

Revision 0

03/08/99

TECHNICAL PROTOCOL FOR IMPLEMENTING INTRINSIC
REMEDATION WITH LONG-TERM MONITORING FOR
NATURAL ATTENUATION OF FUEL CONTAMINATION
DISSOLVED IN GROUNDWATER

VOLUME I

by

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*This United States Air Force guidance was developed in cooperation with United States Environmental Protection Agency (USEPA) researchers but was not issued by the USEPA and does not represent USEPA guidance.

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ADMIN RECORD

SW-A-005904

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ACKNOWLEDGMENTS

The authors would like to thank Mr. Doug Downey, Dr. Robert Edwards, Dr. Robert Taylor, Dr. Guy Sewell, Dr. Mary Randolph, Mr. Randall Ross, Dr. Hanadi Rifai, and Ms. E. Kinzie Gordon for their extensive and helpful reviews of this manuscript. Dr. Robert Edwards for his contributions to the analytical protocol presented in Table 2.1. Mr. Matt Swanson for his contribution to the sections on modeling. Kyle Cannon, R. Todd Herrington, Jeff Black, Dave Moutoux, Bill Crawford, Peter Guest, Leigh Benson, Mark Vesseley, Jeff Fetkenhour, John Hicks, Steve Ratzlaff, Michael Phelps, Don Malone, Tom Richardson, Saskia Hoffer, and Haiyan Liu for their efforts at making this project a success!

SECTION 1

INTRODUCTION

The intent of this document is to present a technical protocol for data collection and analysis in support of intrinsic remediation with long-term monitoring (LTM) for restoration of groundwater contaminated with fuel hydrocarbons. Specifically, this protocol is designed to evaluate the fate in groundwater of fuel hydrocarbons that have regulatory standards. Intrinsic remediation is an innovative remedial approach that relies on natural attenuation to remediate contaminants in the subsurface. In many cases, the use of this protocol should allow the proponent of intrinsic remediation to show that natural degradation processes will reduce the concentrations of these contaminants to below regulatory standards before potential receptor exposure pathways are completed. The evaluation should include consideration of existing exposure pathways, as well as exposure pathways arising from potential future use of the groundwater.

Based on experience at over 40 Air Force sites, the cost to fully implement this protocol ranges from \$100,000 to \$175,000, depending on site conditions. This cost includes site characterization (with monitoring well installation), chemical analyses, numerical modeling, report preparation including comparative analysis of remedial options, and regulatory negotiations. The additional chemical analyses required to implement this protocol typically increase analytical costs by 10 to 15 percent over the analytical costs of a conventional remedial investigation. This modest investment has the potential to save significant taxpayer dollars in unnecessary cleanup activity.

The intended audience for this document is United States Air Force personnel and their contractors, scientists, consultants, regulatory personnel, and others charged with remediating groundwater contaminated with fuel hydrocarbons. This protocol is intended to be used within the established regulatory framework. It is not the intent of this document to prescribe a course of action, including site characterization, in support of all possible remedial technologies. Instead, this protocol is another tool, similar to the Air Force Center for Environmental Excellence (AFCEE) - Technology Transfer Division bioventing (Hinchee *et al.*, 1992) or bioslurping (Battelle, 1995) protocols that allows practitioners to adequately evaluate these alternatives in

subsequent feasibility studies. This protocol is not intended to support intrinsic remediation of chlorinated solvent plumes, plumes that are mixtures of fuels and solvents, or groundwater contaminated with metals. It is not the intent of this document to replace existing United States Environmental Protection Agency (USEPA) or state-specific guidance on conducting remedial investigations.

The AFCEE Remediation Matrix - Hierarchy of Preferred Alternatives has identified intrinsic remediation as the first option to be evaluated for Air Force sites. This matrix implies only that intrinsic remediation should be evaluated prior to proceeding (if necessary) to more costly solutions (e.g., pump and treat), not that intrinsic remediation be selected "presumptively" in every case. The USEPA has not identified intrinsic remediation as a presumptive remedy at the time of this writing (September 1995).

