Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation

Prepared For

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Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation

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INTRODUCTION

Natural attenuation processes affect the fate and transport 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 efficiency 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 United States Environmental Protection Agency (USEPA) published its final policy on the use of natural attenuation, entitled *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (USEPA, 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 the USEPA (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. In addition, all monitoring programs should be designed to accomplish the following goals:

1) Demonstrate that natural attenuation is occurring according to expectations;

2) Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce (or enhance) the efficacy of the natural attenuation processes;

3) Identify any potentially toxic and/or mobile transformation products;

4) Verify that the dissolved contaminant plume is not expanding;

5) Verify that there has been no unacceptable impact to downgradient receptors;

6) 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;

7) Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors; and

8) 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.

According to the USEPA (1998), there are three types of environmental monitoring:

1) Site characterization (i.e., baseline monitoring) to describe the disposition of contamination and forecast its future behavior;

2) Validation monitoring to determine if predictions based on site characterization are accurate; and

3) Long-term monitoring to ensure that the behavior of the contaminant plume does not change.

The collection and interpretation of the first type of monitoring data are described by Wiedemeier *et al*. (1995 and 1998) for fuels and chlorinated solvents, respectively and by Wiedemeier *et al.* (1999). Validation monitoring consists of collecting the complete analytical suites specified by Wiedemeier *et al.* (1995, 1998, and 1999) - for one or two sampling rounds after completion of site characterization. Validation monitoring is used to ensure that the analytical results obtained from the baseline sampling events are accurate. Long-term monitoring involves collecting a subset of the parameters specified by Wiedemeier *et al*. (1995, 1998, and 1999). Ultimately the subset of parameters selected for analysis on an ongoing basis will be site-specific. This document describes how to effectively and efficiently specify the location, frequency, and types of samples and analyses required to meet the objectives of validation monitoring and long-term monitoring. In addition, guidance is provided on developing contingency remedies that will not adversely impact the natural biodegradation reactions occurring at a site, should engineered remediation be required.

Designing an effective monitoring program involves locating groundwater monitoring wells and developing a site-specific groundwater sampling and analysis strategy and contingency plan. The monitoring program should be designed to monitor contaminant plume migration 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 groundwater 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 groundwater and land. The results of a natural attenuation evaluation as described by Wiedemeier *et al.* (1995 and 1998) are critical to the design of a monitoring program. For those sites where the groundwater 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 two types of monitoring to be completed after the initial site characterization and evaluation of natural attenuation are validation monitoring and long-term monitoring (USEPA, 1998). Two types of wells are utilized for both types of monitoring: performance monitoring wells and contingency monitoring wells. Performance monitoring wells (PMWs) are located upgradient from [i.e. background location(s)], within, and just downgradient from the plume. These wells are used to verify that individual constituents of concern concentrations, plume boundaries, and overall progression toward remedial goals are acceptable over time and space. Contingency monitoring wells are used to ensure that the plume is not expanding beyond pre-established boundaries. Detection of unacceptable concentrations of contaminants at the contingency monitoring wells triggers implementation of the contingency remedy.

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 provided and to facilitate CERCLA 5-year reviews, Operating Properly and Successfully determinations, etc. Primary factors to consider include (at a minimum) distance to potential receptor exposure points, groundwater seepage velocity and direction, type(s) of contaminant(s), 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 ten years 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. Secondary factors to consider include (at a minimum) access issues, property lines, and contaminant contributions from offsite 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 groundwater. The combination of these two factors will influence well spacing and sampling frequency. Typically, the greater the groundwater seepage velocity and the shorter the distance to potential receptors, the greater the sampling frequency. The use of seepage velocity is conservative because some sorption and biodegradation of dissolved contaminants likely are occurring which will retard the movement of the contaminants. The analytical protocol developed for a site will be influenced mainly by the

type of contamination. 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. 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. Placement of sample collection points, the analytical protocols to be used for validation and long-term monitoring, and the determination of sampling frequency are described in Section 2.

One of the most important purposes of long-term monitoring is to confirm that the contaminant plume is behaving as predicted. Graphical and statistical tests can be used to evaluate plume stability. 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. Section 3 describes graphical and statistical techniques that can be used to evaluate plume stability.

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 intrinsic bioremediation. The development of contingency plans is discussed in Section 4.

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 a clear objective for long-term monitoring, and should help define the length of time that monitoring will be required. Section 5 discusses exit strategies.

This document is intended for use in conjunction with the U. S. EPA and AFCEE technical protocols for evaluating natural attenuation (Wiedemeier *et al*., 1995 and 1998). If properly

implemented, the technical approach outlined in this document should meet the objectives of the USEPA's second and third types of monitoring (validation monitoring and long-term monitoring). In addition, 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.

SECTION 2

PLACEMENT OF SAMPLE COLLECTION POINTS, ANALYTICAL PROTOCOLS, AND SAMPLING FREQUENCY

Designing an effective monitoring plan involves locating sampling points and developing a site-specific groundwater sampling and analysis strategy. The sampling and analysis strategy should specify a sampling frequency and an analytical protocol. The monitoring plan should be designed to monitor contaminant plume migration 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 groundwater modeling (as appropriate) should be used when preparing the monitoring plan. The design of the monitoring program should include consideration of current receptor exposure pathways, as well as exposure pathways arising from potential future use of the groundwater and land. The results of a natural attenuation evaluation (Wiedemeier *et al.*, 1995 and 1998) should be used in designing a monitoring program. If the groundwater flow field at a site cannot be adequately characterized (e.g., flows in fractured bedrock), the evaluation of natural attenuation, and monitoring program design, can be problematic. The placement of sampling points, analytical protocols, and sampling frequency are discussed in this section.

2.1 PLACEMENT OF SAMPLING POINTS

The post-characterization monitoring strategy for a given site will depend upon several factors. Primary factors to be consider include (at a minimum) distance to potential receptor exposure points, groundwater seepage velocity and direction, type(s) of contaminant(s), 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 ten years 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 critical areas. Secondary factors to consider include (at a minimum) access issues, property lines, and contributing offsite 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 groundwater. These two factors will strongly influence monitoring well spacing and sampling frequency. Typically, the faster the groundwater seepage velocity and the shorter the distance to potential receptor exposure points, the greater the sampling frequency. The use of seepage velocity is conservative because some sorption and biodegradation are likely retarding contaminant migration relative to groundwater 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. It is important however, 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 groundwater flow. The geologic complexity of the site and groundwater 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 (USEPA, 1998). The PMWs, located upgradient from, within, and just downgradient from the plume, are used to verify the predictions made during the evaluation of natural attenuation (Wiedemeier *et al.*, 1995 and 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. If pre-established trigger levels are exceeded at the contingency monitoring wells, then the implementation of the contingency plan will proceed (see Section 4).

Where possible, contaminant, geochemical and hydrogeological data should be used to site monitoring wells, especially those wells downgradient from the plume. For example, data for geochemical parameters such as dissolved oxygen, nitrate, Fe(II), sulfate, and methane can be

used in conjunction with contaminant data to site downgradient contingency monitoring wells in locations with "treated" groundwater. 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 groundwater. To evaluate the behavior of the dissolved contaminant plume over time and to estimate cleanup timeframes, statistical methods should be employed (see Section 3).

2.1.1 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 groundwater 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/or elevated metabolic byproduct concentrations (e.g., iron (II), methane, chloride, alkalinity) relative to background levels provide good evidence that the groundwater 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 groundwater was contaminated at one time and has since been treated (Wiedemeier *et al.*, 1995 and 1998). 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 2.1 and 2.2 illustrate how geochemical data can be used to place monitoring wells. Figure 2.1 illustrates a hypothetical monitoring network for a site contaminated with dissolved organic compounds emanating from a light nonaqueous-phase liquid (NAPL). Figure 2.2 illustrates a hypothetical monitoring network for a site contaminated with dissolved organic compounds emanating from a dense NAPL. These figures depict 1) upgradient (PMW-1A) and crossgradient (PMW-1B and C) wells in unimpacted groundwater; 2) a well(s) 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 groundwater (PMW-5); 5) a well (PMW-6) in treated groundwater; 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.
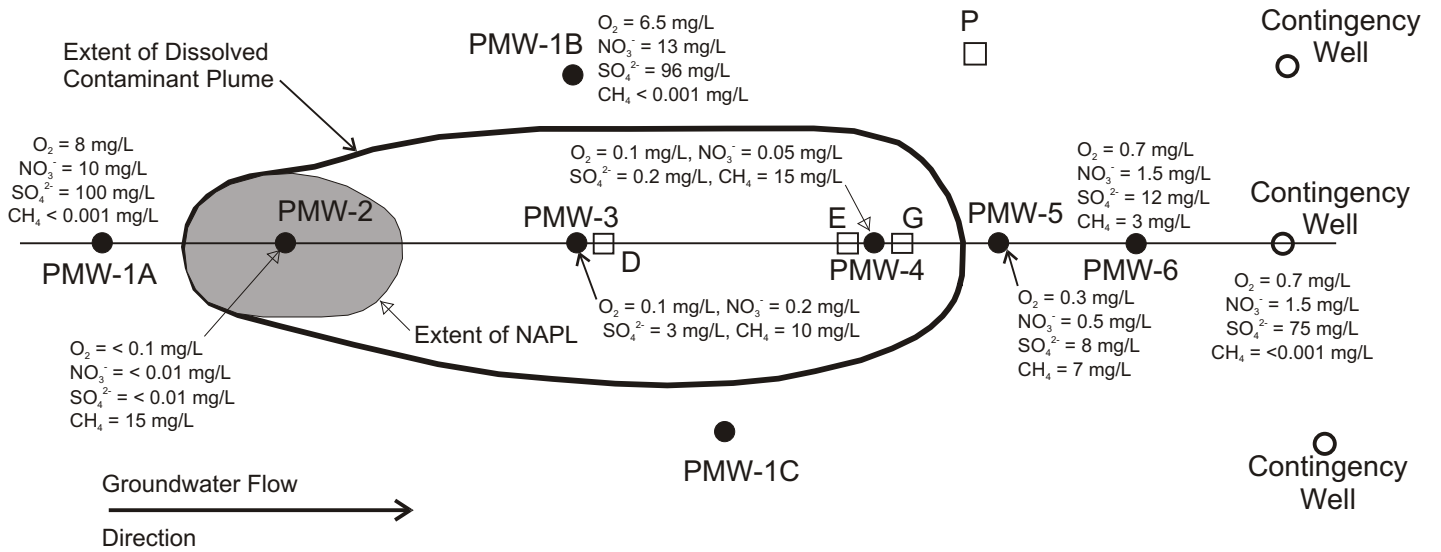
Wells D, E, G, and P have geochemistry similar to wells PMW-1 (A, B, and C) (i.e., Background) so they probably are not screened across the flowpath of the contaminant plume and therefore are not being used for this hypothetical monitoring program.

