Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation

Todd H. Wiedemeier, Michael J. Barden, Patrick E. Haas, and W. Zachary Dickson

CONTENTS

Introduction ........................................................................................................ 574
Purpose of Monitoring for Natural Attenuation ............................................. 576
Types of Monitoring for Natural Attenuation .............................................. 577
  Site Characterization Monitoring .............................................................. 577
  Validation Monitoring .............................................................................. 578
  Long-Term Monitoring .............................................................................. 578
    Performance Monitoring ........................................................................ 578
    Compliance or Contingency Monitoring ................................................ 578
Essential Design Elements of a Monitoring Plan .......................................... 579
  Location and Placement of Monitoring Points ......................................... 580
    Plumes that do not Discharge to Surface-Water Bodies ......................... 582
    Plumes that Discharge to Surface Water Bodies ..................................... 586
Analytical Protocols — What to Analyze for and When ............................... 586
  Typical Ground-Water Analytes for Evaluating the Long-Term Performance of Natural Attenuation ........................................................ 588
    Sampling in the NAPL Source Area ....................................................... 588
    Contaminants and Transformation Products ........................................... 594
    Naturally Occurring Electron Acceptors and Metabolic Byproducts .......... 594
    General Water-Quality Parameters ....................................................... 594
Supplemental Monitoring Parameters .......................................................... 594
Ground-Water Sampling Techniques ............................................................ 595
  Sampling with Peristaltic Pumps ............................................................... 595
  Sampling with Submersible Pumps ............................................................ 595
  Sampling with Bailers ............................................................................... 596
  Diffusion Samplers ................................................................................... 597
  General Ground-Water Sampling Considerations ..................................... 597
  Sampling Frequency ................................................................................. 598
Evaluation and Interpretation of Monitoring Data ......................................... 599
  Evaluating Contaminant Data ................................................................ 600
  Graphical Methods for Evaluating Plume Behavior .................................. 600
  Statistical Methods for Evaluating Plume Behavior .................................. 604
    Nature of Ground-Water Concentration Data and Appropriate Statistical Methods ........................................................................ 607
    Tests for Trend ....................................................................................... 607
    Tests for Differences between Groups of Data ....................................... 612

573
Natural attenuation processes affect the migration and fate of organic compounds in all hydrologic systems. Over the past several years, regulatory agencies and environmental professionals have come to recognize the importance of these natural processes in affecting contaminant attenuation. When they are shown to be protective of human health and the environment, and when a well-designed monitoring program is in place to document the efficacy of these processes, they can be a valuable component of site remediation strategies.

In April 1999, the Office of Solid Waste and Emergency Response (OSWER) of the U.S. Environmental Protection Agency (U.S. EPA) published a directive on the use of natural attenuation, entitled *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (U.S. EPA, 1999). As implied by the title of this policy document, monitoring will be required to evaluate the long-term effectiveness of natural attenuation and to assure protection of human health and the environment. According to U.S. EPA (1999), the monitoring program designed for each site should specify the location, frequency, and types of samples and measurements necessary to evaluate if the remedy is performing as expected and if it is capable of attaining remediation objectives.

Designing an effective monitoring program involves locating ground-water monitoring wells and developing a site-specific ground-water sampling and analysis strategy and
contingency plan. The monitoring program should be designed to monitor contaminant plume behavior over time and to verify that natural attenuation is occurring at rates sufficient to protect potential downgradient receptors. All available site-specific data and information developed during site characterization, conceptual model development, and ground-water modeling (as appropriate) should be used when preparing a monitoring program. The design of the monitoring program should include consideration of existing receptor exposure pathways, as well as exposure pathways arising from potential future use of the ground water and land. The results of a natural attenuation evaluation as described by U.S. EPA (1998) and Wiedemeier et al. (1995, 1999) are critical to the design of a monitoring program. For those sites where the ground-water flow field cannot be determined with certainty (e.g., fractured bedrock), the evaluation of natural attenuation, and the design of a monitoring program, can be problematic.

The monitoring strategy for a given site will depend upon several primary and secondary factors and will likely be modified over time as new information is obtained. Primary technical factors to consider include (at a minimum) distance to potential receptor exposure points, ground-water seepage velocity and direction, types of contaminants, aquifer heterogeneity, the three-dimensional distribution of constituents of concern; areas of unique geochemical conditions; surface-water impacts, and the effects of engineered remediation systems. In addition, primary factors can include the level of understanding of historical plume behavior and site complexity. In other words, if one has 10 yr of defensible data demonstrating a stable or shrinking plume and site conditions that are unlikely to change, the monitoring strategy can be optimized to focus on monitoring critical areas. Primary regulatory factors may include points of compliance, alternate concentration limits, or requirements identified under the Resource Conservation and Recovery Act (RCRA) or site-specific records of decision, remedial action plans, or decision documents. Secondary factors to consider include (at a minimum) access issues, property lines, and contaminant contributions from off-site sources. Each of these factors will influence the final design of the monitoring program. Perhaps the most critical factors to consider when developing a monitoring program are the distance to potential receptor exposure points and the seepage velocity of ground water. The combination of these two factors will influence well spacing and sampling frequency. Typically, the greater the ground-water seepage velocity and the shorter the distance to potential receptors, the greater the sampling frequency. The use of seepage velocity usually (if not always) overestimates the rate of solute movement because some sorption, dispersion, and biodegradation of dissolved contaminants likely are occurring which will retard the downgradient movement of the contaminants. The analytical protocol developed for a site should be influenced mainly by the type of contamination and the geochemical conditions that affect the fate of the chemicals of concern. Sites with chlorinated solvent contamination likely will require a more diverse suite of analytical parameters (e.g., chloride, ethene, ethane, known solvent breakdown products, etc.) than sites contaminated with fuel hydrocarbons. This is because of the differences in the patterns of biodegradation between different contaminants. For example, it is now well known that fuel hydrocarbons almost invariably biodegrade in the shallow subsurface. This is in contrast to chlorinated solvents, which exhibit varying degrees of biodegradation potential under unique geochemical conditions. The degree of aquifer heterogeneity also will influence the placement of the monitoring wells, with more heterogeneous sites typically requiring a more elaborate sampling network. If surface water is impacted, several factors must be considered, including the amount of contaminant flux into the body of water, the regulatory status (e.g., impaired), and the physical characteristics of the water body. Placement of sample collection points, the analytical protocols to be used for monitoring, and the determination of sampling frequency, are described later in this chapter.
One of the most important purposes of long-term monitoring is to confirm that the contaminant plume is behaving as predicted with no unacceptable impacts to human health or the environment. Graphical and statistical methods can be used to evaluate plume stability and behavior. When evaluating the stability of a contaminant plume, it is important that the historical data demonstrate a clear and meaningful trend at appropriate monitoring points. Graphical and statistical techniques that can be used to evaluate plume stability are described later in this chapter.

Changing site conditions can result in variable plume behavior over time. To circumvent potential problems, a contingency plan should be an integral part of the monitoring program. Contingency plans are used to help ensure protection of human health and the environment should a contaminant plume begin to migrate farther or faster than predicted, and typically involve some kind of engineered remediation. It is prudent to update the contingency plan on a periodic basis as the plume attenuates or as new remediation technologies are developed. Although some engineered remediation systems may be effective in achieving plume containment, it should be kept in mind when developing the contingency plan that some remediation systems may have an adverse impact on contaminant degradation. The development of contingency plans is discussed subsequently.

As with any remedial option for sites contaminated with organic compounds, remediation goals and an exit strategy should be established early in the regulatory negotiation process. This will help establish clear objectives for long-term monitoring, and should help define the length of time that monitoring will be required. Exit strategies are discussed later in this chapter.

Decisions regarding remedy effectiveness and the adequacy of the monitoring program will generally result in either continuation of the program, program modification, implementation of a contingency or alternative remedy, or termination of the performance monitoring program (U.S. EPA, 2004). Such decisions are appropriately based on site-specific, quantifiable performance criteria defined in the monitoring plan. Continuation of the program without modification should not be considered a default, but would be best supported by contaminant concentrations behaving according to remedial expectations while ground-water flow and geochemical parameters remain within acceptable ranges. Monitoring programs should be subjected to periodic review and optimization to ensure that goals are being met. Modification of the program, including increases or decreases in monitoring parameters, frequency, or locations, may be warranted to reflect changing conditions or improved understanding of natural attenuation processes at the site. Situations that may trigger implementation of a contingency or alternative remedy are discussed later in this chapter.

The material presented in this chapter is intended for use in conjunction with the Air Force Center for Environmental Excellence (AFCEE), U.S. EPA, and U.S. Department of Energy (DOE) technical protocols for evaluating and monitoring natural attenuation (Wiedemeier et al., 1995, 1999; U.S. EPA, 1998, 1999, 2004). The approach specified herein can lower monitoring costs by reducing the number of monitoring wells, the frequency of sampling, and the number of analytes required to demonstrate the continuing efficacy of natural attenuation.

---

**Purpose of Monitoring for Natural Attenuation**

Although the purpose of natural attenuation monitoring and, thus, the monitoring program will be site-specific, all monitoring programs should be designed to accomplish
the following minimum goals (U.S. EPA, 1999):

- Demonstrate that natural attenuation is occurring according to expectations
- Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce (or enhance) the efficacy of the natural attenuation processes
- Identify any potentially toxic and mobile transformation products
- Verify that the dissolved contaminant plume is not expanding
- Verify that there has been no unacceptable impact to downgradient receptors
- Detect new releases of contaminants to the environment that could create an unacceptable risk to receptors or impact the effectiveness of the natural attenuation remedy
- Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors
- Verify progress toward attainment of cleanup objectives

In addition to meeting all of these requirements, a site-specific contingency plan must be specified as a backup remedy in the event that natural attenuation fails to perform as anticipated.

---

**Types of Monitoring for Natural Attenuation**

In order to meet the objectives required by the U.S. EPA described earlier, three types of environmental monitoring are described, including:

- Site characterization monitoring (i.e., baseline monitoring), to describe the disposition of contamination and forecast its future behavior
- Validation monitoring, to determine if predictions based on site characterization are accurate
- Long-term monitoring, to ensure that the behavior of the contaminant plume does not change over time

Each type of monitoring has specific objectives that are defined and discussed briefly in the following subsections.

**Site Characterization Monitoring**

Site characterization monitoring includes monitoring activities conducted during the initial site characterization of a remedial investigation or a natural attenuation evaluation (feasibility study) that provide data on the contaminant distribution and the hydrogeologic and geochemical conditions at a site. This information is used to identify and quantify the natural attenuation processes involved, to evaluate the geochemical conditions that may govern contaminant transformation or degradation processes, and to determine if monitored natural attenuation is viable as a remediation approach at a site. The collection and interpretation of characterization monitoring data for petroleum hydrocarbons is described by Wiedemeier et al. (1995, 1999). The collection and interpretation of
characterization monitoring data for chlorinated compounds is described by U.S. EPA (1998) and Wiedemeier et al. (1999, 2005).

Validation Monitoring

Validation monitoring is used to ensure that the analytical results obtained from the baseline (i.e., site characterization) sampling events are accurate. Validation monitoring consists of collecting the complete analytical suites specified by Wiedemeier et al. (1995, 1999) and U.S. EPA (1998) for one or two sampling rounds after completion of site characterization. In addition, Wiedemeier et al. (2005) lists site-specific supplemental analytes such as acetylene, isotopes, microbial analyses, and mineralogical analyses for iron minerals which may be useful for validation monitoring at more complex sites.

Long-Term Monitoring

Long-term monitoring involves collecting a subset of the parameters specified by Wiedemeier et al. (1995, 1999), U.S. EPA (1998), and Wiedemeier et al. (2005). Ultimately the subset of parameters selected for analysis on an ongoing basis will be site-specific. This chapter describes how to effectively and efficiently specify the location, frequency, and types of samples and analyses required to meet the objectives of long-term monitoring. In addition, guidance is provided on developing contingency remedies that mitigate unacceptable conditions without adversely impacting the natural biodegradation reactions occurring at a site, should engineered remediation or additional land-use control be required. Two types of monitoring (and monitoring wells) are utilized for long-term monitoring: performance monitoring and compliance, or contingency, monitoring.

Performance Monitoring

Performance monitoring is intended to ensure that the behavior of the contaminant plume does not change over time and that the remedial action is progressing appropriately. It involves collecting a subset of the parameters used in site characterization monitoring that focus on the most significant parameters appropriate to the site. This information is used to evaluate and explain solute plume behavior and any changes in conditions that may affect the efficacy of the natural attenuation remedy.

Performance monitoring wells (PMWs) should be located upgradient from, within, transverse to, and just downgradient from the solute plume. These wells are used to verify that the concentrations of individual constituents of concern, plume boundaries, and overall progression toward remedial goals are acceptable over time and space.

Compliance or Contingency Monitoring

Compliance, or contingency, monitoring is intended to ensure compliance with regulatory requirements associated with a monitored natural attenuation remedy. These include ensuring that the plume does not expand past preestablished boundaries and identifying situations that will “trigger” a change in the monitoring plan or implementation of a contingency plan. It involves collecting data from appropriate locations that focuses on detecting and recognizing “unacceptable” solute plume behavior that indicates potential or real failure of a monitored natural attenuation remedy and allows sufficient time to reevaluate the remedy and implement contingency measures. Statistically significant detection of unacceptable concentrations of contaminants at the contingency monitoring wells may trigger implementation of the contingency remedy.
Essential Design Elements of a Monitoring Plan

The ability to design an appropriate and adequate monitoring plan for natural attenuation is entirely dependent upon the quality of site characterization. The information developed during site characterization defines the spatial distribution of constituents of interest and provides an understanding of the hydrogeological setting and underlying natural attenuation processes. If these aspects are not understood, a monitoring program cannot be designed effectively — if you do not understand the problem, you cannot monitor it.

Adequate site characterization and a sound conceptual model of the site are essential to the design of a long-term monitoring plan and it is important to remember that solute plumes are dynamic, three-dimensional entities. Effective monitoring of natural attenuation processes involves a three-dimensional approach to monitoring network design and clearly defined performance criteria based on site-specific remedial action objectives. A well-designed long-term monitoring program should provide all data necessary to document and evaluate the effectiveness and protectiveness of the current remedy. Periodic evaluations are often required under various regulatory programs (e.g., CERCLA 5-yr reviews) or under site-specific agreements.

The degree of aquifer heterogeneity also will influence the placement of the monitoring wells, with more heterogeneous sites possibly requiring a more elaborate sampling network. If surface water is impacted, several factors must be considered, including the amount of contaminant flux into the body of water. For those sites where the groundwater flow field cannot be determined with certainty (e.g., fractured bedrock), the evaluation of natural attenuation, or any remedial action, and the design of a monitoring program can be problematic.

Designing an effective monitoring program requires the proper placement of groundwater monitoring wells and developing a site-specific groundwater sampling and analysis strategy. The monitoring program should be designed to monitor solute plume behavior over time and to verify that natural attenuation is occurring at rates sufficient to protect potential downgradient receptors. All available site-specific data and information developed during site characterization, conceptual model development, groundwater modeling (as appropriate), and regulatory negotiations should be used when preparing a monitoring program. The monitoring program designed for each site must specify the purpose, location, sampling frequency, and types of samples and measurements necessary to evaluate if the remedy is performing as expected (U.S. EPA, 1999). The data collected during long-term monitoring are used to evaluate changes in three-dimensional solute plume boundaries, contaminant mass and concentrations in the solute plume, and hydrological and geochemical changes that may indicate changes in remedy performance. The design of the monitoring program also must include consideration of existing receptor exposure pathways, as well as those that may arise from potential future land use and groundwater use (U.S. EPA, 1999).

The monitoring strategy for a given site will depend upon a variety of factors and will likely be modified over time as new information is acquired. If adequate data to define seasonal variation in contaminant concentrations, geochemical parameters and water levels (groundwater flow patterns) are not available from the site characterization or natural attenuation evaluation (feasibility study) for the site, monitoring of these parameters should be continued to determine the short-term variation and to verify that data collected from any new monitoring points are consistent with the site conceptual model (validation monitoring). Quarterly groundwater level and contaminant monitoring are often used to determine if a seasonal variation exists. However, one should consider the use of newly
available tools like dedicated water-level loggers to first determine if naturally occurring conditions like water-level fluctuations occur throughout the year or in response to specific climatic changes. This allows the environmental professional to not only identify significant changes in hydrologic conditions, but also to schedule contaminant or geochemical monitoring during these significant events (e.g., snow melt, river ice breakup, seasonal ground-water flow reversals, etc.). Arbitrarily scheduled quarterly monitoring may lead to improperly timed sampling or looking for effects that do not exist. Once this information is available, the sampling parameters and frequency can be adjusted to optimize data collection.

A variety of technical, institutional, and regulatory factors affect the design of a long-term monitoring program for natural attenuation. The technical factors include distance to potential receptor exposure points; ground-water seepage velocity and direction; types of contaminants; aquifer heterogeneity; the three-dimensional distribution of constituents of concern; areas of unique geochemical conditions; surface-water impacts; and the effects of engineered remediation systems. In addition to the technical issues involved, institutional and regulatory factors must also be considered. These include issues of access to the necessary locations, property boundaries, regulatory framework (e.g., RCRA) or site-specific requirements, and contaminant contributions from offsite sources.

In addition, primary factors can include the level of understanding of historical plume behavior and site complexity. In other words, if one has 10 yr of defensible data demonstrating a stable or receding plume and site conditions that are unlikely to change, the monitoring strategy can be optimized to focus on monitoring critical areas.

The use of existing monitoring wells from the site characterization as part of the long-term monitoring program must be considered in light of their location, current condition, and construction. The location of existing monitoring points should be carefully evaluated to determine whether the data obtained will be useful as part of the long-term monitoring program. Monitoring points that are not located along flow paths can provide information on spatial relationships in the solute plume, but the resulting data may be difficult to interpret without the use of detailed spatial analysis. Also, the length of the screened interval of existing monitoring wells may not provide the necessary resolution to provide unequivocal data.

**Location and Placement of Monitoring Points**

Effective monitoring of natural attenuation processes involves a three-dimensional approach to monitoring network design (as required) and clearly defined performance criteria based on site-specific remedial action objectives. Ideally, long-term monitoring points should be located along ground-water flow paths so that the data generated from upgradient monitoring points can be related to the data obtained from downgradient monitoring points. The post-characterization monitoring strategy for a given site will depend upon several factors. Primary factors to be considered when locating monitoring points include (at a minimum) distance to potential receptor exposure points, ground-water seepage velocity and direction, types of contaminants, aquifer heterogeneity, the three-dimensional distribution of constituents of concern; areas of unique geochemical conditions; surface-water impacts, and the effects of engineered remediation systems. In addition, primary factors can include the level of understanding of historical plume behavior and site complexity. In other words, if available information on plume behavior and land use support the position that a significant or unacceptable change in trends or conditions is not plausible, then monitoring frequency can be reduced. Monitoring programs should not be used solely to confirm the obvious. They are more appropriately designed to
provide critical updates and to provide for contingency action in the event that it is required. Secondary factors to consider include (at a minimum) access issues, property lines, and contributing off-site contaminant sources. Each of these factors will influence the final design of the monitoring program. Perhaps the most critical factors to consider when developing a monitoring program are the distance to potential receptors and the seepage velocity of ground water. These two factors will strongly influence monitoring well spacing and sampling frequency. Typically, the faster the ground-water seepage velocity and the shorter the distance to potential receptor exposure points, the greater the sampling frequency. The use of a range of site-specific seepage velocity estimates is conservative because some sorption and biodegradation are likely retarding contaminant migration relative to ground-water flow.