Fuels are released into the subsurface as oily-phase liquids that are less dense than water. As oils, they are commonly referred to as "light nonaqueous-phase liquids," or LNAPLs. The greatest mass of contaminant hydrocarbons are associated with these LNAPL source areas, not with groundwater. For typical spills, 90% of the benzene, 99% of the benzene, toluene, ethylbenzene, and xylenes (BTEX), and 99.9% of total petroleum hydrocarbons (TPH) is associated with the oily-phase hydrocarbons (Kennedy and Hutchins, 1992). As groundwater moves through the LNAPL source areas, soluble components partition into the moving groundwater to generate the plume of dissolved contamination. After further releases have been stopped, these LNAPL source areas tend to slowly weather away as the soluble components, such as BTEX, are depleted. In cases where mobile LNAPL removal is feasible, it is desirable to remove product and decrease the time required for complete remediation of the site. However, at many sites mobile LNAPL removal is not feasible with available technology. In fact, the quantity of LNAPL recovered by commonly used recovery techniques is a trivial fraction of the total LNAPL available to contaminate groundwater. Frequently less than 10% of the total LNAPL mass in a spill can be recovered by mobile LNAPL recovery (Battelle, 1995). At 10 Air Force sites with LNAPL that were evaluated following a draft version of the intrinsic remediation protocol, historical data on groundwater quality are available. The concentration, and total mass, of contaminants in groundwater declined over time at these sites even though mobile LNAPL removal was not successful.

Advantages of intrinsic remediation over conventional engineered remediation technologies include: 1) during intrinsic remediation, contaminants are ultimately transformed to innocuous

byproducts (e.g., carbon dioxide and water), not just transferred to another phase or location within the environment; 2) intrinsic remediation is nonintrusive and allows continuing use of infrastructure during remediation; 3) engineered remedial technologies can pose greater risk to potential receptors than intrinsic remediation because contaminants may be transferred into the atmosphere during remediation activities; 4) intrinsic remediation is less costly than currently available remedial technologies such as pump and treat; 5) intrinsic remediation is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime); and 6) those fuel compounds that are the most mobile and toxic are generally the most susceptible to biodegradation.

Limitations of intrinsic remediation include: 1) intrinsic remediation is subject to natural and institutionally induced changes in local hydrogeologic conditions, including changes in groundwater gradients/velocity, pH, electron acceptor concentrations, or potential future releases; 2) aquifer heterogeneity may complicate site characterization, as it will with any remedial technology; and 3) time frames for completion may be relatively long.

This document describes those processes that bring about intrinsic remediation, the site characterization activities that may be performed to support the intrinsic remediation option, intrinsic remediation modeling using analytical or numerical solute fate and transport models, and the post-modeling activities that should be completed to ensure successful support and verification of intrinsic remediation. The objective of the work described herein is to support intrinsic remediation at sites where naturally occurring subsurface attenuation processes are capable of reducing dissolved fuel hydrocarbon concentrations to acceptable levels. A recent comment made by a member of the regulatory community summarizes what is required to successfully implement intrinsic remediation:

A regulator looks for the data necessary to determine that a proposed treatment technology, if properly installed and operated, will reduce the contaminant concentrations in the soil and water to legally mandated limits. In this sense the use of biological treatment systems calls for the same level of investigation, demonstration of effectiveness, and monitoring as any conventional [remediation] system (National Research Council, 1993).

To support implementation of intrinsic remediation, the property owner must scientifically demonstrate that degradation of site contaminants is occurring at rates sufficient to be protective of human health and the environment. Three lines of evidence can be used to support intrinsic remediation including:

- 1) Documented loss of contaminants at the field scale,
- 2) Contaminant and geochemical analytical data, and
- 3) Direct microbiological evidence.

The first line of evidence involves using statistically significant historical trends in contaminant concentration or measured concentrations of biologically recalcitrant tracers found in fuels in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in the total mass of contaminants is occurring at the site. The second line of evidence involves the use of chemical analytical data in mass balance calculations to show that decreases in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic byproduct concentrations. This evidence can be used to show that electron acceptor concentrations in groundwater are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models can be used to aid mass balance calculations and to collate information on degradation. The third line of evidence, direct microbiological evidence, can be used to show that indigenous biota are capable of degrading site contaminants.

This document presents a technical course of action that allows converging lines of evidence to be used to scientifically document the occurrence, and to quantify rates, of intrinsic remediation. Ideally, the first two lines of evidence listed above should be used in the intrinsic remediation demonstration. To further document intrinsic remediation, direct microbiological evidence can be used. Such a "weight-of-evidence" approach will greatly increase the likelihood of successfully implementing intrinsic remediation at sites where natural processes are restoring the environmental quality of groundwater contaminated with fuel hydrocarbons.