Figure 2.1
Locating Monitoring Wells Using Contaminant and Geochemical Data (LNAPL)
(Modified from Wiedemeier *et al.*, 1999)

Wells F and R have geochemistry similar to wells PMW (A, B, and C) (i.e., Background) so they probably are not screened across the flowpath of the contaminant plume and therefore are not being used for this hypothetical monitoring program.
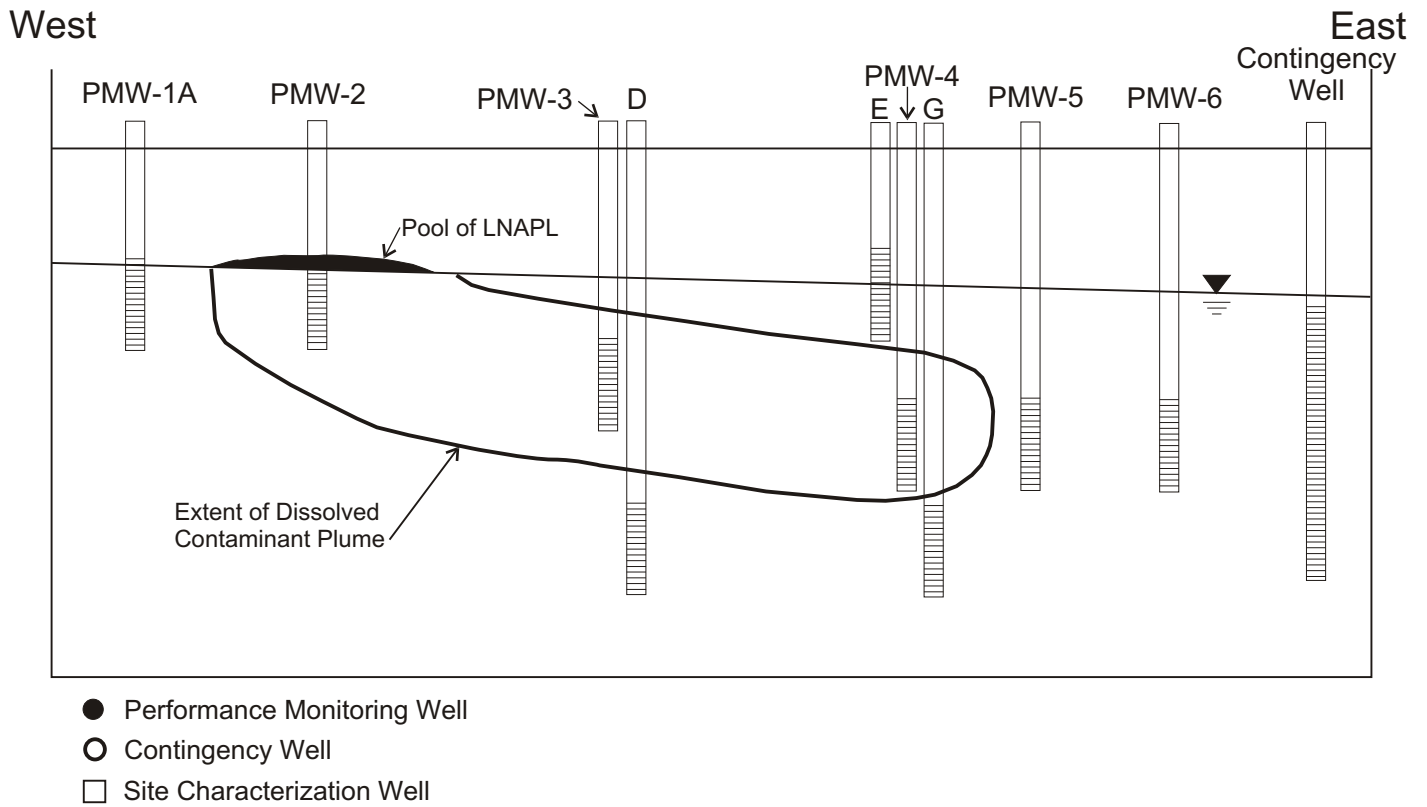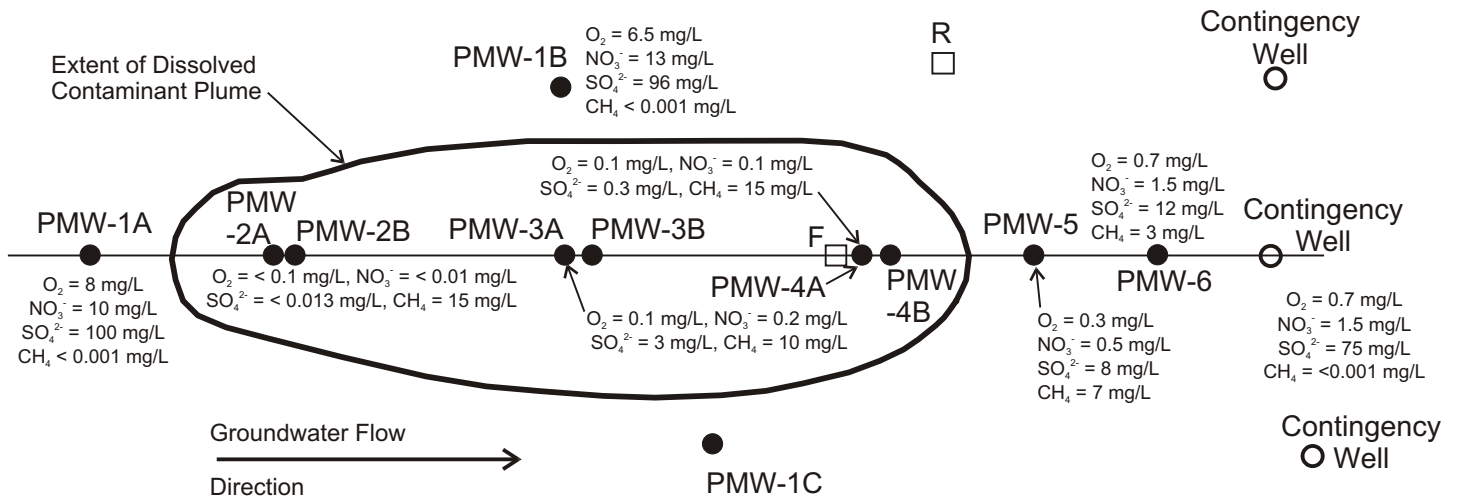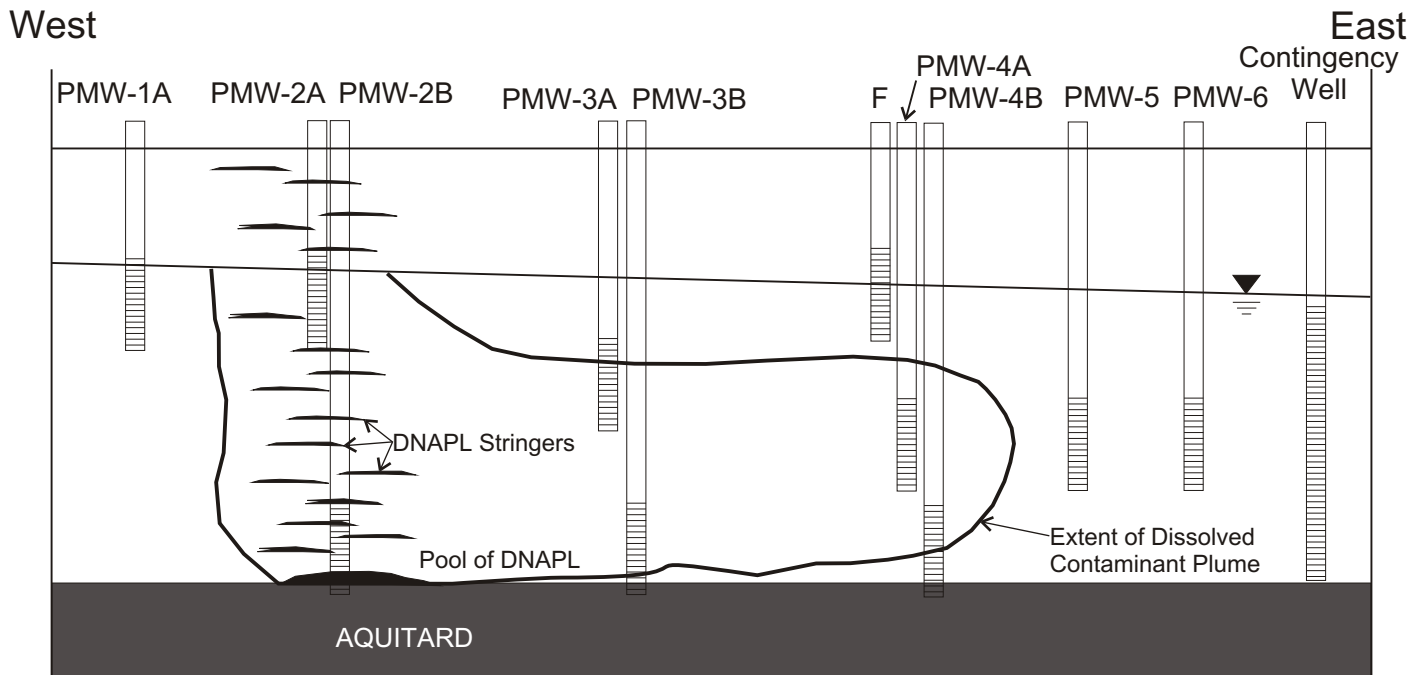
Figure 2.2
Locating Monitoring Wells Using Contaminant and Geochemical Data (DNAPL)
(Modified from Wiedemeier *et al.*, 1999)

Table 2.1 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 PMW(s) in the NAPL source area is (are) intended to monitor changing NAPL composition over time and to give an indication of the changing strength of the NAPL. 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 groundwater flow along the centerline 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 downgradient portion of the plume (PMW-4 in this example) and the well located downgradient 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 2.1 are 500 feet apart and groundwater is flowing at 50 feet per year, it will take at least 10 years 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 2.1 are 100 feet apart, then it will take about 2 years 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 flowpath or potential flowpath 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 the seepage velocity of the groundwater rather than on the solute transport velocity.

Table 2.1
Sampling Locations, Purpose, and Analytical Parameters for Validation Monitoring and Long-Term Monitoring of Groundwater
(Modified from Wiedemeier *et al.*, 1999)

Type of Well	Location	Purpose	Analytical Parameters	
			Validation Sampling	Long-Term Monitoring
PMW-1	Upgradient/Crossgradient	Monitor Background Water Quality	Contaminants, Daughter Products, and Full Suite of Geochemical Parameters[a/]	Limited Suite of Geochemical Parameters[b/,c/]
PMW-2	NAPL Source Area	Monitor Changing NAPL Composition/Source Strength and Plume Behavior over Time	Contaminants, Daughter Products, and Full Suite of Geochemical Parameters[a/]	Contaminants and Daughter Products in NAPL and Groundwater Beneath NAPL and Limited Suite of Geochemical Parameters[b/,c/]
PMW-3 and PMW-4	Downgradient from NAPL Source Area along Plume Centerline	Monitor Plume Behavior over Time	Contaminants, Daughter Products, and Full Suite of Geochemical Parameters[a/]	Contaminants and Daughter Products[c/]
PMW-5	Immediately Downgradient from Plume	Early Detection of Plume Migration	Contaminants, Daughter Products, and Full Suite of Geochemical Parameters[a/]	Contaminants and Daughter Products[c/]
PMW-6	Between Contingency Wells and the Other PMWs	Early Detection of Plume Migration	Contaminants, Daughter Products, and Full Suite of Geochemical Parameters[a/]	Contaminants and Daughter Products[c/]
Contingency Wells	Downgradient from Most Downgradient PMW (PMW-6 in this Case) and Upgradient from Receptor Exposure Point	Monitor for Plume Migration Toward a Potential Receptor and Trigger Contingency Plan	Contaminants, Daughter Products, and Full Suite of Geochemical Parameters[a/]	Contaminants and Daughter Products[c/]
Surface Water	At and Upgradient and Downgradient from Discharge Point	Determine Surface-Water Impacts	Contaminants and Daughter Products	Contaminants and Daughter Products

[a/] For fuel hydrocarbon plumes, the full suite of geochemical parameters should include dissolved oxygen, nitrate, Fe (II), sulfate, methane, temperature, pH, conductivity, alkalinity, and oxidation/reduction potential. For chlorinated solvent plumes chloride, ethane/ethane, total organic carbon, and hydrogen (if necessary) should be added to the full suite of geochemical parameters recommended for fuel hydrocarbon plumes. See Wiedemeier *et al*. (1995, 1998, and 1999) for more information on analytes.

[b/] The limited suite of geochemical parameters should include dissolved oxygen, oxidation/reduction potential, temperature, and pH.

[c/] If plume behavior changes or is suspected of changing, then analyze for contaminants and the full suite of geochemical parameters.

2.1.2 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 ground water/surface water interface. Figure 2.3 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 crossgradient wells (PMW-1B and -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 above 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.

2.2 ANALYTICAL PROTOCOLS

The analytical protocol developed for a site will be influenced mainly by the type of contamination present. Sites with chlorinated solvent contamination will likely require a much more diverse suite of analytical parameters than fuel hydrocarbons. This is because of the differences in the patterns of biodegradation between different contaminants. For example, it is now widely accepted that fuel hydrocarbons almost invariably biodegrade in the shallow subsurface. This is in contrast to chlorinated solvents, which exhibit varying degrees of biodegradation potential.

