 Sampling

The ratios of the initial to final (i.e., post-purging) concentrations of VOCs provided in Table 17 snow the effects of degassing on stored water. The ratios for the five principal contaminants ranged from 0.01 to 1.46. The higher ratios are shewed somewhat by the variable, low concentrations or VOCs in wells 21, 23 and 30. The apparent 15 to 23% lower initial values due to outgassing of the volatiles underscore the need to purge monitoring wells even in this type of transmissive hydrogeologic environment where one might expect the screened interval to be renewed by flow (Robin and Gillham, 1987; Powell and Puls, 1993). The observed differences between the initial and final concentrations are modest in comparison with those reported by some previous workers (Smith *et al.,* 1988; Barcelona and Helfrich, 1992; Gibs and Imbrigiotta, 1990; and Chou *et al.,* 1991). Stagnant water samples from monitoring wells nave teen found to be significantly lower in volatile organic compounds than those measured after purging in a range of hydrogeologic settings.

Low volume, low flow rate pumping was sufficient for stabilization of O_2 and conductance values during purging. The same situation applied generally to the behavior of the VOC compounds. Table 18 contains the results for the VOC concentration changes after an initial period of pumping. The concentration levels for the five principal VOCs began to stabilize after pumping an average of 40% (range of 35 to 52%) of a bore volume at ~1 L/min. This range compares favorably to the average percentage bore-volumes to stabilization of O_2 (i.e. 44 ± 27%) and conductance (i.e. 44 ± 21%). The VOC concentrations on the stabilization plateau varied within ±2.2 to 14% relative standard deviation from the means shown in bold in Table 18. This range of variability is well within expectations for repetitive samples from individual wells for VOC concentrations in the range of 10-500 μg/L. The ranges of acceptable limits for reporting VOC concentrations in USEPA Water Supply Performance Evaluation Studies are ±40 and ±20% from true values at levels less than 10 μg/L and greater than or equal to 10 μg/L, respectively (Britton, 1992). The stabilization of VOC concentrations during purging at levels within these ranges of analytical performance standards should be more than adequate for most routine monitoring investigations. The stabilization of O_2 or conductance values may not necessarily be predictive of volumes to VOC stabilization. However, in this study all constituents reproducibly stabilized within the same volume range.

Weak linear correlations between higher average stabilized concentration values of the VOCs and higher initial volumes of stabilization were observed in the purging experiment. The correlation coefficients were relatively poor (i.e., r^2 for DCE = 0.22; DCA = 0.33; cl2DCE = 0.26; TCA = 0.12; TCE = 0.40). This was due in part to the fact that in some wells with low concentrations of VOCs (21, 23 & 30), negligible changes in concentration were observed during purging. Certainly, well to well variability in VOC concentrations also weakened these correlations. The use of close-fitting dedicated pumps with the intake placed in the middle of the short-screened interval minimized the volume of potentially contaminated water which must be purged at these flow rates prior to sampling. The position of the bladder pump intake and minimal drawdown during pumping provide the basis for consistent measurements of both the purging indicator parameters and VOCs.

Documentation of the behavior of the indicator parameters during purging of individual wells provides a body of data with which the consistency of field sampling procedures can be judged over time. They should be considered as part of QA/QC guidelines in monitoring efforts. Under similar hydrogeologic conditions, a two person crew could easily sample ten or more wells per day following the suggested low flow rate well purging method. In the course of a day of sampling, less than 500 L of potentially contaminated water would need to be bandied by the field crew. This purging method has distinct advantages for long-term monitoring efforts in terms of cost and the minimization of volumes of purged water for treatment or disposal.

Table 18. VOC Purging Behavior: Initial Volume of Stabilization, Mean Stabilized Concentrations, and Standard Deviation.

	Conductance (μS/cm)			Oxygen (mg/L)			1.1DCE			1.1DCA			1.2c-DCE			1.1.1TCA			TCE		
Well No.	Vi	C	STDEV	Vi	C	STDEV	Vi	C	STDEV	Vi	C	STDEV	Vi	C	STDEV	Vi	C	STDEV	Vi	C	STDEV
15	69	816	15	89	2.1	0.1	41	2.1	(0.05)	41	2.1	(0.32)	93	7.8	(0.08)	93	29.5	(0.8)	41	2.0	(0.3)
16							42	19.6	(1.1)	42	53.7	(2.9)	33	50.8	(2.9)	52	213	(15.7)	52	35.1	(3.7)
17	15	781	8.4	15	3.2	1.0	40	8.9	(1.4)	33	32.5	(1.4)	58	13.9	(0.6)	58	36.9	(1.2)	58	3.9	(0.2)
18	30	732	3.5	55	1.8	0.2	156	36.6	(1.5)	85	87.5	(1.5)	85	144	(1.9)	85	394	(3.6)	85	94.3	(0.4)
19	71	859	12	10	2.4	0.1	+	0.5	-	+	0.5	-	+	0.5	-	+	17.5	(2.1)	+	0.5	-
20	19	824	13	31	0.35	0.2	68	17.8	(2.7)	92	237	(0.2)	92	61.4	(0.6)	29	30.7	(1.9)	+	0.5	-
21							32	7.3	(0.5)	52	18.3	(0.80)	52	12.8	(1.2)	52	78.9	(5.0)	52	14.4	(0.8)
22	68	762	2.5	79	1.2	0.2	4.3	0.87	(0.17)	7.7	2.5	(0.70)	7.7	1.3	(0.22)	50	32.7	(1.7)	50	0.94	(0.15)
23	17	745	1.6	83	3.9	0.7	3.4	0.93	(0.10)	21	3.3	(0.20)	6.1	1.1	(0.30)	6.1	23.4	(0.8)	6.1	1.3	(0.12)
24	41	733	4.4	41	3.8	0.1	2.6	0.5	-	7.8	0.5	-	7.8	1.0	-	2.1	6.4	(0.3)	2.1	1.1	(0.1)
27	37	728	3.8	22	4.7	1.0	92	17.3	(3.9)	22	395	(1.8)	22	45.4	(1.6)	32	138	(6.7)	32	43.7	(1.95)
28	62	671	3.7	27	2.5	0.2	110	29.9	(3.2)	15	99.7	(3.0)	15	90.1	(6.5)	1.0	155	(7.8)	1.0	53.2	(1.1)
29	38	791	3.6	38	3.0	0.1	+	-	-	+	-	-	+	-	-	9.6	5.5	(0.3)	9.6	1.0	(0.1)
30	60	797	5.8	37	4.1	0.1	28	5.5	(0.7)	9.3	11.0	(0.6)	19	10.2	(1.0)	28	64.7	(3.3)	28	13.4	(0.6)

Vi = % Bore Volume at which stabilization began.

C = Mean Concentration (in µg/L, except where otherwise indicated) on stabilization plateau.

STDEV = Standard Deviation (in µg/L, except where otherwise indicated) on stabilization plateau.

\+ = No significant delay to stable or non-detectable concentration.

\- = Concentration values too low or intermittent to estimate mean or standard deviation.

VOC Purging Criteria

Recommended criteria in the literature for the stabilization or chemical constituents during purging vary. Most nave centered on the variability or indicator parameters, for example, O_2, conductance, temperature, and pH (Gibb *et al.*, 1981; Barcelona *et al.*, 1985) or the maximum rate of change for indicator parameter and VOC concentrations (Gibs & Imbriggiotta, 1990) over a specified volume. The choice of the level of acceptable variability over the appropriate flow rate and volume (i.e., bore volume, screen volume, sandpack volume, etc.) on the purging plateau should be carefully evaluated for the hydrogeologic setting, monitoring well design, and hydraulic performance.

Even when we applied the apparently stringent equilibration variability criteria suggested by Gibs and Imbriggiotta to the purging data presented in this study, a fraction of a bore volume (i.e., <50%) would be sufficient to achieve stabilization. From the present observations, approximately ±0.2 mg/L O_2 and ±10 μS/cm conductance Ω^{-1} over one-half bore volume, after the initial volume of stabilization, would be considered reasonable field criteria for the indicator parameters (since pH and T were relatively insensitive to purging). This procedure would be expected to minimize the purge value requirement well below that called for by recommendations of three to five bore volumes (Gibb *et al.*, 1981).

Ideally one could take sequential samples during purging for VOC determinations from a "typical" well at a site. This would establish a more site-specific correspondence between the easily measured indicator parameters and the behavior of VOCs during sampling. Low flow rate purging with dedicated bladder pumps or similar devices would certainly avoid the excessive variability and perhaps failure to achieve stable values reported in high flow rate pumping studies (Clarke and Baxter, 1989; Pionke and Urban, 1987; Gibs and Imbriggiotta, 1990). Gibs and Imbriggiotta pumped their wells during purging at rates of 4 to 25 L/min. In fact, in three of their six cases in which "unstable" concentration values for two or more compounds were observed during purging, the entrance velocity through the screen exceeded the optimum screen velocity for production wells of the same diameter (assuming 50% blockage of the open area of the screen). At low flow rates, one avoids: pumping excessive volumes of water, further well development, excess turbidity, and well damage which can lead to systematic error (i.e., bias) in chemical constituent determinations.

Monitoring Well Purging Hydraulics

The extension of the above results to other hydrogeologic settings, well designs, pumping rates, etc. depends on considerations of the hydraulics of the monitoring wells and the distribution of chemical constituents adjacent to the screen. Empirical observations of volumetric purging behavior of VOCs reported in this study and by Gits and Imbriggiotta (1990) did not correlate well with the concentration levels or the constituents, hydraulic conductivity, transmissivity or the critical hydraulic residence times calculated by Schafer's (1978) method.

Robbins (1989) and Robbins and Martin-Hayden (1991) developed a treatment of the purging behavior or wells for VOCs which can be applied to the study results. Their mass-averaging model expression for purging is shown below in equation 1.

$$C_w = C_f + (C_o - C_f) \exp(-V_e/V_w) \qquad (1)$$

where:

C_w = concentration pumped
C_f = concentration at stabilization
C_o = initial concentration (Co=Cw)
V_e = cumulative volume pumped during purging
V_w = well volume

This equation was used to determine the best fit between the purging observations in this study with the model prediction for different water volume values for V_w (i.e. V = V_{BV} , $V_{sp/sc}$ or V_{sc}). The borehole volume V_{BV} was assumed to include water in the casing, screen and sand-pack. $_{sp/sc}V$ included the volume in the screened interval and the sandpack (i.e. the borehole around the screen corrected for porosity). V_{sc} included the volume in the screened interval minus that occupied by the pump.

The predicted concentrations C_w, as a function of the volume pumped for each relevant "storage" volume, V_w, are shown in figure 34 (a - f) for O_2, conductance, and TCA in wells 18 and 24. The plots for these typical wells show that the best-fit of the observed concentrations to those predicted by the mass-averaging equation were calculated when the screen volume was used for V_w.

In general, conductance observations most closely matched predictions. This is probably due to the fact that conductance best reflects major ion chemistry which is less affected by either volatilization or small scale heterogeneity in subsurface formations than oxygen or volatile constituents. Table 19 contains the results for all of the best-fit linear regressions of observations versus predicted values for the selected constituents which consistently showed appreciable purging variability in all wells in the study. Out of 91 total cases, 47 showed both detectable levels and significant concentration variations during purging which permitted meaningful comparison. Of these cases, 34 showed linear correlation coefficients (r^2) above 0.5. Twenty-seven of these were observed when V = V and 8 when V_w = $V_{sp/sc}$. In only one case, the best fit correlation coefficient exceeded 0.5 for V_w = V_{BV}. The higher general correlation between the observed values and those predicted by V_w = V_{sc} or $V_{sp/sc}$ may reflect the fact that minimal drawdown during purging effectively isolates the stored volume in the casing above the screen from the pump intake. The use of relatively close-fitting dedicated bladder pumps further minimized the pathway by which "stored" water by which water could move into the screen. Maltby and Unwin (1992) have previously observed a degree of isolation of stored water in the casing above the screen when pumping slowly from the screened interval. "Fresh" ground-water then may move into the screen nearly at the onset of pumping.

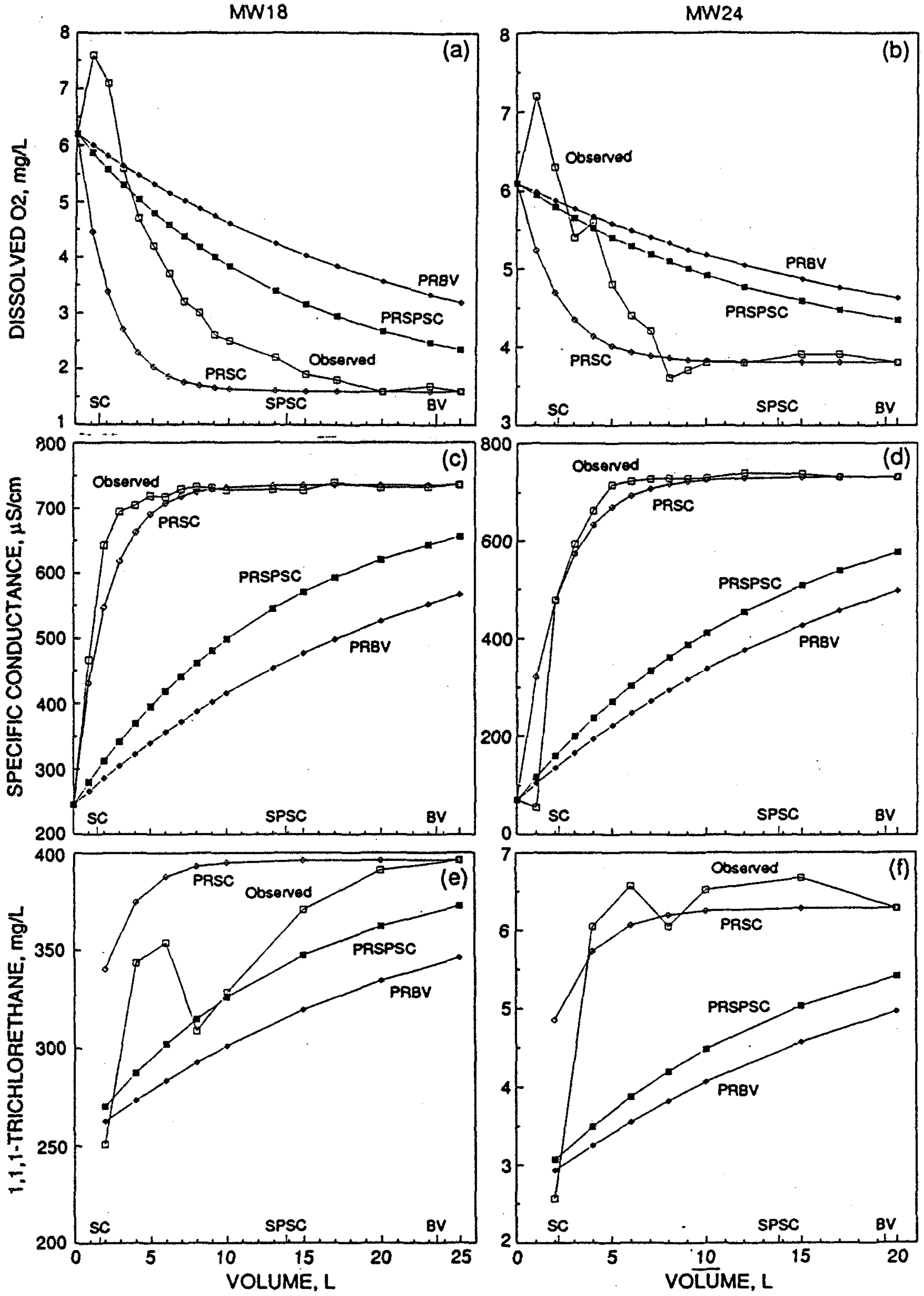


Figure 34. Purging observations and mass-averaging equation predictions for dissolved oxygen, specific conductance, and TCA vs. volume pumped for wells 18 and 24.

Table 19. Best-Fit Volume and Correlation Coefficients
for Predicted and Observed Purging Behavior or Selected Chemical Constituents

WELL	COND	O_2	1,1,1TCA
15	SC* (0.1)** (0.86)	SC (0.1)	SC
17	SC (0.75)	SC (0.1)	SC (0.13)
18	SC (0.95)	SC (0.65)	SPSC,SC (0.69,0.63)
19	SC (0.71)	SC (0.27)	SPSC (0.71)
20	SC (0.92)	SPSC (0.70)	SC (<0.1)
21			SC (0.62)
22	SC (0.85)	SPSC,SC (0.90,0.54)	SC (0.28)
23	SC (0.94)	SPSC,SC (<0.1)	SPSC (0.53)
24	SC (0.92)	SC (0.67)	SC (0.90)
27	SC (0.94)		SC (0.79)
28	BV,SPSC;SC (0.94;0.84)	SC (0.46)	SC (0.51)
29	SC (0.91)	SC (0.83)	
30	SC (0.81)	SC (0.23)	SPSC (0.32)

* = Volume V_w in mass-averaging equation (See Equation 1)

** = r^2 , linear best-fit correlation coefficient

SC = Screen volume

SPSC = Sana/Pack/Screen volume

BV = Casing, screen ana sandpack volume

This encouraging agreement does not constitute a predictive relation for the empirical results one might expect under other hydrogeologic conditions. Robbins and Martin-Hayden nave pointed out that the length or the screen and the concentration distribution adjacent to the screen exert the principal controls on the bias introduced into purging and sampling results due to mass averaging. Attempts were made to linearize their equation to derive a "well-volume" applicable to each parameter fitted to the observations.

Equation 1 was transformed to:

$$\log\left(\left| \frac{C_w - C_f}{C_o - C_f} \right| \right) = \frac{-V_e}{2.3V_w} \qquad (2)$$

The log of the absolute value of the concentration ratio was then plotted versus the cumulative volume pumped (Ve) where the slope was -(1/2.3 V_w). These calculations did not yield reasonable linear relationships by which consistent V_w values could be estimated within ±100% even for the conductance values. Further work is clearly needed to better integrate vertical gradients in chemical constituent concentrations and monitoring well hydraulics, with purging behavior. Care should be taken to avoid screening monitoring wells across variably permeable formations or those with strong vertical chemical concentration gradients (Gibs *et al.*, 1993; Powell and Puls, 1993).

Low flow rate pumping to purge and sample short-screened wells, with dedicated bladder pumps set in the screened interval, causes negligible drawdown. It further permits the in-line observation of stabilization of indicator parameters as a function of volume pumped. At flow rates of ~ 1 L/min., oxygen, conductance and VOC levels stabilized consistently after pumping less than one-half of a bore volume. Stabilization within ±0.2 mg-O_2/L and ±10 μS/cm specific conductance (for wells with conductances < 1,000 μS/cm) over successive bore volumes represents reasonable, initial, field criteria for judging purging effectiveness. Observations of indicator parameter stabilization during low flow rate pumping represent a consistent basis for purging prior to sampling for volatile organic compounds which may not require purging three to five bore volumes. This purging procedure is reasonably consistent with those predicted due to the hydraulic effects of mass-averaging. VOC concentrations stabilized within 15% of annual mean values when these criteria have been applied.