Collection of an adequate database during the iterative site characterization process is an important step in the documentation of intrinsic remediation. Site characterization should provide data on the location and extent of contaminant sources. Contaminant sources generally consist of nonaqueous-phase liquid (NAPL) hydrocarbons present as mobile NAPL (NAPL occurring at sufficiently high saturations to drain under the influence of gravity into a well) and residual NAPL (NAPL occurring at immobile residual saturations that are unable to drain into a well by gravity).

Site characterization also should provide information on the location, extent, and concentrations of dissolved contamination; groundwater geochemical data; geologic information on the type and distribution of subsurface materials; and hydrogeologic parameters such as hydraulic conductivity, hydraulic gradients, and potential contaminant migration pathways to human or ecological receptors. Methodologies for determining these parameters are discussed in Appendix A.

Intrinsic remediation results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization. Appendix B discusses both destructive and nondestructive processes.

The data collected during site characterization can be used to simulate the fate and transport of contaminants in the subsurface. Such simulation allows prediction of the future extent and concentration of the dissolved plume. Several models can be used to simulate dissolved contaminant transport and attenuation. The intrinsic remediation modeling effort has three primary objectives: 1) to predict the future extent and concentrations of a dissolved contaminant plume by simulating the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory levels intended to be protective of human health and the environment; and 3) to provide technical support for the intrinsic remediation option at post-modeling regulatory negotiations. Appendix C discusses data interpretation and pre-modeling calculations. The use of solute fate and transport models is discussed in Appendix D.

Upon completion of the fate and transport modeling effort, model predictions can be used in an exposure pathways analysis. If intrinsic remediation is sufficiently active to mitigate risks to potential receptors, the proponent of intrinsic remediation has a reasonable basis for negotiating this option with regulators. The exposure pathways analysis allows the proponent to show that potential exposure pathways to receptors will not be completed.

Intrinsic remediation is achieved when naturally occurring attenuation mechanisms, such as biodegradation (aerobic and anaerobic), bring about a reduction in the total mass of a contaminant dissolved in groundwater. In most cases, intrinsic remediation will reduce dissolved contaminant concentrations to below regulatory standards such as maximum contaminant levels (MCLs) before the contaminant plume reaches potential receptors. To date (September 1995), this

protocol has been fully or partially implemented at 40 Air Force sites at Hill Air Force Base (AFB), UT; Eglin AFB, FL; Patrick AFB, FL; Dover AFB, DE; Plattsburgh AFB, NY; Elmendorf AFB (two sites), AK; Bolling AFB, D.C.; Madison Air National Guard Base (ANGB), WI; Battle Creek ANGB, MI; King Salmon AFB (two sites), AK; Eaker AFB, AR, Wurtsmith AFB (four sites), MI; Beale AFB, CA; Pope AFB, NC; Fairchild AFB (two sites), WA; Griffis AFB, NY; Langley AFB, VA; MacDill AFB (three sites), FL; Myrtle Beach AFB (two sites), SC; Offutt AFB (two sites), NE; Rickenbacker AFB, OH; Seymour Johnson AFB, NC; Travis AFB, CA; Westover AFRB (two sites), MA; Grissom AFB, IN; Tyndall AFB, FL; Carswell AFB, TX; Ellsworth AFB, SD; and Kessler AFB, MS. In 28 out of 30 Air Force sites that have been fully evaluated using this protocol (Parsons ES, 1994a through 1994d; Parsons ES 1995a through 1995q; Wiedemeier *et al.*, 1995c), intrinsic remediation is expected to reduce concentrations of contaminants to levels below regulatory standards prior to reaching potential receptors, and only two of the 30 plumes have crossed or are projected to cross Air Force boundaries. At the 20 sites where historical data are available, contaminant concentrations and mass have declined over time.

The material presented herein was prepared through the joint effort of the AFCEE Technology Transfer Division; the Bioremediation Research Team at USEPA's National Risk Management Research Laboratory in Ada, Oklahoma (NRMRL), Subsurface Protection and Remediation Division; and Parsons Engineering Science, Inc. (Parsons ES) to facilitate implementation of intrinsic remediation at fuel-hydrocarbon-contaminated sites owned by the United States Air Force and other United States Department of Defense agencies, the United States Department of Energy, and public interests. This document contains three sections, including this introduction, and six appendices. Section 2 presents the protocol to be used to obtain scientific data to support the intrinsic remediation option. Section 3 presents the references used in preparing this document. Appendix A describes the collection of site characterization data necessary to support intrinsic remediation, and provides soil and groundwater sampling procedures and analytical protocols. Appendix B provides an in-depth discussion of the destructive and nondestructive mechanisms of intrinsic remediation. Appendix C covers data interpretation and pre-modeling calculations. Appendix D describes solute fate and transport modeling in support of intrinsic remediation. Appendix D also describes the post-modeling monitoring and verification process. Appendices E and F present case studies of site investigations and modeling efforts that were conducted in support of intrinsic remediation using the methods described in this document.