A groundwater sampling and analysis plan that specifies a sampling frequency and a list of analytes should be prepared in conjunction with sampling point placement. The sampling frequency should be appropriate to detect migration of the plume over time and to define trends in analyte concentrations, and should account for groundwater flow and solute transport rates and monitoring well spacing. Sampling frequency is discussed in Section 2.3. Groundwater analytical parameters for PMW's, contingency wells, and surface water sampling locations (as appropriate) are summarized in Table 2.1. The suggested list of analytes presented in Table 2.1
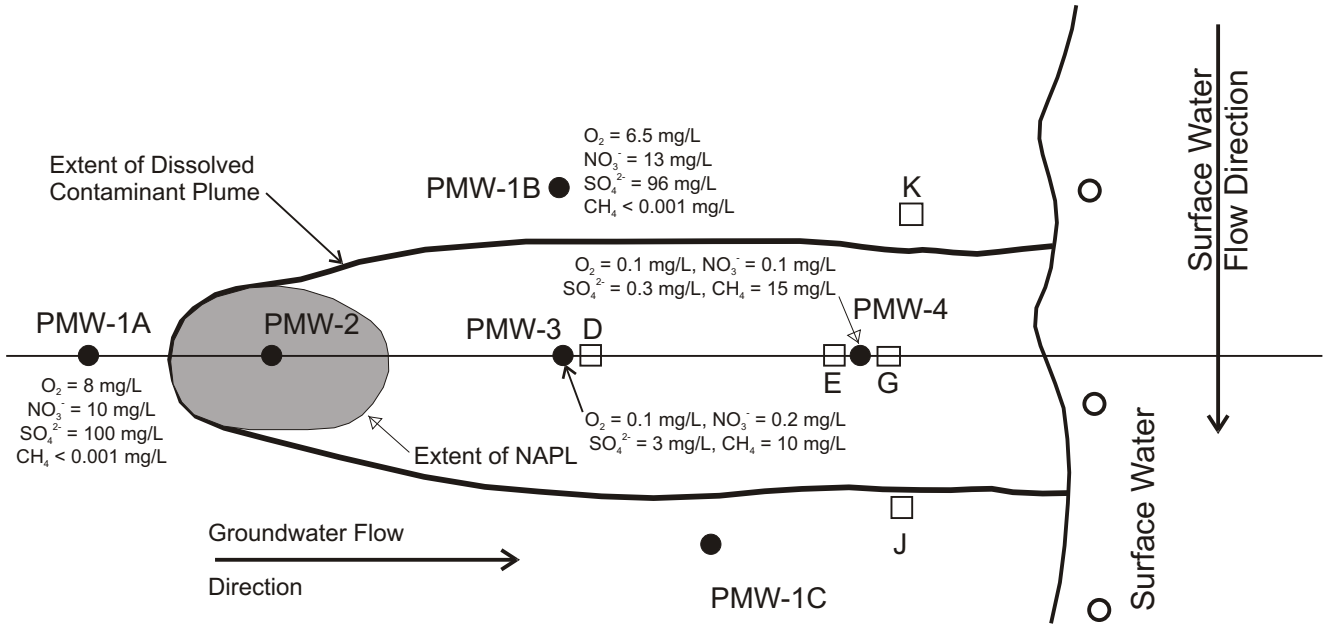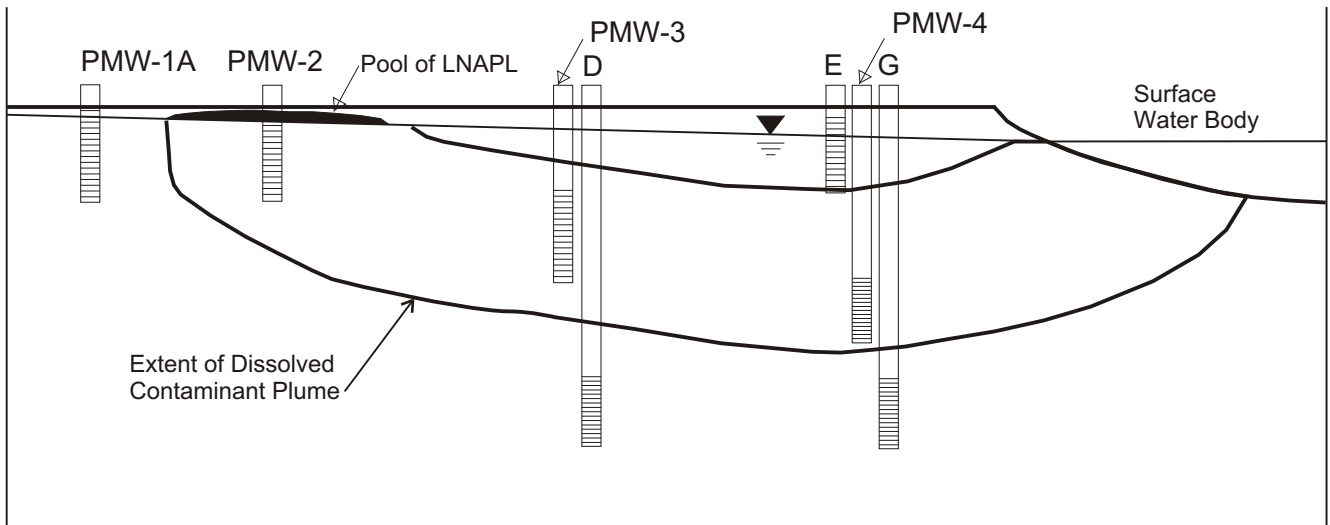
Figure 2.3
Locating Monitoring Wells and Surface Water Sampling Locations for a Discharging Plume
(Modified from Wiedemeier *et al.*, 1999)

includes contaminants and geochemical parameters. One suite of analytical parameters is for validation monitoring, and one is for long-term monitoring. There also are different geochemical analyses suggested for plumes of chlorinated solvents. This is because these plumes are particularly sensitive to changes in groundwater geochemistry, such as depletion of organic carbon or increasing dissolved oxygen concentrations. Such changes may inhibit reductive dechlorination. Any federal or state-specific analytical requirements not listed in Table 2.1 also should be addressed in the sampling and analysis plan to ensure that all data required for regulatory decision-making are collected. Water-level measurements should be made during each sampling event to ensure that the groundwater flow direction has not changed.

The analytes listed in Table 2.1 fall into several broad categories, including source term parameters, contaminants and daughter products, electron acceptors, metabolic byproducts, and general water quality parameters. The analytes listed in Table 2.1 are useful for 1) estimating the composition and strength of a NAPL source, 2) demonstrating that natural attenuation is occurring, and 3) evaluating the relative importance of the various natural attenuation mechanisms. It should be kept in mind that it may be necessary to modify Table 2.1 on a site-specific basis.

Table 2.2 provides a comparison of analytical laboratory costs for potential natural attenuation analyses. Real world unit prices have been listed to provide the user of this protocol an idea of long-term monitoring analytical costs. Mention of company name does not constitute endorsement or recommendation for use.

2.2.1 Sampling in the Nonaqueous-Phase Liquid Source Area

Nonaqueous-phase liquid in the subsurface, whether present at residual saturation or in quantities sufficient to cause formation of a mobile NAPL pool, acts as a continuing source of groundwater contamination; as long as NAPL remains in the subsurface at concentrations sufficient to impact groundwater, aqueous-phase contamination will persist. This has several implications for natural attenuation and the length of time that monitoring must be conducted. 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. Collection and analysis of NAPL samples allows the investigator to determine the composition of the NAPL. In some cases, it may be possible to complete equilibrium partitioning calculations to show that the effective solubility of a compound is no longer high enough to impact groundwater at concentrations above regulatory guidelines.

Table 2.2
Cost Comparison for Analytical Laboratory Natural Attenuation Analyses

Parameter and Method	Unit Cost				
	Columbia Analytical Services[a]	Evergreen Analytical Laboratory	Microseeps[b]	SPL	Quanterra[c]
VOCs (SW8260)	$195.00	$160.00	$100.00	$125.00	$135.00
VOCs (SW8021 or 8260) (PCE, TCE, DCEs, VC)	$115.00	$160.00	$60.00	$75.00	$130.00
Nitrate (SW9056 or 300.0)	$18.00	$15.00	$15.00	$15.00	$30.00
Ethene, Ethane, Methane (RSK SOP 175)	$140.00	$100.00	$100.00	$90.00	$160.00
Dissolved Organic Carbon (SW9060)	$90.00	$35.00	$15.00	$35.00	$55.00
Chloride (SW300.0)	$18.00	$15.00	$15.00	$15.00	$25.00

Notes:

[a] Columbia Analytical Services, Inc. - Discounts are available with consideration to sample volume and laboratory capacity.

[b] Microseeps - Unit costs are based on greater than 10 samples; if less than 10 samples, the unit cost will increase.

[c] Quanterra, Inc. - Volume discounts are based on the following. For any one client that requires "x" dollars in analytical services in one month, analytical services for that client and project, in the following month shall be discounted by "y", where "x" and "y" are as follows: x > $10,000: y = 1%; x > $20,000: y = 2%; and x > $30,000: y = 3%. In addition, a discount is offered of 15% for advanced reservations of ten business days or more, 2% for credit card payment or Purchase Order Number with sample delivery, and 2% for a paperless report.

Mention of company name does not constitute endorsement or recommendation for use.

2.2.2 Contaminants and Daughter Products

The concentrations of contaminants and associated daughter products (which also may be considered contaminants) should be monitored over time. Section 3 describes how to analyze time-series contaminant data.

2.2.3 Electron Acceptors

Naturally occurring electron acceptors commonly used in microbial metabolism include dissolved oxygen, nitrate, Fe(III), sulfate, and carbon dioxide. Measurement of these parameters is useful for evaluating the occurrence of intrinsic bioremediation and the relative importance of the various terminal electron-accepting processes.

Although microbes utilize Fe(III) as an electron acceptor during Fe(III) reduction, one of the metabolic byproducts of this reaction, Fe(II), is measured to confirm the occurrence of Fe(III) reduction. This is because of the difficulty involved in measuring the concentration of biologically available Fe(III) in an aquifer system.

2.2.4 Metabolic Byproducts

Readily measurable byproducts of microbial metabolism in areas contaminated with organic compounds include Fe(II), carbon dioxide, methane, ethane, ethene, alkalinity, lowered ORP, chloride, and hydrogen.

2.2.5 General Water Quality Parameters

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 groundwater contaminated with municipal waste leachates, which often contain elevated concentrations of organic acids (Baedecker and Back, 1979). In groundwater contaminated with sludges from cement manufacturing, pH values as high as 11 have been measured (Chapelle, 1993).

Groundwater 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. Groundwater temperature also affects the metabolic activity of bacteria. Rates of hydrocarbon

biodegradation roughly double for every 10°C increase in temperature ("Q"$_{10}$ rule) over the temperature range between 5 and 25°C.

Conductivity is a measure of the ability of a solution to conduct electricity. The conductivity of groundwater is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases.

Because the pH, temperature, and conductivity of a groundwater sample can change significantly within a short time following sample acquisition, these parameters, along with dissolved oxygen and oxidation/reduction potential (ORP), must be measured in the field in unfiltered, unpreserved, "fresh" water. The measurements should be made in a clean glass container separate from those intended for laboratory analysis, and the measured values should be recorded in the groundwater sampling record.

2.3 SAMPLING FREQUENCY

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. Based on 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 significant variability is encountered during the first year, then additional quarterly sampling may be required. Based on the results of the first year's sampling, the sampling frequency may be reduced to annual (or less frequent) sampling in the quarter showing the highest contaminant concentrations or the greatest extent of the plume.

According to the USEPA (1998), 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, and

3) The reduction in contaminant concentration required to meet the acceptance criteria.

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 estimated 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 groundwater seepage/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 groundwater. For example, consider the contaminant plume depicted on Figure 2.1. If the distance between well PMW-5 and the center contingency well is 500 feet, and the seepage velocity of groundwater is 250 feet per year, then a sampling frequency of 500 ft/250 ft per year = 2 years may be appropriate for this site. Because the exact location of the leading edge of a dissolved contaminant plume generally is not known, some professional judgment may be required when making these calculations.

According to the USEPA (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 appropriate to decrease the monitoring frequency at some point in time, once it has been determined 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.

2.4 SAMPLING TECHNIQUES

In addition to conventional and low-flow sampling techniques, diffusion samplers can be quite effective for sampling during long-term monitoring.