The placement of monitoring wells and the frequency of sampling must yield useful data and allow detection of significant changes in plume configuration and definition of trends in contaminant concentrations over time. In many cases it may be possible to utilize some of the existing monitoring wells at a site, thereby reducing the cost of implementing the long-term monitoring plan. However, it is important that these wells are located in appropriate locations. Not all wells installed during site characterization may be appropriate or necessary for long-term monitoring. Because monitoring wells installed for site characterization purposes will not necessarily provide meaningful long-term monitoring data, it is important to be selective in determining which of the existing wells to sample. The locations and screened intervals of long-term monitoring wells should be based on site stratigraphy and plume behavior as revealed during site characterization. This requires a detailed understanding of the three-dimensional relationship between contaminants and stratigraphy to ensure that monitoring wells are screened in the same hydrogeologic unit as the contaminant plume, and that they are in the path of contaminated ground-water flow. The geologic complexity of the site and ground-water seepage velocity ultimately will dictate the density of the sampling network.

Two types of wells, PMWs and contingency wells, are used for validation monitoring and long-term monitoring after the initial site characterization and baseline evaluation of natural attenuation. The PMWs, located upgradient from, within, and just downgradient from the plume (Figure 9.1), are used to verify the predictions made during the evaluation of natural attenuation (Wiedemeier et al., 1995; U.S. EPA, 1998). Contingency monitoring wells are placed beyond the maximum predicted lateral and downgradient boundaries of the plume, and typically upgradient from known or potential receptor...
exposure points, to ensure that the plume does not threaten human health or the environment (Figure 9.1). If preestablished trigger levels are exceeded at the contingency monitoring wells, they should be verified prior to the implementation of the contingency plan.

Where possible, contaminant, geochemical and hydrogeological data should be used to locate and design monitoring wells, especially those wells downgradient from the plume. For example, geochemical parameters such as dissolved oxygen, nitrate, Fe(II), sulfate, and methane can be used in conjunction with contaminant data to ensure the proper placement of downgradient contingency monitoring wells in locations with “treated” ground water. “Treated” ground water exhibits a predictable change in geochemistry even though it may lack detectable concentration of site contaminants. This approach ensures that the downgradient monitoring network is in the flow path of the contaminant plume. The frequency of sampling will depend on the location of potential receptor exposure points and the seepage velocity of ground water. To evaluate the behavior of the dissolved contaminant plume over time and to estimate cleanup time frames, statistical methods should be employed.

**Plumes that do not Discharge to Surface-Water Bodies**

For plumes that do not discharge to a surface-water body, the monitoring program includes PMWs and contingency monitoring wells. Geochemical data should be used when possible to confirm that downgradient wells are sampling ground water that was once contaminated with organic compounds. Wells downgradient from a contaminant plume, and completed in the same stratigraphic horizon, that do not contain organic compounds but have depleted electron acceptor (e.g., dissolved oxygen, nitrate, sulfate) and elevated metabolic byproduct (e.g., iron(II), methane, chloride, alkalinity) concentrations relative to background levels provide good evidence that the ground water being sampled flowed through the contaminant plume and has been treated. Such wells have been termed “smoking guns” because they provide fairly conclusive evidence that the ground water was contaminated at one time and has since been treated (Wiedemeier et al., 1995, 1999). Because concentrations of electron acceptors and metabolic byproducts typically will return to background concentrations at some distance downgradient from the contaminant plume, it is important to locate at least one PMW close to the downgradient edge of the contaminant plume. This also will allow better resolution of the behavior of the leading edge of the plume to determine if the plume is at steady-state equilibrium, is receding, or is expanding. Figures 9.2 and 9.3 illustrate how geochemical data can be used to place monitoring wells for solute plumes emanating from non-aqueous phase liquid (NAPL) sources. Figure 9.2 illustrates a hypothetical monitoring network for a solute plume from a light non-aqueous phase liquid (LNAPL) source. Figure 9.3 illustrates a hypothetical monitoring network for a solute plume from a dense non-aqueous phase liquid (DNAPL) where the NAPL materials have migrated to a lower confining layer. In contrast, a contaminant source and dissolved phase plume comprised solely of dissolved phase DNAPL materials is more likely to behave like the plume depicted in Figure 9.2b. These figures depict: (1) upgradient (PMW-1A) and crossgradient (PMW-1B and PMW-1C) wells in unimpacted ground water; (2) wells in the NAPL source area (PMW-2); (3) wells downgradient from the NAPL source area in the plume (PMW-3 and PMW-4); (4) a well located downgradient from the plume where contaminants are not detectable, soluble electron acceptors are depleted, and metabolic byproducts are elevated with respect to unimpacted ground water (PMW-5); (5) a well (PMW-6) in treated ground water; and (6) contingency wells. Note that these figures are only examples of monitoring well placement. The actual location and number of monitoring wells must be determined on a site-specific basis.
Table 9.1 summarizes sampling locations. The upgradient and crossgradient PMWs are intended to monitor for changes in background water quality that can provide an indication of changing conditions that could affect natural attenuation. The need for, and placement of, crossgradient PMWs is related to whether ground-water flow directions change due to site-specific seasonal or other hydrological conditions. In contrast, if the ground-water flow direction, plume configuration, and behavior are well-established and unlikely to change, then the number and sampling frequency of upgradient and cross-gradient monitoring points can be reduced. The PMWs in the NAPL source area are intended to monitor changing apparent NAPL thickness, distribution, or composition.
over time and to give an indication of the changing solute concentration in ground water.
PMWs downgradient from the NAPL source area are intended to monitor plume behavior and changing contaminant concentrations over time. Ideally, these wells will be aligned parallel to the direction of ground-water flow and the center line of the plume. It should be kept in mind that this requires good definition of the plume and fairly uniform (unchanging) hydraulic gradients. The PMWs located downgradient from the dissolved contaminant plume are intended to provide early detection of contaminant plume migration toward a contingency well. These wells should be located in the flow path of the contaminant plume. The placement and spacing of the PMWs located in the

---

**FIGURE 9.3**
Locating monitoring wells using contaminant and geochemical data (a) Plan view of DNAPL. (b) Cross-sectional view of DNAPL. (Modified from Wiedemeier et al., 1999. With permission.)
### TABLE 9.1
Sampling Locations, Purpose, and Analytical Parameters for Validation Monitoring and Long-Term Monitoring of Ground Water

<table>
<thead>
<tr>
<th>Type of Well</th>
<th>Location</th>
<th>Purpose</th>
<th>Validation Sampling</th>
<th>Long-Term Monitoring</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMW-1 (A, B, C)</td>
<td>Upgradient/crossgradient</td>
<td>Monitor background water quality</td>
<td>Contaminants, daughter products, and full suite of geochemical parameters</td>
<td>Limited suite of geochemical parameters</td>
</tr>
<tr>
<td>PMW-2</td>
<td>NAPL source area</td>
<td>Monitor changing NAPL composition/source strength and plume behavior over time</td>
<td>Contaminants, daughter products, and full suite of geochemical parameters</td>
<td>Contaminants and daughter products in ground water beneath NAPL and limited suite of geochemical parameters</td>
</tr>
<tr>
<td>PMW-3 and PMW-4</td>
<td>Downgradient from NAPL source area along plume centerline</td>
<td>Monitor plume behavior over time</td>
<td>Contaminants, daughter products, and full suite of geochemical parameters</td>
<td>Contaminants, daughter products, and limited suite of geochemical parameters</td>
</tr>
<tr>
<td>PMW-5</td>
<td>Immediately downgradient from plume</td>
<td>Early detection of plume migration</td>
<td>Contaminants, daughter products, and full suite of geochemical parameters</td>
<td>Contaminants, daughter products, and limited suite of geochemical parameters</td>
</tr>
<tr>
<td>PMW-6</td>
<td>Between contingency wells and the other PMWs</td>
<td>Early detection of plume migration</td>
<td>Contaminants, daughter products, and full suite of geochemical parameters</td>
<td>Contaminants, daughter products, and limited suite of geochemical parameters</td>
</tr>
<tr>
<td>Contingency wells</td>
<td>Downgradient from most downgradient PMW well (PMW-6 in this case) and upgradient from receptor exposure point</td>
<td>Monitor for plume migration toward a potential receptor and trigger contingency plan</td>
<td>Contaminants, daughter products, and full suite of geochemical parameters</td>
<td>Contaminants, daughter products, and limited suite of geochemical parameters</td>
</tr>
<tr>
<td>Surface water</td>
<td>At and upgradient and downgradient from discharge point</td>
<td>Determine surface-water impacts</td>
<td>Contaminants and daughter products</td>
<td>Contaminants and daughter products</td>
</tr>
</tbody>
</table>

*For fuel hydrocarbon plumes, the full suite of geochemical parameters should include dissolved oxygen, nitrate, Fe (II), sulfate, methane, temperature, pH, conductivity, and ORP. For chlorinated solvent plumes ethane or ethene and sulfide should be added to the full suite of geochemical parameters recommended for fuel hydrocarbon plumes. In addition, certain supplemental data may be useful for evaluating complex plumes, most notably solvent plumes. See Section 4.2 for more information on analytes. Additional analytes are suggested below to help evaluate complex plumes:

- **a** For fuel hydrocarbon plumes, the full suite of geochemical parameters should include dissolved oxygen, nitrate, Fe (II), sulfate, methane, temperature, pH, conductivity, and ORP. For chlorinated solvent plumes ethane or ethene and sulfide should be added to the full suite of geochemical parameters recommended for fuel hydrocarbon plumes. In addition, certain supplemental data may be useful for evaluating complex plumes, most notably solvent plumes. See Section 4.2 for more information on analytes.
- **b** At a minimum, the limited suite of geochemical parameters should include dissolved oxygen, ORP, temperature, and pH.
- **c** If plume behavior changes or is suspected of changing, then analyze for contaminants and the full suite of geochemical parameters plus any supplemental data that may be appropriate.
- **d** LNAPL thickness measurements should be obtained.
downgradient portion of the plume (PMW-4 in this example) and the well located down-
gradiant from the contaminant plume (PMW-5 in this example) are particularly important. This is because the closer the downgradient well (i.e., PM-5) is to the contaminant plume, the less time required to confirm that the plume is at steady-state equilibrium, or is receding. For example, if wells PMW-4 and PMW-5 in Figure 9.2 are 500 ft apart and groundwater is flowing at 50 ft per yr, it will take at least 10 yr of monitoring data to show that the contaminant plume is not migrating at the seepage velocity of the groundwater. It will take even longer to show that the contaminant plume is not migrating downgradient at some retarded solute transport velocity. If, on the other hand, wells PMW-4 and PMW-5 in Figure 9.2 are 100 ft apart, then it will take about 2 yr of monitoring data to show that the contaminant plume is not migrating at the seepage velocity of the groundwater, and is thus being retarded by some mechanism of natural attenuation.

Contingency wells are intended to monitor unexpected plume migration and to trigger implementation of the contingency plan. All of the contingency wells should be located in the flow path or potential flow path of the contaminant plume. The distance between downgradient PMWs and contingency wells and the density of the monitoring network should be based on the groundwater seepage velocity, solute transport velocity, and the distance to potential receptor exposure points. Contingency wells should be placed a sufficient distance upgradient from potential exposure points in the flow path of the solute plume to ensure that a contingency plan can be implemented before potential receptors are impacted. To be conservative, these distance calculations should be made based on a representative seepage velocity of the groundwater rather than on the solute transport velocity.

Plumes that Discharge to Surface Water Bodies

For sites where contaminated groundwater discharges to surface water, the monitoring strategy must be highly customized to factor in all the physical, chemical, and biological processes that occur at and beyond the groundwater and surface-water interface. Figure 9.4 is a hypothetical monitoring strategy for a contaminant plume discharging to a body of surface water. This figure depicts (1) an upgradient (PMW-1A) well and cross-gradient wells (PMW-1B and PMW-1C) in unimpacted groundwater; (2) a well in the NAPL source area (PMW-2); (3) wells downgradient from the NAPL source area in the zone of anaerobic treatment (PMW-3 and PMW-4); and (4) surface-water collection points. The purpose of the first three sampling locations is the same as that discussed earlier for contaminant plumes that do not discharge to a surface water body. The fourth type of sampling location is intended to provide information on the impact of the contaminant plume on the surface water body. Mass flux calculations can be completed to estimate the amount of contamination entering the surface water body and the resultant contaminant concentrations in the surface water. In many cases, the relationship between mass flux into the surface water and dilution (and volatilization) will be such that the contamination is not detectable or is quickly diluted or volatilized to nondetectable concentrations a short distance from the point of discharge.

Analytical Protocols — What to Analyze for and When

The analytical protocol for a long-term monitoring program defines the specific parameters that will be analyzed, as well as the locations where samples for these parameters will be collected and when the samples will be collected. The specific analytical parameters that should be collected in a long-term monitoring program for natural attenuation
will depend upon both the contaminants of interest and the particular transformation or degradation mechanisms that are involved. For example, sites with chlorinated solvent contamination will likely require a different suite of analytical parameters than petroleum hydrocarbons. This is because of the differences in the patterns of biodegradation between these different types of contaminants. It is now widely accepted that petroleum hydrocarbon compounds are almost invariably mineralized through oxidation by bacteria in
the shallow subsurface. This is in contrast to chlorinated solvents, which exhibit varying
degrees of biodegradation potential involving oxidation (mineralization) and reduction
(reductive dechlorination). In addition to the biological reactions, chlorinated solvents
can be degraded by abiotic reductive dechlorination reactions. Both biological and
abiotic reactions depend upon the specific compound and the site-specific geochemistry.
This section describes both typical and supplemental ground-water analytes that are
useful for monitoring natural attenuation.

Typical Ground-Water Analytes for Evaluating the Long-Term
Performance of Natural Attenuation

Typical ground-water analytical parameters for monitoring natural attenuation are sum-
marized in Table 9.2. The suggested list of analytes presented in Table 9.2 includes con-
taminants and geochemical parameters. As summarized in Table 9.1, some of the
analytical parameters are for validation monitoring, some are for long-term monitoring,
and some are for both. There also are different geochemical analyses suggested for
plumes of chlorinated solvents. This is because these plumes are particularly sensitive
to changes in ground-water geochemistry, such as depletion of organic carbon or increa-
sing dissolved oxygen concentrations. Such changes may inhibit reductive dechlorination.
Any Federal- or State-specific analytical requirements not listed in Tables 9.1 and 9.2 also
should be addressed in the sampling and analysis plan to ensure that all data required for
regulatory decision-making are collected. In addition, water-level and, if present, light
nonaqueous-phase liquid (LNAPL) measurements, should be made during each sampling
event to ensure that the ground-water flow direction has not changed.

The analytes listed in Table 9.2 fall into several broad categories, including source-term
parameters, contaminants and daughter products, electron acceptors, metabolic bypro-
ducts, and general water-quality parameters. These analytes are useful for: (1) estimating
the composition and strength of a NAPL source, (2) demonstrating that natural attenu-
ation is occurring, and (3) evaluating the relative importance of the various natural attenu-
ation mechanisms. It should be kept in mind that it may be necessary to modify Table 9.2
on a site-specific basis. In addition to the parameters listed in Table 9.2, the supplemental
parameters summarized in Table 9.3 may be useful for monitoring natural attenuation at
sites where degradation mechanisms are not apparent.

Sampling in the NAPL Source Area

NAPL in the subsurface, whether present at a residual saturation or in quantities sufficient
to cause formation of a mobile or immobile pool of NAPL, acts as a continuing source of
ground-water contamination. Thus, as long as NAPL remains in the subsurface at concen-
trations sufficient to impact ground water, the solute plume will persist. This has several
implications for natural attenuation and the length of time that monitoring must be con-
ducted. The degree and rate of weathering of the NAPL, and hence its composition and
strength, dictate the amount of aqueous-phase contamination at a site. Significant
reductions in soluble and toxic constituents in NAPLs can occur due to natural or
enhanced destructive processes (AFCEE, 2003).

Collection and analysis of NAPL samples allows the investigator to determine the
composition and physical properties of the NAPL. In some cases, it may be possible to
complete NAPL-to-water partitioning calculations to show that the effective solubility
of a compound is no longer high enough to impact ground water at concentrations
above regulatory guidelines. Additionally, NAPL samples collected over time can help
define the compositional changes and allow estimates of source decay (weathering)
rates to be made.
TABLE 9.2
Typical Ground-Water Analytes for Evaluating the Long-Term Performance of Natural Attenuationa

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Method/Reference</th>
<th>Comments</th>
<th>Data Use</th>
<th>Sample Volume, Sample Container, Sample Preservation</th>
<th>Field or Fixed-Base Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals of concern</td>
<td>SW8260B</td>
<td>Handbook method</td>
<td>Used to determine presence of parent and daughter compounds and rates of attenuation</td>
<td>Collect 3 x 40 ml VOA vials, preserve with HCL and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>E360.1 — Dissolved oxygen membrane electrode.</td>
<td>Avoid exposure to atmospheric oxygen</td>
<td>Concentrations less than 1 mg/l generally indicate an anaerobic pathway</td>
<td>Measure dissolved oxygen onsite using a flow-through cell</td>
<td>Field</td>
</tr>
<tr>
<td>Nitrate</td>
<td>ICb method E300</td>
<td>Method E300 is a Handbook method</td>
<td>Substrate for microbial respiration if oxygen is depleted. Absence is required for Fe(III) reduction to occur</td>
<td>Collect 1 l poly container and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Iron(II) (Fe2⁺)</td>
<td>Colorimetric hach method</td>
<td>Filter with 0.45 μ inline filter</td>
<td>Indicates an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese. Required for abiotic reductive dechlorination</td>
<td>Collect 100 ml of water in a headspace-free container to eliminate introduction of oxygen and analyze as soon as possible</td>
<td>Field</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>IC method E300</td>
<td>Method E300 is a Handbook method</td>
<td>Substrate for anaerobic microbial respiration</td>
<td>Collect 1 l poly container and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Sulfide</td>
<td>E376.1</td>
<td>Handbook method</td>
<td>Required for abiotic reductive dechlorination</td>
<td>Collect 500 ml in plastic or glass container, preserve with NaOH to pH &lt; 9, cool to 4°C, no headspace</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>ORP</td>
<td>Direct-reading probe</td>
<td>Avoid introduction of oxygen during sampling</td>
<td>The ORP of ground water influences and is influenced by the nature of biologically mediated reactions</td>
<td>Measure ORP onsite using a flow-through cell</td>
<td>Field</td>
</tr>
</tbody>
</table>

(Table continued)
### Table 9.2  Continued

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Method / Reference</th>
<th>Comments</th>
<th>Data Use</th>
<th>Sample Volume, Sample Container, Sample Preservation</th>
<th>Field or Fixed-Base Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, ethane, and ethene</td>
<td>RSK-175 (Kampbell and Vandegrift, 1998)</td>
<td>Method published by researchers at the U.S. EPA</td>
<td>The presence of methane suggests biodegradation via methanogenesis. Ethane and ethene are daughter products of complete dechlorination.</td>
<td>Collect 6 x 40 ml VOA vials, preserve with HCL, and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>pH</td>
<td>E150.1 — Field probe with direct reading meter</td>
<td>Field</td>
<td>Fundamental measurement which is critical for interpretation of carbonate data. Used as a well stabilization criterion</td>
<td>Measure in flow-through cell during well purging</td>
<td>Field</td>
</tr>
<tr>
<td>Temperature</td>
<td>E170.1 — Field probe with direct reading meter</td>
<td>Field only</td>
<td>Fundamental measurement required in all thermodynamic calculations</td>
<td>Measure in flow-through cell during well purging</td>
<td>Field</td>
</tr>
<tr>
<td>Conductivity</td>
<td>E120.1/SW9050, direct reading meter</td>
<td>Protocols/Handbook methods</td>
<td>General water quality parameter that is proportional to the dissolved ions present in solution</td>
<td>Measure in flow-through cell during well purging</td>
<td>Field</td>
</tr>
</tbody>
</table>

*Not all analytes will be required for every site or every sampling event.