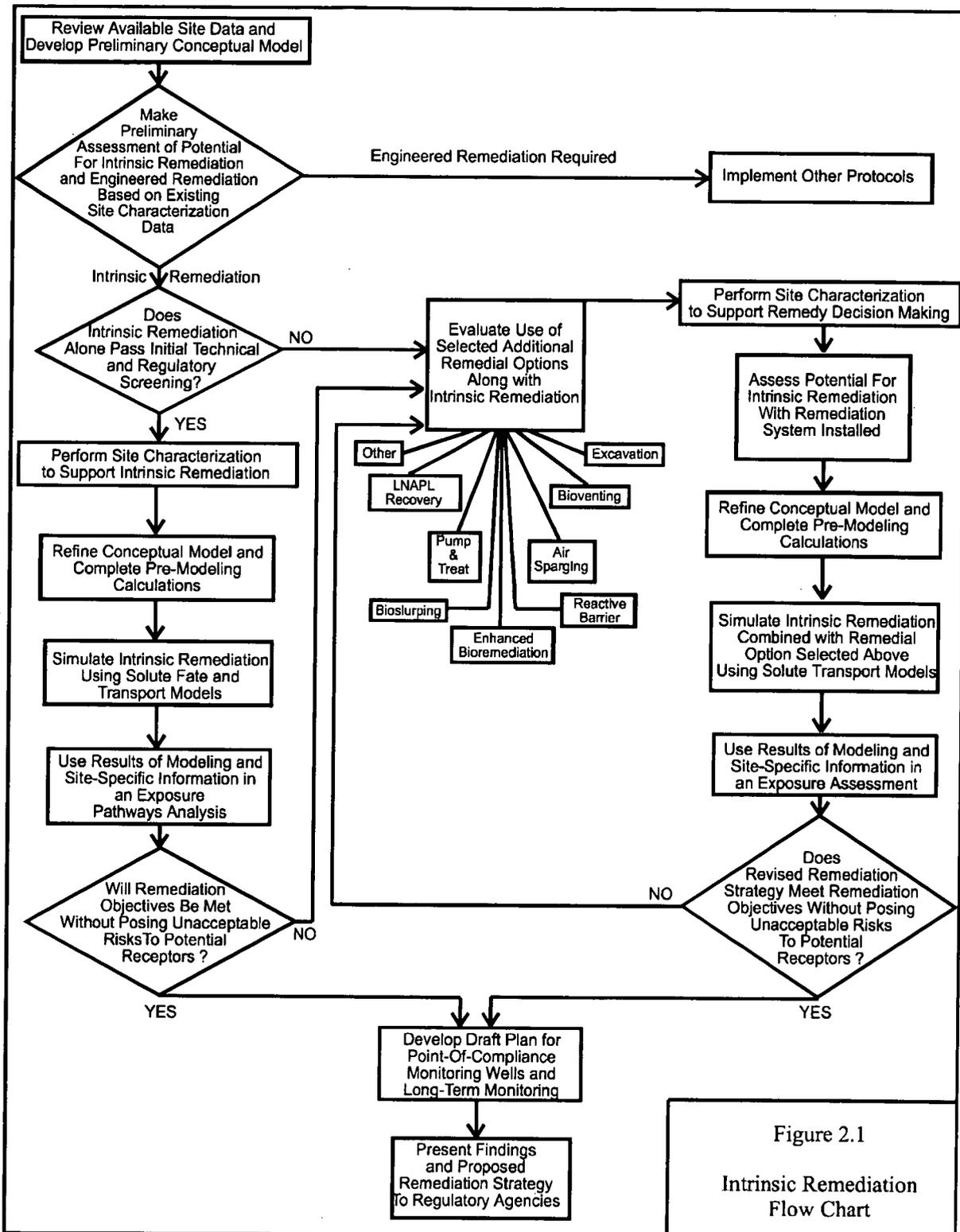
SECTION 2

PROTOCOL FOR IMPLEMENTING INTRINSIC REMEDIATION

The primary objective of the intrinsic remediation investigation is to show that natural processes of contaminant degradation will reduce contaminant concentrations in groundwater to below regulatory standards before potential receptor exposure pathways are completed. Further, intrinsic remediation should be evaluated to determine if it can meet all appropriate federal and state remediation objectives for a given site. This requires that a projection of the potential extent and concentration of the contaminant plume in time and space be made. This projection should be based on historic variations in, and the current extent and concentrations of, the contaminant plume, as well as the measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent of intrinsic remediation to provide sufficient evidence to demonstrate that the mechanisms of intrinsic remediation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of conservative input parameters and numerous sensitivity analyses so that consideration is given to all plausible contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently supports the natural reduction and removal of the dissolved contaminant plume.

This section describes the steps that should be taken to gather the site-specific data necessary to predict the future extent of a contaminant plume and to successfully support the intrinsic remediation option. The flow chart presented in Figure 2.1 presents the information that must be developed and the important regulatory decision points in the process of implementing intrinsic remediation.

Predicting the future extent of a contaminant plume requires the quantification of groundwater flow and solute transport and transformation processes, including rates of natural attenuation. Quantification of contaminant migration and attenuation rates, and successful implementation



of the intrinsic remediation option, require completion of the following steps, each of which is outlined in Figure 2.1 and discussed in the following sections:

- 1) Review available site data;
- 2) Develop preliminary conceptual model and assess potential for intrinsic remediation;
- 3) If intrinsic remediation is selected as potentially appropriate, perform site characterization in support of intrinsic remediation;
- 4) Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of intrinsic remediation;
- 5) Simulate intrinsic remediation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term, as necessary;
- 6) Conduct an exposure pathways analysis;