Monitoring Well - Hydropunch® Intercalibration Experiment

Results of the VOC analyses from the monitoring well - Hydropunch® comparison experiments are shown in Table 20. Scatter plots for each of the five compounds for the three comparisons

Table 20. Analytical Results of Monitoring Well - Hydropunch® Comparisons

Location	DCE	DCA	cl2DCE	TCA	TCE
MW15	0.00	8.19	6.56	45.13	2.49
HP15-1	0.00	4.35	3.96	31.50	0.75
HP15-2	0.00	5.38	4.93	33.70	1.23
MW16	71.23	115.76	176.06	523.76	127.83
HP16-1	70.64	136.13	193.81	586.66	132.33
HP16-2	50.25	105.43	147.15	456.46	102.34
MW17	6.20	31.70	18.08	33.97	4.24
HP17-1	6.11	43.46	23.19	45.93	4.64
HP17-2	7.72	40.60	24.49	47.14	5.99
MW20	37.12	314.29	89.30	101.57	7.88
HP20-1	6.52	535.92	33.16	98.05	0.00
HP20-2	39.19	374.34	103.14	85.45	4.75
MW21	17.66	27.40	31.42	125.39	37.08
HP21-1	13.16	22.28	23.70	90.84	24.59
MW24	0.00	0.00	0.00	4.26	0.56
HP24-1	0.00	0.00	0.00	4.91	0.31
MW30	5.76	10.00	12.66	87.66	23.62
HP30-1	2.14	8.04	9.55	75.54	16.89
HP30-2	1.47	7.29	8.72	72.85	16.29
MW31	39.08	67.40	117.45	285.54	84.06
HP31-1	37.67	64.78	113.86	277.16	82.02
HP31-2	36.86	64.47	116.40	266.39	76.08
MW32	0.00	4.95	4.70	37.14	0.89
HP32-1	0.00	1.80	1.42	26.34	0.00
HP32-2	0.00	3.42	2.89	29.91	0.57
MW35	62.32	110.25	169.21	456.42	117.08
HP35-1	30.13	85.91	102.78	216.71	61.19
HP35-2	33.16	76.86	116.45	296.59	71.14
MW37	25.99	54.80	93.46	279.09	72.73
HP37-1	22.10	50.17	85.10	267.19	64.86
HP37-2	14.19	42.24	70.56	200.22	50.47
MW39	21.84	49.94	82.18	222.51	55.51
HP39-1	22.09	42.36	65.39	196.70	42.93
HP39-2	16.21	40.48	62.33	187.22	37.91
MW42	22.62	39.61	63.51	237.45	51.38
HP42-1	21.07	39.91	62.70	226.08	52.61
HP42-2	19.50	37.56	60.25	216.46	47.09

(monitoring well vs. Hydropunch® 1, monitoring well vs. Hydropunch® 2, and Hydropunch® 1 vs. Hydropunch® 2) are provided in Appendix F. Examples or these graphs for TCA are shown in figures 35 - 37. The data are clearly highly correlated, with correlation coefficients ranging from 0.645 to 0.996 (mean R^2 = 0.884). However, it is also clear that the straight lines drawn as best-fit regressions to the data are not oriented at 45° with the x- and y-axes. There is a negative Lias in the monitoring well - Hydropunch® data; that is, the VOC results from the monitoring wells are higher than corresponding results from the Hydropunch®. The question remained, though, were the differences statistically significant?

The results of statistical comparison of monitoring well - Hydropunch® by the Wilcoxon Signed-Rank test for the five principal VOCs are shown in Tables 21 and 22. Table 21 uses data from all well sites sampled (except for Well 24 as mentioned in the Design section). Examination of the data snowed that results from wellsite 20 may have been in error, particularly for the compounds DCA and cl2DCE. The Wilcoxon Signed-Rank test was run again without data from wellsite 20 to examine whether the data from this site changed overall well - Hydropunch® comparisons. Table 22 summarizes the Wilcoxon results without wellsite 20. Spreadsheets containing the statistical calculations are included in Appendix G.

The Wilcoxon results are somewhat equivocal. the results are fairly consistent for all five compounds in that the Hydropunch® samples from both boreholes are not significantly different from each other (for 4 of the 5 compounds). However, the results are not so consistent when comparing monitoring well samples with the Hydropunch® samples. For the most part, exclusion of wellsite 20 bad no bearing on the statistical results. In both cases, for three of the five compounds (DCA, cl2DCE, and TCA), the Wilcoxon test saw no difference between well and Hydropunch® 1 samples. Oddly, this did not bold true for well and Hydropunch® 2 samples. There is no ready explanation for this; the samples were collected identically. The Wilcoxon test consistently accepted that there was no significant difference between well and Hydropunch® (1 or 2) samples for the compounds DCA and cl2DCE.

The statistical results suggest there may be small differences in the two sampling methods. Because of the consistently negative bias observed in the Hydropunch® samples, it is likely some of the difference (error) may be due to differences similar to the differences experienced between bailing a well sample and pumping with a positive displacement (e.g., bladder) pump. Given the excellent correlation observed between monitoring well and Hydropunch® samples, the Hydropunch® can be considered as an excellent tool for reconnaissance work to select areas and depths to place permanent monitoring well installations.

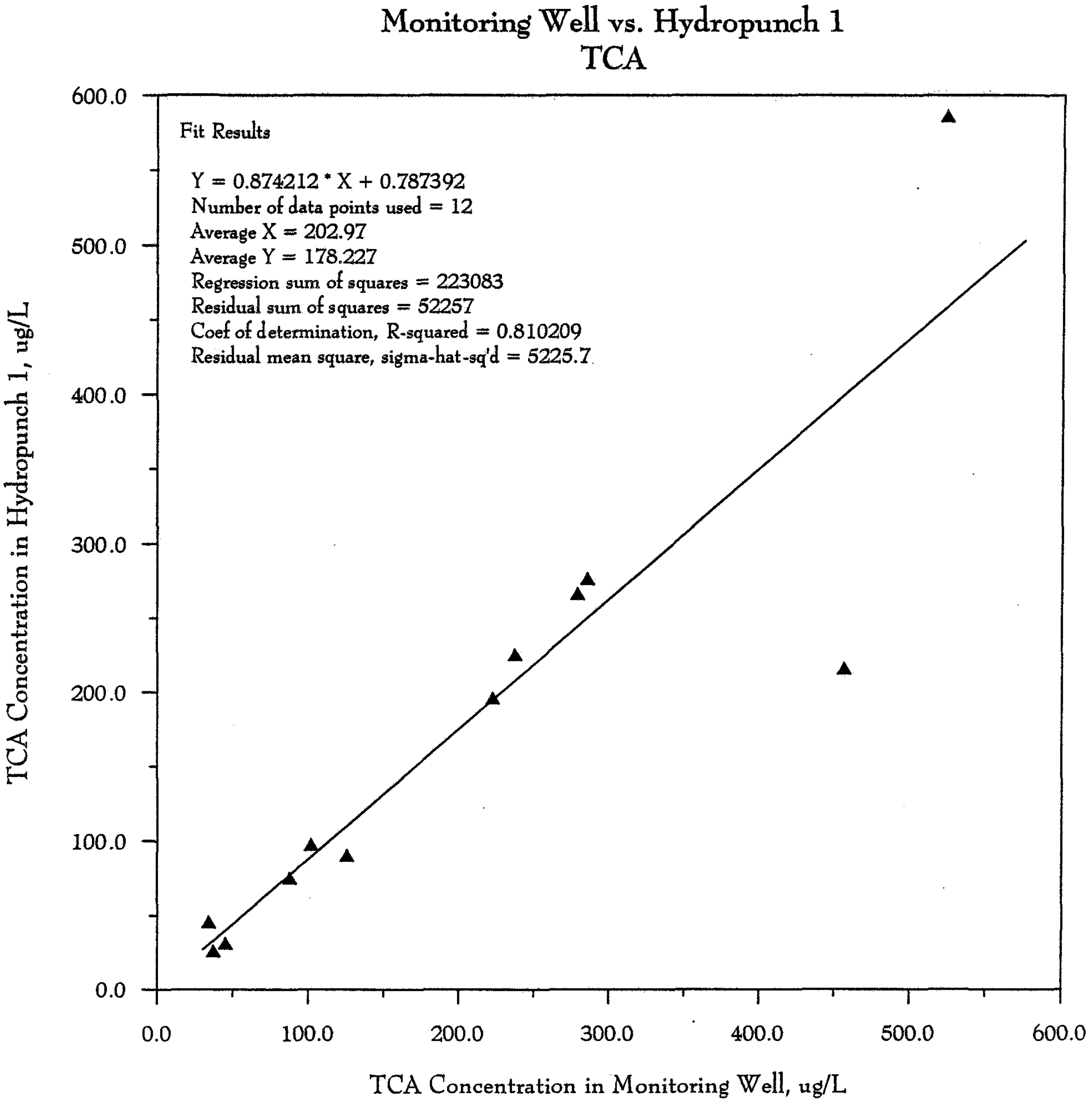


Figure 35. Monitoring well vs. Hydropunch 1 for TCA.

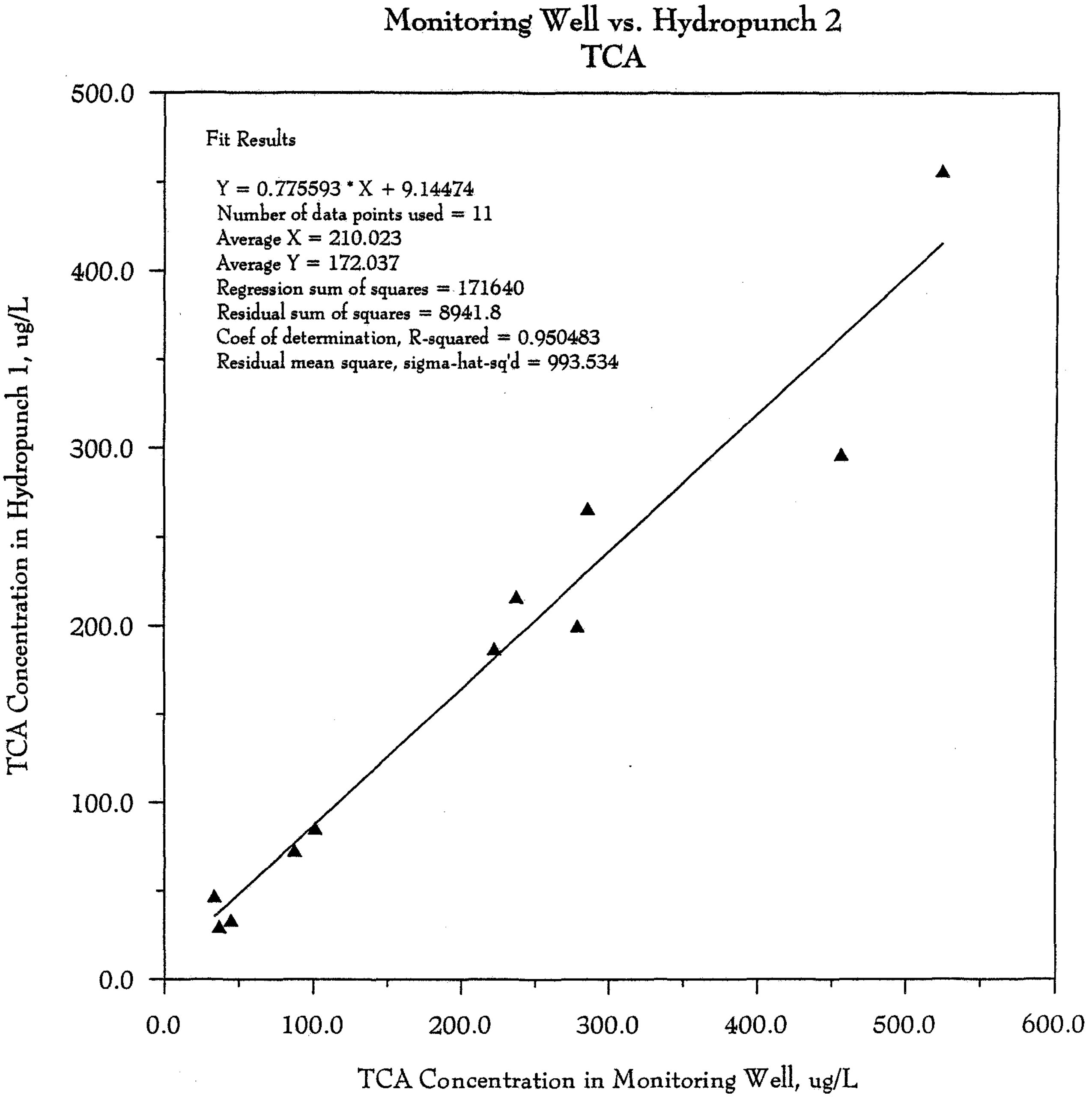


Figure 36. Monitoring well vs. Hydropunch 2 for TCA.

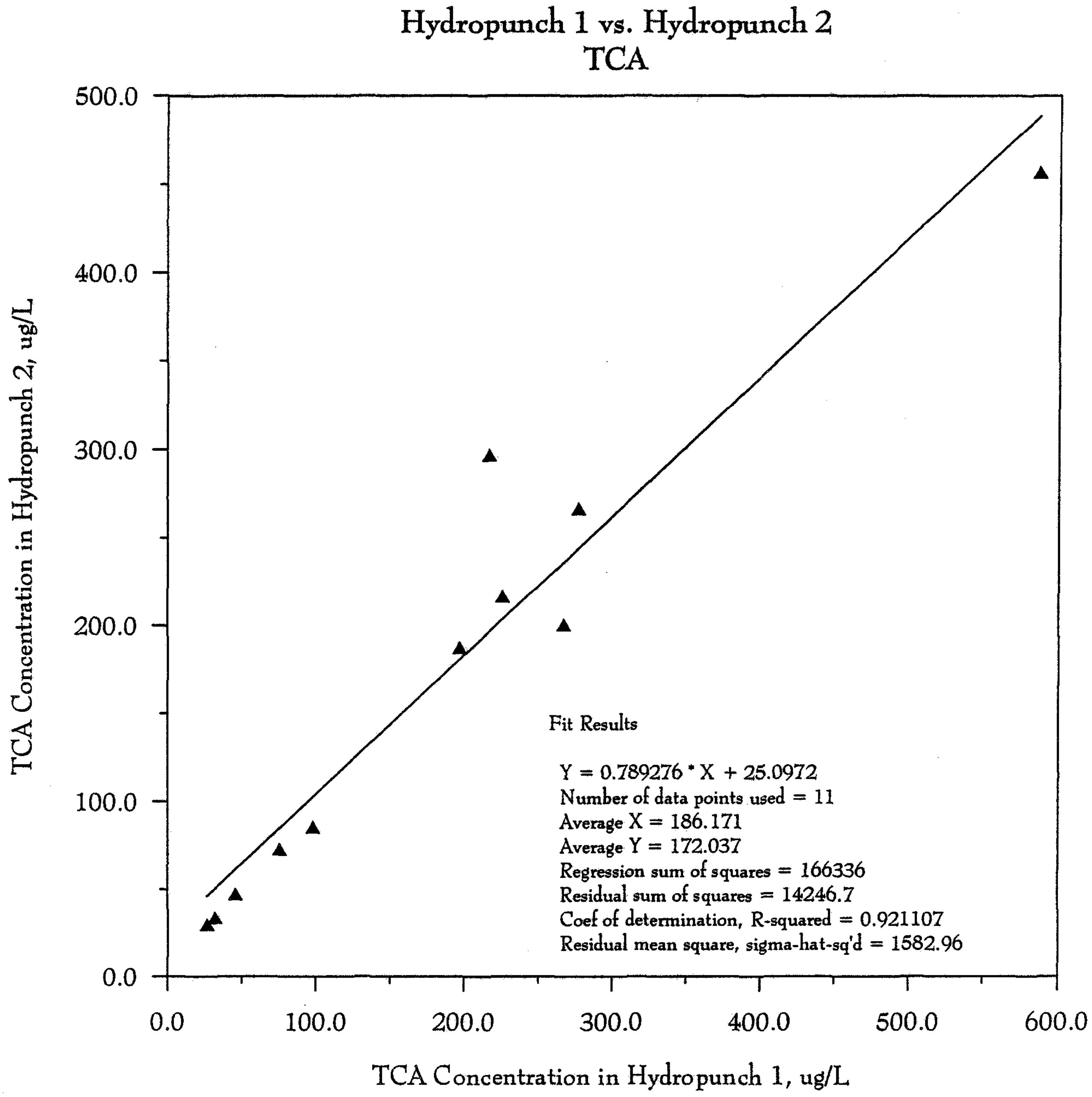


Figure 37. Hydropunch 1 vs. Hydropunch 2 for TCA.

Table 21. Result of Wilcoxon Signed-Rank Statistical Tests for Monitoring Well-Hydropunch® Comparisons including Wellsite 20
$(H_o: \mu_1 = \mu_2; \alpha = 0.05)$

Paired-Comparison Analyte	**Monitoring Well vs. Hydropunck® 1**	**Monitoring Well vs. Hydropunch® 2**	**Hydropunch® 1 vs. Hydropunch® 2**
DCE	Reject Z=2.60	Reject Z=2.31	Do Not Reject Z=0.53
DCA	Do Not Reject *Z=0.55*	Do Not Reject Z=1.42	Reject Z=2.31
cl2DCE	Do Not Reject Z=1.80	Do Not Reject Z=1.78	Do Not Reject *2=0.09*
TCA	Do Not Reject Z=1.78	Reject Z=2.67	Do Not Reject Z=1.42
TCE	Reject Z=2.27	Reject Z=2.67	Do Not Reject Z=1.07

Table 22. Result of Wilcoxon Signed-Rank Statistical Tests for Monitoring Well-Hydropunch® Comparisons without Wellsite 20
$(H_O: \mu_1 = \mu_2; \alpha = 0.05)$

Paired- Comparison Analyte	**Monitoring Well vs. Hydropunch® 1**	**Monitoring Well vs. Hydropunch® 2**	**Hydropunch® 1 vs. Hydropunch® 2**
DCE	Reject Z=2.43	Reject Z=2.38	Do Not Reject Z=1.26
DCA	Do Not Reject Z=1.15	Do Not Reject Z=2.19	Reject Z=2.09
cl2DCE	Do Not Reject *2=1.51*	Reject Z=2.19	Do Not Reject Z=0.46
TCA	Do Not Reject *2=1.65*	Reject Z=2.50	Do Not Reject Z=1.17
TCE	Reject Z=2.04	Reject Z=2.50	Do Not Reject Z=1.27

Aquifer Solids Sampling

Split-spoon cores were collected adjacent to the screens or four monitoring wells, 15, 31, 32, and 37. Table 21 presents the relative concentrations of TCA in the water versus the solids for a representative one liter aquifer element containing ~300 mL of water and 1750 g of aquifer solid. There is a marked difference between the samples preserved in the field with 75% (v/v) methanol versus samples placed in a bulk sampling jar and refrigerated at 4°C prior to analysis. In three out of four cases the bulk jar sample yielded TCA levels below the quantification limit (~5 µg/g). In fact, none of the bulk jar samples snowed any evidence of solvent contamination from other components present in the plume.

Table 21. Relative masses (*µg*) of TCA in ground water and aquifer solids for a representative 1L aquifer element

Well	Ground Water	MeOH Preserved Solid	Bulk Jar 4°C Solid	% Total TCA in Solid
15	13.5	21	-	60
31	85.7	516	52	86
32	11.1	30.9	-	74
37	83.7	239	-	74

The majority of potential errors involved in collection, handling, and analysis of VOC samples may be expected to lead to compound losses and low results. One clearly can avoid gross sampling and analysis errors for VOC determinations by field preservation of solids with methanol.

It should he noted that current regulatory guidance for the collection and handling of VOC samples recommends bulk jar sampling of cored solids or water with 4°C refrigeration for up to 14 days (USEPA, 1986). This presents an obvious conflict between the results of recent research and recommended practice for environmental sampling with major consequences on the accuracy of measured VOC distributions in the subsurface environment.

Temporal Variability

In earlier sections of this report, the control over sampling and anlytical error was established for samples and standards during the study period. The evaluation of temporal variability in water quality, geochemical or contaminant chemical constituents was based on this demonstration of control over analytical and sampling error.

Temporal Variability in Geochemical Constituents

The purging parameters, i.e., O_2, temperature, pH and conductance were the sole geochemical constituents determined routinely during virtually each well sampling event. These data are tabulated in Appendix H. In order to determine if significant difference in geochemical parameter levels occurred over time frames of weeks to months, the Wilcoxon Signed-Rank test was applied to the seven quarterly datasets. The test was applied to all wells (9 - 48) and those wells in the 15 to 18 meter depth plane (Tables 22 and 23). The latter set of wells exluded wells numbered: 10, 11, 13, 14, 18, 25, 26, 28, 29, 40, 41, 43, 45 and 46. The Wilcoxon test alpha level was set at a probability of 0.05 to judge the significance of difference between quarters. Tests which yielded a probability of less than 0.05 would affirm the null hypothesis that significant differences exist between quarters.