*Ion chromatography.
<table>
<thead>
<tr>
<th>Analysis</th>
<th>Method/Reference</th>
<th>Comments</th>
<th>Data Use</th>
<th>Sample Volume, Sample Container, Sample Preservation</th>
<th>Field or Fixed-Base Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>Colorimetric Hach method</td>
<td>Filter with 0.45 μ inline filter</td>
<td>May indicate an anaerobic degradation process due to depletion of oxygen, and nitrate. Interferences can occur if hydrogen sulfide and high concentrations of calcium are present</td>
<td>Collect 100 ml of water in a headspace-free container to eliminate introduction of oxygen and analyze as soon as possible</td>
<td>Field</td>
</tr>
<tr>
<td>Bicarbonate and Carbonate Alkalinity</td>
<td>Hach digital titrate</td>
<td>Field filter with 0.45 μ inline filter. Carbonate alkalinity only significant at pH &gt; 8.5</td>
<td>General water quality parameter used (1) to measure the buffering capacity of ground water and (2) as a marker to verify that all site samples are obtained from the same ground-water system</td>
<td>Collect 100 ml of water in glass container. Analyze as soon as possible</td>
<td>Field</td>
</tr>
<tr>
<td>DOC</td>
<td>E415.1</td>
<td>Field filter with 0.45 μ inline filter. Minimize aeration and fill sample container completely</td>
<td>Used to classify plume and to evaluate the potential for biologic and biologically predicated abiotic degradation</td>
<td>Collect 250 ml glass amber container, preserve with H₂SO₄ and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>DIC</td>
<td>E415.1</td>
<td>Filter in the field with 0.45 μ inline filter. Minimize aeration of sample and fill sample container completely to avoid loss of CO₂</td>
<td>An increase of DIC above background concentrations provides a footprint in ground water that has been remediated by biological processes. Carbon dioxide is the most universal end product of chlorinated hydrocarbon biodegradation. DIC is the sum of dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate</td>
<td>Collect 250 ml glass amber container, preserve with H₂SO₄ and cool to 4°C. (same sample bottle as DOC)</td>
<td>Fixed-base laboratory</td>
</tr>
</tbody>
</table>

(Table continued)
<table>
<thead>
<tr>
<th>Analysis</th>
<th>Method/Reference</th>
<th>Comments</th>
<th>Data Use</th>
<th>Sample Volume, Sample Container, Sample Preservation</th>
<th>Field or Fixed-Base Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anions — Cl, F, NO₃, SO₄, HCO₃, CO₃, Br</td>
<td>Method E300 (Cl, F, SO₄, NO₃, and Br). Method E310.1 (HCO₃ and CO₃)</td>
<td>Filter in the field with 0.45 μ inline filter</td>
<td>Can be used graphically (e.g., Piper and Stiff diagrams) with cations to identify different hydrogeologic units and identify areas impacted by contamination</td>
<td>Collect 1 l poly container and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Cations — Ca, Mg, K, and Na, Mn, Fe</td>
<td>SW6010</td>
<td>Filter in the field with 0.45 μ inline filter</td>
<td>Can be used graphically with anions to identify different hydrogeologic units and identify areas impacted by contamination</td>
<td>Collect 500 ml poly container, preserve with HNO₃ and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Chloride⁺</td>
<td>IC method E300⁺</td>
<td>Method SW9050 may also be used</td>
<td>Final product of chlorinated solvent reduction. Can be used as a tracer</td>
<td>Collect 1 l poly container and cool to 4°C</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Equilibration with gas in the field analyzed with a reducing gas detector in the lab</td>
<td>Supplemental specialized analysis to be completed on select wells</td>
<td>Determine current terminal electron accepting process and if sufficient hydrogen is available for reductive dechlorination</td>
<td>Sampled at well head. Requires the production of 100 ml per min of water for 30 min</td>
<td>Fixed-base laboratory</td>
</tr>
<tr>
<td>Method</td>
<td>Sample Type</td>
<td>Collection Details</td>
<td>Laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------</td>
<td>-------------------------------------------------------------------------------------</td>
<td>------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetylene Light hydrocarbon analysis</td>
<td>GC-FID method&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Product of abiotic reductive dechlorination by iron sulfides</td>
<td>Fixed-base laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VFAs</td>
<td>Can be a useful indicator of microbial metabolism of added substrate</td>
<td>Biomarkers of anaerobic metabolism. Anaerobic bacteria produce these compounds by fermentation</td>
<td>Fixed-base laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLFAs</td>
<td>White et al. (1997) PLFA data can be readily correlated with contaminant and geochemical trends</td>
<td>Provides microbial biomass, community structure and physiological status data</td>
<td>Fixed-base laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGGE</td>
<td>Muyzer et al. (1993) Mainly for use in forensic or failure analyses</td>
<td>Identifies most dominant microorganisms in the ground water</td>
<td>Fixed-base laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotopes</td>
<td>Sherwood-Lollar et al. (1999) May need more than one quarter of data and interpretation may become complicated if there is more than one source</td>
<td>Helps elucidate biotic versus abiotic dechlorination pathways</td>
<td>Fixed-base laboratory</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Included in major anion analysis.
<sup>b</sup>Gas chromatography — flame ionization detector.
<sup>c</sup>Ion chromatography.
Contaminants and Transformation Products

Clearly, the chemicals of concern identified in the site characterization must be part of the analytical protocol. The appropriate analytical methods will depend upon the specific contaminants involved. Analytical methods are often specified by the governing regulatory agency. In addition, the analytical methods used must identify any potentially toxic and mobile transformation products (U.S. EPA, 1999).

Naturally Occurring Electron Acceptors and Metabolic Byproducts

The purpose of sampling geochemical parameters as part of a long-term monitoring program for natural attenuation is to provide salient information regarding changes in conditions that may affect the behavior of the solute plume and the efficacy of natural attenuation. The measurement of geochemical parameters associated with naturally occurring oxidation–reduction processes is useful for evaluating the occurrence and relative importance of the various terminal electron-accepting processes. The monitoring of geochemical parameters during the long-term monitoring program should focus on the specific parameters that are of significant importance at the site as identified during site characterization. For example, if nitrate is present at only very low concentrations in the plume and in background locations, then ground water should not be analyzed for nitrate on a routine basis.

Naturally occurring electron acceptors that are typically monitored for natural attenuation include dissolved oxygen, nitrate, and sulfate. Table 9.2 summarizes analytical methods and data uses for these compounds. The interpretation of electron acceptor data is also discussed later.

Metabolic byproduct data that can be collected during natural attenuation monitoring include Fe(II), sulfide, and methane. Table 9.2 summarizes analytical methods and data uses for these compounds. The interpretation of metabolic byproduct data is discussed later.

General Water-Quality Parameters

General water-quality parameters, including pH, temperature, conductivity, oxidation-reduction potential (ORP), and conductivity, should be a part of every sampling event. Table 9.2 summarizes analytical methods and data uses for these compounds. The interpretation of general water-quality data is discussed later. Because the pH, temperature, and conductivity of a ground-water sample can change significantly within a short-time following sample acquisition, these parameters, along with dissolved oxygen and ORP, must be measured in the field in unfiltered, unpreserved, “fresh” water. The measurements are best made either downhole, or directly from a flow-through cell, and the measured values should be recorded in the ground-water sampling record.

Supplemental Monitoring Parameters

In addition to the analytes described earlier, additional lines of evidence can be collected in the form of supplemental or confirmatory parameters discussed subsequently. These data can be particularly useful if negative indicators of contaminant attenuation or conflicting results are present and the plume is no longer behaving as expected. Some of the potential supplemental analytes include manganese, alkalinity, dissolved inorganic carbon (DIC), anions, cations, hydrogen, acetylene, volatile fatty acids (VFAs), phospholipid fatty acids (PLFAs), denaturing gradient gel electrophoresis (DGGE), and isotope analyses. Table 9.3 summarizes analytical methods and data uses for these compounds. The interpretation of supplemental data is discussed later.
**Ground-Water Sampling Techniques**

The ground-water sampling procedures presented in this section are important, because the quality of several of the biogeochemical indicators used to evaluate degradation can be significantly affected by poor sampling technique. Poor data quality can result in erroneous conclusions regarding the efficacy, or even the occurrence, of degradation, so care must be taken during ground-water sample collection. Because of the accuracy required for many of the analytical procedures required to evaluate natural attenuation, care must be exercised when extracting ground water from the sampling device. Varied equipment and methods are available for the extraction of ground water (see Chapter 15). The approach used should be determined on the basis of application (purging or sampling), hydrogeologic conditions, monitoring location dimensions, and regulatory requirements.

Portable ground-water extraction devices from four generic classifications are commonly used to collect ground-water samples: grab samplers, suction lift samplers, submersible samplers, and passive samplers. Sampling devices discussed in this chapter include peristaltic pumps, electric submersible pumps, positive-displacement pumps, bailers, and diffusion samplers.

**Sampling with Peristaltic Pumps**

Suction-lift sampling technology is best represented in environmental investigations by the peristaltic pump. A peristaltic pump extracts water using a vacuum created by cyclically advancing a sealed compression along flexible tubing. This pumping technique means that extracted water contacts nothing other than tubing that can be easily replaced between sampling locations. This reduces the possibility of cross-contamination. Furthermore, peristaltic pumps can be used to extract minimally disturbed ground water from any diameter monitoring point at variable low-flow rates; however, because of the limited flow rate, peristaltic pumps are impractical for purging and sampling wells that are larger than 2 in. in diameter. Because of the features of the peristaltic pump, representative samples are simple to collect, and reliable flow-through cells are simple to establish. The biggest drawback of sampling with a peristaltic pump is the maximum achievable pumping depth which is equivalent to the height of water column that can be supported by an imperfect vacuum. This effectively limits the use of a peristaltic pump to monitoring locations with ground water depths of less than approximately 25 ft, depending on the altitude of the site. Also, sample degassing can occur in the tubing as a result of the vacuum applied to the sample and the high-rate of cyclical loading. If bubbles are observed in the tubing during purging or sampling, the flow rate of the peristaltic pump should be slowed. If bubbles are still apparent, the lift is probably too great to maintain the dissolved gas content in the sample, and sampling should not be attempted (see Chapter 15 for more detail). The final potential disadvantage with a peristaltic pump is the low flow rate. Although advantageous for sampling, this can be inappropriate during purging at locations requiring large extraction volumes.

To prevent downhole aeration of the sample in wells screened across the water table, well drawdown should not exceed about 5–10% of the height of the standing column of water in the well. The pump tubing should be immersed alongside the dissolved oxygen probe beneath the water level in the sampling container (Figure 9.5). This will minimize aeration and keep water flowing past the dissolved oxygen probe’s sampling membrane.

**Sampling with Submersible Pumps**

Submersible pumps, some of which are positive-displacement pumps, include bladder pumps, progressing cavity pumps (i.e., the Keck® pump), centrifugal electric submersible
pumps (i.e., the Grundfos Redi-Flo II® pump), electric submersible gear pumps (i.e., the Fultz® pump), double-acting piston pumps (i.e., the Bennett® pump) and pumps of other designs (i.e., the Enviro-Tech Purger ES® pump). Most of these pumps operate downhole at lifts of up to a few hundred feet (with the exception of the Bennett pump, which will operate at lifts of more than 1000 ft) and at pumping rates of between 1/2 gallon and several gallons per minute. Some submersible pumps are particularly useful for applications requiring the extraction of large volumes of water, and most can be used for the extraction of ground water from depths in excess of 100 ft. Because the pumps operate downhole, they require appropriately sized wells. A well diameter of at least 2 in. is typically required; however, larger well diameters can be required depending on the selected pump type, extraction depth, and extraction rate. It is important that cavitation is not introduced while using a submersible pump. Because the typical submersible pump design results in contact between the ground water and internal as well as external surfaces of the pump, rigorous decontamination procedures must be implemented to avoid cross-contamination if a pump that is not dedicated to the well is used for sampling.

**Sampling with Bailers**

Bailers are the most common sampling devices in use in most monitoring programs. Bailers can be used at any depth in wells with an inside diameter of at least 0.5 in. However, ground-water sample collection becomes less efficient as the well diameter (and hence the bailer diameter) decreases. Disposable bailers can be used to avoid decontamination expenses and potential cross-contamination problems. Drawbacks of bailers include significant agitation and aeration of the water column in the well, mixing of the water column above the screen with the water column in the screen, and the inability to maintain steady, nonturbulent flow in the well. Agitation and aeration can be minimized, but not eliminated, through careful immersion into and extraction from the standing column of water in the well or sampling point. Aeration also can be an issue during transfer of the sample from the bailer to the sample container. Once again, this aeration can be
minimized, but not eliminated. Because of aeration, accurate dissolved oxygen and ORP measurements can be difficult or impossible to obtain when using a bailer. Bailers cannot be used with flow-through cells.

When using a bailer, the bailer should be slowly immersed in the standing column of water in the well to minimize aeration. After sample collection, the water should be drained from the bottom of the bailer (using bottom-emptying tubing) into the sampling container. The tubing used for this operation should be immersed alongside the dissolved oxygen probe beneath the water level in the sampling container (Figure 9.5). This will minimize aeration and keep water flowing past the dissolved oxygen probe’s sampling membrane.

**Diffusion Samplers**

Diffusion samplers can be useful for sampling low-solubility, low vapor pressure volatile organic compounds (VOCs) (such as benzene and tetrachloroethylene), but not high-solubility, high vapor pressure VOCs (such as methyl tertiary butyl ether [MTBE] and acetone), during long-term monitoring. The diffusion sampler technology utilizes a deionized water-filled, low-density polyethylene bag to collect water samples from groundwater monitoring wells for VOC laboratory analyses. The bag allows selected VOCs in groundwater to diffuse into the deionized water. Chemical equilibrium between the selected VOCs in groundwater and the deionized water in the sampler will occur over time, resulting in a water sample (from the diffusion sampler) that is representative of the concentrations of those selected VOCs in the ground water. Diffusion samplers can be used to rapidly and inexpensively obtain ground-water samples for selected VOCs in monitoring wells in which horizontal flow dominates (Vroblesky et al., 1996; Vroblesky and Hyde, 1997). They should not be used in wells in which vertical flow occurs within the well screen. When used appropriately, representative samples can be obtained without well purging to identify temporal changes in ground-water chemistry for selected VOCs (Vroblesky, 2001). Potentially large cost savings in long-term ground-water monitoring efforts may be realized due to the simplicity of the diffusion samplers compared with traditional purge-and-sample techniques. One drawback of the diffusion sampler is that insufficient water is collected to allow measurement of many of the parameters listed in Table 9.2.

**General Ground-Water Sampling Considerations**

Purging consists of the evacuation of water from the monitoring location prior to sampling, so that “fresh” formation water will enter the monitoring location and be available for sampling. Because sampling can occur immediately upon completion of purging, it is best to limit ground-water agitation, and consequently, aeration of the ground water and volatilization of contaminants. Two sources for agitation include the purging device and the cascading of water down the screen as drawdown occurs in the well. To avoid agitation, a low-disturbance device such as a peristaltic pump (at low lifts) or a positive-displacement pump is recommended for purging, while equipment such as bailers should be avoided. To avoid aeration, wells or sampling points screened below the water table should be pumped at a rate that prevents lowering of the water table to below the top of the screen. If practical, wells or sampling points screened across the water table should be pumped at a rate that lowers the total height of the water column no more than 5–10%.

A flow-through cell, such as the simple one pictured in Figure 9.5, should be used for the measurement of ground-water quality indicator parameters such as pH, temperature,
specific conductance, dissolved oxygen, and ORP. Measurements of these parameters should be taken during well purging and immediately before sample acquisition using a multi-parameter sonde or a direct-reading meter (see Chapter 15). Because most well purging techniques can allow aeration of collected ground-water samples, it is important to minimize potential aeration by taking the following precautions:

1. Use a submersible pump of some type to purge the well when possible. To prevent downhole aeration of the sample in wells screened across the water table, drawdown should not exceed about 5–10% of the height of the standing column of water in the well. The discharge end of the pump tubing should be attached to a flow-through cell or immersed alongside the dissolved oxygen and ORP probes beneath the water level in a sampling container (Figure 9.5). This will minimize aeration and keep water flowing past the dissolved oxygen probe’s sampling membrane.

2. If bubbles are observed in the tubing during purging using a peristaltic pump, the flow rate of the peristaltic pump must be slowed. If bubbles are still apparent, sampling should be discontinued.

3. When using a bailer, the bailer should be slowly immersed in the standing column of water in the well to minimize aeration. After sample collection, the water should be drained from the bottom of the bailer through tubing into the sampling container. The tubing used for this operation should be immersed alongside the dissolved oxygen and ORP probes beneath the water level in the sampling container (Figure 9.5). This will minimize aeration and keep water flowing past the dissolved oxygen probe’s sampling membrane.

4. Downhole dissolved oxygen probes are preferred for dissolved oxygen analyses, but such probes must be thoroughly and carefully decontaminated between wells. Some decontamination solutions can be harmful to the dissolved oxygen probe (see Chapter 15).

Samples should be collected directly from the pump discharge tubing or bailer into a sample container of appropriate size, style, and preservation for the desired analysis. Water should be directed down the inner walls of the sample bottle to minimize aeration of the sample. All samples to be analyzed for volatile constituents (e.g., SW8010, SW8020, SW8240, SW8260, and TPH-g) or dissolved gases (e.g., methane, ethane, and ethene) must be filled and sealed so that no headspace remains in the container.

**Sampling Frequency**

The determination of appropriate sampling frequency requires a balancing of several factors including, among others, the chemical characteristics of the contaminants of concern, distance to potential receptors, ground-water seepage velocity, solute transport velocity, the amount of historical data, and how well the contaminant plume is understood.