- 7) If intrinsic remediation alone is acceptable, prepare LTM plan; and
- 8) Present findings to regulatory agencies and obtain approval for the intrinsic remediation with LTM option.

2.1 REVIEW AVAILABLE SITE DATA

The first step in the intrinsic remediation investigation is to review available site-specific data to determine if intrinsic remediation is a viable remedial option. A thorough review of these data also allows development of a preliminary conceptual model. The preliminary conceptual model will help identify any shortcomings in the data and will allow placement of additional data collection points in the most scientifically advantageous and cost-effective manner possible.

When available, information to be obtained during data review includes:

- Nature, extent, and magnitude of contamination:
 - Nature and history of the contaminant release:
 - Catastrophic or gradual release of LNAPL ?
 - More than one source area possible or present ?
 - Divergent or coalescing plumes ?
 - Three-dimensional distribution of mobile and residual LNAPL and dissolved contaminants. The distribution of mobile and residual LNAPL will be used to define the dissolved plume source area.
 - Groundwater and soil chemical data.
 - Historical water quality data showing variations in contaminant concentrations through time.

- Chemical and physical characteristics of the contaminants.
- Potential for biodegradation of the contaminants.
- Geologic and hydrogeologic data (in three dimensions, if feasible):
 - Lithology and stratigraphic relationships.
 - Grain-size distribution (sand vs. silt vs. clay).
 - Aquifer hydraulic conductivity.
 - Groundwater flow gradients and potentiometric or water table surface maps (over several seasons, if possible).
 - Preferential flow paths.
 - Interactions between groundwater and surface water and rates of infiltration/recharge.
- Locations of potential receptors:
 - Groundwater wells.
 - Downgradient and crossgradient groundwater discharge points.

In some cases, few or no site-specific data are available. If this is the case, and if it can be shown that intrinsic remediation is a potential remedial option (Section 2.2), all future site characterization activities should include collecting the data necessary to support this remedial alternative. The additional costs incurred by such an investigation are greatly outweighed by the cost savings that will be realized if intrinsic remediation is selected. Even if not selected, most of the data collected in support of intrinsic remediation can be used to design and support other remedial measures.