2.4.1 Diffusion Samplers

The diffusion sampler technology utilizes a deionized water-filled, low-density polyethylene diffusion membrane to collect water samples from groundwater monitoring wells for VOC laboratory analyses. The membrane of the sampler allows VOCs in groundwater to diffuse into the deionized water. Chemical equilibrium between the groundwater and sampler water typically occurs within 14 days resulting in a water sample (from the diffusion sampler) that is representative of VOC concentrations in the well water. The diffusion samplers can be used to rapidly and inexpensively obtain groundwater samples for VOCs in monitoring wells (Vroblesky *et al.,* 1996; Vroblesky and Hyde, 1997.) When used appropriately, representative samples can be obtained without well purging or to identify temporal changes in well water chemistry (Vroblesky and Robertson, 1996). Potentially large cost savings in long-term groundwater monitoring efforts may be realized due to the simplicity of the diffusion samplers compared to traditional purge-and-sample techniques.

Passive diffusion membrane samplers installed in groundwater monitoring wells have been found to be capable of yielding representative water samples of groundwater contaminated with VOCs. In previous field investigations, the VOC concentrations in water samples obtained using diffusion samplers without purging were comparable to concentrations in water samples obtained from the respective wells using traditional purge-and-sample procedures (Vroblesky and Hyde, 1997). Similar sampling devices have been utilized to collect groundwater samples at the groundwater/surface water interface when buried directly into sediment (Vroblesky *et al.*, 1991; Vroblesky *et al.*, 1996). The devices and methodology are potentially applicable to groundwater monitoring for most volatile and many semivolatile organic compounds that will diffuse through the polyethylene membrane.

Water samples from groundwater monitoring wells can be collected using diffusion samplers without purging of the well water. The typical approach for sampling groundwater-monitoring wells for VOCs involves purging water from well casings prior to collecting the groundwater sample. In accordance with current standard operating procedures (SOPs), purging requires the removal of at least three well casing volumes of water and stabilization of water-quality parameters such as dissolved oxygen (DO), pH, temperature, and conductance. However, recent studies suggest that removing three to five casing volumes of water prior to sampling, as suggested by the U.S. EPA, is sometimes unnecessary. In some cases, well purging may produce undesirable effects (Powell and Puls, 1993; Kearl *et al.*, 1992; Barcelona *et al.*, 1994). Insertion of sampling devices (e.g., submersible pumps) can significantly increase the size and number of suspended colloidal particles (Kearl *et al.*, 1992). The turbidity decreases with time, raising the possibility that insertion of a sampling device and subsequent sampling may yield water samples and colloids not representative of the ambient aquifer conditions. Increasing the purge volumes can also increase the radius of aquifer influenced by the pumping, resulting in a sample that may represent an integration of differing water types. Mixing of groundwater from contaminated and uncontaminated zones may result in dilution of the true nature of contamination in the contaminated zone, or by suggesting that the contaminated zone is larger than it actually is. Furthermore, the costs for well purging, including labor, equipment, and disposal of purge water may be substantial. Thus in order to lower costs, it often is desirable to minimize well purging prior to obtaining representative samples. Using diffusion samplers for groundwater monitoring can eliminate well purging while collecting representative samples and minimize wastewater requiring further disposal.

Data from recent investigations suggest that the water immediately adjacent to a well screen can be representative of aquifer water prior to purging. Robin and Gillbam (1987) showed that groundwater at their site moved through the screened portion of a well with little interaction or

mixing with water in the overlying well casing. Powell and Pols (1993) used tracer studies to show that, for three of the four wells that examined, the water in the screened interval exchanged with formation water and did not significantly mix with overlaying casing water unless disturbed. In the fourth well, Powell and Pols (1993) found that the casing was constantly replenished with formation water throughout its volume with little or no time available for stagnation of casing water. The results of these studies implied that flow through the well across the screened interval was often horizontal and laminar and representative of formation water. Kearl *et al.*, (1992) used a downhole colloidal borescope to provide visual support of this hypothesis by showing advection of suspended sediment across the borehole. Thus, in a well with horizontal, laminar flow across the screened interval and little interaction or disturbance of the overlying water column, a sampling device in the screened interval potentially could be used to collect a representative sample while minimizing disturbance of the overlying water column in the well.

Unlike traditional purge-and-sample methods of groundwater sample collection, the diffusion samplers allow collection of samples from discrete depths intervals within the well casing. By placing multiple samplers within a monitoring well's screened interval, it is possible to develop a vertical profile of the VOC contamination along length of the well screen and identify specific horizons (*i.e.,* geologic units), if any, that may be contributing the highest concentrations reported in the well. This methodology eliminates the potential for collecting samples that represent an integration of different water types. In addition, once the vertical profile of the well's contamination is defined, a sampling program can be developed that monitors only the horizon, or horizons, that are contributing the highest VOC concentrations. In most cases, the diffusion sampler placed at the midpoint of the well screen may be sufficient to collect a sample that is representative of water in the entire well. A previous field investigation of the methodology showed a close match between VOC concentrations in water obtained using the samplers without prior purging and sampling approaches (Vroblesky and Hyde, 1997).

The sampling methodology described in this section is for the use of water-filled, low-density polyethylene diffusion samplers as an alternative approach to allow routing monitoring of VOCs in groundwater at monitoring wells. This method allows VOCs in groundwater to diffuse through semipermeable membranes (*i.e.,* polyethylene bags) into the deionized water inside the membrane. Samplers are typically constructed in 1.5-foot sections from 2-or 3-inch diameter, 40 mil polyethylene tubing, filled with retail-grade deionized water, and heat sealed on both ends. A typical diffusion sampler contains approximately 300 mL of water. The samplers are placed into "flex-guard" low-density polyethylene mesh tubing for structural support, attached to a weighted rope with nylon cable ties, and lowered into the well. Knots can be positioned in the rope if multiple samples are to be collected from one well. Stainless steel weights are attached to the

end of the rope to ensure the samplers are located at the proper depths and not floating at, or above, the water surface.

The diffusion samplers remain undisturbed in the wells until equilibrium between the water in the well casing and water in the diffusion samplers is achieved. VOCs will move from the contaminated groundwater, through the semipermeable membranes, into the (initially) uncontaminated deionized due to the diffusion transport mechanism. Diffusion causes solutes, in this case VOCs, in water to move from an area of high concentration to an area of lower concentration, and typically occur in the absence of water velocity. One-dimensional mass transport in the water due to diffusion can be estimated using Fick's first law of diffusion:

$$F_x = -D_d \left(\frac{dC}{dx} \right)$$

Where, F_x = mass flux $(M/L^2/T)$

D_d = diffusion coefficient (L^2/T)

dC/dx = concentration gradient $(M/L^3/L)$

Equilibrium time is variable, but for the purposes of this study, a minimum of 14 days should be suitable. Laboratory data indicate that the diffusion samplers equilibrate within approximately 3 to 4 days, depending on the hydrogeologic characteristics of the aquifer (Vroblesky and Campbell, 1999). Periods of longer than 14 days are also acceptable, with no adverse impacts on data quality. In that diffusive transport will allow VOCs in the samplers and the aquifer to remain in equilibrium assuming that relatively steady-state conditions are present.

Upon recovery of the diffusion samplers from the wells, the samplers are opened and water samplers transferred into 40-milliliter (mL) volatile organic analysis (VOC) bottles. The samples are preserved and submitted to a laboratory for VOC analysis. Upon collection of groundwater samples from the diffusion samplers, the wells can be purged and sampled for other parameters such as DO, ORP, temperature, etc. in accordance with the site-specific long-term monitoring plan.

The diffusion sampler methodology has many advantages over currently available sampling protocols, such as:

- capable of collecting groundwater VOC samples that are representative of concentrations directly adjacent to the well screen;
- capable of collecting samples from discrete depth intervals (1.5 feet long) along the length of the well screen;
- samples collected do not represent an integration of contaminated concentrations along the length of the well screen where vertically dissimilar contamination profiles exist;
- does not require well purging prior to sample collection, thus minimizing labor costs and eliminating costs for purging/sampling equipment and minimizing wastewater disposal;
- no capital and low material costs; and
- no dedicated equipment to maintain.

The diffusion sampler methodology has potential disadvantages and limitations compared to conventional technologies, including:

- the methodology is not applicable to metals and other contaminants that do not readily diffuse through the semipermeable polyethylene membranes;
- may not be applicable for sites where water in well casting is stagnant or otherwise not representative of the aquifer adjacent to the well screen.

SECTION 3

EVALUATING PLUME STABILITY AND BEHAVIOR

An historical database showing statistically significant plume stabilization and/or loss of contaminant mass over time can be used to demonstrate that natural attenuation is occurring at a site, and is perhaps the best line of evidence to have when trying to implement natural attenuation as a remediation approach. It is important to note that plume stabilization can occur with or without destructive attenuation mechanisms such as intrinsic bioremediation or hydrolysis. In certain cases (e.g., for some MTBE plumes), nondestructive mechanisms of natural attenuation such as dilution, dispersion, sorption, and volatilization may be sufficient to cause the dissolved contaminant plume to reach steady-state equilibrium, or even recede if the strength of the NAPL source is decreasing due to natural weathering or engineered remediation. Thus, it generally is necessary to use the second line of evidence, chemical and geochemical data, to isolate the component of natural attenuation attributable to destructive attenuation mechanisms, especially intrinsic bioremediation. Although possible, plume stabilization or decline typically will not be achieved before receptors are impacted without destructive attenuation mechanisms such as intrinsic bioremediation.

One of the most important purposes of long-term monitoring is to confirm that the contaminant plume is behaving as predicted. This section describes graphical (i.e., visual) and statistical tests can be used to evaluate plume stability. It is important when evaluating the stability of a contaminant plume that the historical data demonstrate a clear and meaningful trend at appropriate monitoring or sampling points. Graphical techniques for evaluating plume stability 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 downgradient for several wells along the groundwater flow path over several sampling events.

In addition to methods presented by the USEPA (1989 and 1992), two other, fairly straightforward statistical approaches can be used to evaluate plume stability. The Mann-Whitney U test is performed for every contaminant at every monitoring well at a site where this plume stability test is being applied. The test is nonparametric, which means that the outcome of the test is not determined by the overall magnitude of the data points, but depends on the ranking

of individual data points. The Mann-Kendall test is another nonparametric test that can be used to define the stability of a solute plume based on concentration trends at individual wells. To evaluate plume stability using the Mann-Kendall test, four or more independent sampling events are required. As with the Mann-Whitney U test, this test is applied to data for each contaminant of interest at each monitoring well located in the plume. Another statistical technique that can be used to evaluate plume stability is an analysis of the location and movement of the center of mass of a contaminant plume. One method is the Thiessen analysis. In addition, some computer modeling programs can estimate the center of mass of a contaminant plume.

To help aid in designing long-term monitoring programs, AFCEE developed the Long Term Monitoring Decision Support Software. Figure 3.1 shows the opening screen of this software package. This program is especially useful for evaluating plume stability and includes both graphical and statistical techniques.

3.1 GRAPHICAL TESTS FOR PLUME STABILITY

There are several ways to present data showing changes in contaminant concentrations and plume configuration over time. One method consists of preparing isopleth maps of contaminant concentrations over time. Figure 3.2 shows isopleth maps of total volatile organic compound (VOC) concentrations in groundwater 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 groundwater geochemistry, and an apparent reduction in plume size and/or contaminant concentrations could simply be the result of seasonal dilution. Also plotted on Figure 3.2 is the projected extent of contamination if intrinsic bioremediation were not occurring. This projection was made using an analytical model that incorporated the effects of advection, dispersion, and sorption only; biodegradation was assumed not to occur in these simulations. Model predictions suggest that if biodegradation were not occurring at this site, the plume would advance approximately 1,500 feet per year. Chemical data show that this is not the case, so plume stabilization is likely the result of intrinsic bioremediation. This type of analysis provides good evidence for the occurrence of intrinsic bioremediation, and geochemical data can be used to provide additional confirmation of intrinsic bioremediation.