The results of these tests for which there were more than 6 valid pairs of differences for comparison showed significance levels lower than $p = 0.05$. The wells in-plane showed roughly the same number of significant differences for conductance, oxygen and pH as did the total well set. In general, the in-well temperature data set was limited to three quarters which yielded insufficient numbers of pairs for valid comparison. These results clearly show the value of quarterly sampling frequency to evaluate temporal variability in geochemical conditions as was shown by our previous study (Barcelona *et al.*, 1989b).

Appropriate annual data sets were also subjected to the Wilcoxon Signed-Rank test for the geochemical parameters. The results of these tests for all wells are shown in Table 24.

The results in the table show that annual conductance and pH values were significantly different at the $p = 0.05$ level, while the oxygen levels were not. This reflects the general increases in the former parameters over the study period. Oxygen levels varied substantially across the datasets with no clear overall trend. Clearly, if significant differences in these geochemical parameters are of interest, sampling frequencies higher than annual (i.e., quarterly) must be made part of the monitoring network design.

Temporal Variability in Volatile Organic Compounds

The purpose of the temporal analysis was to draw conclusions about the general trend of contaminant concentrations at certain wells over the course of the project. Differences in quarterly datasets were analyzed utilizing the Wilcoxon Signed-Rank test on the VOC concentration data set. There was no definite temporal trend in the data; selected wells are plotted in figures 38-41. Additional graphs for the well pairs 16/16A, 17/17A, and 21/21A for the five principal VOCs are compiled in Appendix I. An increasing trend was observed most consistently in well 17, where increases continued throughout the study. A noticeable concentration spike occurred in August 1991, in a

Table 22. Wilcoxon Signed-Rank Test Probabilities for Quarterly Geochemical Parameters Data - All Wells

Quarterly Sampling Periods	Conductance	O_2	Temperature	PH
Nov 90 - Feb 91	0.0277*	-	-	0.0087*
Feb 91 - May 91	0.0135*	0.2721	-	0.9929*
May 91 - Aug 91	0.0002*	0.0332*	-	0.00004*
Aug 91 - Dec 91	0.0001*	0.0007*	-	0.000001*
Dec 91 - Mar 92	0.000002*	0.0379*	0.0005*	0.000002*
Mar 92 - Sep 92	0.00002*	0.4140	0.0002*	0.00003*

* $p < 0.05$

- = insufficient data for meaningful comparison

Table 23. Wilcoxon Signed-Rank Test Probabilities for Quarterly Geochemical Parameters Data - Wells in 15 to 18m Plane

Quarterly Sampling Periods	Conductance	O_2	Temperature	pH
Nov 90 - Feb 91	0.0679	-	-	0.0423*
Feb 91 - May 91	0.0077*	0.3139	-	0.0109*
May 91 - Aug 91	0.0014*	0.0296*	-	0.0001*
Aug 91 - Dec 91	0.0024*	0.00006*	-	0.00002*
Dec 91 - Mar 92	0.00004*	0.0082*	0.0050*	0.00003*
Mar 92 - Sep 92	0.0001*	0.6894	0.0025*	0.000005*

* $p<0.05$

- = insufficient data for meaningful comparison

Table 24. Wilcoxon Signed-Rank Test Probabilities for Annual Geochemical Parameters Data for All Wells

Annual Sampling Periods	Conductance	Oxygen	pH
Nov 90-Dec 91/Aug 91-Sept 92	0.0277*		0.0051*
Feb 91-Dec 91/Aug 91-Sept 92		0.0754	
Valid N	(6)	(11)	(10)

*$p <0.05$

majority of the well pairs. A noticeable decrease was observed in December 1991, when concentrations dipped to some extent. In March 1992, increases occurred in nine out or 15 cases

which were greater than the increase observed in August 1991. Since these concentration variabilities were generally greater than those attributable to laboratory or field sources or error they must be considered part or the natural variability in contaminant concentrations. A reasonable hypothesis for fluctuating concentrations may be related to recharge processes. Concentration highs may be expected to occur after recharge events when infiltrating water enters the system and flushes contaminant from the soil matrix. However, the appearance of such a "recharge" related peak may be delayed in time and dampened over an entire season from the time major precipitation events occur. No particular recharge event (e.g., large rainfall event just prior to sampling) could be related to the increase experienced in August 1991.

In order to determine if significant concentration differences occurred between quarterly sampling periods, the Wilcoxon test was applied to data gathered from the sampling events of November 1990 - February 1991, February 1991 - May 1991, May 1991 - August 1991, August 1991 - December 1991, December 1991 - March 1992, and March 1992 - September 1992. This again was done for all wells and those in the 15 to 18m plane. Four of the five statistical tests result in a rejection of the null hypothesis for TCA for both well sets (Tables 25 & 26). This means that significant temporal concentration differences exist between four of the seven quarterly sampling events.

A noticeable rejection of the null hypothesis was observed in the testing of period May 1991 and August 1991 which showed rejections for all five volatile organic compounds. For well pairs 16/16A, 17/17A, and 21/21A this significant statistical difference may have been due to the large increase in concentrations which occurred for the August 1991 period. In most cases, dramatic increases in concentration were evident from May 1991 and August 1991. Three out five tests showed statistical differences from August 1991 and December 1991. Referring to figures 38-41, there was a sharp decrease in concentration from August 1991 to December 1991.

Annual Wilcoxon Signed-Rank tests were performed on the quarterly sampling periods between November 1990 and December 1991, and August 1991 and September 1992 (Table 27). These periods were chosen because they represent approximately one year between sampling periods. The results indicated statistical differences for all five VOCs.

The contaminant TCE yielded three statistical rejections in comparisons of quarterly data over the sampling period for all wells and two rejections in the in-plane dataset. The contaminant cl2DCE yielded one rejection in five tests for all wells (Table 26) and two in the in-plane dataset (Table 25) which means that a difference in contamination level existed only between the sampling period from May 1991 to August 1991. Four of the 5 quarterly sampling events for DCA yielded probabilities less than the stated alpha level in all wells and thus, were actually different from each other. The in-plane well set showed 5 of six significant statistical differences. DCE showed three statistical

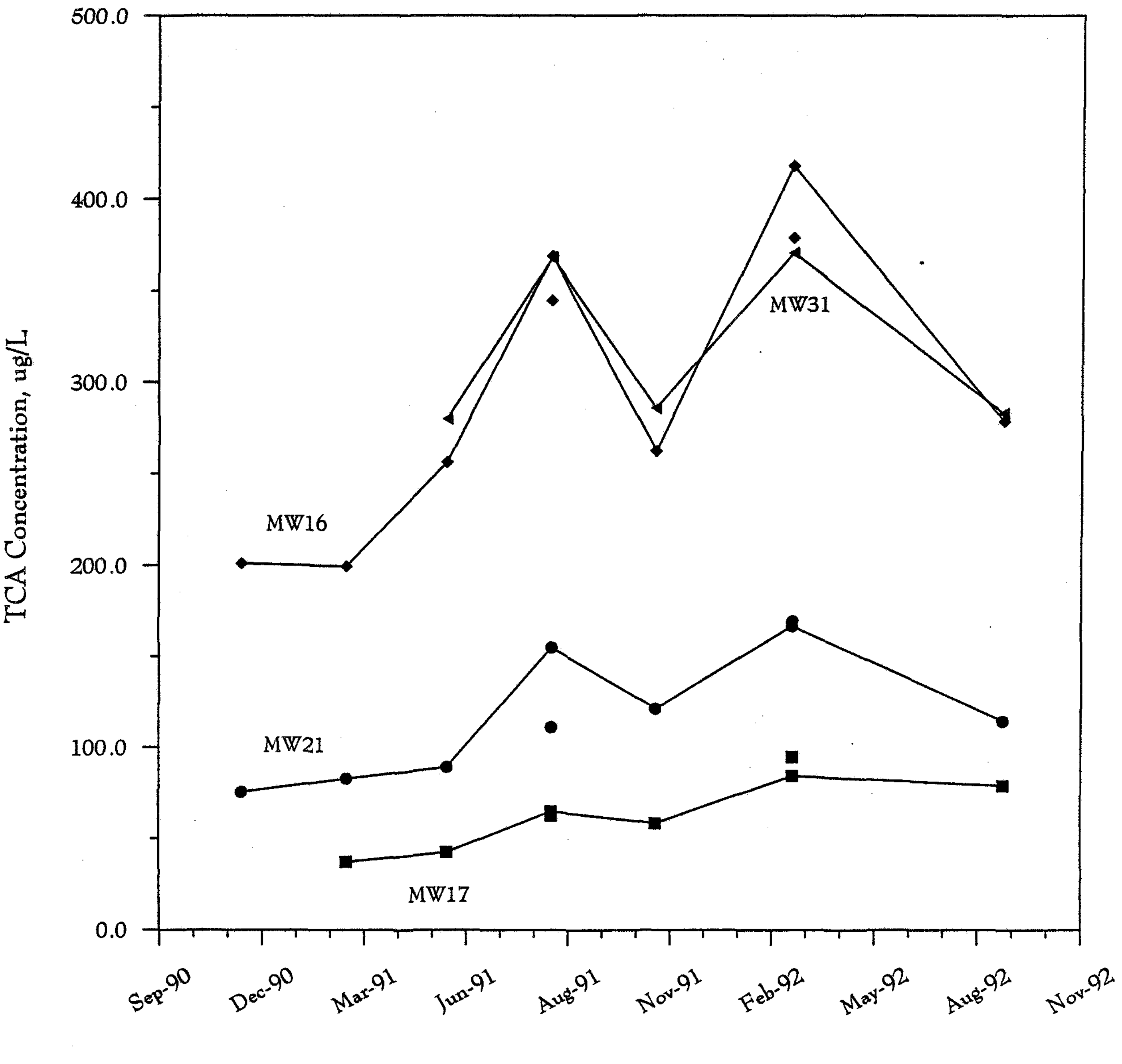


Figure 38. Quarterly sampling results for TCA at wells 16, 17, 21, and 31. Separate points on graph denote well-pair data from 16A, 17A, and 21A.

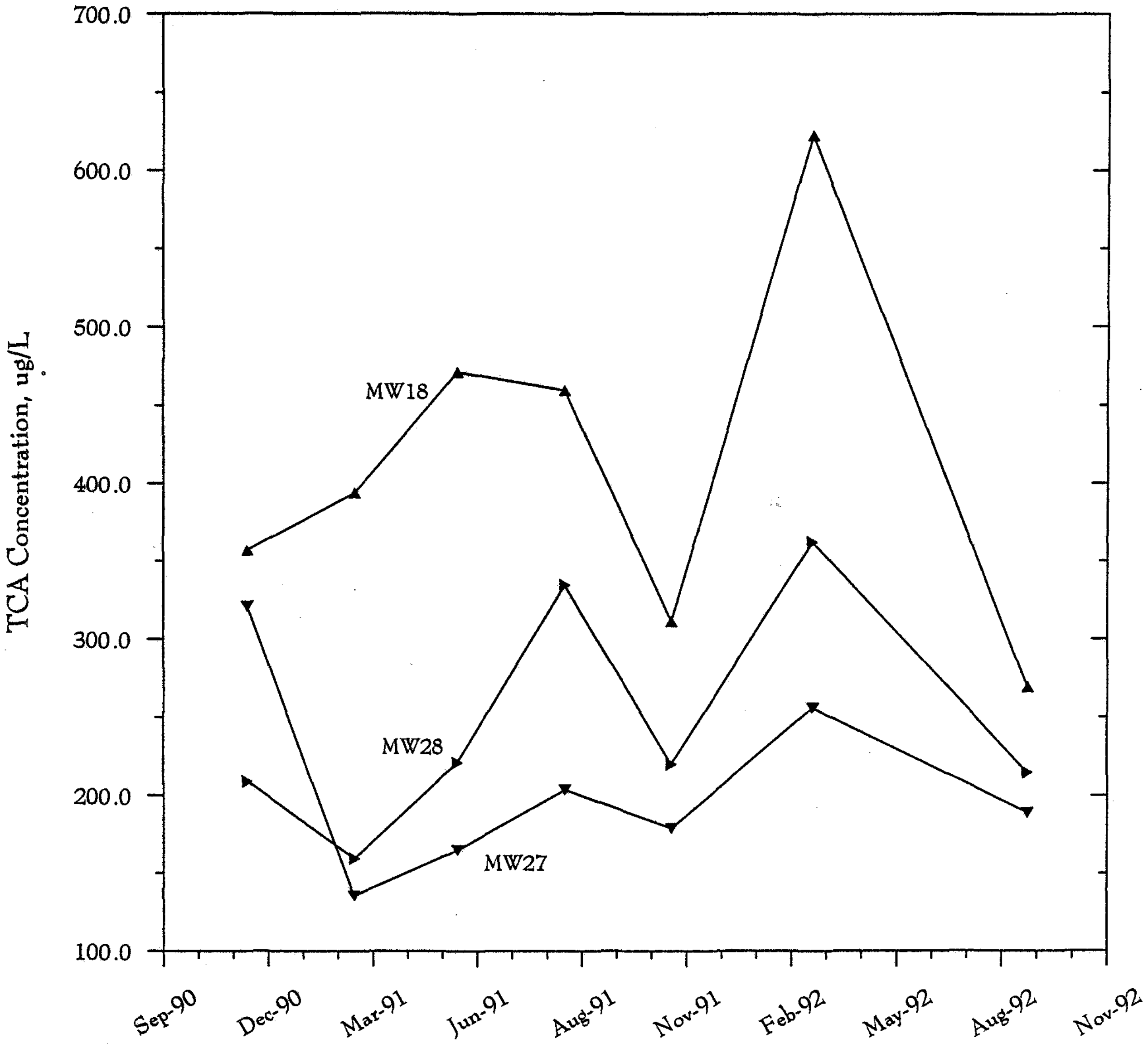


Figure 39. Quarterly sampling results for TCA at wells 18, 27, and 28.

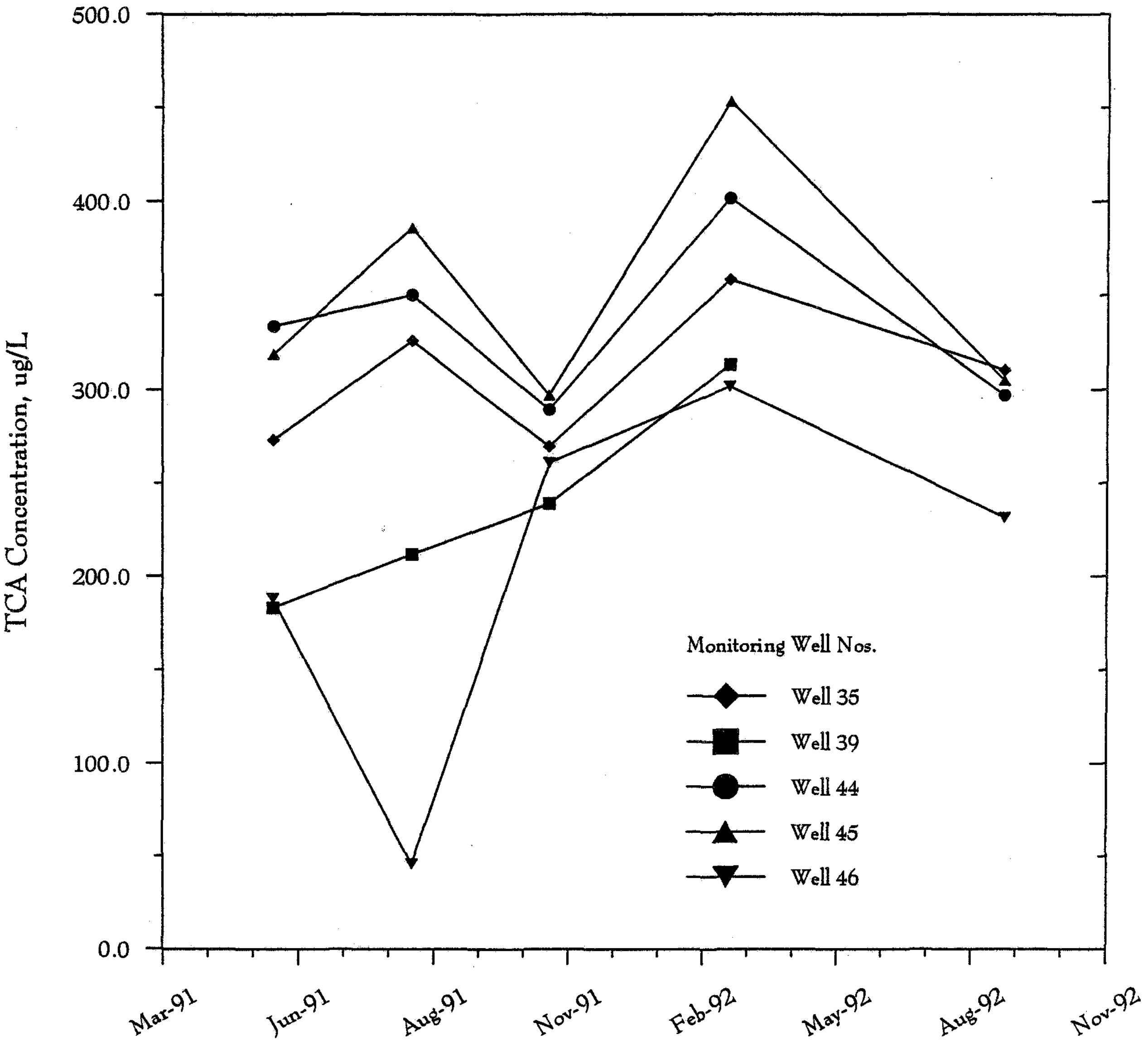


Figure 40. Quarterly sampling results for TCA at wells 35, 39, 44, 45, and 46.

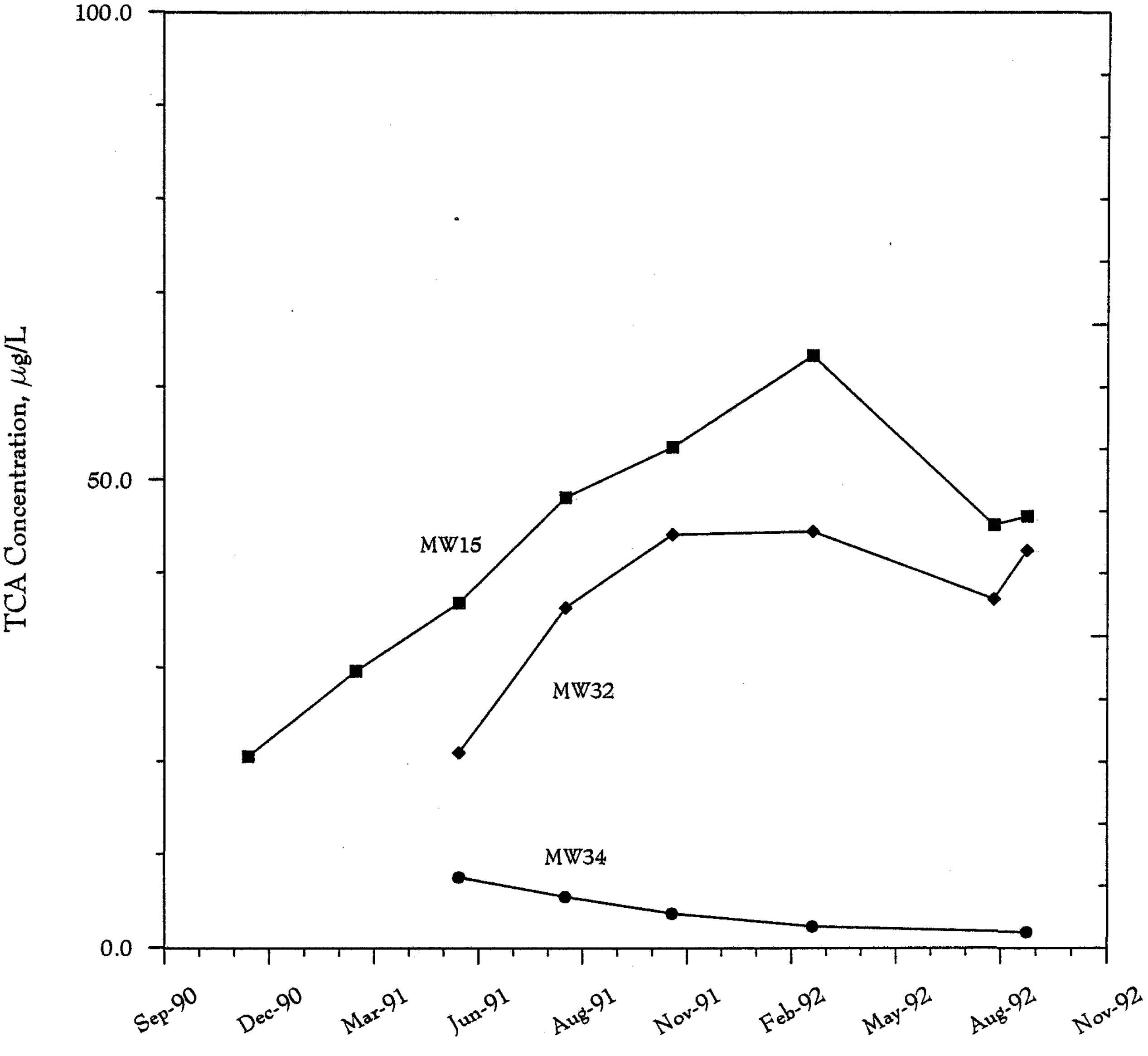


Figure 41. Quarterly sampling results for TCA at wells 15, 32, and 34.