2.2 DEVELOP PRELIMINARY CONCEPTUAL MODEL AND ASSESS POTENTIAL FOR INTRINSIC REMEDIATION

After reviewing existing site characterization data, a conceptual model should be developed, and a preliminary assessment of the potential for intrinsic remediation should be made. The conceptual model is a three-dimensional representation of the groundwater flow and solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data for the site. This type of conceptual model differs from the conceptual site models commonly used by risk assessors that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. However, the groundwater system conceptual model facilitates identification of these risk-assessment elements for the exposure pathways analysis. After development, the conceptual

model can be used to help determine optimal placement of additional data collection points as necessary to aid in the intrinsic remediation investigation and to develop the solute fate and transport model. Contracting and management controls must be flexible enough to allow for the potential for revisions to the conceptual model and thus the data collection effort.

Successful conceptual model development involves:

- Definition of the problem to be solved (generally the unknown nature and extent of existing and future contamination).
- Integration and presentation of available data, including:
 - Local geologic and topographic maps,
 - Geologic data,
 - Hydraulic data,
 - Biological data,
 - Geochemical data, and
 - Contaminant concentration and distribution data.
- Determination of additional data requirements, including:
 - Borehole locations and monitoring well spacing,
 - An approved sampling and analysis plan, and
 - Any data requirements listed in Section 2.1 that have not been adequately addressed.

After conceptual model development, an assessment of the potential for intrinsic remediation must be made. As stated previously, existing data can be useful in determining if intrinsic remediation will be sufficient to prevent a dissolved contaminant plume from completing exposure pathways, or from reaching a predetermined point of compliance (POC), in concentrations above applicable regulatory standards. Determining the likelihood of exposure pathway completion is an important component of the intrinsic remediation investigation. This is achieved by estimating the migration and future extent of the plume based on contaminant properties, including biodegradability, aquifer properties, groundwater velocity, and the location of the plume and contaminant source relative to potential receptors (i.e., the distance between the leading edge of the plume and the potential receptors). Appendix B discusses the biodegradability of BTEX under laboratory conditions and in the field.

If intrinsic remediation is determined to be a significant factor in contaminant reduction, site characterization activities in support of this remedial option should be performed. If exposure pathways have already been completed and contaminant concentrations exceed regulatory levels, or if such completion is likely, other remedial measures should be considered. Even so, the collection of data in support of the intrinsic remediation option can be integrated into a comprehensive remedial plan and may help reduce the cost and duration of other remedial measures such as intensive source removal operations or pump-and-treat technologies.

2.3 PERFORM SITE CHARACTERIZATION IN SUPPORT OF INTRINSIC REMEDIATION

Detailed site characterization is necessary to document the potential for intrinsic remediation. As discussed in Section 2.1, review of existing site characterization data is particularly useful before initiating site characterization activities. Such review should allow identification of data gaps and guide the most effective placement of additional data collection points.

There are two goals during the site characterization phase of the intrinsic remediation investigation. The first is to collect the data needed determine if natural mechanisms of contaminant attenuation are occurring at rates sufficient to protect human health and the environment. The second is to provide sufficient site-specific data to allow prediction of the future extent and concentration of a contaminant plume through solute fate and transport modeling. Because the burden of proof for intrinsic remediation is on the proponent, very detailed site characterization is required to achieve these goals and to support this remedial option. Adequate site characterization in support of intrinsic remediation requires that the following site-specific parameters be determined:

- Extent and type of soil and groundwater contamination.
- Location and extent of contaminant source area(s) (i.e., areas containing mobile or residual NAPL).
- The potential for a continuing source due to leaking tanks or pipelines.
- Aquifer geochemical parameters.
- Regional hydrogeology, including:
 - Drinking water aquifers, and
 - Regional confining units.

- Local and site-specific hydrogeology, including:
 - Local drinking water aquifers.
 - Location of industrial, agricultural, and domestic water wells.
 - Patterns of aquifer use (current and future).
 - Lithology.
 - Site stratigraphy, including identification of transmissive and nontransmissive units.
 - Grain-size distribution (sand vs. silt vs. clay).
 - Aquifer hydraulic conductivity.
 - Groundwater hydraulic information.
 - Preferential flow paths.
 - Locations and types of surface water bodies.
 - Areas of local groundwater recharge and discharge.
- Identification of potential exposure pathways and receptors.

The following sections describe the methodologies that should be implemented to allow successful site characterization in support of intrinsic remediation.

2.3.1 Soil Characterization

In order to adequately define the subsurface hydrogeologic system and to determine the amount and three-dimensional distribution of mobile and residual NAPL that can act as a continuing source of groundwater contamination, extensive soil characterization must be completed. Depending on the status of the site, this work may already have been completed during previous remedial investigation work. The results of soils characterization will be used as input into a solute fate and transport model to help define a contaminant source term and to support the intrinsic remediation investigation.