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 groundwater flow path over several sampling events. It

Figure 3.1
Screen Capture of the AFCEE LTM Decision Support Tool

August 1993

July 1994

September 1995

8,000

4,000

ND

20,000

8,000

4,000

ND

8,000

4,000

ND

4,000

Groundwater Flow Direction

Projected Extent
of Plume with Advection,
Dispersion, and Sorption
Only, Biodegradation Omitted

4,000 — Line of Equal Total
BTEX Concentration (g/L)
Groundwater Flow
Velocity = 1,600 feet per year

Modified from Wiedemeier *et al.* (1999)
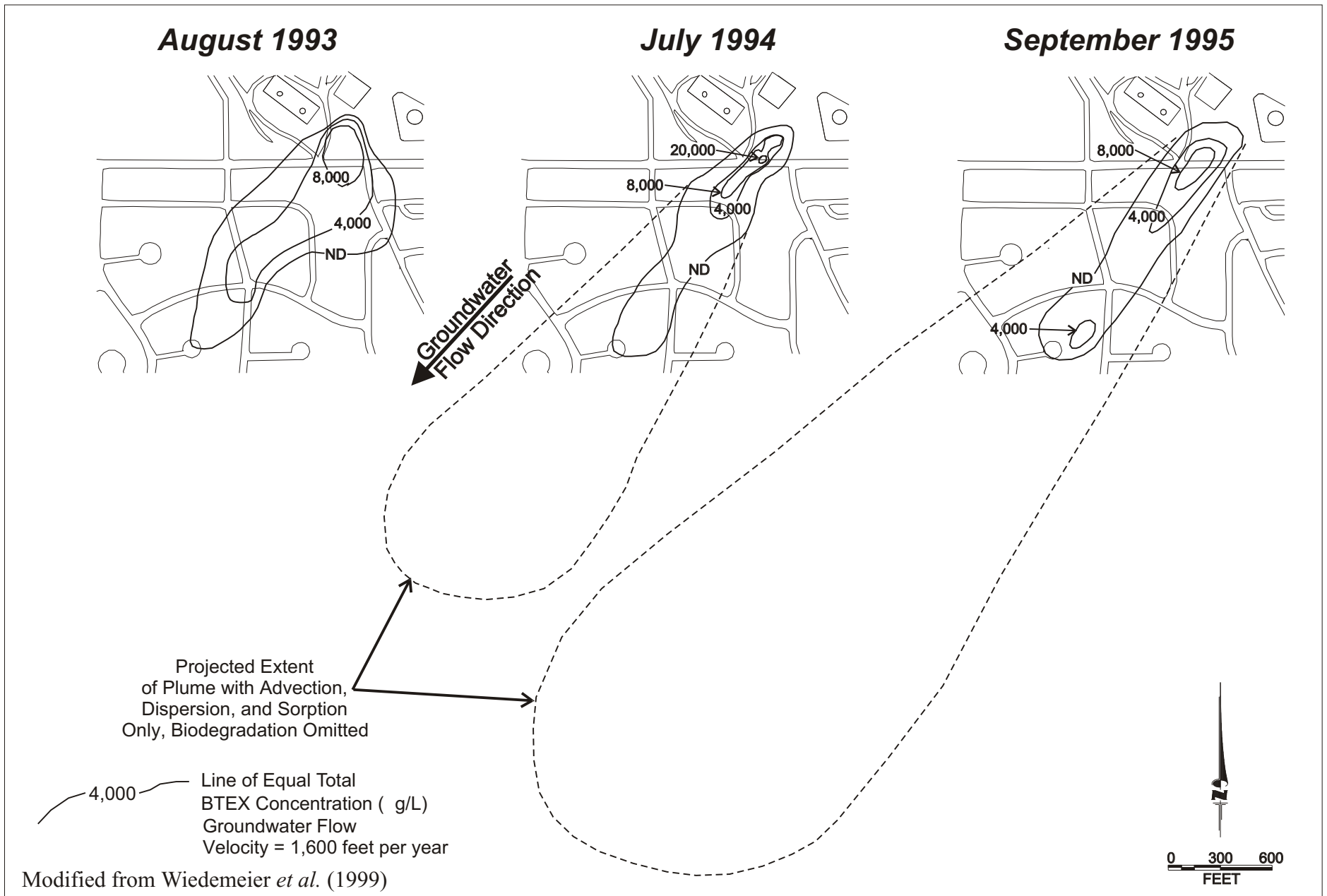
N

0   300   600
FEET

Figure 3.2
Isopleth Maps Showing Contaminant Distribution Over Time

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 groundwater 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 migrating downgradient, it is important that downgradient wells are located in the path of contaminated groundwater flow. Geochemical data can be used to confirm that downgradient wells are sampling groundwater that was once contaminated with organic compounds, as discussed in Section 2.

Figure 3.3 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. Based on the geochemical data presented on 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 feet apart, and the groundwater seepage velocity is 50 feet per year; with 8 years 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 on Figure 3.3, and the lack of contaminant migration provide reasonable evidence for natural attenuation and contaminant mass destruction. The chemical and geochemical data discussed by Wiedemeier *et al*. (1995 and 1998) can be used to show that this loss of contaminant mass is the result of intrinsic bioremediation.

The AFCEE Long Term Monitoring Decision Support Software package can be used to aid in graphical plume stability analysis. Figure 3.4 is a plot of contaminant concentration versus time generated by the program.

3.2 STATISTICAL TESTS FOR PLUME STABILITY

In addition to the methods presented by the USEPA (1989 and 1992), two different and fairly straightforward statistical approaches can be used to evaluate plume stability. First, trends can be analyzed by plotting concentration data versus time, usually on semi-log paper with log concentration being plotted against linear time. Plotting the concentration data on the log scale counters the relatively large changes in concentration data (e.g., a concentration reduction from 1 mg/L to 1 µg/L represents a 1000-fold reduction).

West   East

Extent of Dissolved
Contaminant Plume

I
O_2 = 6.5 mg/L
NO_3^- = 13 mg/L
SO_4^{2-} = 96 mg/L
CH_4 < 0.001 mg/L

J
O_2 = 8.5 mg/L
NO_3^- = 13 mg/L
SO_4^{2-} = 89 mg/L
CH_4 < 0.001 mg/L

Extent of NAPL

A   B   C D   E F G   H

O_2 = 8 mg/L
NO_3^- = 10 mg/L
SO_4^{2-} = 100 mg/L
CH_4 < 0.001 mg/L

O_2 = 0.1 mg/L, NO_3^- = 0.2 mg/L
SO_4^{2-} = 3 mg/L, CH_4 = 10 mg/L

100 feet

O_2 = 0.3 mg/L
NO_3^- = 0.5 mg/L
SO_4^{2-} = 8 mg/L
CH_4 = 7 mg/L

L

Groundwater Flow

Velocity = 50 feet per year

K

West   East

A   B   C D   E F G   H

Extent of Dissolved
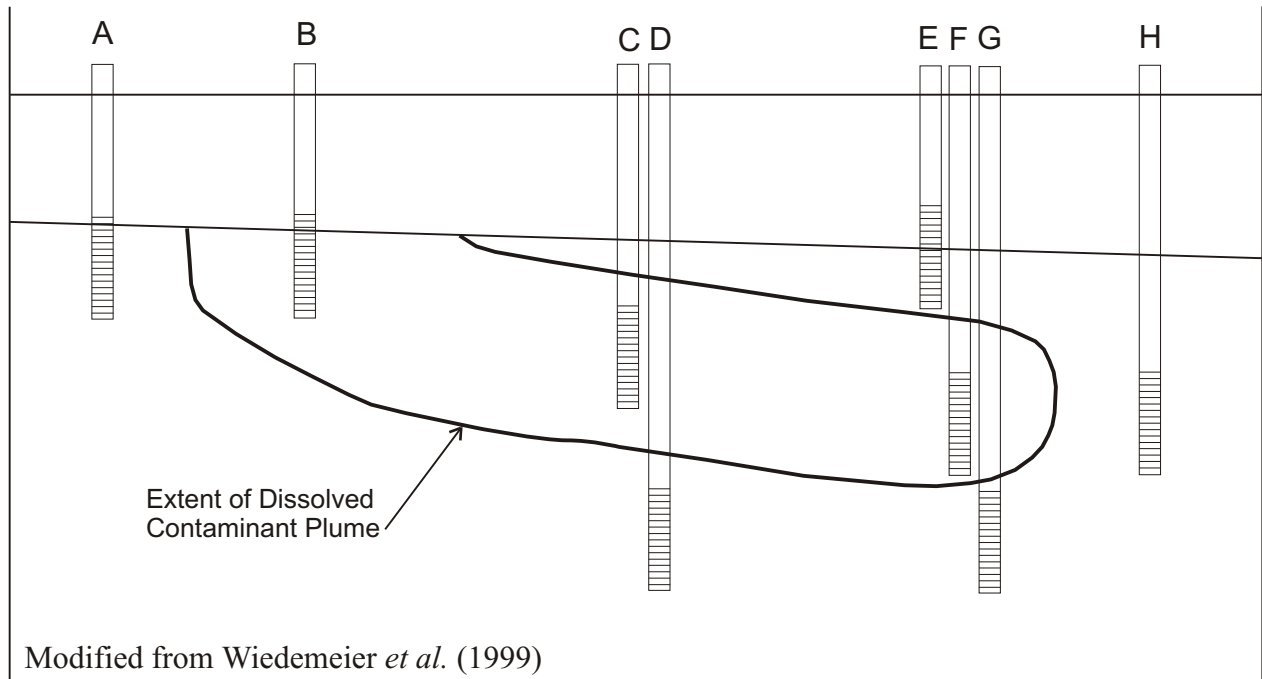Contaminant Plume

Modified from Wiedemeier *et al.* (1999)

Figure 3.3a
Sampling Locations for the Plots of Contaminant Concentration Versus Time
and Distance Downgradient Presented on Figure 3.3b

6/89

Well C

6/91

6/93

6/95

6/97

Concentration

Time

B   C   F

June, 1989

June, 1991

June, 1993

June, 1995

June, 1997

Concentration

Distance Downgradient
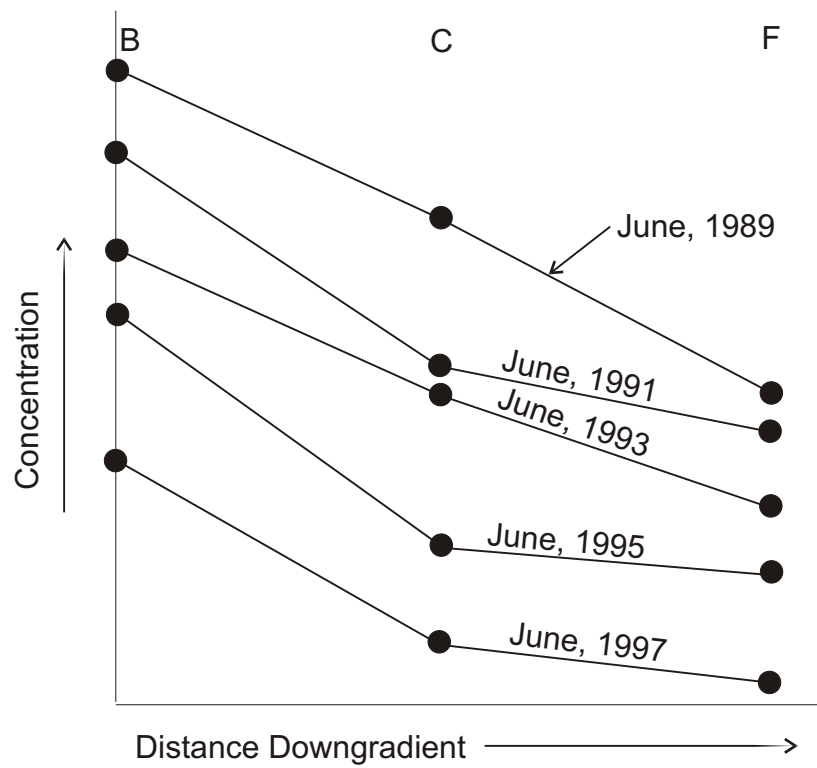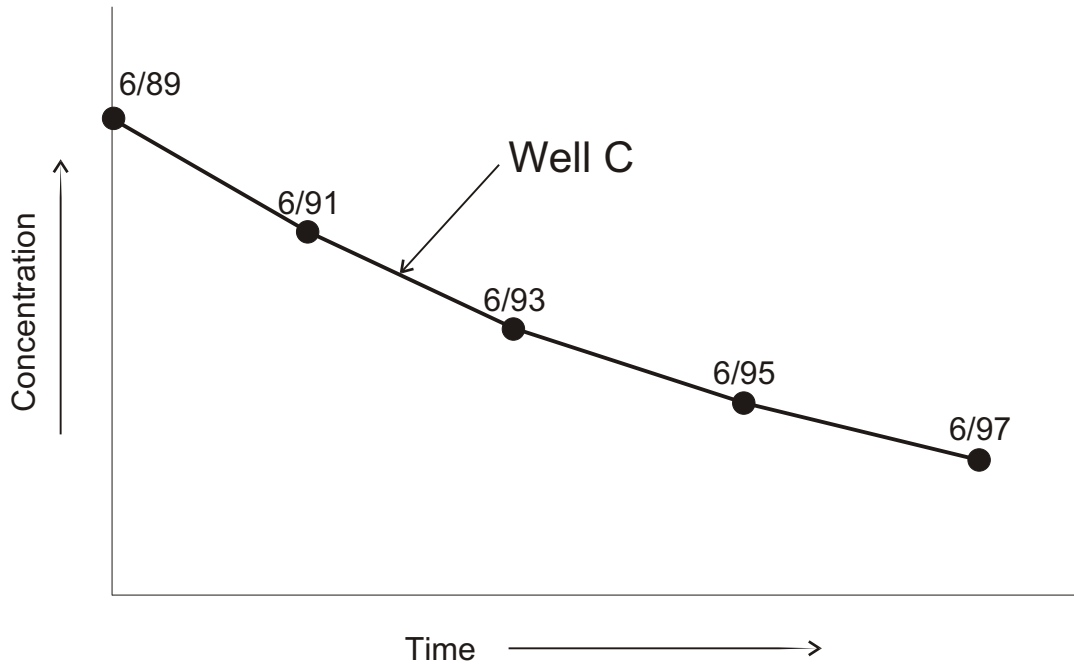
Modified from Wiedemeier *et al.* (1999)