Table 25. Wilcoxon Signed-Rank Test Probabilities
for Quarterly Volatile Organic Compound Data - Wells in 15 to 18m Plane

Sampling Periods	TCA	cl2DCE	DCA	DCE	TCE
Nov 90 - Feb 91	0.8785	0.7671	0.2604	0.5751	0.0687
Feb 91 - May 91	0.0186*	0.1731	0.0109*	0.9594	0.9594
May 91 - Aug 91	0.00008*	0.0002*	0.0002*	0.0299*	0.0001*
Aug 91 - Dec 91	0.0126*	0.0582*	0.0005*	0.0759	0.00002*
Dec 91 - Mar 92	0.0019*	0.1221	0.0002*	0.1128	0.9032
Mar 92 - Sep 92	0.0731	0.8313	0.0016*	0.6791	0.8813

* $p < 0.05$

Table 26. Wilcoxon Signed-Rank Test Probabilities
for Quarterly Volatile Organic Compound Data - All Wells

Sampling Periods	TCA	cl2DCE	DCA	DCE	TCE
Nov 90 - Feb 91	0.9721	1.0000	0.5937	0.9375	0.0164*
Feb 91 - May 91	0.0076*	0.8589	0.2478	0.3882	0.4631
May 91 - Aug 91	0.0004*	0.0003*	0.0002*	0.0180*	0.000004*
Aug 91 - Dec 91	0.0071*	0.1531	0.0027*	0.0459*	0.000001*
Dec 91 - Mar 92	0.0019*	0.3458	0.00003*	0.0221*	0.3389
Mar 92 - Sep 92	0.0731	0.8076	0.0005*	0.0919	0.5677

* $p < 0.05$

Table 27. Wilcoxon Signed-Rank Test Probabilities
for Annual Volatile Organic Compound Data - All Wells

Sampling Period	TCA	cl2DCE	DCA	DCE	TCE
Nov 90-Dec 91/ Aug 91-Sept 92	0.0331*	0.0077*	0.0058*	0.0597*	0.0010
Meaningful N	(13)	(13)	(14)	(14)	(14)

rejection tor the periods May 1991 and August 1991 for all wells and one significant difference for the in-plane wells.

Overall, the tests or significance snowed that sampling on a quarterly basis may be expected to yield at least statistical differences while snorter sampling intervals may not be statistically different. These results provide support for using quarterly sampling frequency to provide non-redundant data in preliminary network designs. This was found to be the case for temporal variability of inorganic constituents by Barcelona *et al.*, (1989b).

Given the fact that the estimated bulk flow velocity at this site is estimated to be in the range of 0.2 to 0.8 m/day and there was some variation in flow direction, it was anticipated that substantial temporal variability would be observed in VOC concentrations. The data analysis suggests significant variability over quarterly and annual time frames. These results support the conclusions of previous work (Barcelona *et al.*, 1989b; Bell and DeLong, 1988) that permit resampling and analysis within weeks to check questionable results in natural gradient situations done to minimal short-term variations during this timeframe. Also, significant longer term variability (months to years) argues for a minimal quarterly sampling frequency for initial monitoring network designs.

Spatial Variability

Volatile Organic Compounds

Several spatial data analysis objectives were approached by kriging techniques. First, maps of TCA concentrations were obtained and estimated error maps were also produced. Kriged contour maps of TCA concentrations for each quarterly sampling period and their associated error maps are shown in figures 42 through 52. These maps agree fairly closely with a map TCA concentrations based on the analysis of samples from domestic wells in July 1990 (figure 52). In general, the plume follows the direction of ground-water flow quite closely, extending from east to west over one mile. Peak concentrations vary with the greatest concentrations often exceeding 250 µg/L on the eastern edge of our study area. A distinct zone of higher concentrations follows a ridge through the middle of the plume to the west-northwest. Smaller TCA peaks occur along the this ridge suggesting possible source pulses, potentially seasonal in nature (with a ground-water velocity or approximately 0.8 m/day, a separation distance of 1000 feet between peaks is roughly a one year travel time). While the plume tends to "disappear" ' to the west, this may be an artifact of the depth of our monitoring wells. The plume is, in all likelihood descending through the aquifer as it moves westward toward the Rock River. In addition, a moderately sized industrial well is located on the western edge of the plume; our monitoring well 46. is located within 150 feet of this pumping well and the TCA "halo" seen on the western edge of the plume is a reflection of the redistribution of contaminant caused by that pumping center. Also quite distinguishable within the plume is an area of depressed TCA concentrations located in the vicinity of monitoring wells 33 and 34. This area of smaller TCA

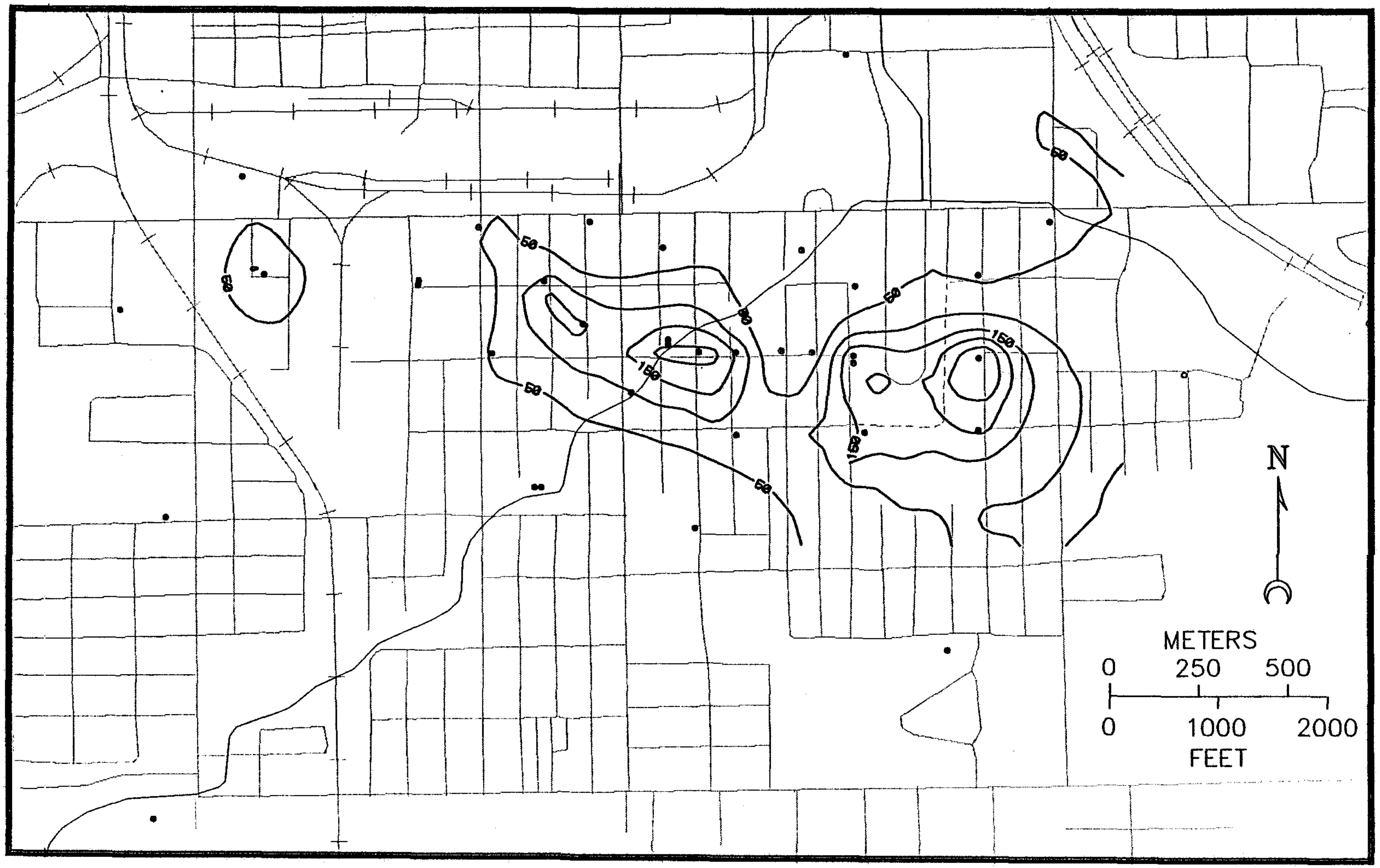


Figure 42. TCA concentrations within the intensive study area for May 1991.

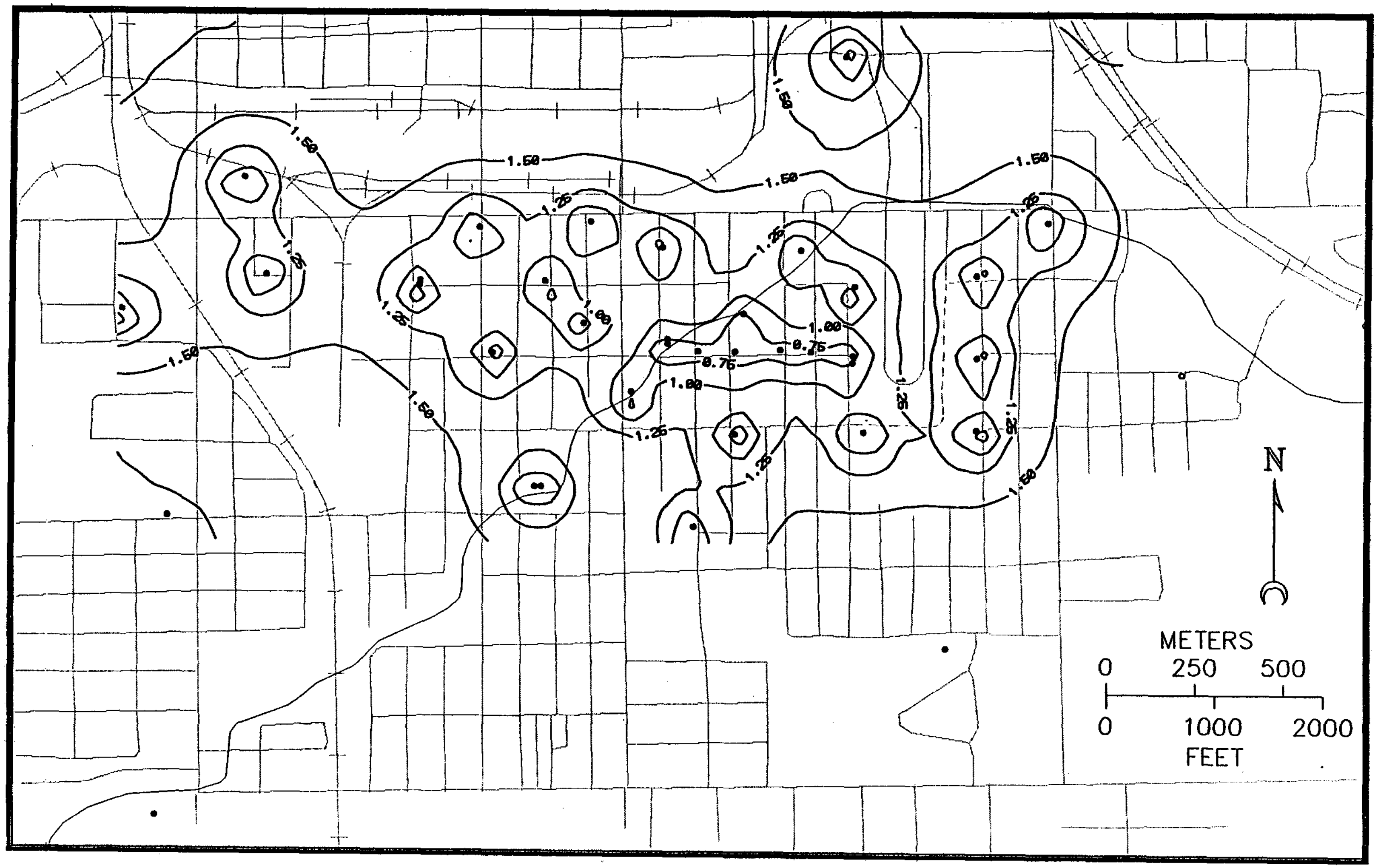


Figure 43. Standard deviation of estimated ln(TCA) concentrations for May 1991.

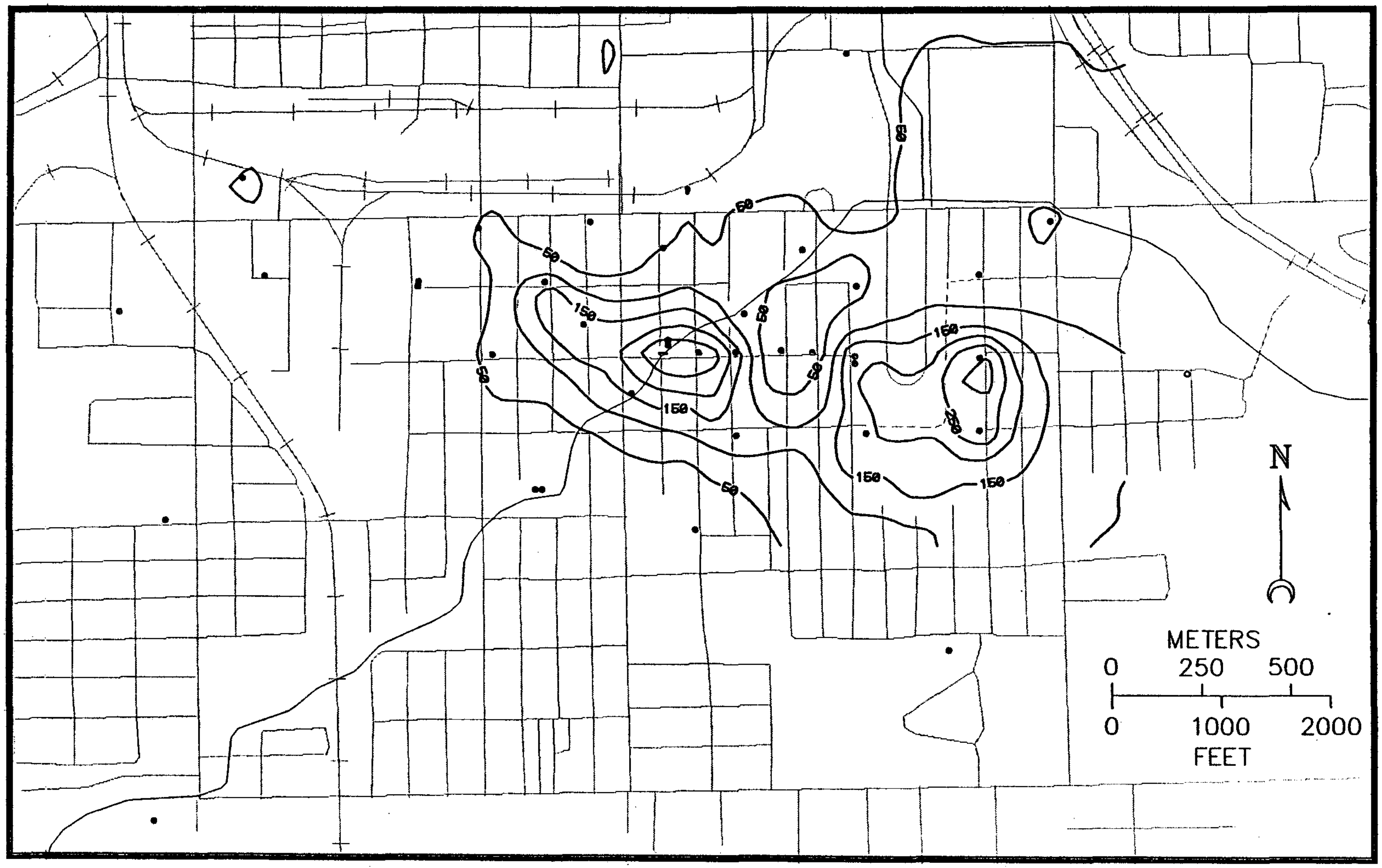


Figure 44. TCA concentrations within the intensive study area for August 1991.

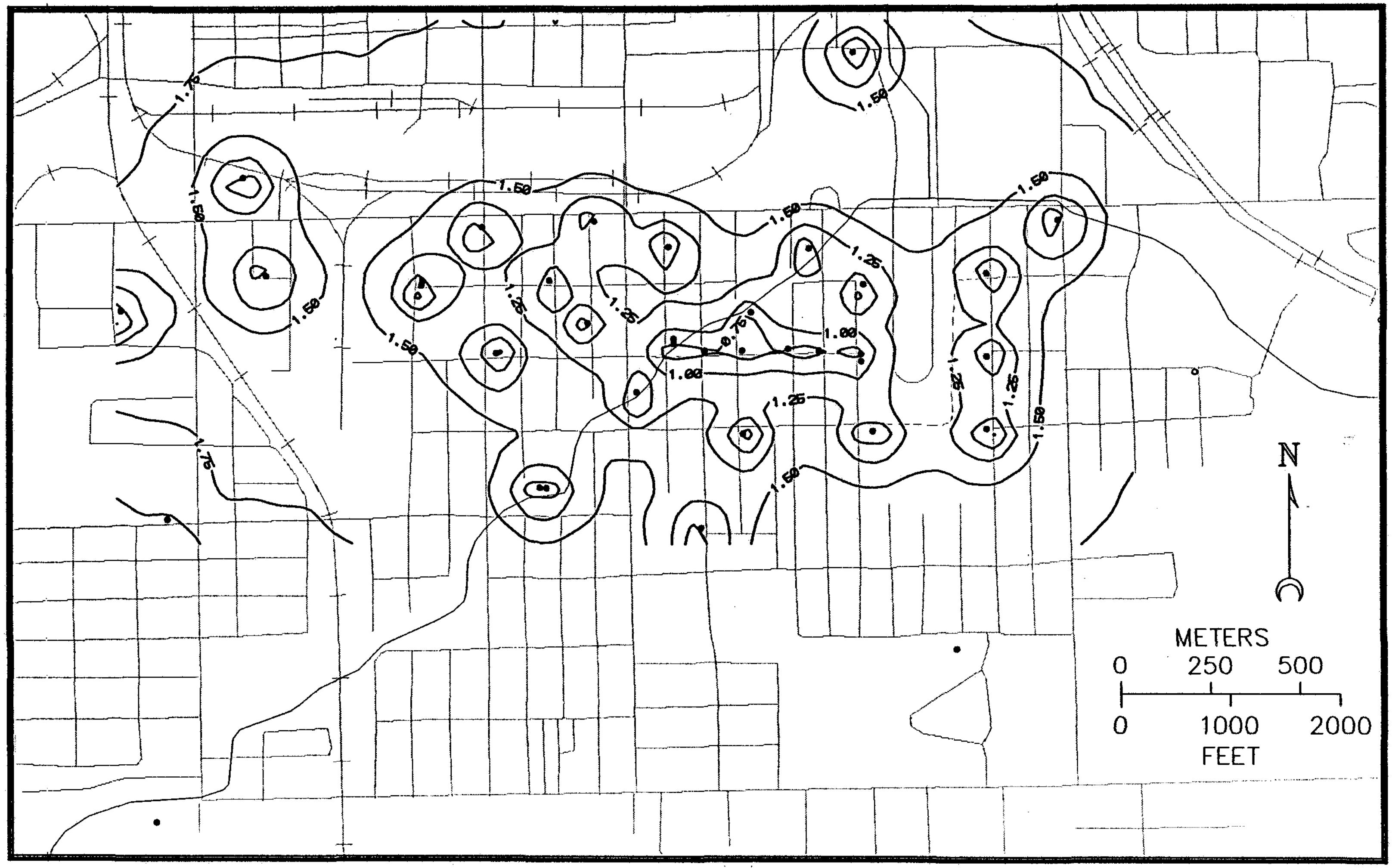


Figure 45. Standard deviation of estimated ln(TCA) concentrations for August 1991.