In the past, the monitoring of dissolved contaminant plumes typically was needlessly time- and location-intensive and, in many cases, involved the quarterly sampling of every monitoring well at a site. On the basis of our current understanding of the behavior of dissolved contaminant plumes, this may not be necessary in many cases. However, quarterly sampling of long-term monitoring wells during the first year of sampling may be useful to help confirm the direction of plume migration and to better establish baseline conditions and seasonal variability. If variability due to seasonal and climatic events is suspected, the installation of dedicated water-level loggers in selected wells may be the best
technique to determine the presence and timing of significant events. The probability the
prescheduled quarterly monitoring will occur during a unique temporal event may be
low at many sites. Quarterly monitoring may represent more of a misplaced tradition
than a technically sound approach. Thus, information should be compiled to identify the
nature, probability, and timing of significant seasonal or climatic events. If significant vari-
bility is encountered during the first year, then more frequent and precisely timed sampling
may be required. On the basis of the results of the first year’s sampling, the sampling fre-
quency may be reduced to annual (or less frequent) sampling during the period showing
the highest contaminant concentrations or the greatest extent of the plume.

At a minimum, the frequency of long-term monitoring should be related to:

1. The natural variability in contaminant concentrations.
2. The distance and travel time from the source to the location where acceptance
criteria are applied.
3. The reduction in contaminant concentrations required to meet the acceptance
criteria.
4. The occurrence of a significant seasonal or climatic event (e.g., snow melt, rainy
season, river ice breakup, spring thaw, etc.).

Ideally, the number of wells to be sampled and the frequency of sampling will be based on
plume behavior and the variability in contaminant concentrations, the distance and esti-
imated time of contaminant travel between long-term monitoring wells, and the distance
and estimated time of contaminant travel between PMWs and contingency wells. Sampling
frequency should be determined by the final placement of the PMWs and contingency
monitoring wells and the ground-water seepage and contaminant transport velocity.

One method of estimating sampling frequency is to divide the distance between a point
just downgradient from the leading edge of the contaminant plume and a downgradient
contingency well located in the plume’s flow path by the seepage velocity of ground water.
For example, consider the contaminant plume depicted in Figure 9.2. If the distance
between well PMW-5 and the center contingency well is 500 ft, and the seepage velocity
of ground water is 250 ft per yr, then a sampling frequency of 2 yr (500 or 250 ft per yr)
may be appropriate for this site. Because the exact location of the leading edge of a dis-
solved contaminant plume generally is not known, some professional judgment may be
required when making these calculations.

According to U.S. EPA (1999), flexibility for adjusting the monitoring frequency over the
life of the remedy should be included in the monitoring plan. For example, it may be approp-
iate to decrease the monitoring frequency at some point in time, once it has been deter-
mined that natural attenuation is progressing as expected and very little change is
observed from one sampling round to the next. Conversely, the monitoring frequency
may need to be increased if unexpected conditions (e.g., plume migration) are observed.
Remedial process optimization (RPO) is a value-added process aimed at determining that
monitoring programs and remedial alternatives are effective, protective, and cost-effective.
This approach should be applied to long-term monitoring programs (AFCEE, 2001).

Evaluation and Interpretation of Monitoring Data

One of the essential components of a long-term monitoring plan is the evaluation and
interpretation of the resulting data. Too often, monitored natural attenuation remedies
are proposed and implemented with little or no consideration of why the monitoring data are being collected. The evaluation and interpretation of long-term monitoring data focuses on detection of spatial and temporal changes, the relation of these changes to natural attenuation processes and plume behavior, and assessment of their impacts on the achievement of site-specific goals.

Long-term monitoring data should be examined in the context of relevant natural attenuation processes and the hydrogeologic setting. This includes evaluation and interpretation of contaminant concentration data, geochemical data, and other parameters to provide empirical evidence for how the ground-water solute plume is behaving over time, to provide insight into how the natural attenuation processes are affecting this behavior, and to allow the identification and explanation of changes that may alter solute plume behavior and affect the performance of the natural attenuation remedy. The purpose is to explain what is happening in the solute plume, not just observe it.

Of particular interest are changes in conditions that may affect the efficacy of the natural attenuation remedy or signal a change in solute plume behavior. These can include indications of additional contaminant releases, changes in geochemical conditions (e.g., redox conditions) that may alter contaminant transformation processes and rates, detections of contaminants at the horizontal and vertical plume boundaries that may indicate plume expansion, and changes in ground-water flow velocities or directions that may move contaminants into previously unaffected areas.

Evaluating Contaminant Data

The fundamental reason for monitoring of natural attenuation is to establish the behavior of the ground-water solute plume so it can be evaluated in relation to remediation objectives for the site. This evaluation typically relies on ground-water monitoring data for locations within the solute plume that indicate how concentrations of constituents of interest are changing over time.

On a conceptual level, the behavior of ground-water solute plumes is a continuum with three major phases: plume expansion, plume stabilization, and plume recession (Figure 9.6). These phases represent the interaction between mass loading to ground water from the source and the action of various attenuation mechanisms in the aquifer. Different portions of a solute plume, as well as different individual constituents, may exhibit different behaviors that can change over time in response to changes in environmental conditions (Figure 9.6).

Evaluation of solute plume behavior can be qualitative or quantitative, or both, depending upon the availability of the necessary data. The particular methods used depend on the availability and quality of monitoring data and will change over time as more monitoring data are generated. The approaches for evaluating solute plume behavior can be separated into two classes: (1) graphical methods that rely on visual interpretation of monitoring data and (2) statistical methods that rely on quantitative analysis of the monitoring data.

Graphical Methods for Evaluating Plume Behavior

Graphical methods are essential tools for evaluating plume behavior. There are several ways to present data to illustrate changes in contaminant concentrations and plume configuration over time. The most common graphical techniques include: (1) preparing isopleth maps of contaminant concentration over time; (2) plotting contaminant concentrations versus time for individual monitoring wells; and (3) plotting contaminant
concentrations versus distance for several wells along the ground-water flow path over several sampling events.

Isopleth maps of contaminant concentrations prepared for successive monitoring rounds are useful for depicting spatial distribution of the solute plume over time. The example in Figure 9.7 shows isopleth maps for total VOC concentrations in ground water at the depth of greatest contaminant concentration. Note that the plotted contaminant data were collected during the same season. This is important because seasonal variations in recharge can cause significant changes in contaminant concentrations and ground-water geochemistry, and an apparent change in plume size and contaminant concentrations could simply be the result of seasonal dilution.

Another method that can be used to present data showing changes in contaminant concentrations and plume configuration over time is to plot contaminant concentrations versus time for individual monitoring wells, or to plot contaminant concentrations versus distance downgradient for several wells along the ground-water flow path over several sampling events. It is important when plotting data in this manner that a least one data point be located a short distance downgradient from the contamination in the ground-water flow path. This ensures that contaminant concentrations in the aquifer as a whole are decreasing and that a pulse of contaminant is not simply migrating downgradient from the observation wells. To ensure that contaminants are not moving downgradient, it is important that downgradient wells are located in the path of contaminated ground-water flow. Geochemical data can be used to confirm that downgradient wells are sampling ground water that was once contaminated with organic compounds.

**FIGURE 9.6**
Solute plume behavior illustrated by concentration trends over time for monitoring points in the vicinity of the source, mid-plume, and the distal part of the plume.
Contaminant concentration versus time plots should only be completed using data from events that are considered comparable. Data from different events may not always be comparable due to abnormal conditions like high water levels due to 100-yr flood events or other unique events.

Figure 9.8 presents a plot of contaminant concentration versus time in one well, and contaminant concentrations versus distance downgradient along the flow path for several sampling events. On the basis of the geochemical data presented in this figure, it is reasonably certain that well H is in the plume’s flow path. Therefore, if the plume were migrating downgradient, this migration should be detected. Wells F and H are...
spaced 100 ft apart, and the ground-water seepage velocity is 50 ft per yr; with 8 yr of sampling data from the same season, we can conclude with reasonable certainty that the plume is not migrating downgradient. The combination of decreasing contaminant concentrations shown by the plots in Figure 9.8b, and the lack of contaminant migration provide converging lines of evidence for natural attenuation and contaminant mass destruction. The chemical and geochemical data discussed by Wiedemeier et al. (1995, 1999) and U.S. EPA (1998) can be used to show that this loss of contaminant mass is the result of degradation.

While plotting concentration data versus time is recommended for any plume stability analysis, discerning trends in the plotted data can be a subjective process, particularly if the data do not display a uniform trend, but show some variability over time (Figure 9.9).

**FIGURE 9.8**

(a) Sampling locations for the (b) plots of contaminant concentration versus time and distance downgradient.
Statistical methods are powerful tools for identifying significant changes and trends in ground-water concentration data. They provide for an objective evaluation of the data and allow statements to be made about the confidence in results. This provides a quantitative indication of the likelihood that conclusions drawn from the data are correct. In evaluating natural attenuation, statistical methods are used to assess ground-water monitoring data for the presence of significant trends or changes in concentrations over time that can provide insight into solute plume behavior. Once again, it is paramount to verify that the monitoring events and data subject to statistical analyses are comparable. If high water levels correlate with higher contaminant concentrations, then data from high and low water table events may not be comparable. If sampling was conducted during an extreme weather event (e.g., a 100-yr flood), then it may not be comparable to previous events. A more detailed discussion of the concept of comparability is found in Gilbert (1987).

**FIGURE 9.8**
Continued.

*Statistical Methods for Evaluating Plume Behavior*

Statistical methods are powerful tools for identifying significant changes and trends in ground-water concentration data. They provide for an objective evaluation of the data and allow statements to be made about the confidence in results. This provides a quantitative indication of the likelihood that conclusions drawn from the data are correct. In evaluating natural attenuation, statistical methods are used to assess ground-water monitoring data for the presence of significant trends or changes in concentrations over time that can provide insight into solute plume behavior. Once again, it is paramount to verify that the monitoring events and data subject to statistical analyses are comparable. If high water levels correlate with higher contaminant concentrations, then data from high and low water table events may not be comparable. If sampling was conducted during an extreme weather event (e.g., a 100-yr flood), then it may not be comparable to previous events. A more detailed discussion of the concept of comparability is found in Gilbert (1987).
The application of statistics requires an understanding of the underlying assumptions of the tests and nature of the data because these determine the selection of appropriate methods and interpretation of the results. While a detailed review of the statistical analysis of concentration data and its application are beyond the scope of this chapter, a brief discussion of the significant factors and some methods that are applicable in the majority of situations is provided. More detailed discussion is available in several statistics texts (e.g., Gilbert, 1987; Gibbons, 1994; U.S. EPA, 2000; Helsel and Hirsch, 2002). This is not a theoretical discussion; rather, it provides practical considerations where statistical results are used in decision-making.

Statistical tests are a form of hypothesis testing and their basis is the comparison of what statisticians call the “null hypothesis” (H₀) to an alternative hypothesis (H₁). The null hypothesis is the statistical hypothesis being tested; generally that the test results are merely a product of chance factors. For example, to test for a trend in a concentration time series, H₀ would be that there is no change in concentration over time, and H₁ would be that the concentration is either increasing or decreasing with time. The two hypotheses are compared using a test statistic that is calculated from the data series being tested.

Most statistical tests are intended to detect a significant difference between a group of samples or from a predefined condition. This is determined by comparing the value for the test statistic calculated from the data set to the probability of obtaining that value purely due to chance. The probability values are determined from the “null” distribution for the test statistic that is the distribution of values for the test statistic under the null hypothesis (H₀). The significance level is a means of determining whether the test statistic value calculated from the data set is less than the level of significance, the null hypothesis (H₀) can be rejected in favor of the alternative hypothesis (H₁).

There are two possible types of decision errors associated with statistical hypothesis testing. A Type I error is when H₀ is incorrectly rejected. A Type II error is when H₀ is accepted when H₁ is true. Both types of decision errors have implications for the conclusions drawn from results of statistical tests.

A Type I error is rejecting the null hypothesis (H₀) when it is in fact true. This is essentially equivalent to a “false positive” result, such as concluding that there is an increasing or decreasing trend in concentration over time when no trend is actually present. The
probability of incorrectly rejecting $H_0$ is the “significance level” ($\alpha$) of the test. Type I errors are controlled by selecting an appropriate $\alpha$-value to reduce the likelihood of drawing an incorrect conclusion from the test.

The inability to reject the null hypothesis (failure to accept the alternative hypothesis) at some level of significance does not imply that the null hypothesis is true. A Type II error is failing to reject (accepting) the null hypothesis ($H_0$) when it is false and the alternative hypothesis ($H_1$) is true. This is essentially equivalent to a “false negative” result, such as concluding that there is no trend in concentration over time when an increasing or decreasing trend is actually present. The probability of this occurring is $\beta$ and the power of a statistical test to detect a significant difference is $1 - \beta$. The statistical power of a test is related to both the $\alpha$-value selected and the sample size ($n$).

Ideally, we would like to minimize both Type I and Type II errors in using statistical tests, but this is difficult in practice. The importance of either type of decision error should be evaluated in terms of the ultimate use of the results of the statistical test. A pragmatic approach is to specify an acceptable value for $\alpha$ and concurrently reduce $\beta$ by (1) increasing the sample size and (2) using a statistical test with the greatest power for the type of data being evaluated (Helsel and Hirsch, 2002).

Statistical tests are described as one- or two-sided depending upon the specific alternative hypothesis involved. A two-sided test is used when a difference in either direction from $H_0$ would cause $H_0$ to be rejected, such as a test for detecting the presence of a trend or change in concentration. For example, if there is no reason to assume that concentrations are not stable or that departures from $H_0$ in only one direction are of interest, a two-sided test is appropriate. A one-sided test is used when a change in only one direction from $H_0$ would cause $H_0$ to be rejected, such as a test for detecting an increase (or decrease) in concentration over time. For example, if only evidence that concentration is increasing (or decreasing) over time is considered important, $H_0$ would be stated as “the change in concentration over time is less (or greater) than or equal to zero (0)” and $H_1$ would be “the change in concentration over time is greater (less) than zero (0).”

The null distributions for most test statistics are symmetrical and the probability values for only one “tail” of the distribution are given. For detecting an increase (or decrease), only the difference in one direction is important and the critical test statistic value at $\alpha$ is used (one-sided tail). For detecting the presence of a trend or change in concentration, both a positive or negative difference is important and the critical test statistic value at $\alpha/2$ is used (two-sided tail).

The issue of confidence levels, or significance levels, and their meaning is a source of considerable confusion on the part of users. The practical implication of the confidence level is that there is error associated with the decision to reject the null hypothesis. If the calculated value of the test statistic leads you to reject the null hypothesis, it does not mean that the value for the test statistic you obtained could not have occurred by chance. It means that the probability of obtaining that value by chance alone is sufficiently small that it is reasonable to conclude that the result is not due to chance and that the decision to reject the null hypothesis is correct. The confidence level simply quantifies the likelihood that rejecting the null hypothesis is appropriate.

The confidence level for a statistical test is related to the significance level ($\alpha$) and is simply described by the value $1 - \alpha$, typically expressed as a percentage. The significance level ($\alpha$) is specified in advance of the test and defines the “acceptable” level of Type I error that the user is willing to tolerate in deciding to reject the null hypothesis. For example, if the desired confidence level for a statistical test is 95% (0.95), the significance level would be specified as 0.05 and the null hypothesis would be rejected if the calculated test statistic value has a probability $\leq 0.05$. This means that the likelihood of making an incorrect decision to reject the null hypothesis is 5 in 100 (1 in 20) and,
conversely, the likelihood that the decision to reject the null hypothesis is correct is 95 in 100 (19 in 20).

The confidence level simply quantifies the “confidence” associated with obtaining a “significant” result for a statistical test, such as concluding that there is a trend in concentration over time or a difference in concentrations. There is no magic to defining the appropriate confidence level and adjusting the confidence level simply changes the tolerance for Type I error in decision-making. In most scientific applications, a 95% confidence level is used as there is general concurrence that the associated error (5%) is sufficiently small. Decreasing the confidence level for a statistical test will increase the likelihood of obtaining a “significant” result, but will also increase the chances that the null hypothesis will be incorrectly rejected. The specified confidence level is simply a reflection of the user’s willingness to accept a mistaken conclusion for a statistical test.

Nature of Ground-Water Concentration Data and Appropriate Statistical Methods

Issues involved with the statistical analysis of ground-water concentration data are myriad, but most commonly involve missing values, nondetect (censored) values, small number of data points, and the lack of certain knowledge of the underlying distribution. All of these complicate the application of statistical methods and either require significant data manipulation or the use of methods that are little affected by these data characteristics. Trend analysis, in particular, is sensitive to these issues, as well as to changes in sampling and analytical procedures, seasonal or other cyclic variation in the data, and correlated data (Gilbert, 1987).

Statistical approaches can be separated into parametric and nonparametric methods. The familiar parametric statistics, such as regression analysis, rely on data conforming to an underlying distribution, such as normal (Gaussian) or log-normal. Parametric statistics are sensitive to missing data points and outliers, how nondetect values are handled, and departures from the assumed distribution. Nonparametric statistical methods do not depend on assumptions regarding the underlying data distribution and are also known as “distribution-free” methods. They can accommodate missing data points and nondetect values that are common in ground-water concentration data sets. These methods rely on the ranks or relative magnitudes of the data rather than the actual values and are fairly straightforward to use. In many situations, particularly those involving small data sets, nonparametric methods perform as well or better than parametric ones (Helsel and Hirsch, 2002).

The selection of statistical methods is frequently limited by the availability of sufficient data. Aside from the issues mentioned earlier, parametric methods are sensitive to sample size and their power is reduced for small data sets, such as are common in ground-water concentration data. Nonparametric methods typically are equally or more powerful for discerning trends and changes for small data sets.

Due to the issues associated with most ground-water concentration data, the use of nonparametric techniques are generally preferred (Gilbert, 1987; Gibbons, 1994) and some commonly used methods are described briefly below. Additional information on these nonparametric methods is provided in Hollander and Wolfe (1999), Conover (1999), and Helsel and Hirsch (2002).

Tests for Trend

The Mann–Kendall test for trend (Mann, 1945; Kendall, 1975) is used to determine the presence or absence of a trend in concentration over time for individual monitoring points. It is a test for zero slope of time-ordered data that is based on a nonparametric analog of linear regression. The basic methodology and its variants (such as the Seasonal
Mann–Kendall test) are described in Gilbert (1987) and Helsel and Hirsch (2002) and four or more independent sampling events are required. The results of the Mann–Kendall test indicate the presence or absence of a statistically significant increasing or decreasing trend in concentrations over time at a monitoring point. These results can be used to help evaluate whether the solute plume is receding, expanding, or stable.

The Mann–Kendall test for between 4 and 40 data points is very straightforward to apply and an example calculation is provided in Table 9.4. Concentration data are ordered sequentially over time and a matrix is constructed comparing each data value to subsequent values. Starting with the earliest data point, each subsequent data point is compared and a value entered into the matrix:

\[
\begin{array}{l}
+1 & \text{if the later value is greater,} \\
-1 & \text{if the later value is less, and} \\
0 & \text{if the later value is equal to the earliest data point.}
\end{array}
\]

The process is repeated for the next data point in the sequence, comparing its value to subsequent ones, until all data points in the sequence have been compared and appropriate values entered into the matrix. The values in each row in the matrix are then summed and the row sums are then summed to generate the Mann–Kendall statistic \( S \).