Figure 3.3b
Plots of Contaminant Concentration Versus Time and Distance Downgradient
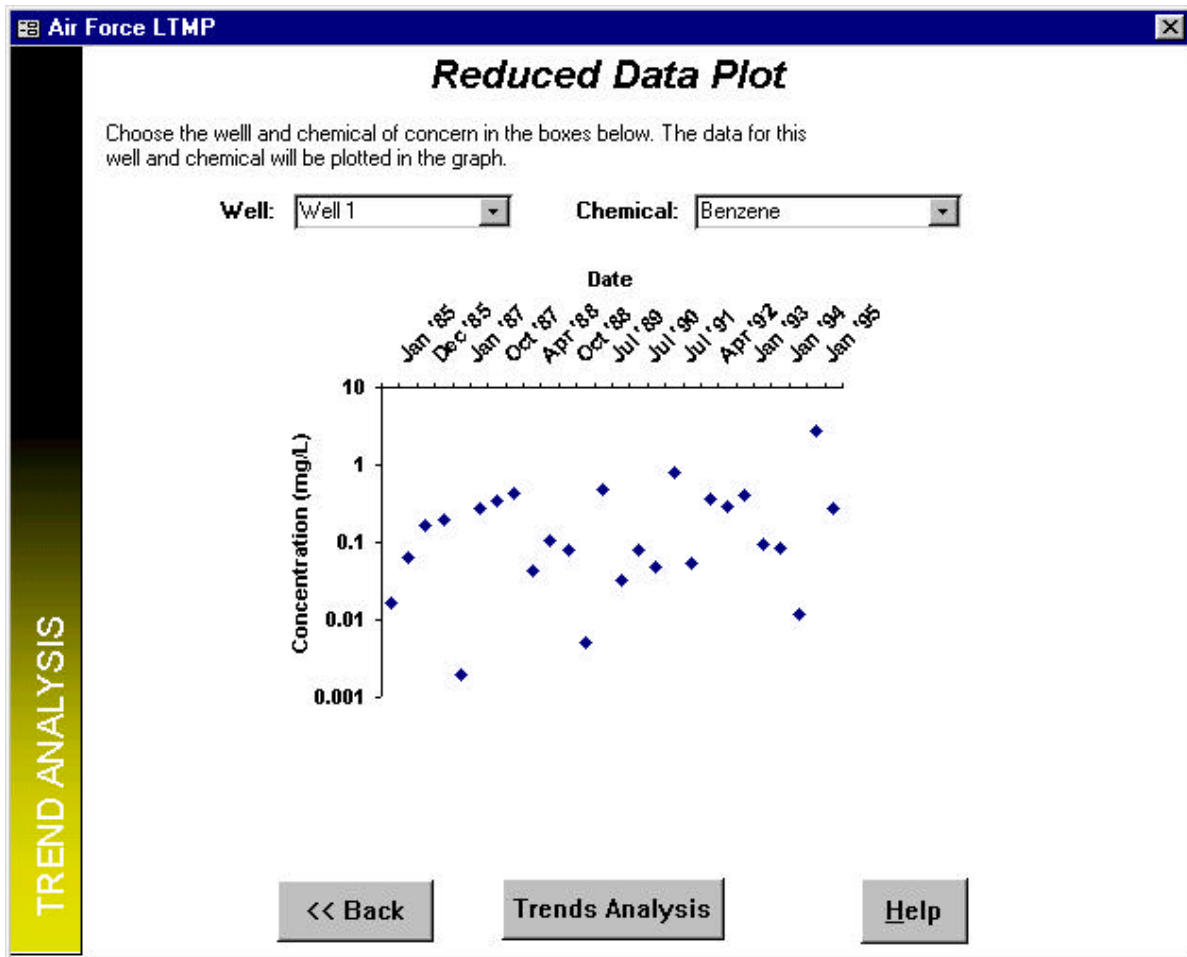
Figure 3.4
Screen Capture of the AFCEE LTM Decision Support Tool Showing a
Plot of Contaminant Concentration versus Time

While plotting concentration data versus time is recommended for any plume stability analysis, discerning trends in the plotted data can be subjective process, particularly if the data do not display a uniform trend, but show some variability over time (Figure 3.5). In these cases a statistical test such as the Mann-Whitney U Test or Mann-Kendall Test can be useful.

3.2.1 Mann-Whitney U Test

The Mann-Whitney U test (also called the Wilcoxon Rank-Sum Test) is currently being used by the State of New Jersey to determine plume stability (28 N.J.R. 1143). The test is performed using data for every contaminant at every monitoring well at a site where this plume stability test is being applied. The test is nonparametric (Mann and Whitney, 1947), which means that the outcome of the test is not determined by the overall magnitude of the data points, but depends on the ranking of individual data points.

In the New Jersey approach, eight consecutive quarters of monitoring data are divided into two groups representing the first four quarters (each point designated with an "A") and the last four quarters (each point designated with an "B"). The Mann-Whitney U method tests the hypothesis that the two populations are statistically equivalent.

The test is conducted by vertically ranking the eight data points from lowest to highest, with the lowest value on top and greatest value on the bottom. For each individual "A" concentration, the number of "B" concentrations that occur below the "A" concentration are counted. The four values (either zero or some positive number) are summed together to obtain the U statistic. All nondetect values are considered zero. If two or more concentrations are identical, then two vertical columns are constructed. In the first column, the tying "B" concentration is ranked first, and in the second column the tying "A" concentration is ranked first. An interim U is calculated for each column, and the average of the interim U values is used as the final U value. If $U = 3$ then the null hypothesis is rejected, and it is concluded with at least 90% confidence that the concentration for the individual contaminant at that well has decreased over time. If $U > 3$, the null hypothesis is accepted, and it cannot be concluded with at least 90% confidence that the concentration for the individual contaminant has decreased with time at that well. Table 3.1 presents an example of the Mann-Whitney U Test as applied in the New Jersey methodology. Note that this is a relatively low-power test, and many datasets that may appear to exhibit a declining trend may not yield a declining result with the U test.
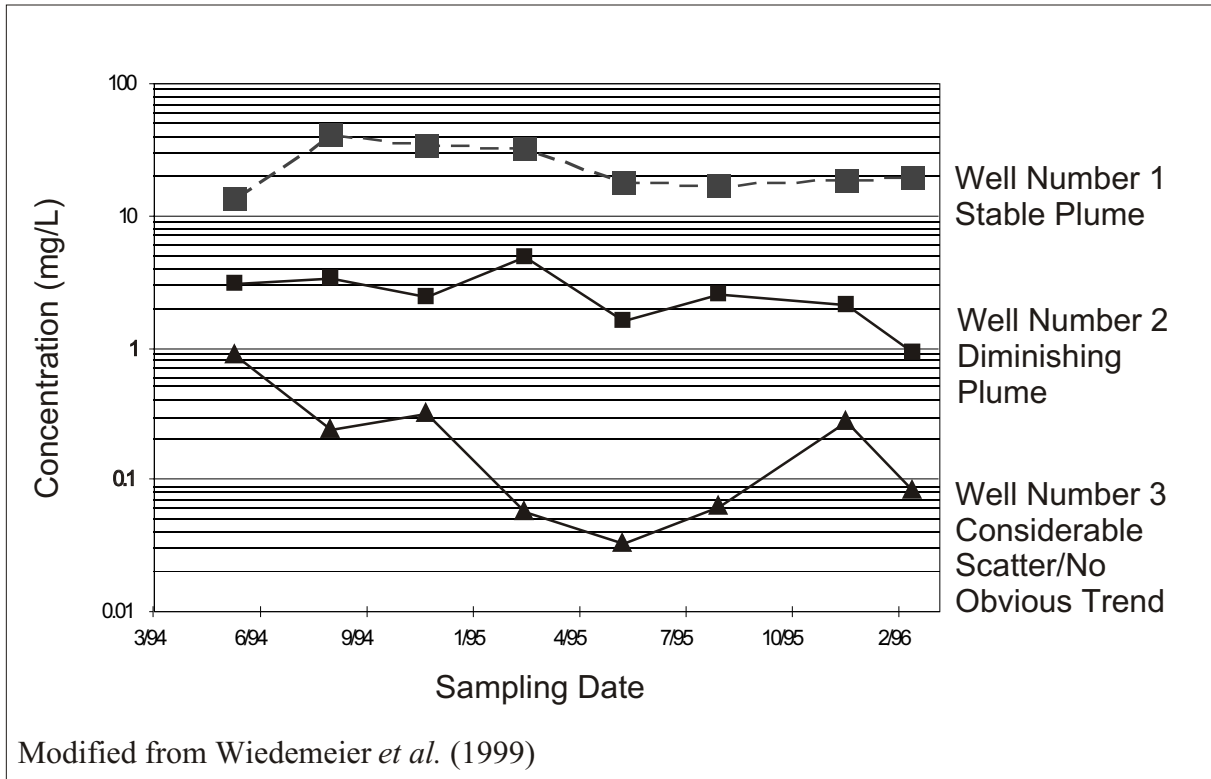
Figure 3.5
Example Plume Stability Plots

Table 3.1

Example of Mann-Whitney U Test for Plume Stability Using New Jersey Methodology*

Date	Concentration (mg/L)	Group
1st Q. 95	3.5	A
2nd Q. 95	2.9	A
3rd Q. 95	2.6	A
4th Q. 95	2.4	A
1st Q. 96	2.3	B
2nd Q. 96	0.9	B
3rd Q. 96	2.8	B
4th Q. 96	2.2	B

Ranked Conc. (mg/L)	Group	Is Group B Value > 2.4 mg/L?	Is Group B Value > 2.6 mg/L?	Is Group B Value > 2.9 mg/L?	Is Group B Value > 3.5 mg/L?
0.9	B	No	No	No	No
2.2	B	No	No	No	No
2.3	B	No	No	No	No
2.4	A	---	---	---	---
2.6	A	---	---	---	---
2.8	B	Yes	Yes	No	No
2.9	A	---	---	---	---
3.5	A	---	---	---	---
	NUMBER:	1	1	0	0

* Data are for single contaminant at a single well.

ANALYSIS:

Number of Yes Values: 2

U Statistic = 2

Because the U Statistic is < 3; contaminant concentrations are stable.

3.2.2 Mann-Kendall Test

The Mann-Kendall Test is another nonparametric test (Gilbert, 1987) that can be used to define the stability of a solute plume (i.e., stable, diminishing, or expanding) based on concentration trends at individual wells. To evaluate plume stability, four or more independent sampling events are required. As with the Mann-Whitney test, the Mann-Kendall test is applied to data for each contaminant of interest at each monitoring well located in plume area. However, as shown in a Mann-Kendall worksheet presented on Figure 3.6, the calculation approach is different.

The worksheet is used by completing the following steps (Figure 3.6):

Step 1: Well Data: Enter contaminant concentrations for each sampling event. Include only events for which numeric or nondetect (ND) values are available.

Step 2: Data Comparisons: Complete Row 1, comparing the results of Events 2, 3, etc. to Event 1, as follows:

- Concentration of Event x > Event 1: Enter 1
- Concentration of Event x = Event 1: Enter 0
- Concentration of Event x < Event 1: Enter -1

Complete all rows in same manner until data for all sampling events have been entered.