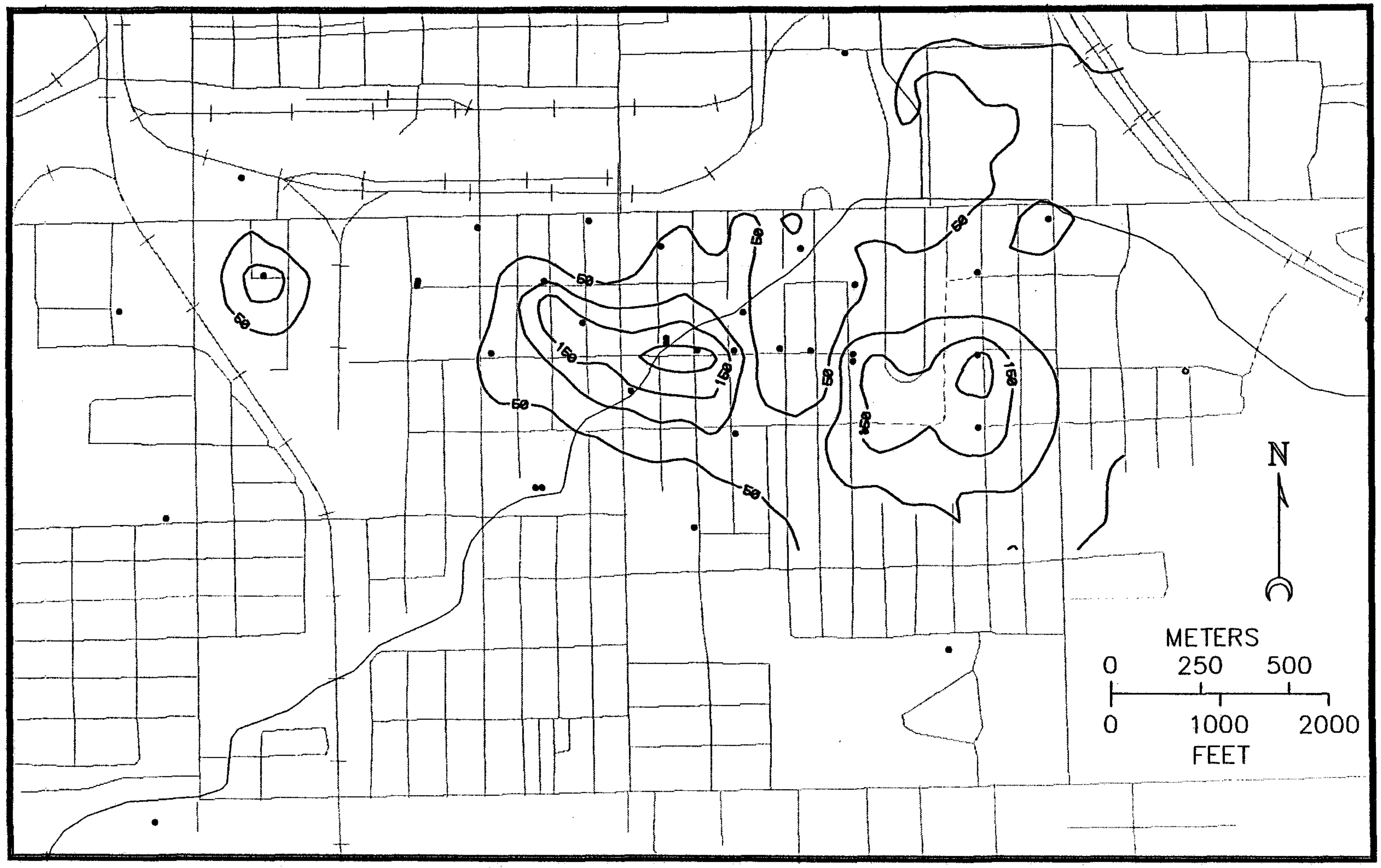


Figure 46. TCA concentrations within the intensive study area for December 1991.

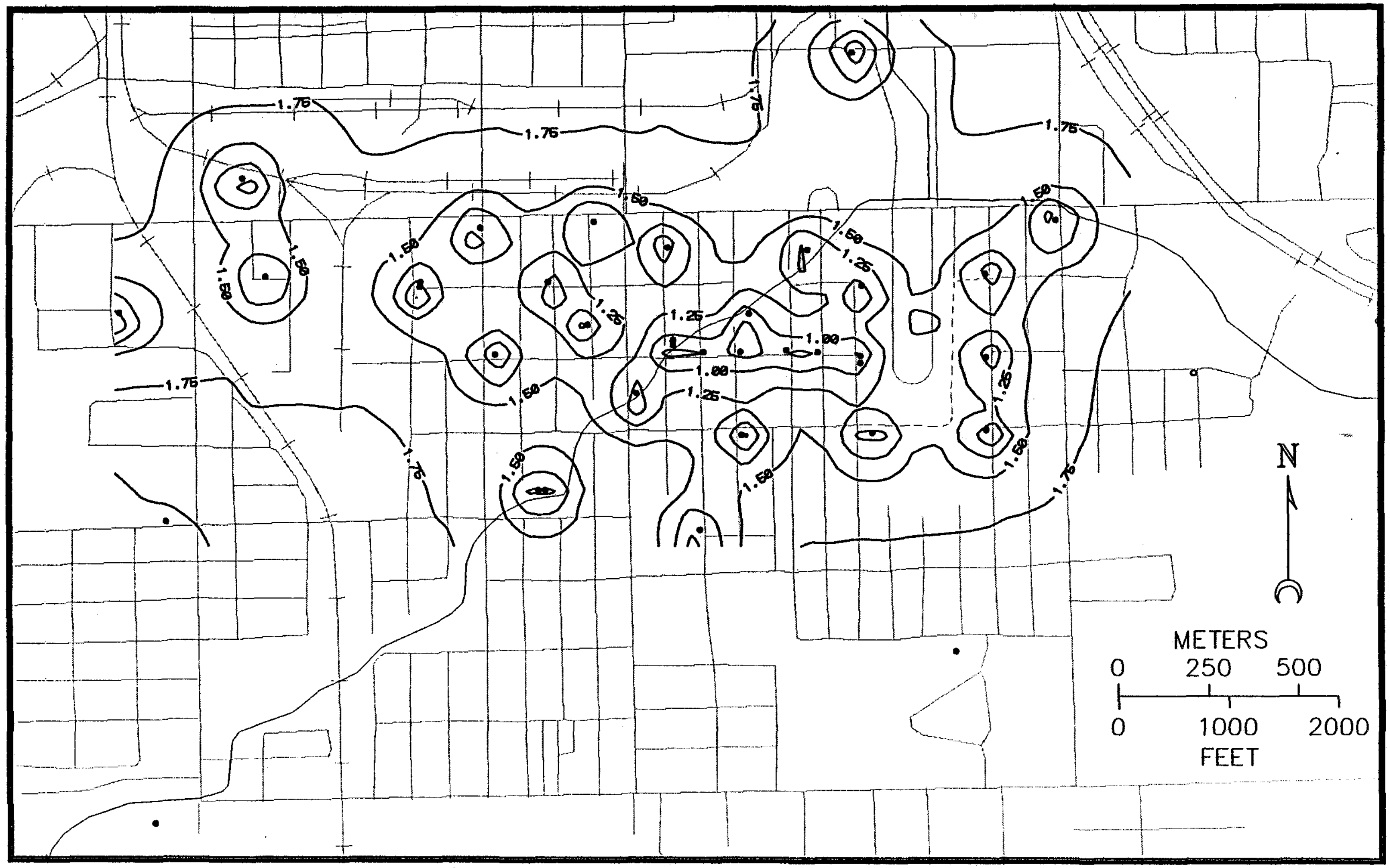


Figure 47. Standard deviation of estimated ln(TCA) concentrations for December 1991.

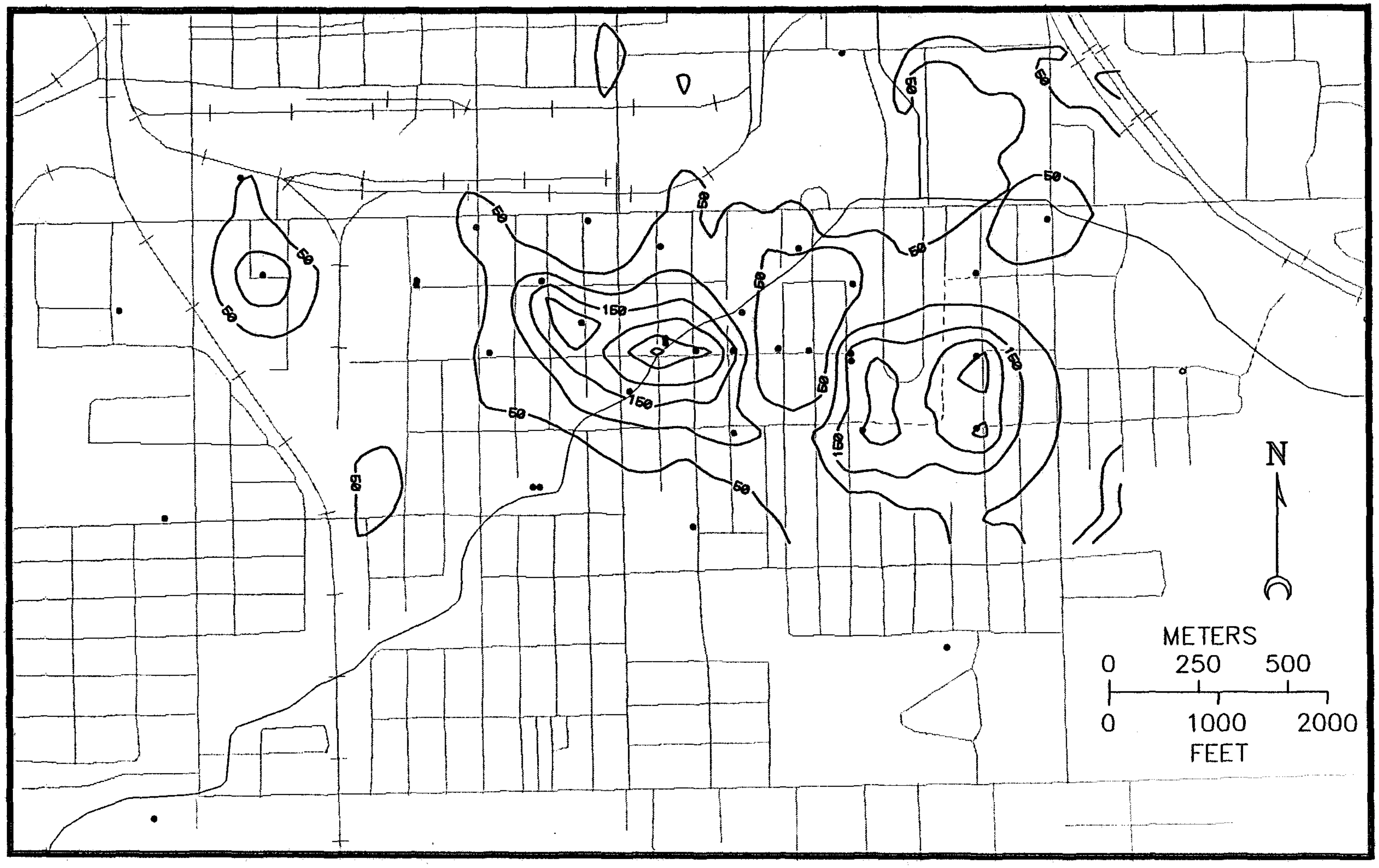


Figure 48. TCA concentrations within the intensive study area for March 1992.

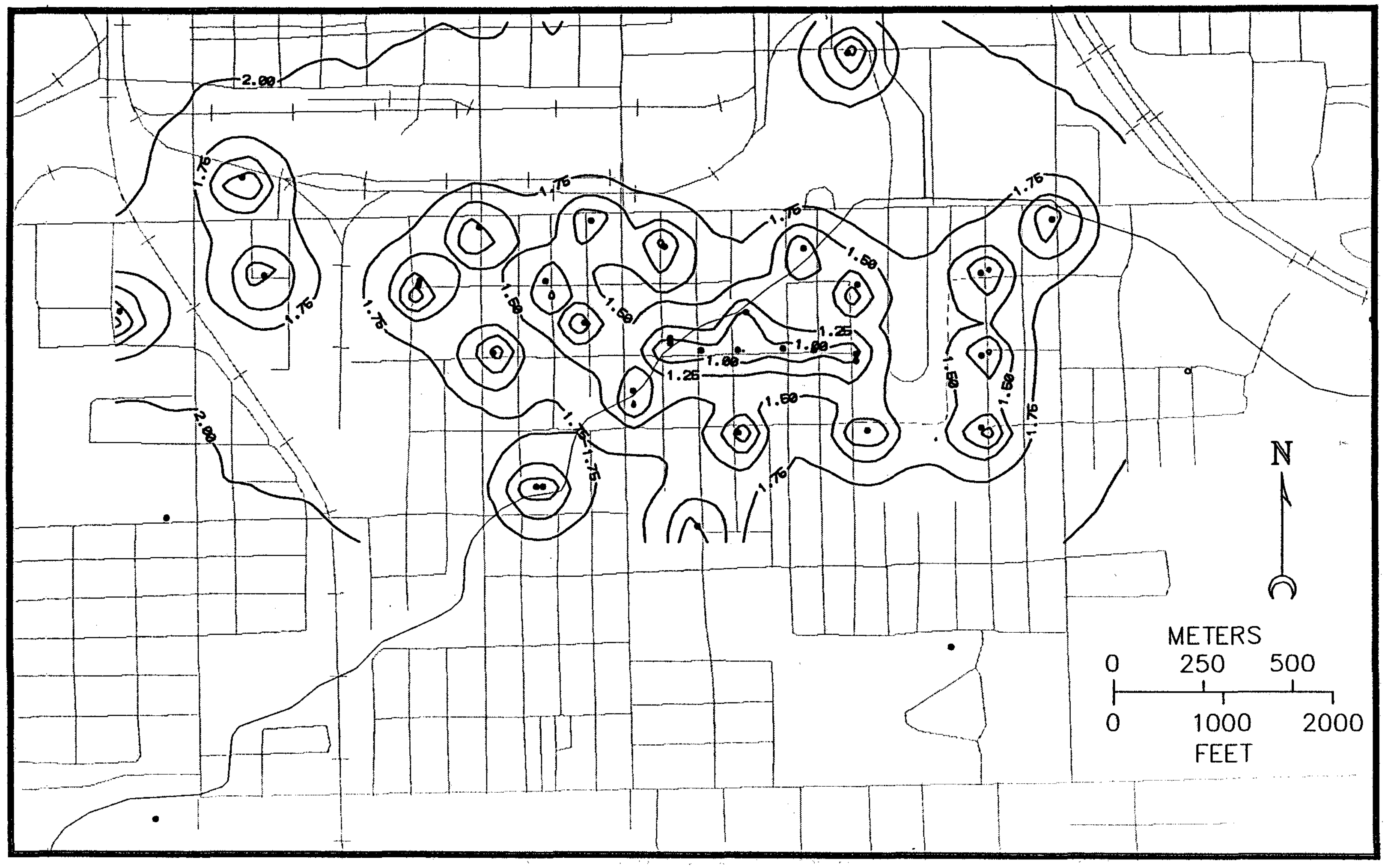


Figure 49. Standard deviation of estimated ln(TCA) concentrations for March 1992.

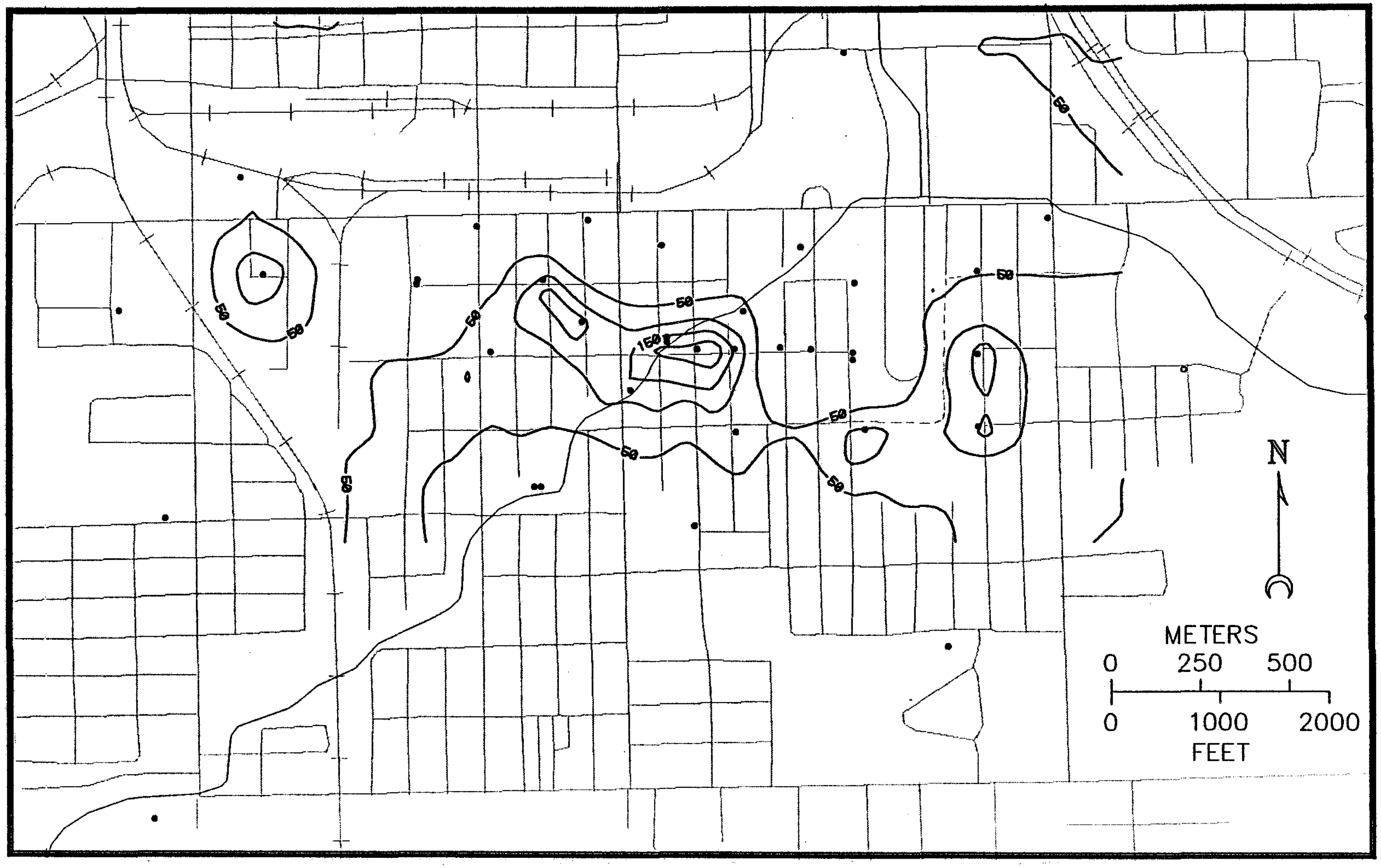


Figure 50. TCA concentrations within the intensive study area for September 1992.