Once the \( S \)-statistic has been calculated, it is compared with the table of null probability values of \( S \) for the number of data points \( n \) in the series (Table 9.5). If the probability value for the calculated \( S \)-statistic and the number of data points \( n \) is less than the specified significance level for the test (\( \alpha \) for one-sided; \( \alpha/2 \) for two-sided), the result is significant at the \( 1 - \alpha \) confidence level and a trend is present. The calculated \( S \)-statistic \( -17 \) and \( n \) (10) for the example calculation in Table 9.4 correspond to a probability of 0.078 in Table 9.5. For a one-sided test, this result is less than the \( \alpha \) for the 90% confidence level (\( \alpha = 0.1 \)), indicating a significant result, but is greater than the \( \alpha \) for the 95% confidence level (\( \alpha = 0.05 \)), indicating that the result is not significant at this level of confidence.
### TABLE 9.5
Null Probabilities for the Mann–Kendall Statistic, \( n = 4–20 \)

| \( s \) | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 19  | 20  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0     | 0.625 | 0.592 | 0.548 | 0.540 | 0.527 | 0.524 | 0.518 | 0.516 | 0.513 | 0.513 | 0.513 | 0.513 | 0.513 | 0.513 | 0.513 | 0.513 |
| ±1    | 0.375 | 0.408 | 0.452 | 0.460 | 0.473 | 0.476 | 0.482 | 0.484 | 0.487 | 0.487 | 0.487 | 0.487 | 0.487 | 0.487 | 0.487 | 0.487 |
| ±2    | 0.167 | 0.242 | 0.235 | 0.281 | 0.360 | 0.381 | 0.420 | 0.429 | 0.447 | 0.452 | 0.441 | 0.445 | 0.441 | 0.441 | 0.441 | 0.441 |
| ±3    | 0.042 | 0.117 | 0.136 | 0.191 | 0.300 | 0.324 | 0.374 | 0.385 | 0.411 | 0.418 | 0.411 | 0.418 | 0.411 | 0.411 | 0.411 | 0.411 |
| ±4    | 0.042 | 0.199 | 0.238 | 0.319 | 0.338 | 0.378 | 0.388 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 |
| ±5    | 0.136 | 0.191 | 0.274 | 0.306 | 0.364 | 0.381 | 0.369 | 0.383 | 0.415 | 0.423 | 0.412 | 0.420 | 0.411 | 0.418 | 0.418 | 0.418 |
| ±6    | 0.042 | 0.199 | 0.238 | 0.319 | 0.338 | 0.378 | 0.388 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 |
| ±7    | 0.042 | 0.199 | 0.238 | 0.319 | 0.338 | 0.378 | 0.388 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 |
| ±8    | 0.042 | 0.199 | 0.238 | 0.319 | 0.338 | 0.378 | 0.388 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 | 0.411 |

(Table continued)
Because the $S$ value is negative, we can conclude that a decreasing trend in concentration over time is present at the 90% confidence level. Whether this result is “significant” would depend upon the significance level ($a$) specified for the test.

The Mann–Kendall test is robust to missing data points and nondetect values. Missing data points are simply ignored because they do not influence the test result. Nondetect values are replaced with a common value less than the smallest concentration value in the data series. If multiple detection limits are involved, the data must be further censored at the highest detection limit (Helsel and Hirsch, 2002). This decreases the power of the test to detect trends due to the increased number of tied values, but the impact in most situations involving small data sets is not significant. If the number of tied values is a significant proportion of the data series, the tie correction for the large-sample approximation described subsequently can be used.

<table>
<thead>
<tr>
<th>$S$</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>±58</td>
<td>0.004</td>
<td>0.009</td>
<td>0.032</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±59</td>
<td>0.000</td>
<td>0.001</td>
<td>0.013</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±60</td>
<td>0.001</td>
<td>0.003</td>
<td>0.007</td>
<td>0.011</td>
<td>0.017</td>
<td>0.027</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±61</td>
<td>0.002</td>
<td>0.005</td>
<td>0.009</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±62</td>
<td>0.001</td>
<td>0.002</td>
<td>0.004</td>
<td>0.012</td>
<td>0.020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±63</td>
<td>0.000</td>
<td>0.007</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±64</td>
<td>0.001</td>
<td>0.003</td>
<td>0.017</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±65</td>
<td>0.005</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±66</td>
<td>0.001</td>
<td>0.002</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±67</td>
<td>0.004</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±68</td>
<td>0.001</td>
<td>0.002</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±69</td>
<td>0.003</td>
<td>0.006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±70</td>
<td>0.000</td>
<td>0.001</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±71</td>
<td>0.003</td>
<td>0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±72</td>
<td>0.001</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±73</td>
<td>0.002</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±74</td>
<td>0.001</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±75</td>
<td>0.001</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±76</td>
<td>0.000</td>
<td>0.006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±77</td>
<td>0.001</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±78</td>
<td>0.001</td>
<td>0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±79</td>
<td>0.001</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±80</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±81</td>
<td>0.001</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±82</td>
<td>0.001</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±83</td>
<td>0.000</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±84</td>
<td>0.000</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±85</td>
<td>0.000</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±86</td>
<td>0.000</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±87</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±88</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±89</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±90</td>
<td>0.002</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±91</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±92</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±93</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±94</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±95</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±96</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±97</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±98</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±99</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>±100</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Adapted from Hollander and Wolfe (1999). Used with permission.
In the unusual circumstance that more than 40 data points are available, a modification of the Mann–Kendall test based on the normal approximation can be used. This version of the Mann–Kendall test uses \( Z \) as the test statistic. The test is performed by calculating the \( S \)-statistic for the data set as described earlier. The variance of the \( S \)-statistic is then calculated as:

\[
\text{VAR}(S) = \frac{1}{18} \left[ n(n-1)(2n+5) - \sum_{p=1}^{q} t_p(t_p - 1)(2t_p + 5) \right]
\]

where \( n \) is the number of data points in the data set, \( q \) is the number of groups of tied values, and \( t_p \) is the number of data points in \( p \)th group of tied values. If the calculated \( S \) is 0, the \( Z \)-statistic is also 0. Otherwise, the \( Z \)-statistic is calculated as follows:

\[
Z = \begin{cases} 
\frac{S-1}{\sqrt{\text{VAR}(S)}} & \text{if } S > 0 \\
\frac{S+1}{\sqrt{\text{VAR}(S)}} & \text{if } S < 0 
\end{cases}
\]

The sign of the calculated \( Z \) indicates whether a trend is increasing (positive) or decreasing (negative). Once the \( Z \)-statistic has been calculated, it is compared with the table of null probability values for \( Z \) that can be found in most statistics texts. Critical values for the \( Z \)-statistic at probabilities for the commonly used significance levels for one-sided (\( p = \alpha \)) and two-sided (\( p = \alpha/2 \)) tests are 1.29 (\( p = 0.1 \)), 1.64 (\( p = 0.05 \)), and 1.96 (\( p = 0.025 \)).

A general consideration for using the Mann–Kendall test is that a nonsignificant result does not demonstrate stability because the result could be due to concentrations at the monitoring point actually being at steady-state (stable) or to the data set being inadequate to provide a statistically significant result (Barden, 2003). Failing to reject \( H_0 \) does not mean that it was “proven” that there is no trend. Rather, it is a statement that the evidence available is not sufficient to conclude that there is a trend at the specified confidence level.

A suggested approach to dealing with the issue of a nonsignificant result for the Mann–Kendall test is to use the coefficient of variation as an indication, or “test,” of stability (GSI, 1998; Wiedemeier et al., 1999; Ling et al., 2003). The coefficient of variation (CV) measures the spread of a set of data as a proportion of its mean and the suggested approach concludes that a Mann–Kendall test that is not significant at the 90% confidence level where CV < 1 indicates stability. However, the coefficient of variation is a relative measure of variation described by the ratio of the sample standard deviation to the sample mean. Thus, it depends upon both values and has no implicit meaning. If the mean value is large, even a small CV can include significant variation. Data series with “low” values for CV certainly show less scatter in the data, but there is no objective basis for using a particular value of CV to determine “stability.”

A useful variation on the Mann–Kendall test is a test for “homogeneity of stations” (Gilbert, 1987; Helsel and Hirsch, 2002). This test essentially pools the results for Mann–Kendall tests at individual monitoring points and allows statements to be made about consistency of trends throughout the plume or portions of the plume (e.g., whether the trends at all monitoring points are in the same direction — all increasing or all decreasing). Such a general statement about the presence or absence of monotonic trends is useful for making interpretations of the overall behavior of the entire plume or specific portions of the plume. For chlorinated solvent solute plumes, these results can be used in combination with geochemical data to discern different types of environments.
The presence of seasonal variability in ground-water concentration time series data can make discerning trends difficult because it contributes short-term variation, caused by water-level fluctuations and other seasonal effects, that appear as background noise in a Mann–Kendall test for the whole time series. If the source of the seasonal effect can be identified, one way to “remove” the effect is to normalize the concentration data to the source variable. For example, if ground-water concentrations are shown to be correlated with water levels in monitoring wells, they could be “normalized” by dividing concentrations by water levels. This is a simplistic approach and more sophisticated data normalization techniques can be used (Helsel and Hirsch, 2002).

The “Seasonal Kendall test” (Hirsch et al., 1982; Hirsch and Slack, 1984) is a modification of the Mann–Kendall test that addresses this short-term variability due to seasonality and allows evaluation of overall trends in the time series. In a seasonal Kendall test, the Mann–Kendall test is applied to each season (e.g., quarter) separately and then the results are combined for an overall test (Hirsch et al., 1982). Each season by itself may show a positive trend, none of which is significant, but the overall seasonal Kendall statistic can be quite significant. The test has all the advantages of the Mann–Kendall test, but is more robust because it removes short-term variability caused by seasonality. When successive seasons are correlated, a correction must be used based on the covariance among seasons (Hirsch and Slack, 1984).

The seasonal Kendall test consists of calculating the Mann–Kendall statistic, $S$, and its variance, $\text{VAR}(S)$, for the data from each season collected over a period of years. These “seasonal” statistics are then summed and the test statistic $Z$ is calculated as described earlier using the summed values. As with the normal approximation described earlier, the sign of the calculated $Z$ indicates whether a trend is increasing (positive) or decreasing (negative). The calculated $Z$-statistic then is compared with the table of null probability values for $Z$ that can be found in most statistics texts. There is some question regarding the direct application of the standard $Z$ table values for a small number of “seasons” and few years of sampling data (Gilbert, 1987). However, the exact distribution for the test statistic can be determined using the technique described in Hirsch et al. (1982).

A practical limitation on the use of the seasonal Kendall test for evaluating ground-water data in long-term monitoring of natural attenuation is that seasonal (e.g., quarterly) data must be available. If the monitoring frequency is changed to annual or semi-annual basis, these seasonal data may be lost. If seasonal effects are identified during site characterization, or in the early stages of the long-term monitoring program, continued quarterly monitoring may be warranted to adequately define the impact of seasonal effects on trend results and to determine the appropriate frequency for later monitoring. Additionally, the number of data points for each season and the number of seasons considered can impact the results of the seasonal Kendall test. Generally, at least 3 yr of monitoring data should be included in the analysis.

**Tests for Differences between Groups of Data**

Another type of statistical test that is commonly suggested for evaluating ground-water concentration data for natural attenuation is a test for significant differences between groups of data. Several nonparametric methods are available for performing such comparisons and the appropriate method depends upon the number of groups to be compared and whether the data are paired (Gilbert, 1987; Helsel and Hirsch, 2002). All of these methods are nonparametric analogs of the Student’s $t$-test. These methods test whether measurements from one data set are consistently larger or smaller than those from another data set, either using relative ranks of the data or the differences.

Two-sample tests are typically used for comparing earlier data sets to those from later time periods. These can include comparing concentrations for several monitoring points
at two time points or comparing concentrations from an individual monitoring point for one time period to those for another time period (e.g., quarterly monitoring results for 1 yr to those for another year). Such a comparison can essentially identify the presence or absence of a step trend in concentrations over time. Two-sample procedures should only be used when the data sets being analyzed can be naturally broken into two distinct time periods or when a known event has occurred that is likely to have resulted in a significant change in concentrations (Helsel and Hirsch, 2002). In general, the monotonic trend methods discussed previously are more appropriate.

The Mann–Whitney U-test (Mann and Whitney, 1947), also called the Wilcoxon rank sum test, is commonly suggested for the purpose of identifying step trends and has been specified in some States’ regulations (e.g., New Jersey, Wisconsin). The typical application of this test is to compare concentrations from individual monitoring points for one time period to those for another time period (e.g., quarterly monitoring results for 1 yr to those for another year). The Mann–Whitney U-test is based on the assumption that the two data sets are independent, meaning that there is no natural way to pair the data. However, in the typical use of this test for evaluating natural attenuation, the data for the two groups can be considered paired by “seasons” and are not really independent. Use of the Mann–Whitney U-test should be limited to the situations noted above and where data set independence can be assured.

Data are considered paired when there is a natural way to spatially or temporally associate data values in each group. In many cases, the data involved in evaluating natural attenuation will be paired by location or by season (e.g., quarterly data). In such situations, a paired-sample test, such as the “sign test” or the “Wilcoxon signed rank test” (not to be confused with the Wilcoxon rank sum test), is more appropriate (Gilbert, 1987).

The sign test is more versatile than the Wilcoxon signed rank test because it has no distributional assumptions and can accommodate a few nondetect values. However, it has less ability to detect differences between populations. The test statistic is the number of data pairs where \( x_{1i} > x_{2i} \) (the number of positive differences). However, at small sample sizes the sign test has limited utility. The Wilcoxon signed rank test is a more powerful alternative to the sign test that is more likely to detect significant differences between data sets. However, it does require that the underlying distribution is symmetrical. In some cases where the differences are not symmetric in the original units, but a logarithmic transformation of the two data sets produces symmetric differences, the Wilcoxon signed rank test is also appropriate (Helsel and Hirsch, 2002).

The Wilcoxon signed rank test involves calculating and ranking the differences \( D_i \) of the data pairs. The \( H_0 \) for the test is the median of the differences is zero (0). Example calculations are shown in Table 9.6 for quarterly concentration data in a monitoring well from 2 yr, and in Table 9.7 for concentration data from multiple monitoring wells.

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Year 1 (x)</th>
<th>Year 2 (y)</th>
<th>Difference</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>32</td>
<td>27</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>2nd</td>
<td>46</td>
<td>42</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td>3rd</td>
<td>28</td>
<td>30</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td>4th</td>
<td>30</td>
<td>26</td>
<td>4</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\( W^+ = 9 \)

**Table 9.6**
Example Calculations for the Wilcoxon Signed-Rank Test Comparing Groups of Paired Data for Quarterly Concentration Data in a Single Monitoring Well for 2 yr (\( \mu g/l \))
for 2 yr. The difference between each pair of values \((x_i - y_i)\) in the two data sets is calculated and the absolute value of the differences \(|D_i|\) is then ranked from smallest to largest. The test uses only nonzero differences, so tied values \((x_i - y_i = 0)\) are deleted and the sample size is reduced by the number of tied values. When two nonzero differences are tied, the average of the ranks involved is assigned to the tied values.

The signed rank \((R_i)\) for each pair is determined by the sign of the difference for each pair \((x_i - y_i)\); “+” for a positive difference and “−” for a negative difference. The test statistic \(W^+\) is then calculated as the sum of the positive ranks. The \(W^+\)-statistic is compared with a table of critical values for \(W^+\) quantiles (Table 9.8). For the appropriate sample size

<table>
<thead>
<tr>
<th>Well</th>
<th>Year 1 ((x))</th>
<th>Year 2 ((y))</th>
<th>Difference</th>
<th>Rank</th>
<th>Difference</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-1</td>
<td>1045</td>
<td>890</td>
<td>155</td>
<td>8</td>
<td>0.070</td>
<td>5</td>
</tr>
<tr>
<td>MW-2</td>
<td>352</td>
<td>241</td>
<td>111</td>
<td>7</td>
<td>0.165</td>
<td>8</td>
</tr>
<tr>
<td>MW-3</td>
<td>256</td>
<td>287</td>
<td>−31</td>
<td>−6</td>
<td>−0.050</td>
<td>−3</td>
</tr>
<tr>
<td>MW-4</td>
<td>132</td>
<td>128</td>
<td>4</td>
<td>2.5</td>
<td>0.013</td>
<td>1</td>
</tr>
<tr>
<td>MW-5</td>
<td>46</td>
<td>40</td>
<td>6</td>
<td>5</td>
<td>0.061</td>
<td>4</td>
</tr>
<tr>
<td>MW-6</td>
<td>28</td>
<td>30</td>
<td>−2</td>
<td>−1</td>
<td>−0.030</td>
<td>−2</td>
</tr>
<tr>
<td>MW-7</td>
<td>30</td>
<td>25</td>
<td>5</td>
<td>4</td>
<td>0.079</td>
<td>6</td>
</tr>
<tr>
<td>MW-8</td>
<td>10</td>
<td>14</td>
<td>−4</td>
<td>−2.5</td>
<td>−0.146</td>
<td>−7</td>
</tr>
</tbody>
</table>

\[ W^+ = 26.5 \]

\[ W^+ = 24 \]

for 2 yr. The difference between each pair of values \((x_i - y_i)\) in the two data sets is calculated and the absolute value of the differences \(|D_i|\) is then ranked from smallest to largest. The test uses only nonzero differences, so tied values \((x_i - y_i = 0)\) are deleted and the sample size is reduced by the number of tied values. When two nonzero differences are tied, the average of the ranks involved is assigned to the tied values.

The signed rank \((R_i)\) for each pair is determined by the sign of the difference for each pair \((x_i - y_i)\); “+” for a positive difference and “−” for a negative difference. The test statistic \(W^+\) is then calculated as the sum of the positive ranks. The \(W^+\)-statistic is compared with a table of critical values for \(W^+\) quantiles (Table 9.8). For the appropriate sample size

### Table 9.8

<table>
<thead>
<tr>
<th>(n)</th>
<th>0.025</th>
<th>0.05</th>
<th>0.1</th>
<th>0.025</th>
<th>0.05</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td></td>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>15</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>21</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>26</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>5</td>
<td>8</td>
<td>33</td>
<td>31</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>40</td>
<td>37</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>10</td>
<td>14</td>
<td>47</td>
<td>45</td>
<td>41</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>13</td>
<td>17</td>
<td>56</td>
<td>53</td>
<td>49</td>
</tr>
<tr>
<td>12</td>
<td>13</td>
<td>17</td>
<td>21</td>
<td>65</td>
<td>61</td>
<td>57</td>
</tr>
<tr>
<td>13</td>
<td>17</td>
<td>21</td>
<td>26</td>
<td>74</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>14</td>
<td>21</td>
<td>25</td>
<td>31</td>
<td>84</td>
<td>80</td>
<td>74</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
<td>30</td>
<td>36</td>
<td>95</td>
<td>90</td>
<td>84</td>
</tr>
<tr>
<td>16</td>
<td>29</td>
<td>35</td>
<td>42</td>
<td>107</td>
<td>101</td>
<td>94</td>
</tr>
<tr>
<td>17</td>
<td>34</td>
<td>41</td>
<td>48</td>
<td>119</td>
<td>112</td>
<td>105</td>
</tr>
<tr>
<td>18</td>
<td>40</td>
<td>47</td>
<td>55</td>
<td>131</td>
<td>124</td>
<td>116</td>
</tr>
<tr>
<td>19</td>
<td>46</td>
<td>53</td>
<td>62</td>
<td>144</td>
<td>137</td>
<td>128</td>
</tr>
<tr>
<td>20</td>
<td>52</td>
<td>60</td>
<td>69</td>
<td>158</td>
<td>150</td>
<td>141</td>
</tr>
</tbody>
</table>

Source: Adapted from McCornack (1965). Used with permission.
in Table 9.8 the critical values \((w \text{ and } w')\) are obtained for the significance level of the test. For a two-sided test \((p = \alpha/2)\), the null hypothesis is rejected if \(W^+ \leq w\) or \(W^+ \geq w'\) (x tends to be larger or smaller than \(y\)). For a one-sided test \((p = \alpha)\), the null hypothesis is rejected if either \(W^+ \leq w\) (x tends to be smaller than \(y\); concentrations increase) or \(W^+ \geq w'\) (x tends to be larger than \(y\); concentrations decrease).