Step 3: Mann-Kendall Statistic: Sum across each row (e.g., 0 + 0 + -1 + -1 + 0 = -2), and record the result in far right-hand column. Sum the right-hand column down to get TOTAL sum. This TOTAL value represents Mann-Kendall "S" statistic for the data from this well.

Step 4: Results: Use the Confidence Level Chart in Figure 3.6 to determine the percent confidence in the plume trend based on the S value and the number of sampling events.

Step 5: Analysis: Compare results from all monitoring wells for all contaminants and evaluate overall plume stability.

This approach has its limitations, as a dataset can show a tremendous amount of scatter but still return the conclusion that the plume is stable (i.e., no significant trend could be established statistically). To counter this problem, one can apply a more sophisticated analysis using Mann-Kendall by comparing the Mann-Kendall S statistic, a calculated confidence level, and the coefficient of variance for the sample data. Figure 3.7 is a conceptual representation of the three types of information, where the S statistic shows the direction of the trend, the confidence factor shows how strong the trend is, and the coefficient of variation indicates how much scatter there is

MANN-KENDALL ANALYSIS OF PLUME: MONITORING WELL NO. _____ CONTAMINANT_____

	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6	Event 7	Event 8	Event 9	Event 10	Sum Rows
Total BTEX (mg/L)											
Row 1: *Compare to Event 1:*											
Row 2: *Compare to Event 2:*											
Row 3: *Compare to Event 3:*											
Row 4: *Compare to Event 4:*											
Row 5: *Compare to Event 5:*											
Row 6: *Compare to Event 6:*											
Row 7: *Compare to Event 7:*											
Row 8: *Compare to Event 8:*											
Row 9: *Compare to Event 9:*											

Mann-Kendall Statistic (S) = TOTAL [   ]

CHARACTERIZATION OF GROUNDWATER PLUME BASED ON DATA FROM THIS WELL

Use the Confidence Level Chart with the Mann-Kendall Statistic computed above (S) and the number of sampling events to estimate confidence level in the presence of a plume trend (i.e., expanding plume or diminishing plume):

Confidence Level Chart

S	Total No. of Sampling Events						
Value	4	5	6	7	8	9	10
0							
± 1			No Trend				
± 2			Indicated				
± 3							
± 4							
± 5							
± 6							
± 7							
± 8							
± 9							
± 10							
± 11							
± 12							
± 13							
± 14		Trend Probably Present					
± 15		(≥90% Confidence)					
± 16							
± 17							
± 18							
± 19							
≥ 20							

Stability Evaluation Results

❏ **No Trend Indicated** ❷ Plume Not Dimishing or Expanding (Plume is Stable)

❏ **Trend Is Present** (>90% Confidence
   ❏ S < 0   ❷   Diminishing Plume
   ❏ S > 0   ❷   Expanding Plume

Figure 3.6
Worksheet for Plume Stability Analysis Using the Mann-Kendall Test
(Modified from Wiedemeier *et al.*, 1999)

S Stat <1

S Stat >1

Confidence
Factor HIGH

Confidence
Factor LOW

Coeff. of
Variation
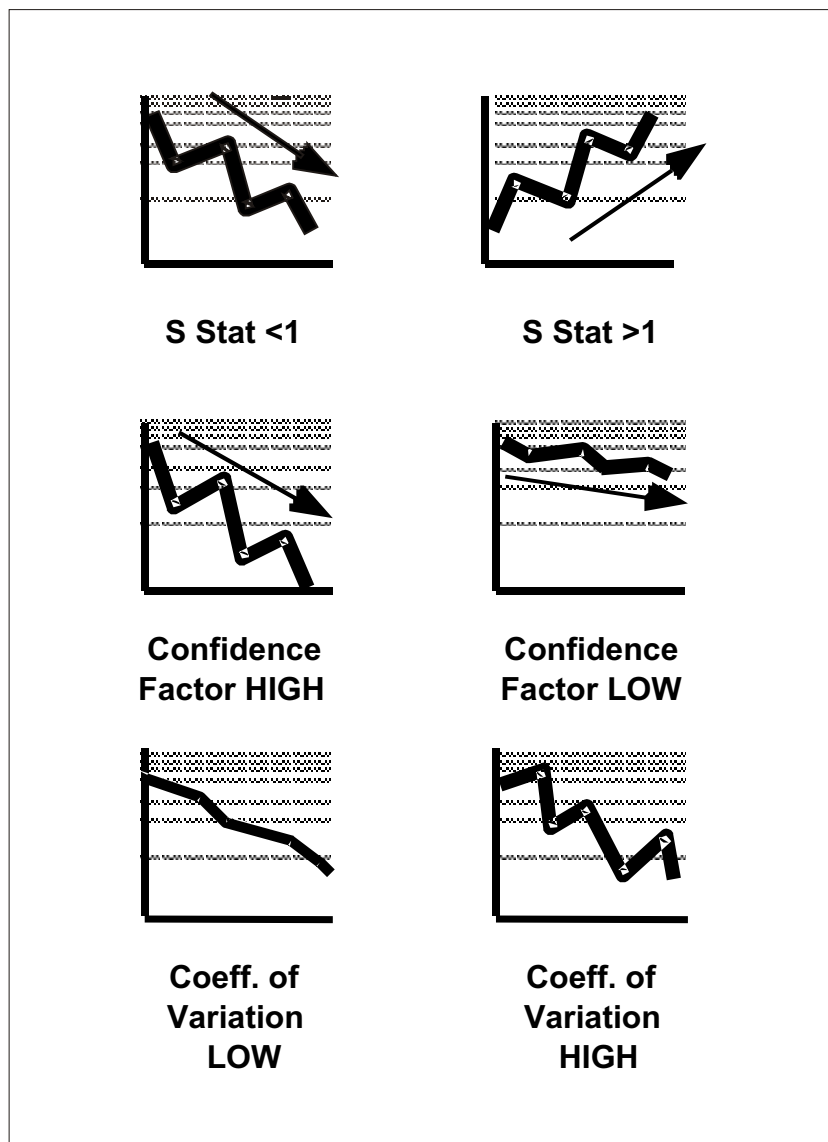LOW

Coeff. of
Variation
HIGH

Figure 3.7
Conceptual Representation of Mann-Kendall "S" Statistic,
Confidence Factor, and Coefficient of Variation
(Modified from Wiedemeier et al., 1999)

in the data. With this approach, for example, sites with confidence factors less than 90% can be classified as stable if the coefficient of variation is small (e.g., < 1). One software package designed for analyzing plume stability, the RNA Tool Kit (Groundwater Services, Inc., 1998) uses these three variables together in a conservative fashion to analyze stability, and will classify any dataset as declining, probably declining, stable, no trend, probably increasing, or increasing. The rules used in this software package to classify plume stability are listed in Table 3.2.

3.2.3 Statistical Analysis using the AFCEE Long Term Monitoring Decision Support Software Package

The AFCEE Long Term Monitoring Decision Support Software package can be used to evaluate plume stability using the following statistical techniques; 1) Mann-Kendall statistics, moving average, and linear regression. Figure 3.8 is a screen capture of the software package showing the trend analysis menu. Figure 3.9 is a screen capture of the results of a Mann-Kendall statistical analysis using the AFCEE software. Figure 3.10 is a screen capture summarizing the results of a statistical analysis using Mann-Kendall statistics, moving average, and linear regression.

3.3 GROUNDWATER GEOCHEMICAL DATA

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

1) Demonstrate that natural attenuation, and specifically intrinsic bioremediation, 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 intrinsic bioremediation of fuel hydrocarbons is discussed in detail by Wiedemeier *et al*. (1995 and 1999). The interpretation of geochemical data as they apply to intrinsic bioremediation of chlorinated solvents is discussed in detail by Wiedemeier *et al*. (1998 and 1999).

Table 3.2
RNA Tool Kit Rules to Classify Plume Stability

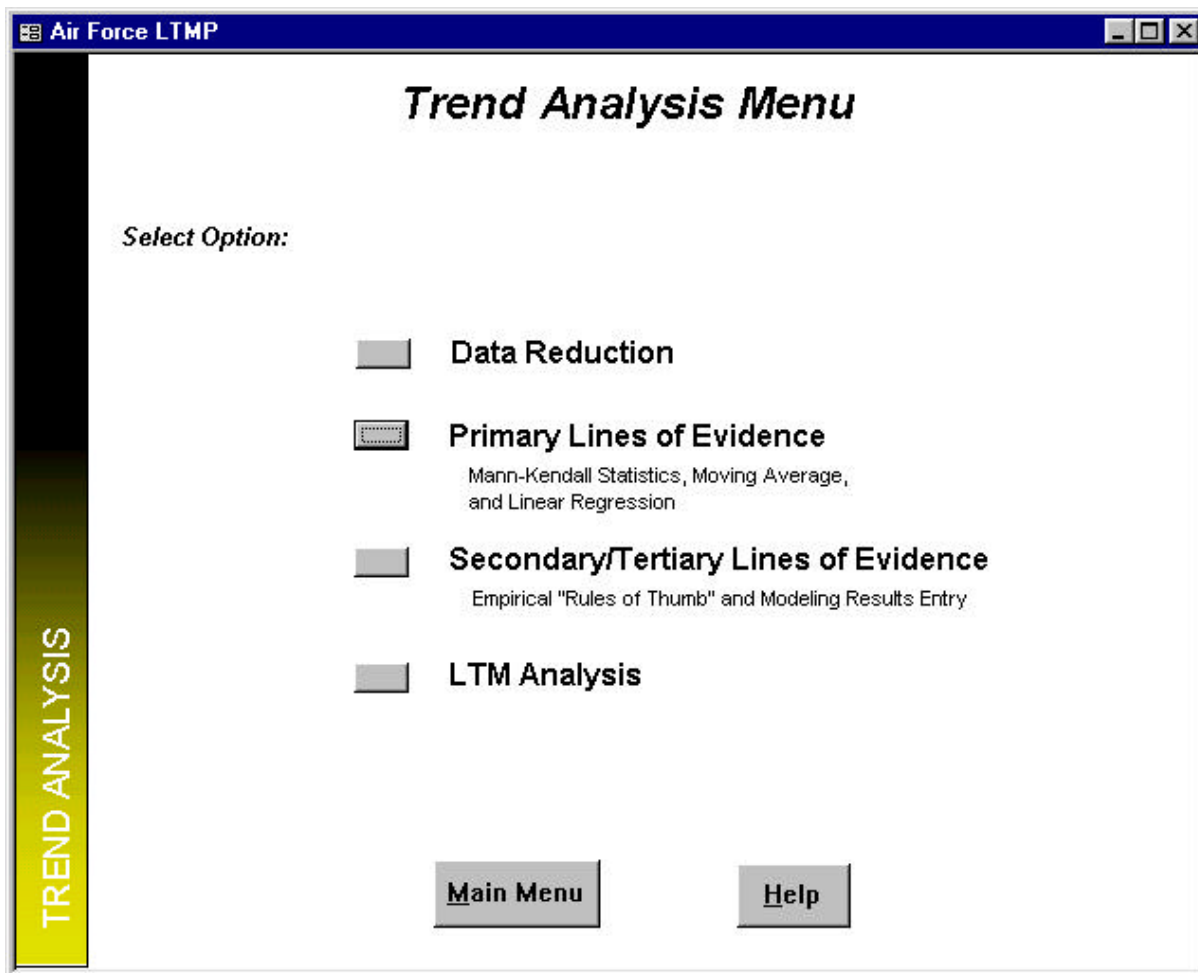| S Statistic	Confidence Factor	Coefficient of Variation	Interpretation
< 1	> 95 %	-	Declining
< 1	90% > CF < 95 %	-	Probably Declining
< 1	< 90 %	< 1	Stable
< 1	< 90 %	> 1	No Trend
• 1	< 90 %	-	No Trend
• 1	90% > CF < 95 %	-	Probably Increasing
• 1	> 95 %	-	Increasing