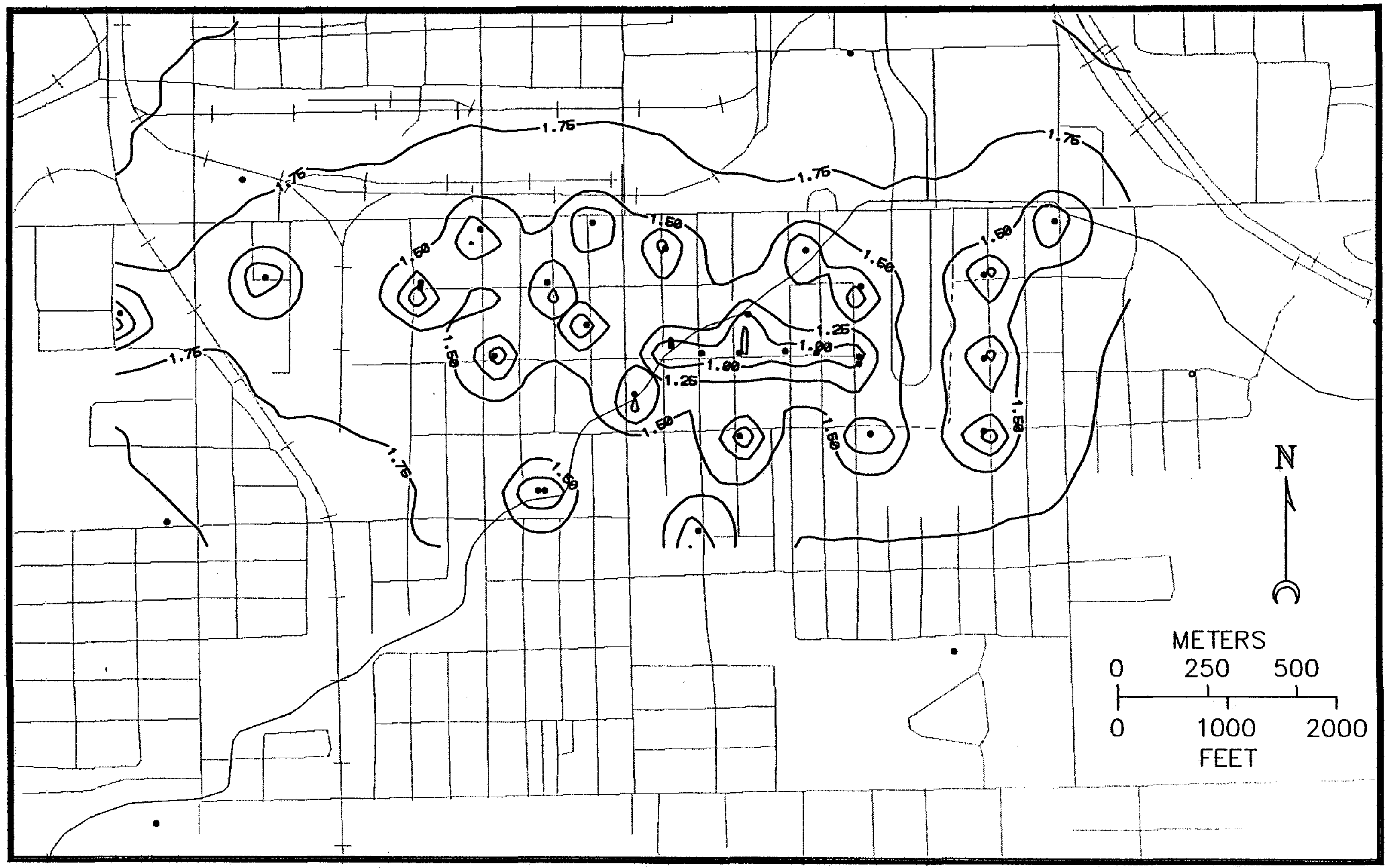


Figure 51. Standard deviation of estimated ln(TCA) concentrations for September 1992.

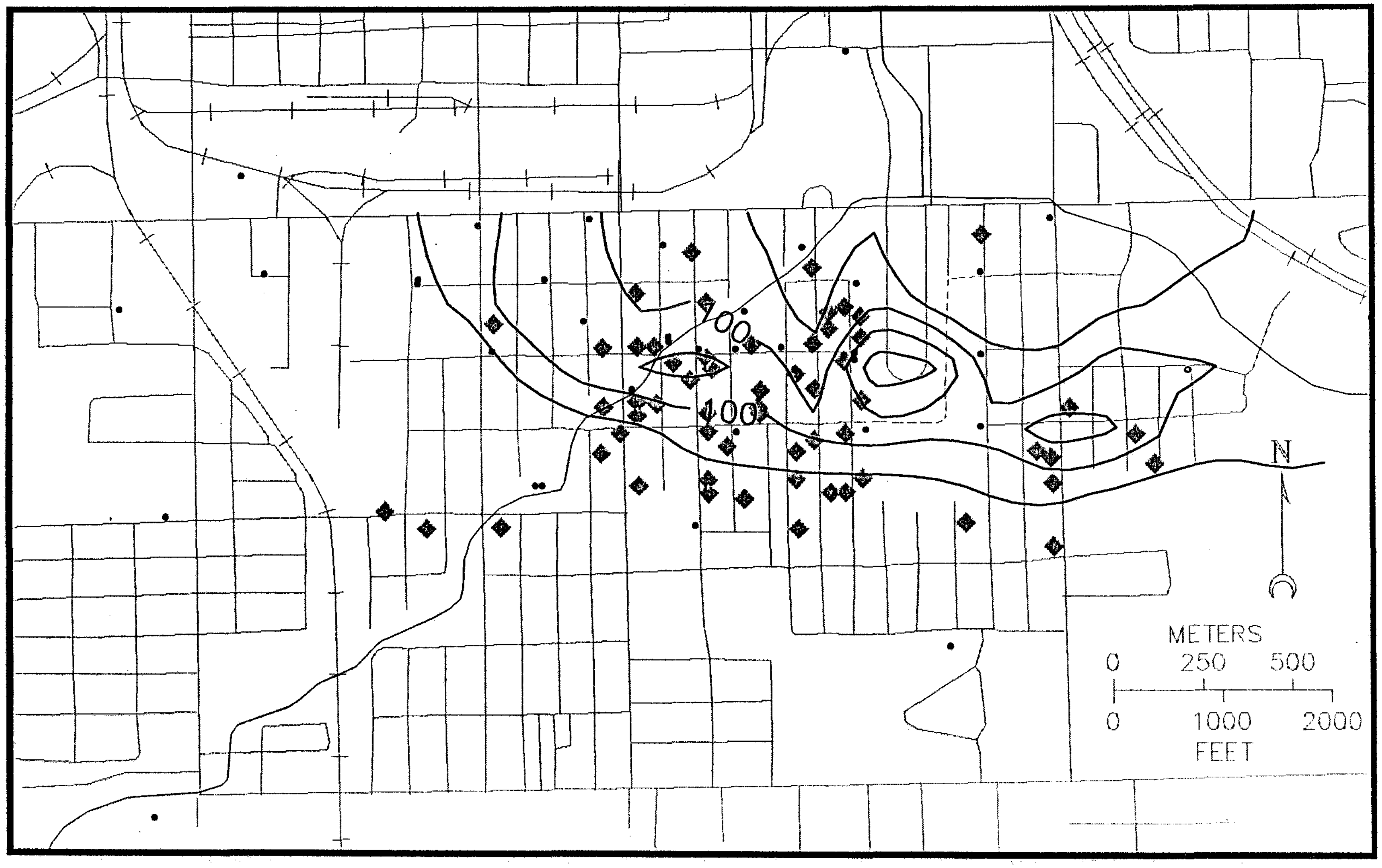


Figure 52. TCA concentrations based on domestic well sampling in July 1990.

concentration appears repeatedly as a tongue or less than 50 µg/L jutting into the northern edge of the plume.

An examination or the temporal variability or the plume by more rigorous means than simple visual inspection was attempted. An analysis or the time series (across the five quarterly sampling periods) or interpolated values at each of the 38x20 blocks used in the kriging analysis was performed. A contour map or the standard deviation of these interpolated values is presented in figure 53. This map suggests that the absolute magnitude of the temporal variability was greatest in the southeastern portion of the plume.

This variability may match the variability associated with hydraulic gradient changes shown in figure 28. This may be misleading, however, if one is interested in the dynamics of the plume because the absolute magnitude of temporal change could be greatest simply where concentrations are highest (e.g., one cannot have a change of 100 µg/L if the maximum concentration is only 25 µg/L). To examine where concentrations were changing based on the mean concentration in that area, a map was prepared which expresses the ratio of the standard deviation to the average concentration (figure 54). This map suggests that the area of greatest change was on the western edge of the study area, closer to the leading edge of the plume. Conceptually, the occurrence of greater changes along or near the leading edge of the plume makes sense. TCA temporal variability here also may coincide with hydraulic gradient variability shown in figure 28.

Jackknife Approach. Results of structural analyses for TCA concentrations for the five quarterly sampling periods and the two domestic well samplings (December 1989 and July 1990), with accompanying jackknife confidence bands, are shown in figures 55 - 61. the estimated semivariograms for each sampling interval are somewhat different (figure 62), leading one to believe that temporal change in the spatial correlation structure had occurred. the confidence bands for each estimated semivariogram are large enough however to indicate that any differences are not statistically significant (figure 63). For ease of examination, figure 64 shows the results for only the

December 1989 and July 1990 sampling events overlaid. Note that the overlap of confidence limits is complete.

The notion that there nave teen no temporal changes in spatial correlation is consistent with the physical process that we expect are controlling the distribution or contaminants. The contaminant source is thought to be at least 1 mile (1,609 m) upgradient from the most upgradient monitoring well used for this study, and the plume is thought to be quite old (decades) and is quite stable within the area we were monitoring (Camp, Dresser & McKee, 1995).

Perhaps the most interesting feature of the sample semivariograms and the associated jackknife confidence bands is the relative differences in the width of the confidence bands. Clearly, confidence in semivariogram estimates is extremely sensitive to sample size. Note the differences in the widths

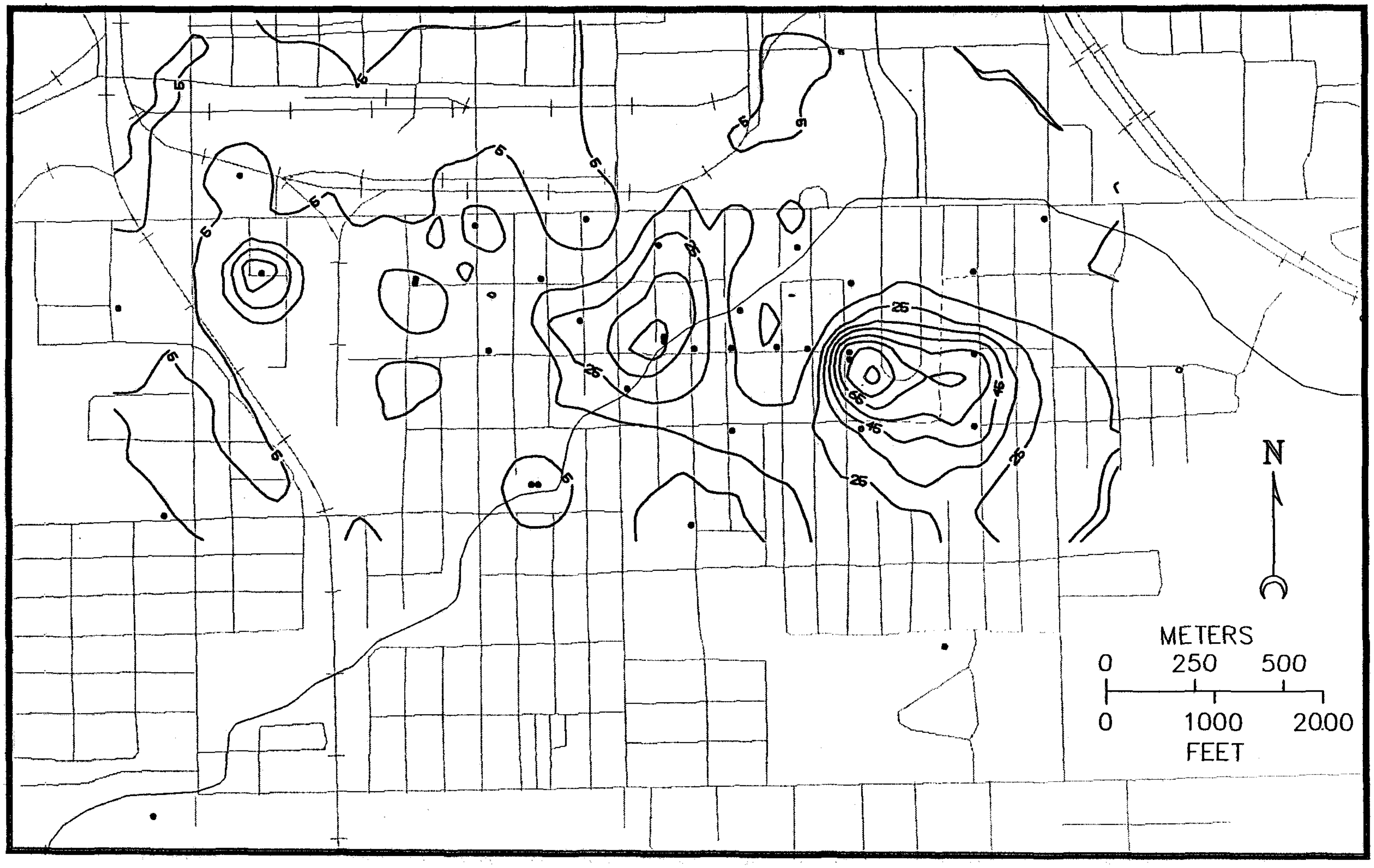


Figure 53. Standard deviation of estimated ln(TCA) concentrations for the five quarterly sampling periods.

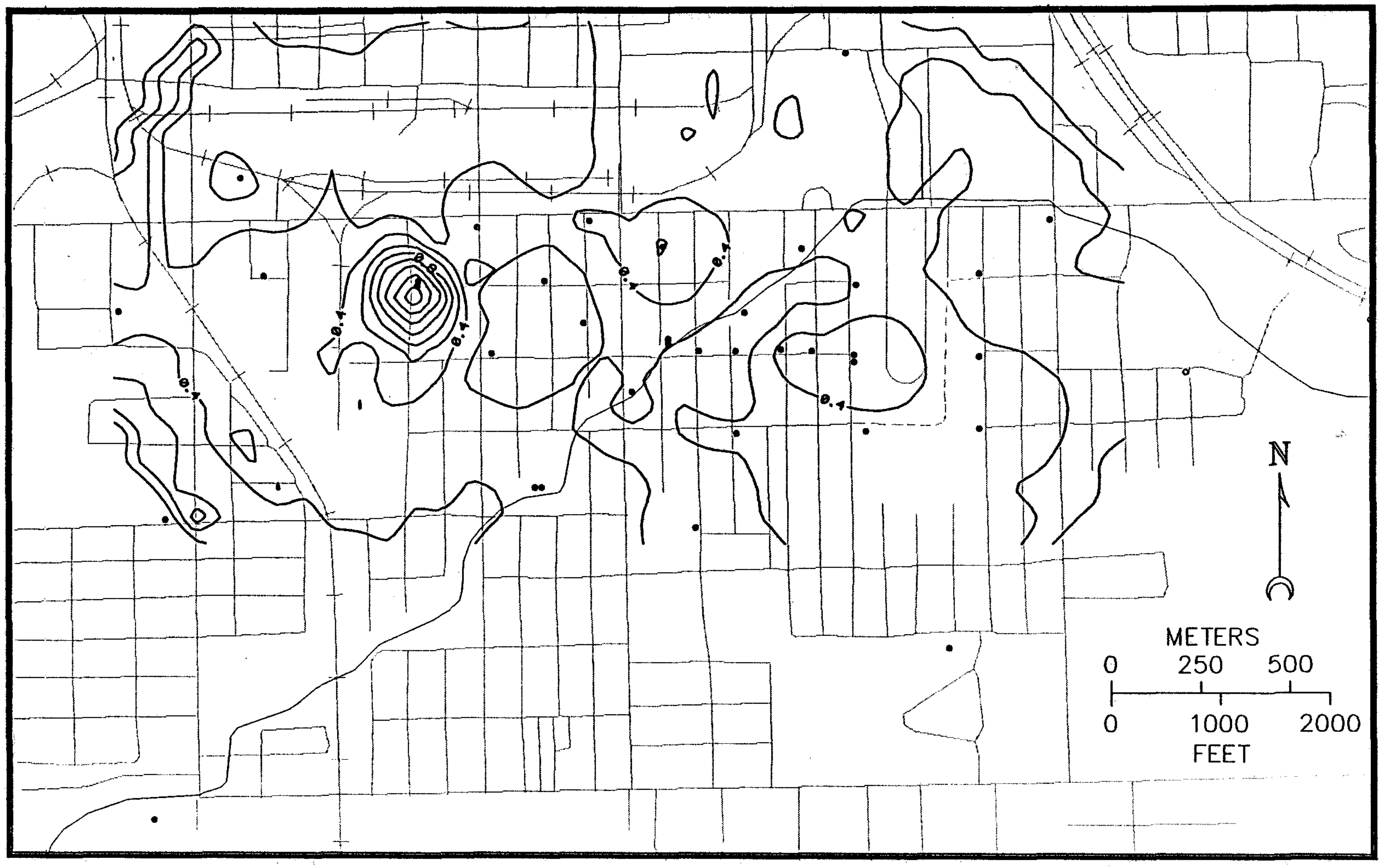


Figure 54. Ratio of the standard deviation to the mean ln(TCA) concentrations for the five quarterly samling periods.