The calculated \(W^+\)-statistic (9) for the example shown in Table 9.6 is greater than the critical value for a significant increase \((w = 0)\) or less than the critical value for a significant decrease \((w' = 10)\) for a one-sided test at the 90% confidence level \((\alpha = 0.1)\) for the sample size, \(n\) (4). The null hypothesis of no increase, or decrease, of concentration in this monitoring well cannot be rejected and no significant change in overall concentration is indicated at this confidence level. For the sample size in this example, the 95% confidence level for a one-sided test cannot be resolved and neither the 90 or 95% confidence levels can be resolved for a two-sided test. This illustrates the limitation of small sample sizes for such tests.

In the example shown in Table 9.7, the symmetry of the differences for the data pairs is questionable. Recalculating the differences using the logarithms of the data values, \(\log(x_i) - \log(y_i)\), gives a distribution of differences that is more symmetrical. These differences are then ranked as described earlier and the \(W^+\)-statistic is calculated. The calculated \(W^+\)-statistic (24) for the example shown in Table 9.7 is greater than the critical values for \(w\) and less than the critical values for \(w'\) at the 90% \((\alpha = 0.1)\) and 95% \((\alpha = 0.05)\) confidence levels for the sample size, \(n\) (8). This indicates a non-significant result for either a one- or two-sided test at these confidence levels so the null hypotheses would be accepted and no significant change in overall concentrations for these monitoring wells is indicated.

Using Statistical Results

The use of results from statistical tests in evaluating the performance of a natural attenuation remedy allows quantifiable patterns in contaminant concentrations over time to be determined. These can provide insight into solute plume behavior and changes over time in different parts of the solute plume that reflect the performance of natural attenuation. An important note is that none of the statistical tests described earlier are tests for solute plume stability; none presently exist. In evaluating solute plume stability, it is important to combine statistical results with observations of the solute plume boundaries. The presence or absence of statistically significant trends in concentration over time at monitoring points do not necessarily translate into spatial changes in solute plume configuration. The lack of statistically significant trends in concentration over time can generally be taken to represent a steady-state condition at a given monitoring point, but this implies nothing about solute plume behavior. Consideration of results at all the monitoring points is necessary.

In evaluating statistical results for concentration data, it is necessary to consider all of the performance monitoring points. Depending on the dynamics of mass transfer from the source and the specific natural attenuation processes involved, different portions of a solute plume may exhibit different types of behavior (Figure 9.6). No single monitoring point can provide statistical results that are definitive because different monitoring points will be located in different geochemical environments that impact the ambient degradation and transformation processes.

A general consideration for the use of statistical methods in identifying trends and evaluating solute plume behavior is that statistical significance does not necessarily imply real-world significance and statistical test results can provide a false sense of assurance regarding conclusions (Barden, 2003). It is important to always relate statistical results and evaluation back to the physical problem in the field to ensure that the results are meaningful. Changes in concentration and trends in concentration time series should be evaluated in the context of the scientific understanding of the relevant natural attenuation processes. The point is to be able to explain why the observed patterns
(Figure 9.6) indicated by the statistical results are occurring. The reason for a “statistically significant” change in concentrations is not provided by the statistics themselves.

As an example, consider the results from tests for step trends. Comparison of concentration data for two successive years does not imply that the result is meaningful. The fact that concentrations in the second year are lower (or higher) than those from the previous year only demonstrates a “statistically significant” difference. This does not imply that data from subsequent years would produce the same result. A fundamental flaw in this sort of analysis is that 2 yr of data in most hydrogeologic settings is not a very large amount and the resulting evaluation may not be substantive in the real world.

A consideration with the seasonal Mann–Kendall test is that trends of opposite sign in different seasons may offset each other, giving the impression that no trends are present. This is typically not a substantive concern because the point of the test is to determine overall trends in the data series that may help to describe solute plume behavior. However, the individual seasonal trends may be of importance for helping to unravel relationships between parameters, in which case they could be examined individually in more detail.

Similarly, it is common for the test for “homogeneity of stations” to show no significant overall trend, even though trends are significant within contiguous portions of the solute plume. Careful consideration of how monitoring points should be grouped is necessary to evaluate portions of the solute plume. Graphical evaluation of the data combined with a scientific understanding of the problem should be a good guide on how to group contiguous monitoring points for statistical analysis.

**Evaluation of Ground-Water Geochemical and Supplemental Data**

The ground-water geochemical data collected during validation monitoring and subsequent long-term monitoring should be evaluated to:

1. Demonstrate that natural attenuation, and specifically degradation, is occurring according to expectations.
2. Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of the natural attenuation process.

The interpretation of geochemical data as they apply to degradation of fuel hydrocarbons is discussed in detail by Wiedemeier et al. (1995, 1999). The interpretation of geochemical data as they apply to degradation of chlorinated solvents is discussed in detail by U.S. EPA (1998) and Wiedemeier et al. (1999, 2005).

The evaluation of ground-water geochemical data during long-term monitoring of natural attenuation is similar to that in site characterization monitoring. The same basis for interpretation is used that is described in the various protocols for evaluating natural attenuation (e.g., Wiedemeier et al., 1995, 1999, 2005; U.S. EPA, 1998). However, the focus during long-term monitoring is on using the geochemical parameters to help explain observed changes in contaminant concentrations and solute plume behavior.

Ground-water geochemical data (Table 9.2) and supplemental data (Table 9.3) can be useful for providing ongoing information on conditions in and around the solute plume. This information is used to provide a mechanistic interpretation of plume behavior (i.e., why the observed changes in contaminant concentration are occurring).

Geochemical data collected during long-term monitoring should be evaluated to determine changes in parameters associated with significant site-specific transformation or degradation processes and changes in background conditions that might impact natural
attenuation processes. The interpretation of geochemical data relies on the availability of an established baseline that includes the range of variation in the parameter values. The significance of changes in geochemical parameter values depends on the expected variation based on existing observations. If such a baseline is not available from the site characterization or natural attenuation evaluation (feasibility study), ground-water geochemical data collected during validation monitoring should be evaluated to determine consistency with the data collected during the site characterization and expected variability in the parameters.

Sampling of geochemical parameters in upgradient, background locations can provide an “early warning” of changes that might adversely impact solute plume stability. In most cases, sampling of geochemical parameters alone is adequate because they are more sensitive to potential problems than sampling for contaminants. For example, if a hydrocarbon solute plume undergoing MNA is stable or receding and a new hydrocarbon release occurs upgradient, the development of the new solute plume could deplete available dissolved oxygen, nitrate, and sulfate in ground water. The observation of a sustained reduction in concentrations of dissolved oxygen, nitrate, or sulfate or the sustained increase in Mn(II), Fe(II), alkalinity or methane concentrations in upgradient, background monitoring locations would indicate that the geochemical “shadow” of the new solute plume is encroaching on the original plume. Such a situation would be expected to affect the efficacy of natural attenuation in the original hydrocarbon solute plume by affecting the dynamics of biodegradation. Whether this would substantively affect the MNA remedy would depend on the site-specific circumstances, but some readjustment of the solute plume would likely occur in response to the changed conditions and reevaluation would be warranted.

Similarly, the geochemical indicators of a sustained reduction in concentrations of dissolved oxygen, nitrate, or sulfate or the sustained increase in Mn(II), Fe(II), methane, or alkalinity concentrations in sentry or point-of-action monitoring locations can provide an “early warning” that a solute plume may be moving downgradient. A sustained increase in chloride concentrations could provide a similar indicator for chlorinated solvent solute plumes.

**Evaluation of Daughter Product Data**

Concentrations of chlorinated solvents and their transformation products give a direct indication of the presence or absence of transformation processes. In many cases the production of cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride (VC), and chloride ions along ground-water flow paths is direct evidence of biodegradation. For example, if trichloroethylene (TCE) was the only contaminant released at a site, then any cis-1,2-DCE or VC present at the site must have come from the degradation of the parent TCE. In some cases, the presence of cis-1,2-DCE and lack of VC may be indicative of abiotic degradation.

**Evaluation of Electron Acceptor Data**

Naturally occurring electron acceptors affect the degradation of petroleum hydrocarbons and chlorinated solvents in different ways. In general, the more electron acceptors present in ground water contaminated with petroleum hydrocarbons, the better. This is because microbes consume these compounds while degrading the hydrocarbons. In contrast, naturally occurring electron acceptors can compete with reductive dechlorination of chlorinated solvents, thus reducing the efficiency of the reaction.

The stabilization of hydrocarbon solute plumes typically is controlled by naturally occurring biodegradation processes that use naturally occurring inorganic electron
acceptors. The scenario of a hydrocarbon solute plume “running out” of electron acceptors to support biodegradation is a common concern on the part of regulators.

For all intents and purposes, electron acceptors dissolved in ground water, such as dissolved oxygen, nitrate and sulfate, will be readily available unless there is a change in background ground-water geochemistry that depletes these constituents. Similarly, methanogenesis is effectively self-perpetuating because it is driven by fermentation reactions that only require reduced organic carbon, so methane would be expected to be present as long as fermentable organic matter is available. However, if the major biodegradation reaction is iron reduction or manganese reduction that relies on bioavailable solid-phase Fe(III) or Mn(IV), there is a limited in situ supply available. Depending upon the mass of hydrocarbon present, it is possible to use up the bioavailable electron acceptor, resulting in a cessation of these reactions. This can cause a solute plume that was stable to shift position downgradient (Cozzarelli et al., 2001). A similar, though much less likely, situation could be envisioned for a solute plume with sulfate reduction as the predominant terminal electron-accepting process where the sulfate is produced by in situ dissolution of sulfate minerals.

Such a situation can cause consternation if the underlying natural attenuation processes are not understood and the significant biodegradation processes monitored using geochemical parameters. The depletion of bioavailable solid-phase Fe(III) or Mn(II) would be accompanied by a steady decrease in measured Fe(II) or Mn(II) concentrations in parts of the plume where they were previously elevated as the soluble, reduced ions are transported downgradient and precipitated as mineral phases.

An important consideration for evaluating geochemical parameters is that Fe(II), Mn(II), and methane are mobile in ground water. Therefore, the detection of these constituents at a given monitoring location is not necessarily indicative of iron-reducing, manganese-reducing, or methanogenic conditions at that location; instead, detection of these constituents could indicate that such conditions are present upgradient from the monitoring location.

In the case of solute plumes derived from chlorinated solvents, the redox conditions in the aquifer are of paramount importance for controlling what transformation reactions will occur. Nitrate, Fe(III) and sulfate are electron acceptors that compete with dehalorespiration. The presence of nitrate, Fe(II) and sulfate could indicate conditions where biological reductive dechlorination may not occur or be inefficient. However, less-chlorinated compounds, such as DCE and VC, can be mineralized through direct oxidation by bacteria under iron-reducing conditions (Bradley and Chapelle, 1996, 1997). The occurrence of elevated Fe(II) together with depleted sulfate concentrations is indicative that the ground water is sulfate reducing. In this case, biological and abiotic reductive dechlorination reactions may be important.

Dissolved Oxygen

Dissolved oxygen is the favored electron acceptor used by microbes for the biodegradation of many forms of organic carbon. Strictly anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/l and hence Fe(III) reduction, sulfate reduction, methanogenesis, and reductive dechlorination (biological or abiotic) cannot occur. This is why it is important to have a source of carbon in the aquifer that can be used by aerobic microorganisms as a primary substrate. During aerobic respiration, dissolved oxygen concentrations decrease and the aquifer quickly becomes anaerobic. The concentration of dissolved oxygen in an aquifer is a very important parameter for determining if the system is capable of supporting the degradation of chlorinated solvents.

Dissolved oxygen measurements should be taken during well purging and immediately before sample acquisition using a direct-reading meter, preferably in a flow-through cell. Each of these measurements should be recorded. Because many well purging techniques
can allow aeration of collected ground-water samples, it is important to minimize the potential for aeration. Because of the difficulty in obtaining accurate dissolved oxygen measurements, especially when the concentration falls below about 1 mg/l, these measurements should be used in a qualitative manner. One use of dissolved oxygen measurements is during well purging. Stabilization of dissolved oxygen concentrations, in conjunction with pH, temperature, and conductivity, can be useful during well purging to determine when the well has been purged sufficiently to provide representative samples.

Measurements of dissolved oxygen should always be interpreted with an eye toward possible sampling errors and should never be relied upon alone or interpreted without consideration of other geochemical parameters, particularly Fe(II), sulfate, methane, and ORP. Inconsistencies between these parameters and dissolved oxygen measurements almost invariably indicate aeration of the sample. In the authors’ experience, more time has been wasted in dealing with misinterpretation of spurious dissolved oxygen measurements than any other single parameter. Due to its reactivity with dissolved oxygen, the presence of Fe(II) is a strong indicator of anaerobic conditions in the aquifer. With these observations in mind, if Fe(II) concentrations are elevated, sulfate concentrations are depleted, and methane concentrations are elevated within the solute plume and dissolved oxygen concentrations greater than between about 0.5 and 1 mg/l were measured within the plume, then the dissolved oxygen measurements should be viewed with a high degree of skepticism and in many cases should be discarded.

If dissolved oxygen is present in the aquifer, the measurement of reduced dissolved gasses such as sulfide and methane should not be undertaken. The reason for this is that the presence of dissolved oxygen precludes the formation of these gasses.

**Nitrate**

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate is used as an electron acceptor for anaerobic biodegradation of organic carbon via denitrification. During denitrification, nitrate concentrations measured in ground water decrease. Thus, nitrate concentrations below background in areas with dissolved contamination provide evidence for denitrification. Denitrification is a reaction that competes with reductive dechlorination. The absence of nitrate is a prerequisite for iron and sulfate reduction, so it is important that this compound is absent in ground water for biological and abiotic reactions to proceed.

**Sulfate and Sulfide**

Sulfate is used as an electron acceptor for anaerobic biodegradation during sulfate reduction wherein sulfate ($SO_4^{2-}$) is reduced to sulfide ($HS^-$ or $H_2S$). During this process, sulfate concentrations measured in ground water decrease and sulfide is produced. The sulfide produced during sulfate reduction is very reactive and in most cases is quickly complexed with Fe(II) and solid-phase iron minerals. From the standpoint of chlorinated solvent degradation, sulfate reduction is important for two reasons: (1) reductive dechlorination caused by biological processes does not become efficient until the dominant terminal electron accepting process is sulfate reduction or methanogenesis and (2) sulfate reduction is important for abiotic mechanisms of reductive dechlorination because it results in the production of sulfide. High sulfate concentrations will likely have the following ramifications:

1. They will reduce the efficiency of biological reductive dechlorination because sulfate is a competing electron acceptor.
2. They will increase the efficiency of abiotic reductive dechlorination, especially if appreciable amounts of Fe(II) are present.
Evaluation of Metabolic Byproduct Data

**Fe(II)**

When Fe(III) is used as an electron acceptor during anaerobic biodegradation of organic carbon, it is reduced to Fe(II), which is somewhat soluble in water. Elevated Fe(II) concentrations are an indication that anaerobic degradation of organic carbon has occurred via Fe(III) reduction. The presence of Fe(II) (and sulfide) is required in order for many of the abiotic reactions described elsewhere in this document to occur. In addition, Bradley and Chapelle (1996, 1997) have shown that VC and DCE can be biologically oxidized under iron-reducing conditions. Fe(III) reduction is a reaction that competes with dehalorespiration.

**Methane**

As implied by the name, methanogenesis results in the production of methane during the biodegradation of organic carbon. The presence of methane in ground water is indicative of strongly reducing conditions and biologically mediated reductive dechlorination is typically very efficient under these conditions. Analysis of methane concentrations in ground water should be conducted by a qualified laboratory. It is important that the detection limit for methane be on the order of 1 μg/l, especially when evaluating the degradation of chlorinated solvents.

The presence of methane generally is indicative of a strongly reducing environment where reductive dechlorination of chlorinated ethenes to cis-1,2-DCE and VC and then to ethene or ethane is likely. If no VC is present then abiotic reactions should be evaluated. Methane can also be transported by advective ground-water flow. Because of this, its presence in ground water does not ensure that the immediate environment is methanogenic; only that methanogenic conditions exist in the vicinity. Evaluating the presence of methane in concert with the other geochemical indicators (e.g., Fe[II] and SO₄²⁻) is essential.

**Ethene and Ethane**

Ethene and ethane are the end products of reductive dechlorination. Because these compounds are extremely transitory, their concentrations typically remain low with concentrations at sites with active reductive dechlorination in the order of hundreds of micrograms per liter.

Evaluation of General Ground-Water Monitoring Parameters

**Oxidation–Reduction Potential (ORP)**

The ORP of ground water is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Oxidation–reduction reactions in ground water containing organic compounds (natural or anthropogenic) are usually biologically mediated, and therefore, the ORP of a ground-water system depends on and influences rates of degradation (both biological and abiotic). The ORP of ground water generally ranges from −400 to +600 mV. ORP readings should only be used on a qualitative basis. In general, the lower the ORP of ground water, the more reducing the system is, and the more likely that reductive dechlorination will be efficient.

ORP measurements can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Mapping the ORP of the ground water in the field helps the field scientist determine the approximate location of the contaminant plume. To map the ORP of the ground water in the field, it is important to have at least one ORP measurement (preferably more) from a well.
located upgradient from, or peripheral to, the plume. ORP measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected ground-water samples that can affect ORP measurements, it is important to minimize potential aeration by using a flow-through cell.

\[ pH \]

Bacteria generally prefer environments with a neutral or slightly alkaline pH. The optimal pH range for most microorganisms is between 6 and 8 standard units; however, many microorganisms can tolerate pHs well outside of this range. For example, pH values may be as low as 4 or 5 in aquifers with active oxidation of sulfides, and pH values as high as 9 may be found in carbonate-buffered systems (Chapelle, 1993). In addition, pH values as low as 3 have been measured for ground water contaminated with municipal waste leachates, which often contain elevated concentrations of organic acids (Baedecker and Back, 1979). In ground water contaminated with sludges from cement manufacturing, pH values as high as 11 have been measured (Chapelle, 1993).

\[ Temperature \]

Ground-water temperature directly affects the solubility of oxygen and other geochemical species. For example, dissolved oxygen is more soluble in cold water than in warm water. Ground-water temperature also affects the metabolic activity of bacteria. Rates of hydrocarbon biodegradation roughly double for every 10°C increase in temperature (the “Q10” rule) over the temperature range between 5 and 25°C. However, in the authors’ experience, the temperature of ground water rarely is a limiting factor for degradation of organic compounds. For example, degradation of these compounds has been observed at ground-water temperatures as low as 34°F and as high as 85°F.

\[ Conductivity \]

Conductivity is a measure of the ability of a solution to conduct electricity. The conductivity of ground water is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases. The conductivity of ground water emanating from a landfill or other waste unit may be significantly different from that of native ground water or surface water. Thus, the conductivity of ground water in the plume may be a useful indicator of the ground-water flow path and may indicate that a plume-resident tracer is present.