Figure 3.8
Screen Capture of the AFCEE LTM Decision Support Tool Showing
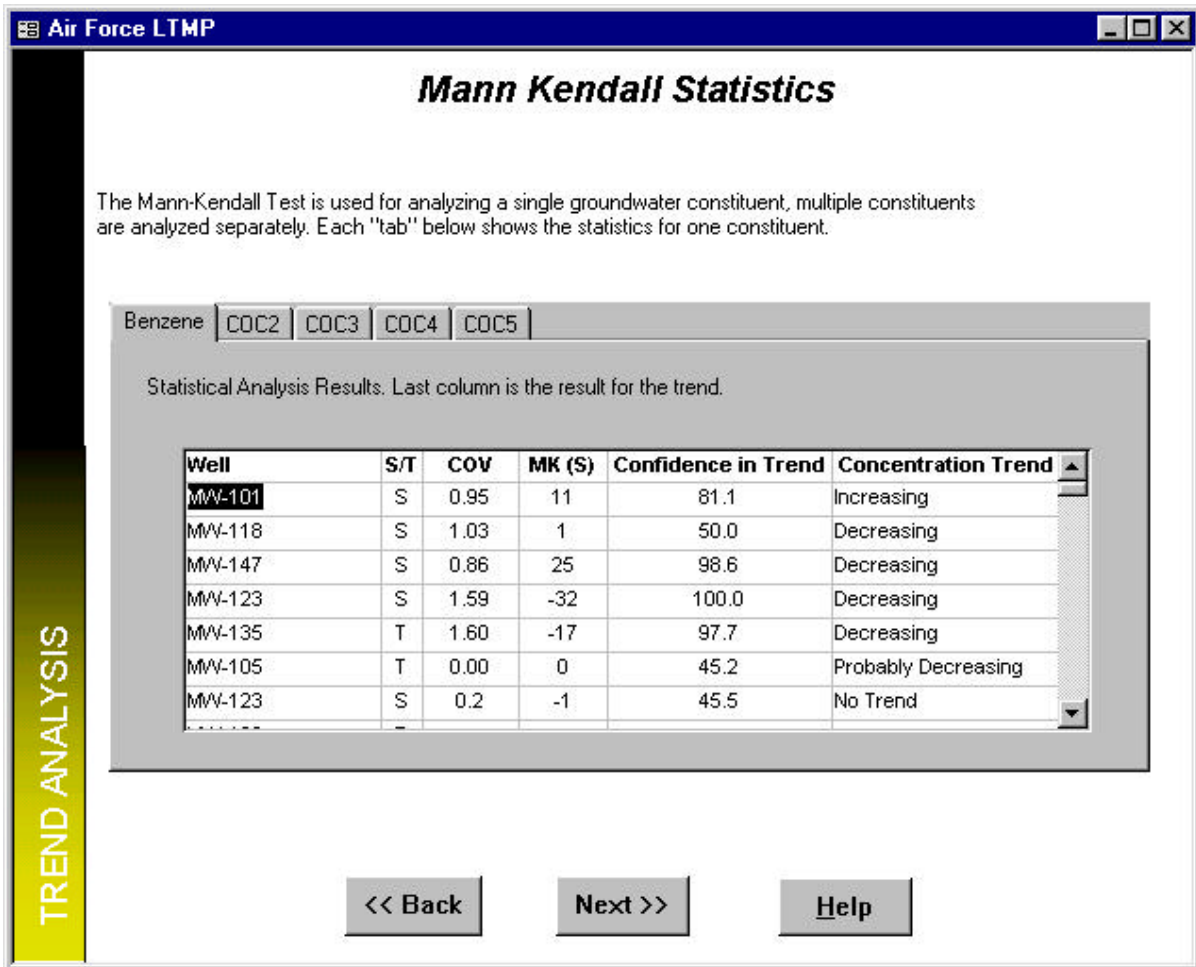the Trend Analysis Menu

Figure 3.9
Screen Capture of the AFCEE LTM Decision Support Tool Showing
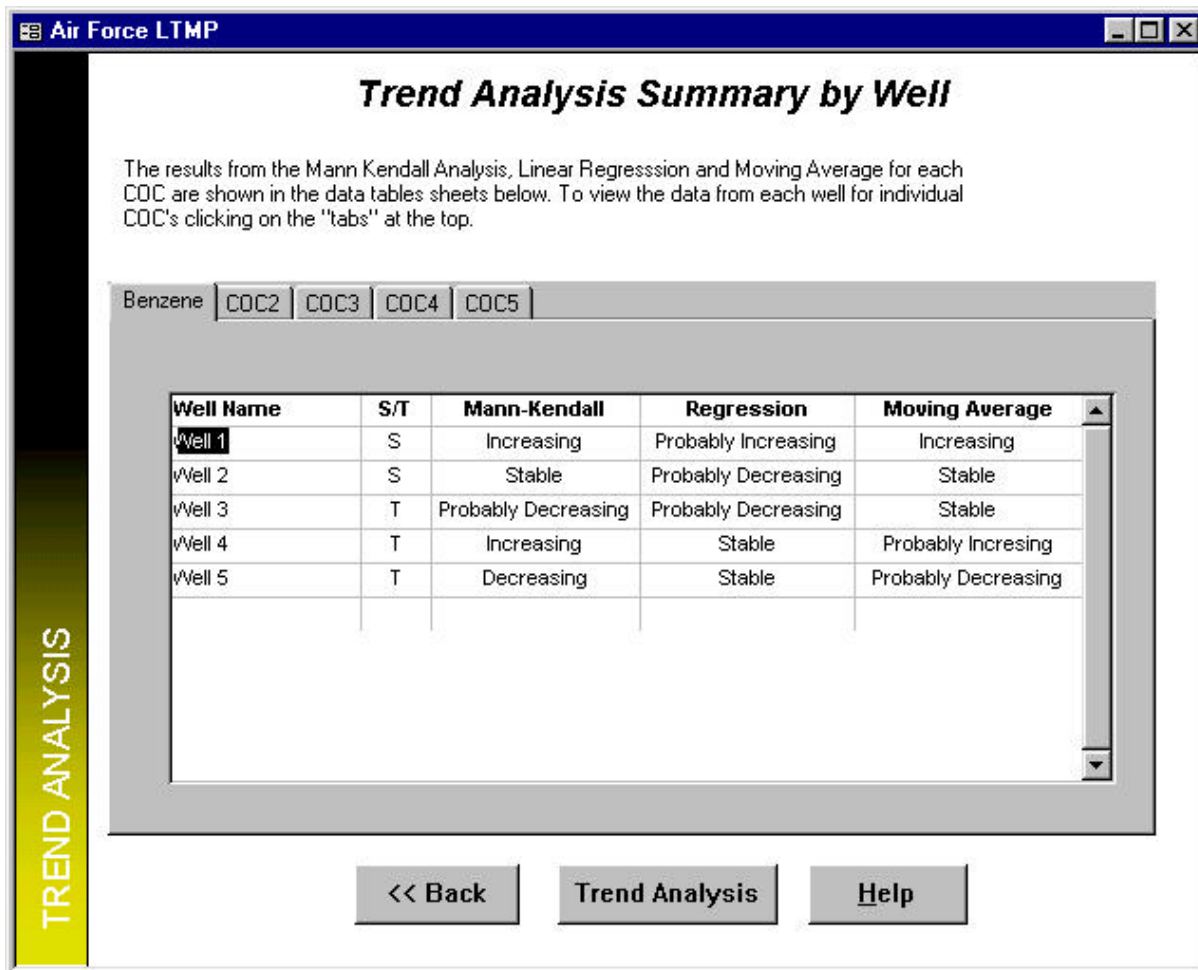the Mann-Kendall Statistics Package

Figure 3.10
Screen Capture of the AFCEE LTM Decision Support Tool Showing
the Trend Analysis Summary by Well

SECTION 4

CONTINGENCY PLANS

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 technology, 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 USEPA (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 USEPA 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 of 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 (USEPA, 1999):

1) Contaminant concentrations in soil or groundwater at specified locations exhibit an increasing trend not originally predicted during remedy selection;

2) Near-source wells exhibit large concentration increases indicative of a new or renewed release;

3) Contaminants are identified in monitoring wells located outside of the original plume boundary;

4) Contaminant concentrations are not decreasing at a sufficiently rapid rate to meet the remediation objectives; and

5) Changes in land and/or groundwater use will reduce the protectiveness of the monitored natural attenuation remedy.

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 concentration(s) at a well(s), which may set off a trigger, might not be a true indication of a change in trend. Trends in contaminant concentrations can be analyzed using the statistical techniques described in Section 3.

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 timeframes 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 intrinsic bioremediation. Table 4.1 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 groundwater to the point that reductive dechlorination can no longer occur and the natural treatment system is destroyed. A groundwater pump-and-treat system can have the same effect by drawing oxygen-rich groundwater 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.

Table 4.1
Interactions Between Active Remediation Technologies and Natural Attenuation
(From Wiedemeier and Chapelle, 1998)

Technology	Possible Benefits		Possible Detriments	
	Petroleum Hydrocarbons	Chlorinated Solvents	Petroleum Hydrocarbons	Chlorinated Solvents
Bioslurping	Source removal, volatilization, enhanced oxygen delivery/aerobic biodegradation	Source removal, volatilization, enhanced oxidation of dichloroethene (DCE) and vinyl chloride (VC), possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Pump and Treat	Plume containment, enhanced oxygen delivery/aerobic biodegradation	Plume containment, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Air Sparging	Volatilization, enhanced oxygen delivery/aerobic biodegradation	Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Soil Vapor Extraction (SVE)/Bioventing	Source reduction, particularly benzene, toluene, ethylbenzene, and xylenes (BTEX)	SVE reduces source in unsaturated zone	None	Air injection can spread non-degradable volatiles
In-Well Circulation/Stripping	Volatilization, enhanced oxygen delivery/aerobic biodegradation	Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination

Table 4.1 (Continued)
Interactions Between Active Remediation Technologies and Natural Attenuation

Technology	Possible Benefits		Possible Detriments	
	Petroleum Hydrocarbons	**Chlorinated Solvents**	**Petroleum Hydrocarbons**	**Chlorinated Solvents**
Landfill Caps	Source containment/ isolation	Source containment/ isolation, reduced oxygen delivery through elimination of recharge/stimulation of reductive dechlorination	Reduced oxygen delivery/aerobic biodegradation	Decreased oxidation of DCE and VC, decreased aerobic cometabolism
Phytoremediation	Plant-specific transpiration/enzymatically mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment	Plant-specific transpiration/enzymatically mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment	None	Unknown
Excavation/Backfilling	Source removal, enhanced oxygen delivery/aerobic biodegradation	Source removal, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Chemical Oxidation (e.g., Fenton's Reagent, potassium permanganate, etc.)	Enhanced oxidation	Enhanced oxidation	None	Enhanced oxygen delivery/decreased reductive dechlorination through oxidation and removal of fermentable carbon substrates. Lowered pH possibly inhibits microbial activity

Table 4.1 (Concluded)
Interactions Between Active Remediation Technologies and Natural Attenuation

Technology	Possible Benefits		Possible Detriments	
	Petroleum Hydrocarbons	**Chlorinated Solvents**	**Petroleum Hydrocarbons**	**Chlorinated Solvents**
Chemical Reduction (e.g., sodium dithionate)	Unknown	Scavenges inorganic electron acceptors/enhanced reductive dechlorination	Scavenges inorganic electron acceptors/decreased oxidation	Decreased oxidation of DCE and VC, decreased aerobic cometabolism
Oxygen-Releasing Materials	Enhanced oxygen delivery/aerobic biodegradation	Enhanced oxidation of DCE and VC	None	Decreased reductive dechlorination through oxidation and removal of fermentable carbon substrates.
Carbon Substrate Addition	None	Stimulation of reductive dechlorination	Competing carbon source	Decreased oxidation of DCE and VC, decreased aerobic cometabolism at injection point
Zero-Valent-Iron Barrier Walls	Unknown	Enhanced reductive dechlorination	Unknown	None
Biological Barrier Walls	Unknown	Enhanced reductive dechlorination	Unknown	None

SECTION 5

EXIT STRATEGIES

As with any remedial option for sites contaminated with organic compounds, remediation goals should be established early in the negotiation process. This will help establish a purpose for long-term monitoring and should help define the length of time that monitoring will be required. Monitoring should continue until the data gathered show that remedial goals have been met and adequately support a decision for closure of the site or implementation of another remedial solution. Continuing a monitoring program after the data being gathered cease to be useful is counterproductive and should be avoided. In many cases, removal of NAPL can dramatically reduce the amount of time required to meet remediation goals, and thus the length of time required for long-term monitoring.

According to the USEPA (1999), 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. Typically, monitoring is continued for a specified period (e.g., one to three years) after remediation objectives have been achieved to ensure that concentration levels are stable and remain below target levels.

SECTION 6

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