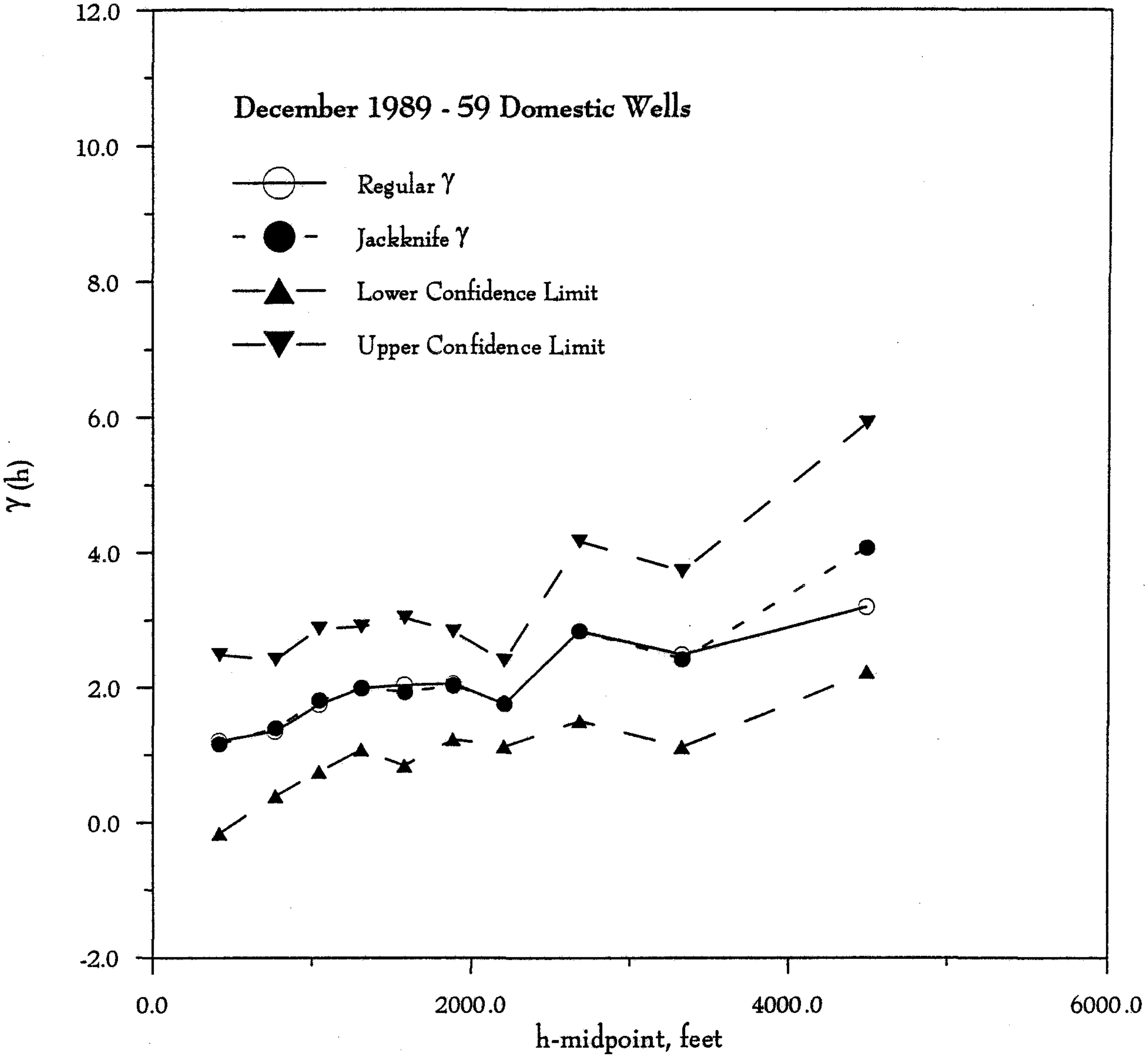


Figure 55. Jackknifed confidence intervals on the semivariogram of December 1989 ln(TCA) domestic well data.

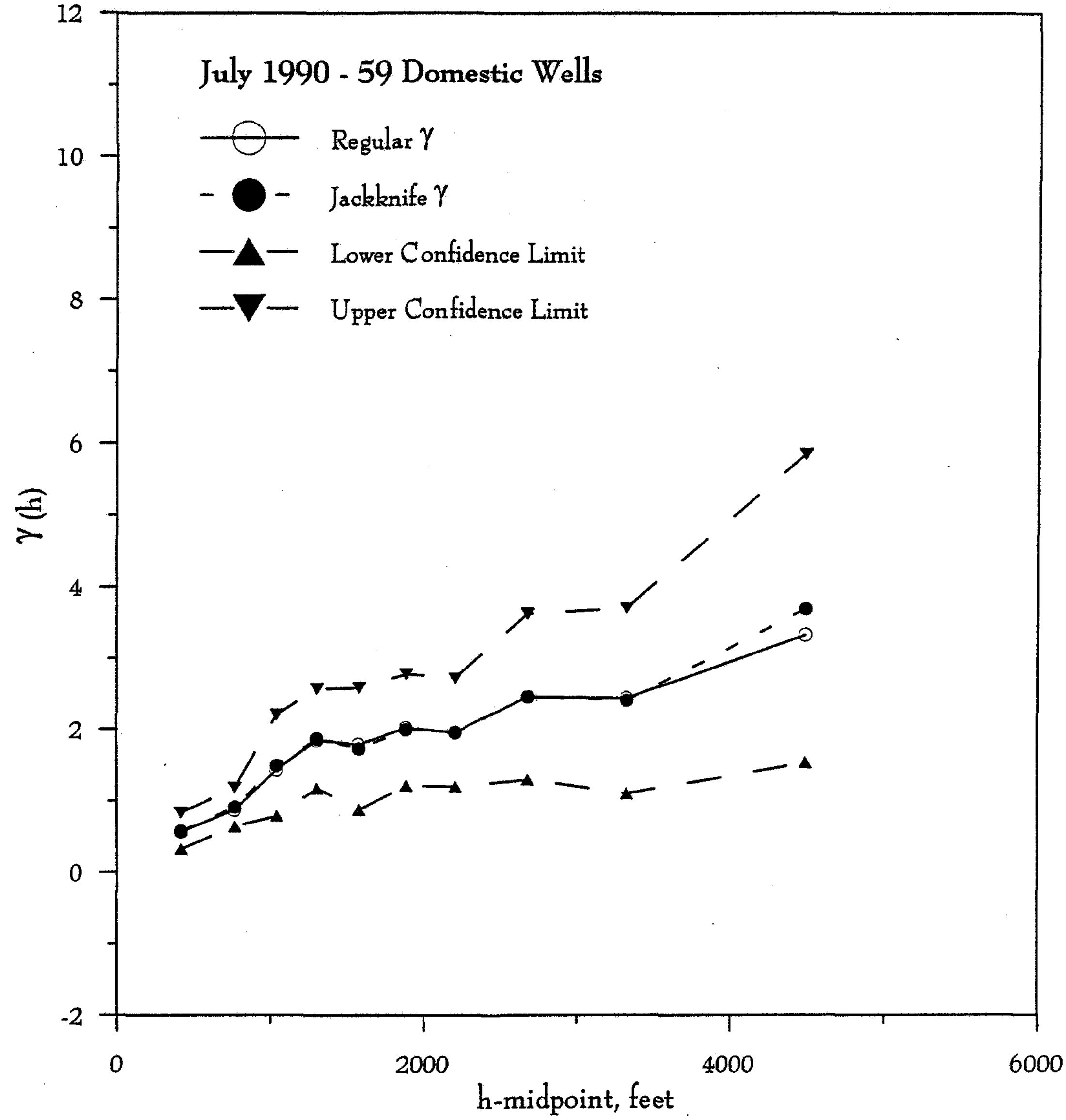


Figure 56. Jackknifed confidence intervals on the semivariogram of July 1990 ln(TCA) domestic well data.

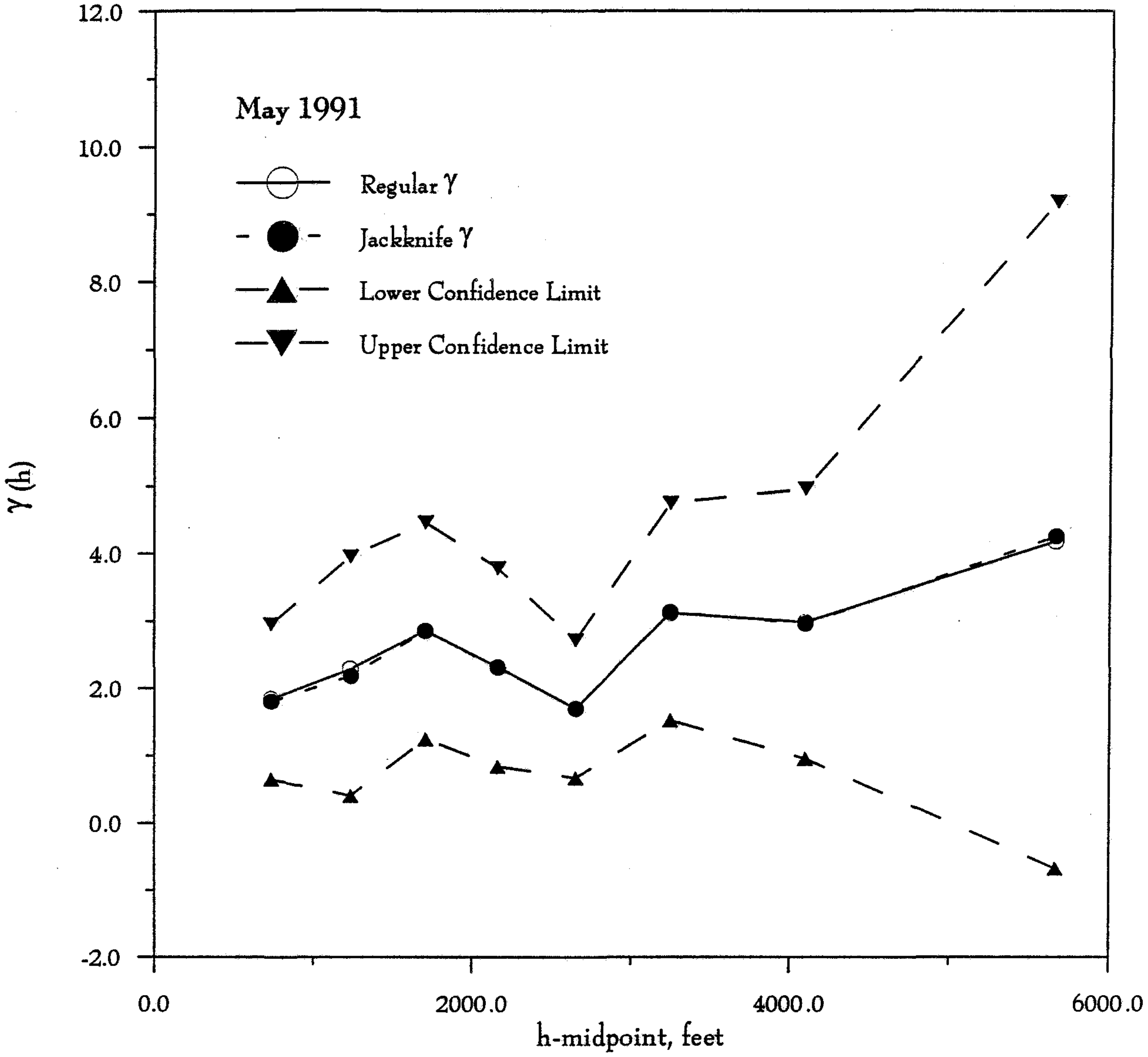


Figure 57. Jackknifed confidence intervals on the semivariogram of May 1991 ln(TCA) monitoring well data.

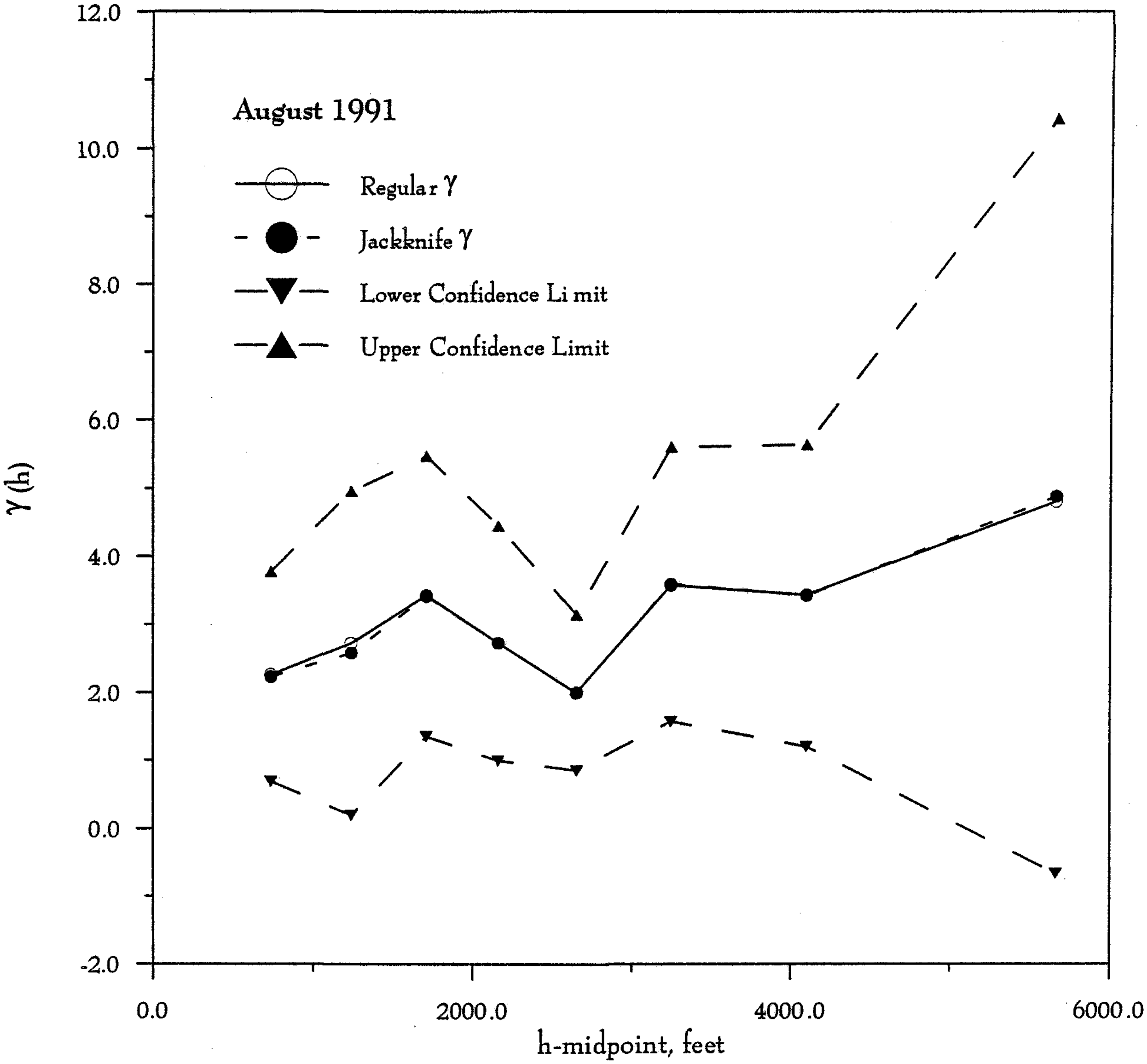


Figure 58. Jackknifed confidence intervals on the semivariogram of August 1991 ln(TCA) monitoring well data.

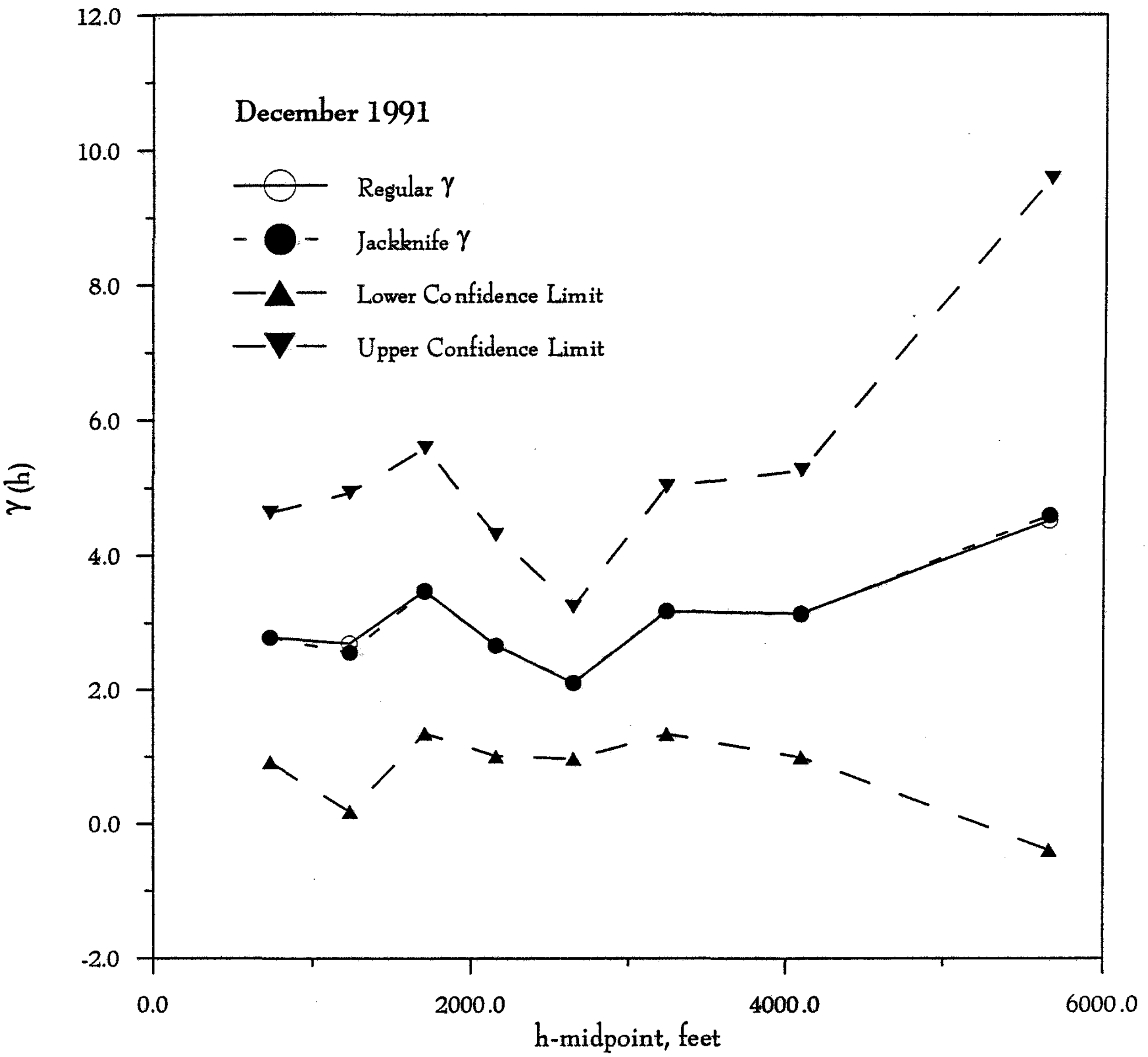


Figure 59. Jackknifed confidence intervals on the semivariogram of December 1991 ln(TCA) monitoring well data.