**Evaluation of Supplemental Data**

Supplemental data should only be collected for sites where the operant mechanisms of natural attenuation are not obvious. For sites contaminated with petroleum hydrocarbons the collection of supplemental data will only very rarely, if ever, be required. For sites contaminated with chlorinated solvents, the collection of supplemental data will be required only on rare occasions. One example of where supplemental data may be useful is for a site where the degradation of PCE appears to “stall” at cis-1,2-DCE (i.e., no VC or ethene and ethane are being produced). This could be caused by at least two scenarios: (1) the system does not contain the microbial consortium required to completely degrade the PCE to ethene; or (2) the cis-1,2-DCE that is being produced may be degraded by abiotic mechanisms that bypass the production of VC and convert the chlorinated compounds to acetylene and ethene. Even without supplemental data, one may be able to deduce the operant
mechanisms by evaluating plume stability if an adequate historical database is available. For sites without significant historical data, supplemental data may be valuable.

**Supplemental Daughter Product Data**

**Acetylene**: Acetylene is a product of the abiotic dechlorination of chlorinated aliphatic hydrocarbons (e.g., PCE and TCE) by iron sulfides. Although the exact pathway has not been fully determined, it is thought that the pathway for TCE oxidation is via the cis-dichlorovinyl radical directly to acetylene (Butler and Hayes, 1999). Therefore, its presence suggests that abiotic dechlorination is occurring. Practical field experience has shown that the volatile and labile nature of acetylene often precludes its detection. Therefore, the absence of detectable concentrations of acetylene does not indicate that abiotic reactions are not occurring. Research is underway to provide a means of preserving samples to be analyzed for acetylene so that laboratory analysis is possible.

**Supplemental Geochemical Data**

In some cases additional geochemical data can be useful for evaluating the predominant geochemical environment in ground water. Table 9.3 summarizes some of the supplemental data that may be useful for evaluating natural attenuation.

**Mn(II)**: When Mn(IV) is used as an electron acceptor during anaerobic biodegradation of organic carbon, it is reduced to Mn(II). Mn(II) concentrations can be used as an indicator that anaerobic degradation of organic carbon has occurred via Mn(IV) reduction. Changes in Mn(II) concentrations inside the contaminant plume versus background concentrations can be used to estimate the mass of contaminant that has been biodegraded by Mn(IV) reduction. Mn(IV) reduction is a reaction that competes with reductive dechlorination. In addition, manganese can react with the hydrogen sulfide created during sulfate reduction, which could result in the formation of abiotically reactive manganese sulfide minerals.

**Carbon Dioxide**: Metabolic processes operating during biodegradation of organic compounds leads to the production of carbon dioxide (CO₂). However, CO₂ released into ground water rapidly reacts to form carbonic acid (H₂CO₃) and its dissociated ions. Accurate measurement of the amount of carbon dioxide produced during biodegradation is difficult because carbonate in ground water (measured as alkalinity) serves as both a source and sink for free carbon dioxide. If the carbon dioxide produced during metabolism is not completely removed by the natural carbonate buffering system of the aquifer, carbon dioxide concentrations higher than background may be observed. However CO₂ measurements alone typically are uninformative.

**Alkalinity**: Biologically active portions of a dissolved contaminant plume typically can be identified by an increase in alkalinity. This increase in alkalinity is brought about by the production of carbon dioxide during the biodegradation of organic carbon. Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of cations such as calcium, magnesium, sodium, and potassium. These species result from the dissolution of rock (especially carbonate rocks), the transfer of carbon dioxide from the atmosphere, and respiration of microorganisms. Alkalinity is important in the maintenance of ground-water pH because it buffers the ground-water system against acids generated during both aerobic and anaerobic biodegradation. In general, areas with reduced organic carbon exhibit a total alkalinity that is higher than that seen in those areas with low organic carbon concentrations. This is expected because the microbially mediated reactions involved in biodegradation of organic carbon cause an increase in the total
alkalinity in the system. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, Fe(III) reduction, and sulfate reduction, and less pronounced during methanogenesis (Morel and Hering, 1993).

**Dissolved Organic Carbon:** Dissolved organic carbon of anthropogenic or natural origin represent an important parameter at sites impacted with chlorinated solvents because it is a necessary ingredient in chlorinated solvent degradation. Thus, its presence and relative concentration is an important parameter for periodic monitoring. A statistically significant decline over time or space may indicate that conditions less conducive to biotic or abiotic reductive dechlorination may be forthcoming.

**Dissolved Hydrogen:** Concentrations of dissolved hydrogen can be used to evaluate terminal electron-accepting processes in ground-water systems (Lovley and Goodwin, 1988; Lovley et al., 1994; Chapelle et al., 1995). Because each terminal electron-accepting process has a characteristic hydrogen concentration associated with it, hydrogen concentrations can be an indicator of predominant terminal electron-accepting processes. These characteristic ranges are as follows:

<table>
<thead>
<tr>
<th>Process</th>
<th>Hydrogen Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic respiration</td>
<td>0 nM</td>
</tr>
<tr>
<td>Denitrification</td>
<td>0.03–0.1 nM</td>
</tr>
<tr>
<td>Iron reduction</td>
<td>0.2–1 nM</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>1–5 nM</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>&gt;5 nM</td>
</tr>
</tbody>
</table>

ORP measurements are based on the concept of thermodynamic equilibrium and, within the constraints of that assumption, can be used to evaluate terminal electron-accepting processes in ground-water systems. The use of dissolved hydrogen to classify the system is based on the ecological concept of interspecies hydrogen transfer by microorganisms and, within the constraints of that assumption, can also be used to evaluate terminal electron-accepting processes. These methods, therefore, are fundamentally different. A direct comparison of these methods (Chapelle et al., 1997) has shown that while ORP measurements were effective in delineating oxic from anoxic ground water, they could not reliably distinguish between nitrate-reducing, Fe(III)-reducing, sulfate-reducing, or methanogenic zones in an aquifer. In contrast, the measurement of dissolved hydrogen could readily distinguish between different anaerobic zones. At those sites where distinguishing between different anaerobic processes is important (such as at sites contaminated with chlorinated solvents), hydrogen measurements can be useful for delineating the distribution of terminal electron-accepting processes.

In practice, it is preferable to interpret hydrogen concentrations in the context of electron acceptor [dissolved oxygen, nitrate, Mn(IV), Fe(III), sulfate] availability and the presence of the final products [Mn(II), Fe(II), hydrogen sulfide, methane] of microbial metabolism (Chapelle et al., 1995). For example, if sulfate concentrations in ground water are less than 0.5 mg/l, methane concentrations are greater than 0.5 mg/l, and hydrogen concentrations are in the 5–20 nM range, it can be concluded with a high degree of certainty that methanogenesis is the predominant terminal electron-accepting process in the aquifer. Similar logic can be applied to identifying denitrification (presence of nitrate, hydrogen <0.1 nM), Fe(III) reduction [production of Fe(II), hydrogen 0.2–0.8 nM], and sulfate reduction (presence of sulfate, production of sulfide, hydrogen 1–4 nM).

Chapelle et al. (1997) compare three methods for measuring hydrogen concentrations in ground water; a downhole sampler, a gas-stripping method, and a diffusion sampler. The downhole sampler and gas-stripping methods gave similar results. The diffusion sampler
appeared to overestimate hydrogen concentrations. Of these methods, the gas-stripping method is better suited to field conditions because it is faster (approximately 30 min for a single sample collection as opposed to 2 h for the downhole sampler and 8 h for the diffusion sampler), the analysis is easier (less sample manipulation is required), and the data computations are more straightforward (hydrogen concentrations need not be corrected for water sample volume) (Chapelle et al., 1997). At least one commercial laboratory uses the gas-stripping method (called the “bubble-strip” method) for hydrogen sampling and analysis.

Chloride: During biodegradation of chlorinated hydrocarbons dissolved in ground water, chloride is released into the ground water, resulting in the accumulation of biogenic chloride. This results in chloride concentrations in ground water in the contaminant plume that are elevated relative to background concentrations. In aquifers with low background concentrations of chloride, the concentration of this material in the solute plume can be seen to increase as chlorinated solvents are degraded. Although site-specific, chlorinated solvent concentrations must be above about 10 mg/l and display significant reductions to raise dissolved chloride concentrations above background levels at sites with “low” background concentrations of chloride. Other anthropogenic sources of elevated chloride (e.g., road salt, landfill, evaporation ponds, brine disposal, etc.) can still be useful in assessing ground-water flow paths and dispersion effects.

Elemental chlorine is the most abundant of the halogens. Although chlorine can occur in oxidation states ranging from Cl\(^{-}\) to Cl\(^{7+}\), the chloride ion (Cl\(^{-}\)) is the only form of major significance in natural waters (Hem, 1985). Chloride forms ion pairs or complex ions with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of fresh water (Hem, 1985). The chemical behavior of chloride is neutral. Chloride ions generally do not enter into oxidation–reduction reactions, form no important soluble complexes with other ions (unless the chloride concentration is extremely high), do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (Hem, 1985). Thus, physical processes control the migration of chloride ions in the subsurface. Kaufman and Orlob (1956) conducted tracer experiments in ground water, and found that chloride moved through most of the soils tested more conservatively (i.e., with less retardation and loss) than any of the other tracers tested. Because of the neutral chemical behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates.

Microcosm Studies

Although several types of microbiological data may be used, the most common type of data collected for evaluating the degradation of organic contaminants in aquifer material is the laboratory microcosm study. If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the potential for biodegradation and abiotic reductive dechlorination. Microcosm studies are the only “line of evidence” that allows an unequivocal mass balance on the biodegradation of environmental contaminants. If the microcosm study is properly designed, it will be easy for decision makers with nontechnical backgrounds to understand. The results of a microcosm study are strongly influenced by the nature of the geological material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Therefore, relating laboratory microcosm results back to in situ field conditions can be difficult. Additionally, microcosm studies are time consuming and expensive to conduct. For these reasons, microcosm studies should be used very selectively in assessing the efficiency of natural attenuation and enhanced remediation.
There are some circumstances, however, when laboratory studies are useful. When specific questions are raised concerning conditions under which degradation processes occur or do not occur, controlled laboratory studies are often required. For example, if concentrations of a particular compound are observed to decrease in the field, it is often not clear whether this decrease is due to sorption, dilution, or biological or abiotic degradation. Laboratory studies in which the effects of each process can be isolated and controlled (they usually cannot be controlled in the field) are the only available method of answering these questions.

**Volatile Fatty Acids (VFAs)**

The VFAs pyruvate, lactate, formate, acetate, propionate, and butyrate are used as biomarkers of anaerobic metabolism. Anaerobic bacteria produce these compounds by fermentation, while under aerobic conditions these compounds are rapidly oxidized for carbon and energy by aerobic bacteria. The VFAs are analyzed by ion chromatography and represent a specialized method. The presence of these compounds is an indication that fermentation is occurring and that the environment may be conducive for reductive dechlorination.

**Phospholipid Fatty Acids (PLFAs)**

Examining the PLFAs in environmental samples provides an indication of the different types of bacteria that may be present at a site. Distinct classes of microbes have different cell membrane compositions. PLFAs are essential components of the membranes of all cells (except for the Archaea), so their sum includes most of the important actors in microbial communities. Methanogens are members of the Archaea and are not included in this analysis. There are four different types of information in PLFA profiles — biomass, community structure, diversity, and physiological status. Thus, PLFA analyses may be useful indicator of the presence of certain classes of microbes. This information may be used qualitatively to correlate that the observed phospholipid profile observed at the site is consistent with a particular class of microorganism with a unique and interesting metabolic capability (e.g., sulfate reduction).

**Biomass:** PLFA analysis is purported to be a reliable and accurate method available for the determination of viable microbial biomass. Because phospholipids break down rapidly upon cell death (White et al., 1979; White and Ringelberg, 1995), the PLFA biomass does not contain “fossil” lipids of dead cells. The sum of the PLFAs, expressed as picomoles (1 pmol = 1 × 10^{-12} mol), is proportional to the number of cells. The proportions used typically are taken from cells grown in laboratory media, and vary somewhat with the type of organism and environmental conditions. Starving bacterial cells have the lowest cells/pmol, and healthy eukaryotic cells have the highest. Biomass can be useful for evaluating the possibility for reductive dechlorination. If biomass appears low, but evidence of active reductive declination is high and credible, then PLFA data is uninformative. If evidence of active reductive dechlorination is low and PLFA data suggests low biomass, then there may be microbial limitations and unfavorable geochemical conditions present.

**Community Structure:** The PLFAs in an environmental sample is the sum of the microbial community’s PLFAs, and reflects the proportions of different organisms in the sample. PLFA profiles are routinely used to classify bacteria and fungi (Tighe et al., 2000) and are one of the characteristics used to describe new bacterial species (Vandamme et al., 1996). Broad phylogenetic groups of microbes have different fatty acid profiles, making it possible to distinguish among them (Edlund et al., 1985; Dowling et al., 1986; White et al., 1996, 1997). Because reductive chlorination results from the work of a microbial
consortium, community structure can be useful for evaluating the possibility for reductive dechlorination.

**Diversity:** The diversity of a microbial community is a measure of the number of different organisms and the evenness of their distribution. Natural communities in an undisturbed environment tend to have high diversity. Contamination with toxic compounds will reduce the diversity by killing all but the resistant organisms. The addition of a large amount of a food source will initially reduce the diversity as the opportunists (usually Proteobacteria) over-grow organisms less able to reproduce rapidly. The formulas used to calculate microbial community diversity from PLFA profiles have been adapted from those applied to communities of macro-organisms (Hedrick et al., 2000). Because reductive dechlorination results from the work of a microbial consortium, an analysis of microbial diversity can be useful for evaluating the possibility for reductive dechlorination.

**Physiological Status:** The membrane of a microbe must adapt to the changing conditions of its environment, and these changes are reflected in the PLFA. Toxic compounds or environmental conditions that disrupt the membrane cause some bacteria to make *trans* fatty acids from the usual *cis* fatty acids (Guckert et al., 1986). Many Proteobacteria and others respond to starvation or highly toxic conditions by making cyclopropyl (Guckert et al., 1986) or mid-chain branched fatty acids (Tsitko et al., 1999). The physiological status biomarkers for toxic stress and starvation or toxicity are formed by dividing the amount of the stress-induced fatty acid by the amount of its biosynthetic precursor.

**Denaturing Gradient Gel Electrophoresis (DGGE)**

The recovery of DNA and RNA and its subsequent analysis after amplification by polymerase chain reaction (PCR) provides a powerful tool for characterizing microbial community structure that complements the PLFA analysis. As with PLFA analysis, numerous studies have used PCR amplification of ribosomal RNA genes (rDNA) to characterize microbial populations in a number of different environments and have demonstrated that the dominant microorganisms isolated by culture frequently do not match those identified by molecular techniques (Amann et al., 1995). Given that only 0.1–10% of visually countable bacteria in samples are cultured and previous studies have demonstrated that organisms obtained from culturing are not necessarily the numerically dominant organisms *in situ*, it is apparent that the results from culture-based community structure assessments can be noticeably incomplete.

DGGE analysis can be used to detect and identify organisms from a whole community of organisms and thus can be used to determine if the requisite microbes for reductive dechlorination are present. The DGGE approach directly determines the species composition of complex microbial assemblages based on the amplification of conserved gene sequences (16S rDNA fragments for prokaryotes, 18S or 28S rDNA for eukaryotes). In DGGE analysis, differences in gene sequences among organisms allow DNA from various organisms to be physically separated in a denaturing gradient gel, thereby allowing one to generate profiles of numerically dominant bacterial community members for a sample. The profiles are visible as bands (or lines) in a gel. The banding patterns and relative intensities of the bands provide a measure of difference among the communities. Gel bands from dominant species, which constitute at least 1% of the total bacterial community, can be excised and sequenced. Sequence analysis of individual bands is used to infer the identity of the source organism based on database searches and phylogenetic methods. Phylogenetic affiliations are determined by comparing the rDNA sequences retrieved from samples to rDNA sequences of known bacterial sequences in national databases, such as the Ribosomal Database Project (RDP) or GenBank.
Practical Considerations for Microbial Characterization Techniques

Microbial characterization techniques like those mentioned earlier are only indicated when quantitative evidence in the form of contaminant mass loss over time and space and confirmatory geochemical data are limited, conflicting, or indicate that a site-specific deficiency exists. Microbes tend to exist and thrive on the solid matrix. Interestingly, ground-water sampling techniques have evolved to collect a clean, clear, sediment-free sample. Ground water from monitoring wells is the most common sample material for the microbial characterization techniques discussed earlier. In summary, a “dirty,” turbid, sediment-rich sample represents a better source of microbial biomass. Thus, a deliberate effort should be made to collect some sediment to increase the chances that a sufficient and representative amount of biomass is collected. Practitioners should verify with the laboratory staff conducting these specialized analyses that sufficient biomass and microbial DNA were obtained from site samples to complete an acceptable analysis. In other words, a sample with insufficient microbial biomass will give an inconclusive or negative result.

Stable Isotopes

Analysis of stable isotope ratios between parent and daughter compounds can be useful for identifying the biodegradation of chlorinated compounds because isotopic fractionation commonly occurs during biodegradation. This fractionation results in a characteristic pattern of isotope ratios between parent compounds and daughter products. For the chlorinated ethenes, non-destructive subsurface processes such as dissolution, sorption, and volatilization do not involve isotopic fractionation greater than 0.5% (Slater et al., 2001). This is the typical accuracy and reproducibility of continuous flow isotope analysis techniques (Slater et al., 2001).

Hunkeler et al. (1999) studied the occurrence of stable carbon isotope ($^{13}$C/$^{12}$C) fractionation during the reductive dechlorination of PCE to ethene in the field and in the laboratory using aquifer material from the same site located in Toronto, Ontario, Canada. According to these researchers, all dechlorination steps in the microcosm were accompanied by stable carbon isotope fractionation with similar results for the field study. In the microcosm study the largest fractionation occurred during dechlorination of cis-1,2-DCE and VC, resulting in a large enrichment of $^{13}$C in the remaining cis-1,2-DCE and VC. Stable carbon isotope ratios ($\delta^{13}$C) of cis-1,2-DCE and VC increased from −25.7 to 1.5‰ and −37 to −2.5‰, respectively. The $\delta^{13}$C of ethene was initially −60.2‰ and approached the $\delta^{13}$C of the added PCE (−27.3‰) as dechlorination came to completion. On the basis of their work, they conclude that strong enrichment of $^{13}$C in cis-1,2-DCE and VC during microbial dechlorination may serve as a powerful tool to monitor the last two steps of dechlorination. These steps frequently determine the rate of dechlorination of chlorinated ethenes at field sites where degradation is occurring.