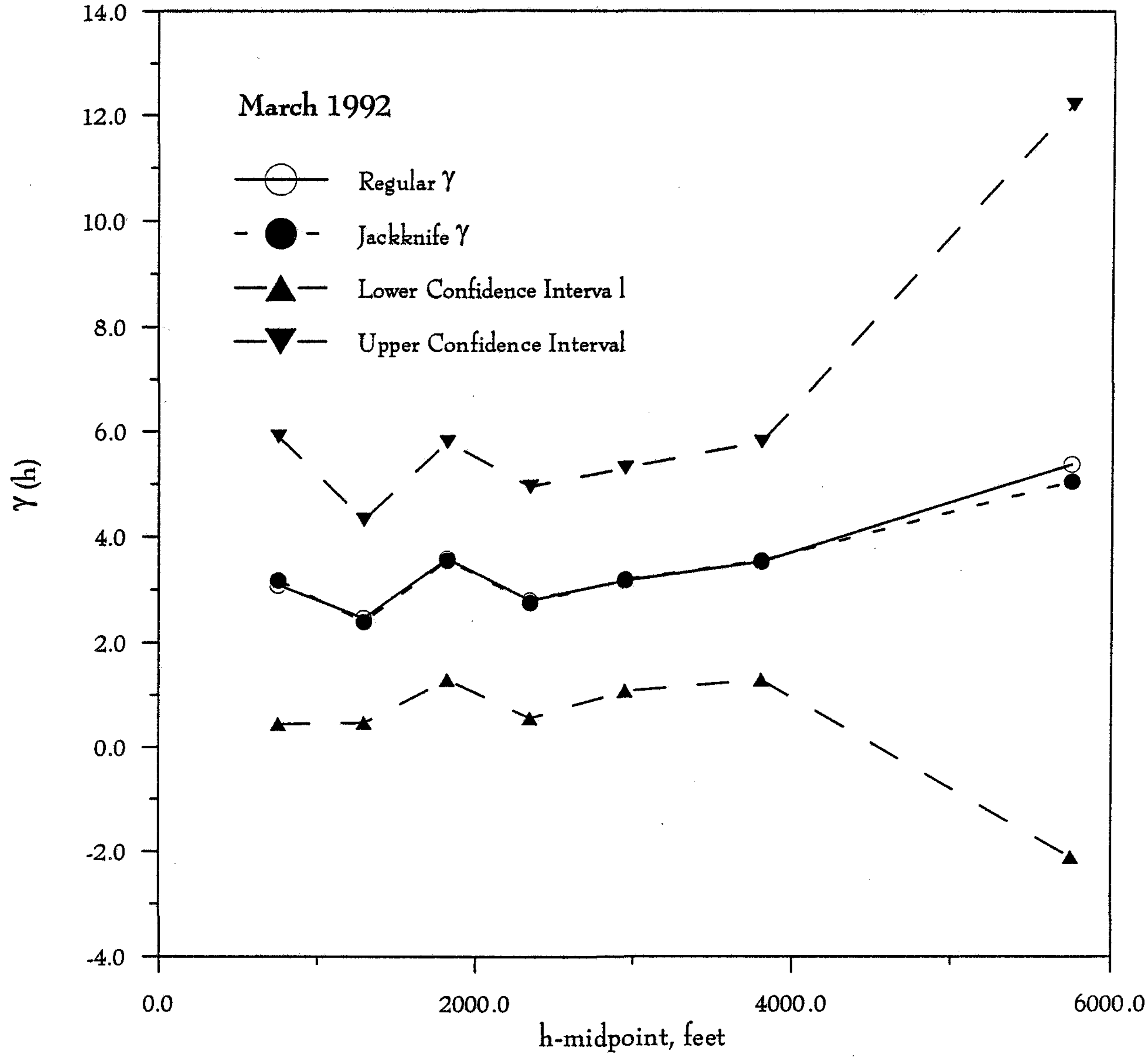


Figure 60. Jackknifed confidence intervals on the semivariogram of March 1992 ln(TCA) monitoring well data.

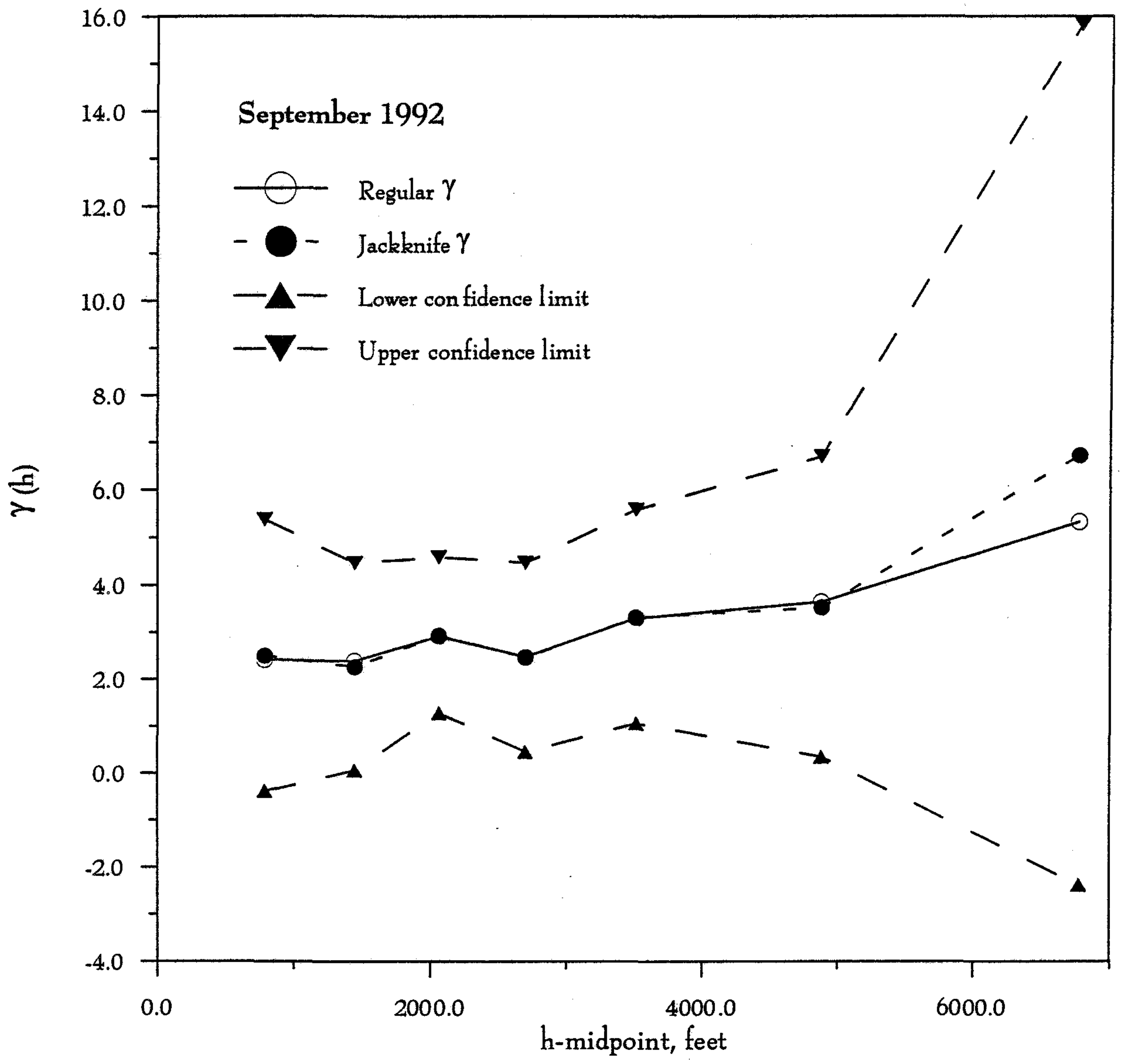


Figure 61. Jackknifed confidence intervals on the semivariogram of September 1992 ln(TCA) monitoring well data.

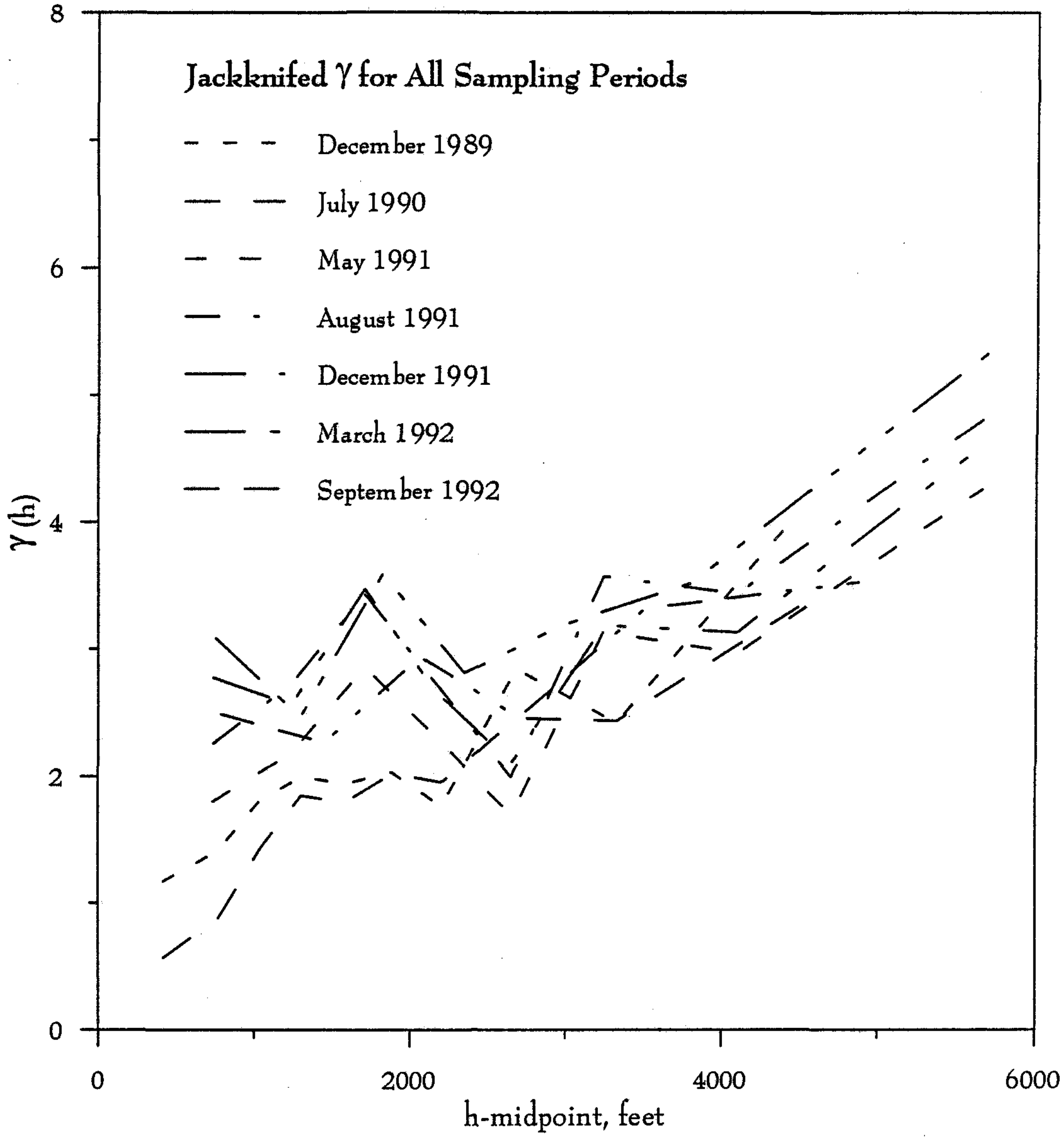


Figure Jackknifed γ for all sampling periods.

Figure 62. Jackknifed γ for all sampling periods.

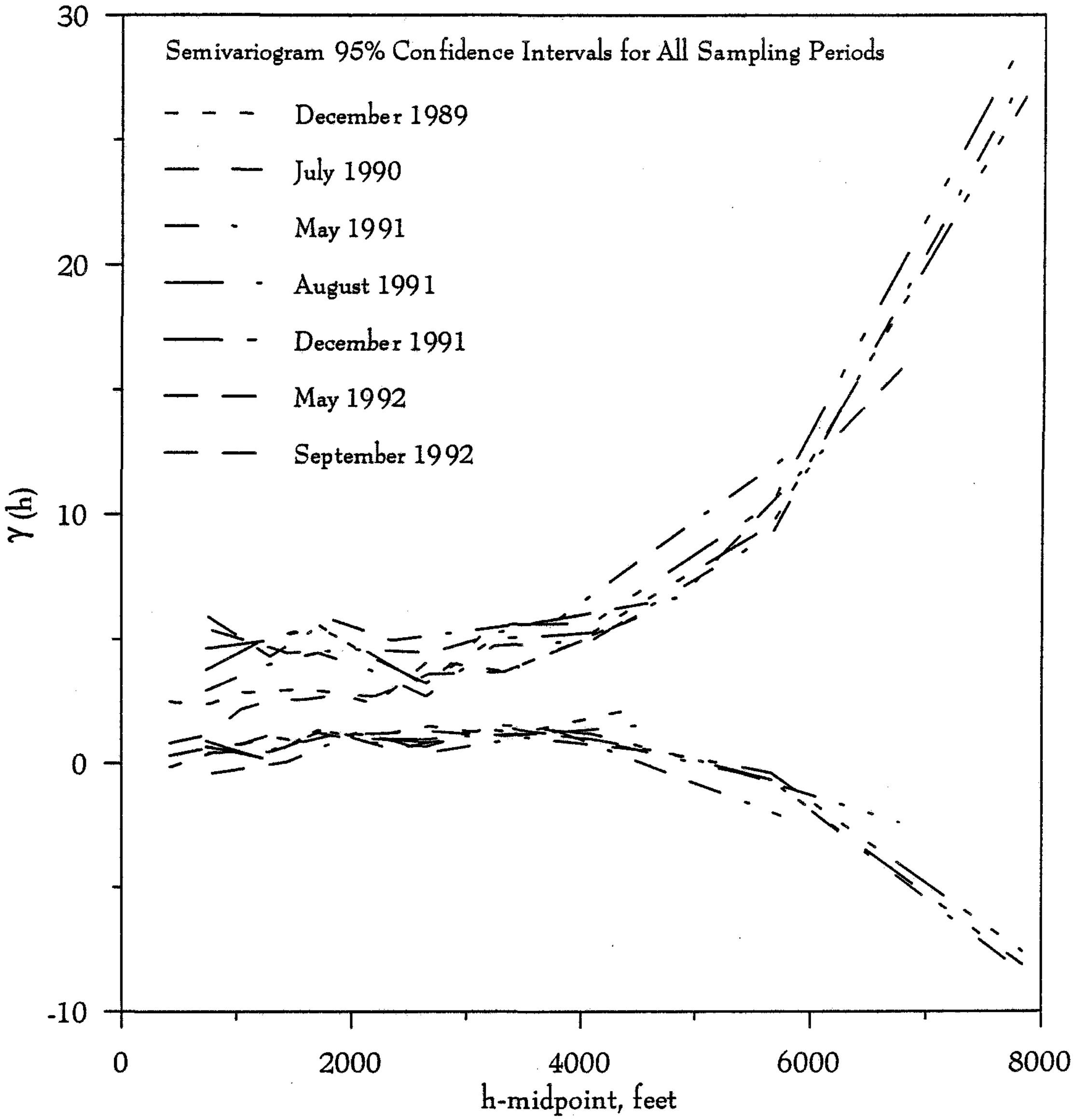


Figure 63. Jackknifed 95% confidence intervals on semivariograms for all sampling periods.

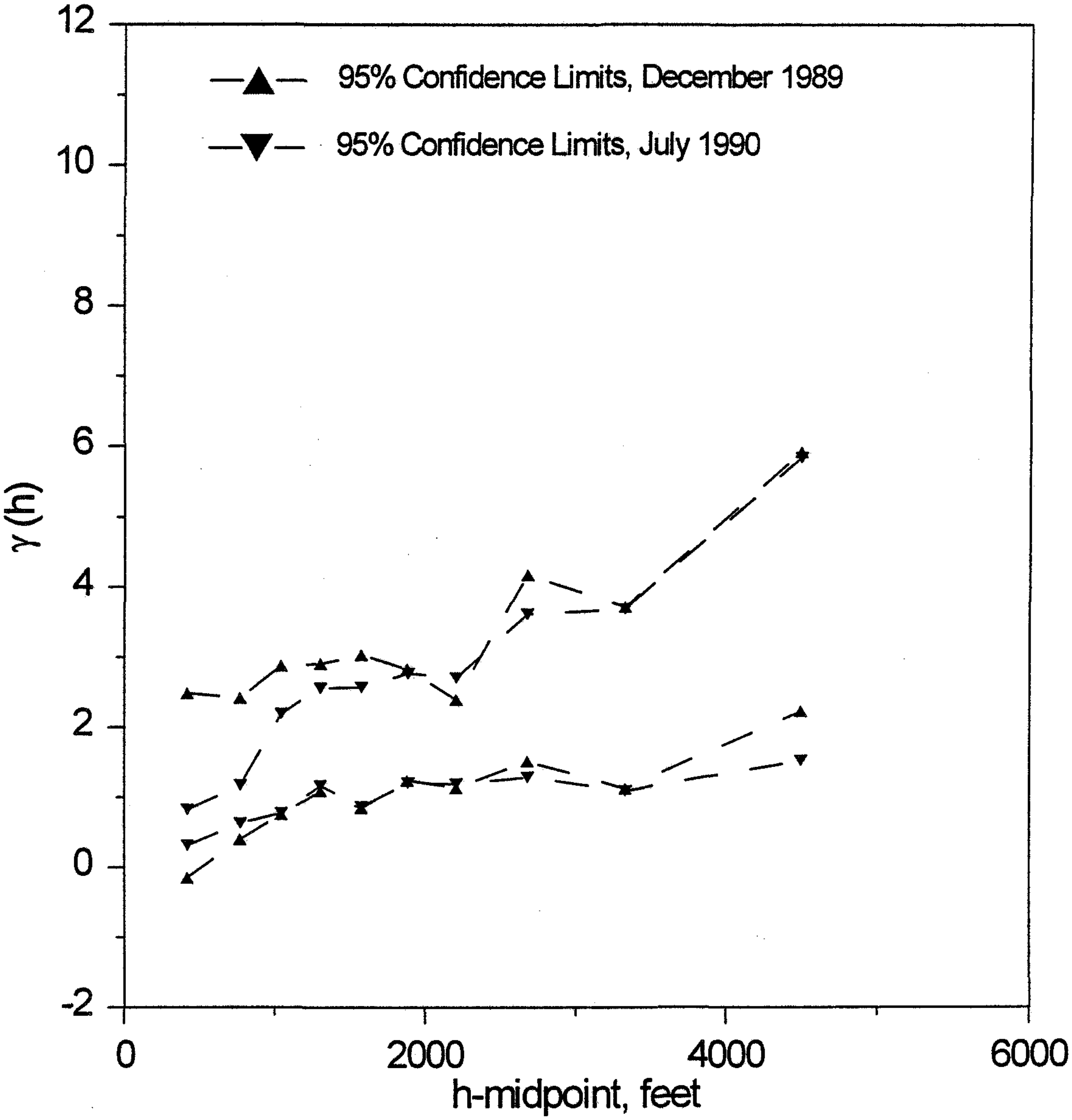


Figure 64. Jackknifed 95% confidence intervals on semivariograms of December 1989 and July 1990 ln(TCA) domestic well data.

of the confidence bands for the sampling periods where 59 wells were used (the December 1989 and July 1990 samplings) vs. 30 wells (the quarterly samplings).

The effect of sample size is somewhat intuitive and was not unexpected. What was unexpected, however, was the difference in the confidence bands between the December 1989 and July 1990 sampling periods (figures 55 and 56). We did not expect to see such a difference because the exact same sampling points were used for each period. We interpret the difference in the confidence band to illustrate the effect of sampling and laboratory variability. Different field personnel, sampling protocol, and laboratories were used for the two periods. We suspect that stricter protocol implemented by the July 1990 sampling team resulted in less noise in the data. The data set with less added variability allowed for more confidence in the estimation of the semivariogram.

Conclusions on Spatial Variability

We conclude from our analysis of jackknife estimates of sample semivariograms (and the associated confidence limits) that our data set could not identify any significant temporal changes in the spatial correlation of TCA over the three years that the study spanned. More importantly, however, we demonstrated the high level of uncertainty that is associated with the estimation of semivariograms from field data sets. We also demonstrated how careful control of artificial variability can improve our confidence in estimates of spatial correlation. The fact that sample size had such a profound effect on uncertainty in estimates or the semivariogram, coupled with the fact that we did not observe much in the way of temporal change in the plume, indicates that the information return for our characterization would have been greater if we had used more sampling points and fewer sampling events. The loss of the domestic wells as potential sampling points had a profound effect on our geostatistical analyses.

Although we recognize that some of these conclusions are specific to our investigation, we conclude generally that variability and uncertainty in estimated spatial correlation is quite significant and should be considered in the application of geostatistics to ground-water contamination problems. Applications such as probability kriging to define clean-up boundaries or sampling network optimization based on kriging standard deviations are particularly sensitive to semivariogram uncertainty. We believe the jackknife technique is an appropriate approach to quantifying this uncertainty.

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