Contingency Plans

A contingency plan is an integral part of a monitored natural attenuation remedy as per the U.S. EPA OSWER Directive 9200-4.17 (U.S. EPA, 1999). Interestingly, contingency remedies are specifically requested in guidance for other remedial alternatives. However, it makes good technical sense to actively evaluate remedial performance and to have a well-formulated contingency plan when a remedy fails to achieve the desired level of effectiveness or protectiveness. The purpose of a contingency plan is to
define the appropriate actions to be taken in the event that natural attenuation proves inadequate to achieve remedial goals. Changing site conditions can result in variable plume behavior over time. To circumvent potential problems, a contingency plan that specifies a contingency remedy should be an integral part of the monitoring program. A contingency remedy is a cleanup technology or approach specified in the site remedy decision document that functions as a backup remedy in the event that the selected remedy fails to perform as anticipated. A contingency remedy may specify a technology (or technologies) that is (are) different from the selected remedy, or it may simply call for modification and enhancement of the selected remedy, if needed. Contingency remedies generally should be flexible to allow for the incorporation of new information about site risks and technologies. Contingency remedies should be developed where the selected technology is not proven for the specific site application, where there is significant uncertainty regarding the nature and extent of contamination at the time the remedy is selected, or where there is uncertainty regarding whether or not a proven technology will perform as anticipated under the particular circumstances of the site. The U.S. EPA (1999) recommends that remedies employing monitored natural attenuation be evaluated to determine the need for including one or more contingency measures that would be capable of achieving remediation objectives. The U.S. EPA believes that a contingency measure may be particularly appropriate for a monitored natural attenuation remedy that has been selected based primarily on predictive analysis rather than on historical trends from actual monitoring data.

One or more criteria (“triggers”) that will signal unacceptable performance of the selected remedy and indicate when to implement contingency measures should be established. Such criteria might include the following (U.S. EPA, 1999, 2004):

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

Care is needed when establishing triggers for contingency remedies to ensure that sampling variability or seasonal fluctuations do not unnecessarily trigger implementation of a contingency remedy. For example, an anomalous spike in dissolved concentrations at wells, that may set off a trigger, might not be a true indication of a change in trend. Trends in contaminant concentrations can be analyzed using statistical techniques.

The most common remedial systems for complementing natural attenuation are source reduction technologies. Source reduction can be an important element of site remediation if site closure or shortened monitoring time frames are desired.

It is prudent to update the contingency plan on a periodic basis as the plume attenuates or as new remediation technologies are developed. Although some engineered remediation systems may be effective in achieving plume containment, other remediation systems may have an adverse impact on degradation. Table 9.9 summarizes some of the potential interactions between remediation systems and natural attenuation. For example, the introduction of oxygen via air sparging into an aquifer contaminated with chlorinated solvents may alter the geochemistry of the ground water to the point that reductive dechlorination can no longer occur and the natural treatment system is destroyed.
### TABLE 9.9
Interactions between Active Remediation Technologies and Natural Attenuation (Wiedemeier and Chapelle, 2000)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Petroleum Hydrocarbons</th>
<th>Chlorinated Solvents</th>
<th>Possible Detriments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioslurping</td>
<td>Source removal, volatilization, enhanced oxygen delivery or aerobic biodegradation</td>
<td>Source removal, volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism</td>
<td>None</td>
</tr>
<tr>
<td>Pump and treat</td>
<td>Plume containment, enhanced oxygen delivery or aerobic biodegradation</td>
<td>Plume containment, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism</td>
<td>None</td>
</tr>
<tr>
<td>Air sparging</td>
<td>Volatilization, enhanced oxygen delivery or aerobic biodegradation</td>
<td>Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism</td>
<td>None</td>
</tr>
<tr>
<td>SVE or Bioventing</td>
<td>Source reduction, particularly BTEX</td>
<td>SVE reduces source in unsaturated zone</td>
<td>None</td>
</tr>
<tr>
<td>In-well circulation or stripping</td>
<td>Volatilization, enhanced oxygen delivery or aerobic biodegradation</td>
<td>Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism</td>
<td>None</td>
</tr>
<tr>
<td>Landfill caps</td>
<td>Source containment or isolation</td>
<td>Source containment or isolation, reduced oxygen delivery through elimination of recharge or stimulation of reductive dechlorination</td>
<td>Reduced oxygen delivery or aerobic biodegradation</td>
</tr>
</tbody>
</table>

(Table continued)
<table>
<thead>
<tr>
<th>Technology</th>
<th>Petroleum Hydrocarbons</th>
<th>Chlorinated Solvents</th>
<th>Possible Benefits</th>
<th>Possible Detriments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoremediation</td>
<td>Plant-specific transpiration or enzymatically mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment</td>
<td>Plant-specific transpiration or enzymatically mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment</td>
<td>None</td>
<td>Unknown</td>
</tr>
<tr>
<td>Excavation or backfilling</td>
<td>Source removal, enhanced oxygen delivery or aerobic biodegradation</td>
<td>Source removal, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism</td>
<td>None</td>
<td>Enhanced oxygen delivery or decreased reductive dechlorination</td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>Enhanced oxidation</td>
<td>Enhanced oxidation</td>
<td>None</td>
<td>Enhanced oxygen delivery or decreased reductive dechlorination</td>
</tr>
<tr>
<td>(e.g., Fenton's reagent, potassium permanganate, etc.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical reduction</td>
<td>Unknown</td>
<td>Scavenges inorganic electron acceptors or enhanced reductive dechlorination</td>
<td>Scavenges inorganic electron acceptors or decreased oxidation</td>
<td></td>
</tr>
<tr>
<td>(e.g., sodium dithionate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen-releasing materials</td>
<td>Enhanced oxygen delivery or aerobic biodegradation</td>
<td>Enhanced oxidation of DCE and VC</td>
<td>None</td>
<td>Decreased reductive dechlorination through oxidation and removal of fermentable carbon substrates</td>
</tr>
<tr>
<td>Carbon substrate addition</td>
<td>None</td>
<td>Stimulation of reductive dechlorination</td>
<td>Competing carbon source</td>
<td>Decreased oxidation of DCE and VC, decreased aerobic cometabolism at injection point</td>
</tr>
<tr>
<td>Zero-valent iron barrier walls</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biological barrier walls</td>
<td>Unknown</td>
<td>Enhanced reductive dechlorination</td>
<td>Unknown</td>
<td>None</td>
</tr>
</tbody>
</table>
A ground-water pump-and-treat system can have the same effect by drawing oxygen-rich ground water through the contaminant plume. Because of these potential adverse affects, the impacts of any proposed remediation system on naturally occurring processes should be evaluated when developing a contingency plan.

Monitoring Duration and Exit Strategies

The duration of monitoring and the exit strategy for a long-term monitoring program are interrelated issues. Because the long-term monitoring of natural attenuation is effectively the implementation of the remedial action, the exit strategy consists of the decision criteria that will allow the long-term monitoring program to end. Defining the decision points and criteria will depend upon the specific remedial action objectives for a given site and, thus, the regulatory framework. This discussion does not purport to address all the considerations or situations that might arise at a particular site; rather it presents a practical approach to the issues that provides a framework for developing an exit strategy for a site.

In general, the objectives of performance monitoring for natural attenuation are derived from the site-specific remedial action objectives (e.g., what the remedy is intended to accomplish) and applicable target concentrations (U.S. EPA, 2004). As with any remediation option for sites with ground-water contamination, remedial goals should be established early in the process. This will help define the specific purposes for the long-term monitoring program and should help define the length of time that monitoring will be required. Long-term monitoring should continue until remediation objectives have been achieved, and longer if necessary to verify that the site no longer poses a threat to human health or the environment (U.S. EPA, 1999, 2004). Typically, verification monitoring is continued for a specified period (e.g., 3–5 yr) after remediation objectives have been achieved to ensure that concentrations are stable and remain below target levels (U.S. EPA, 1999, 2004). While this sounds relatively straightforward, it means different things in different regulatory settings and presumes that the decision criteria are concentration-based.

The duration of a long-term monitoring program for natural attenuation is perhaps the most perplexing and uncertain aspect from a design standpoint. For sites with a NAPL source (the typical case), the major control on persistence of a solute plume is the source mass available to dissolve into ground water. Unfortunately, this is commonly one of the more uncertain parameters. Additional complications arise from mass-transfer limitations on source decay (Chapelle et al., 2003). Projections regarding solute plume duration, regardless of how they are developed, are only as good as the quality of the available data and, in the vast majority of cases, uncertainties of an order of magnitude are the norm. These estimates can be better refined over the course of long-term monitoring as data are developed that characterize the source decay rate (AFCEE, 2003). Even small differences in estimates of mass-transfer from the source can have significant impacts on monitoring duration in practical terms. For example, a factor of two difference in the ground-water flow velocity can change the estimated plume duration from 30 to 60 yr (Chapelle et al., 2003). This presents a quandary for practitioners who are faced with regulatory requests, as well as those from site owners, to define the remediation time frame, or how long the cleanup will take.

Typically, the remediation time frame for a site is based on achieving compliance with some concentration-based target level. While methodologies for making such estimates are available (e.g., Chapelle et al., 2003), the reality is that in most cases the results are uncertain and the time frame will be several decades, or longer, to approach
concentration-based target levels. However, the ultimate remedial goals for a site (e.g., attaining MCLs throughout the solute plume) can be different than the decision criteria for continuing the long-term monitoring program. From the regulatory standpoint, the question is one of whether the site continues to warrant regulatory concern and oversight. Site “closure” is not the hard and fast determination that many perceive; rather it is a decision on the part of the regulatory agency that, based on the available information, the site warrants “no further action,” with various qualifications and stipulations. Viewed in this context, the necessary duration of the long-term monitoring program is the time needed to unequivocally support a decision regarding management of the site. Simply stated, long-term monitoring should continue until the data gathered adequately support a decision for closure of the site (no further action) or the need to implement another remediation option. The monitoring program should focus on providing the data needed to support decision-making and address outstanding questions or concerns. Continuing a monitoring program past the point where the data collected are useful in supporting decisions becomes an exercise in collecting data for the sake of collecting data rather than providing necessary information. In essence, if the additional data will not change decisions regarding management of the site, there is little point in collecting it; if it will, it should be collected.

The single difference between a natural attenuation remedy and other remediation approaches is that, if natural attenuation is effective and the conditions do not change, it will continue to operate whether the solute plume is monitored or not. The underlying question then becomes why is the solute plume being monitored? The answer to this question will depend upon both the technical basis for the monitoring (e.g., what information is needed) and the site-specific remediation objectives and regulatory requirements. However, an important point is that the fundamental cleanup objective for most sites, the reduction of contaminant concentrations in ground water to specified levels, is not changed. The question is only whether continued monitoring is needed.

The duration of long-term monitoring and the criteria for ending the monitoring program are directly related to the purpose for monitoring natural attenuation and specific remedial goals (remedial action objectives) for a given site. These involve both technical and institutional considerations. The technical considerations involve the specific objectives for the performance monitoring; what information is needed and what changes in conditions are of interest and importance for success of the remedy. The institutional considerations involve issues related to land use, ground-water use, preventing exposure to the contaminants, and management of the site.

The technical basis for long-term monitoring will depend on the specific chemicals of concern and the natural attenuation processes that act upon them. These factors determine the conditions necessary for the various degradation and transformation processes to occur, the controls on those processes, and the changes in conditions that might impact the efficacy of the natural attenuation remedy. If the factors are well understood and solute plume behavior is adequately defined at a site, a case may be made for ending the monitoring program. For example, a solute plume from a petroleum hydrocarbon release, where all of the constituents of concern are readily mineralized by direct microbial oxidation, presents one situation. If a case can be made that environmental conditions are consistent and the available long-term monitoring data unequivocally demonstrate that the solute plume is stable or receding, the decision to end the long-term monitoring program can be supported on a technical basis. Biodegradation of the constituents of concern [e.g., benzene, toluene, ethylbenzene, and xylenes (BTEX)] to innocuous products would continue under both anaerobic and aerobic conditions and, over time, ultimately eliminate the solute plume as the source is depleted. Barring a change in conditions that directly alters the mass balance of the solute plume, such as a new release, or causes an
increase in the potential for exposure to the contaminants, a cogent technical argument can be made that continued monitoring of remedy performance is not needed.

A practical way to address the issue of monitoring duration is to consider the specific concerns that are important for the efficacy of natural attenuation in a given situation. For example, consider the case of chlorinated solvent solute plumes undergoing reductive dechlorination. In the case of a solute plume where natural attenuation appears to be effective due to a strongly reducing environment resulting from a source of anthropogenic organic carbon (e.g., the Type 1 environment of Wiedemeier et al., 1999), one of the major considerations is whether there is adequate reduced organic carbon available to maintain the strongly reducing environment until all of the chlorinated solvent constituents are gone. In such a situation, long-term monitoring must continue until this can be unequivocally established; most likely until contaminant concentrations reach MCLs. The situation would be different for a similar solute plume where the reduced organic carbon is naturally occurring in the aquifer (e.g., the Type 2 environment of Wiedemeier et al., 1999) and the availability of an adequate supply of reduced organic carbon to maintain the strongly reducing conditions can be reasonably assured. In this setting, a case might be made that environmental conditions are consistent and, similar to the petroleum hydrocarbon example above with the same qualifications, a cogent technical argument might be made that continued monitoring of remedy performance is not needed. Clearly, the weight of evidence needed to support such an argument must be available from the specific site and is not trivial. These examples illustrate on a conceptual level the type of considerations that should be incorporated into the development of an exit strategy.

In many, if not most cases, the decision to stop the long-term monitoring program and “close” the site depends more on the availability and efficacy of land use and other institutional controls for site management than on the technical aspects. A sound technical case may be made for ceasing long-term monitoring of the solute plume, but long-term management questions may necessitate its continuing in some form.

In some cases, the concern may have management and technical connotations. For example, a solute plume from a petroleum hydrocarbon product release could be demonstrably stable and contained within the property boundaries of the site. If the point of compliance is the property boundary, there is no potential for another release at the site, and adequate institutional controls are in place, such a site could meet the criteria for “closure” in some situations. However, the proximity of another facility immediately upgradient of the site and the potential for a release of petroleum hydrocarbons there could raise concerns over the long-term efficacy of the natural attenuation remedy. A new release at the upgradient facility could place the site in the geochemical “shadow” of depleted electron acceptors. This may not have a substantive impact on the overall efficacy of natural attenuation at the site, but could cause a shift in location of the plume boundaries that might put it out of compliance. Such a situation could warrant continued monitoring of the site in some form, particularly at upgradient locations.

The reliability of land use and other institutional controls are an essential consideration for an exit strategy that provides for an end to long-term monitoring before the target concentrations for a site (e.g., MCLs) are reached. Because the solute plume will still be present at the site, measures to ensure that exposure to the contaminants is prevented and the site is managed appropriately are necessary. Due to the lack of uniformity in the way institutional controls are handled in different legal and regulatory jurisdictions, the specific approach to this issue at a given site will likely vary. However, effective controls on land use and ground-water use must be implemented. In the case where verification of the attainment of target ground-water concentrations is necessary, either for regulatory compliance or to justify the removal of institutional controls, an
“event-driven” approach to future monitoring should be developed. Such an approach would schedule additional monitoring events when estimated plume behavior suggests that cleanup goals will be achieved.

To summarize, the focus of developing an exit strategy should be on identifying what are the specific questions and concerns at a given site and tailoring the long-term monitoring program to address those questions and concerns. The monitoring data collected should have a specific purpose in terms of elucidating plume behavior and supporting decisions regarding management of the site. As a final note, long-term monitoring should continue until it is certain that protection of human health and the environment is ensured.

References

Designing Monitoring Programs to Evaluate the Performance of Natural Attenuation


Lovley, D.R., F.H. Chapelle, and J.C. Woodward, Use of dissolved H₂ concentrations to determine
distribution of microbially catalyzed redox reactions in anoxic ground water, *Environmental
Mann, H.B. and D.R. Whitney, On a test of whether one or more random variables is statistically
larger than the other, *Annual of Mathematical Sciences*, 18, 52–54, 1947.
McCornack, R.L., Extended tables of the Wilcoxon matched pair signed rank statistic. *Journal of the
Morel, F.M.M. and J.G. Hering, *Principles and Applications of Aquatic Chemistry*, John Wiley & Sons,
Muyzer, G., E.C. De Waal, and A.G. Uitterlinden. Profiling of complex microbial populations by
denaturing gradient gel electrophoresis analysis of polymerase chain reaction-amplified
Sherwood-Lollar, B., G.F. Slater, J. Ahad, B. Sleep, J. Spivack, M. Brennan, and P. MacKenzie, Con-
trasting carbon isotope fractionation during biodegradation of TCE and toluene — implications
Slater, G.F., B.S. Lollar, B.E. Sleep, and E.A. Edwards, Variability in carbon isotopic fractionation
during biodegradation of chlorinated ethenes — Implications for field applications, *Environ-
fatty acids and phenotypic relationships of Agrobacterium, Bradyrhizobium, Mesorhizobium,
Rhizobium and Sinorhizobium species using the Sherlock microbial identification system, *Inter-
Tsitko, I.V., G.M. Zaitsev, A.G. Lobanok, and M.S. Salkinoja-Salonen, Effect of aromatic compounds
on cellular fatty acid composition of *Rhodococcus opacus*; *Applied and Environmental Microbiology*,
600/R-98/128, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency
U.S. EPA, Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Under-
ground Storage Tank Sites, OSWER Directive 9200.4-17P, U.S. Environmental Protection Agency,
(QA00 Update), U.S. Environmental Protection Agency, Office of Environmental Information,
U.S. EPA, Performance Monitoring of MNA Remedies for VOCs in Ground Water, EPA/600/R-04/
027, U.S. Environmental Protection Agency, Office of Research and Development, National
Vandamme, P., B. Pot, M. Gillis, P. de Vos, K. Kersters, and J. Swings, Polyphasic taxonomy, a consen-
Vroblesky, D.A., User’s Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain
Volatile Organic Compound Concentrations in Wells. Part 1: Deployment, Recovery, Data
Interpretation, and Quality Control and Assurance. U.S. Geological Survey, Water-Resources
Vroblesky, D.A. and W.T. Hyde, Diffusion samplers as an inexpensive approach to monitoring VOCs
Vroblesky, D.A., M.M. Loray, and P. Trimble, Mapping zones of contaminated ground water dis-
charge using creek-bottom sediment vapor samples, Aberdeen Proving Grounds, Maryland,
Vroblesky, D.A., L.C. Rhodes, and J.F. Robertson, Locating VOC contamination in a fractured rock
aquifer at the ground-water/surface-water interface using passive vapor collectors, *Ground


Practical Handbook of
ENVIRONMENTAL SITE CHARACTERIZATION
AND
GROUND-WATER MONITORING
SECOND EDITION

Edited by
DAVID M. NIELSEN