2.3.1.1 Soil Sampling

The purpose of soil sampling is to determine the subsurface distribution of hydrostratigraphic units and the distribution of mobile and residual NAPL. These objectives can be achieved through the use of conventional soil borings or direct-push methods (e.g., Geoprobe[®] or cone penetrometer testing). All soil samples should be collected, described, analyzed, and disposed of in accordance with local, state, and federal guidance. Appendix A contains suggested procedures

for soil sample collection. These procedures may require modification to comply with local, state, and federal regulations.

2.3.1.2 Soil Analytical Protocol

The analytical protocol to be used for soil sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and biodegradation (aerobic and anaerobic) of fuel hydrocarbons. Each analyte is discussed separately below.

2.3.1.2.1 *Total Volatile and Extractable Hydrocarbons*

Knowledge of the location, distribution, concentration, and total mass of TPH sorbed to soils or present as mobile NAPL is required to calculate contaminant partitioning from these phases into groundwater. The presence or absence of TPH also is used to define the edge of the NAPL plume. One of the greatest areas of uncertainty remaining in the conventional remedial investigation process is delineation of NAPL in the subsurface. Knowledge of the location of the leading edge of the NAPL plume is important in proper model implementation because it defines the extent of the contaminant source area.

2.3.1.2.2 *Aromatic Hydrocarbons*

Knowledge of the location, distribution, concentration, and total mass of fuel-derived hydrocarbons of regulatory concern (especially BTEX) sorbed to soils or present as mobile NAPL is required to calculate contaminant partitioning from mobile and residual NAPL into groundwater.

2.3.1.2.3 *Total Organic Carbon*

Knowledge of the total organic carbon (TOC) content of the aquifer matrix is important in sorption and solute-retardation calculations. TOC samples should be collected from a background location in the zone(s) where most contaminant transport is expected to occur.

Table 2.1 Soil and Groundwater Analytical Protocol*

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Soil	Total volatile and extractable hydrocarbons.	Gas chromatography (GC) method SW8015 [modified]	Handbook method; reference is the California LUFT manual	Data are used to determine the extent of soil contamination, the contaminant mass present, and the need for source removal	Each soil sampling round	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Soil	Aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX]; trimethylbenzene isomers)	Purge and trap GC method SW8020	Handbook method modified for field extraction of soil using methanol	Data is used to determine the extent of soil contamination, the contaminant mass present, and the need for source removal	Each soil sampling round	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Soil	Total organic carbon (TOC)	SW9060 modified for soil samples	Procedure must be accurate over the range of 0.5–15 percent TOC	The rate of migration of petroleum contaminants in groundwater is dependent upon the amount of TOC in the aquifer matrix.	At initial sampling	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Soil	Moisture	ASTM D-2216	Handbook method	Data are used to correct soil sample analytical results for moisture content (e.g., report results on a dry weight basis)	Each soil sampling round	Use a portion of soil sample collected for another analysis	Fixed-base

Table 2.1. (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Total hydrocarbons, volatile and extractable	GC method SW8015 [modified]	Handbook method; reference is the California LUFT manual	Data used to monitor the reduction in concentrations of total fuel hydrocarbons (in addition to BTEX) due to natural attenuation; data also used to infer presence of an emulsion or surface layer of petroleum in water sample, as a result of sampling	One time per year or as required by regulations	Volatile hydrocarbons—collect water samples in a 40 mL VOA vial; cool to 4°C; add HCl to pH 2 Extractable hydrocarbons—collect 1 L of water in a glass container; cool to 4°C; add HCl to pH 2	Fixed-base
Water	Aromatic hydrocarbons (BTEX, trimethylbenzene isomers)	Purge and trap GC method SW8020	Handbook method; analysis may be extended to higher molecular weight alkyl benzenes	Method of analysis for BTEX, which are the primary target analytes for monitoring natural attenuation; BTEX concentrations must also be measured for regulatory compliance; method can be extended to higher molecular weight alkyl benzenes; trimethylbenzenes are used to monitor plume dilution if degradation is primarily anaerobic.	Each sampling round	Collect water samples in a 40 mL VOA vial; cool to 4°C; add hydrochloric acid to pH 2	Fixed-base
Water	Polycyclic aromatic hydrocarbons (PAHs) (optional)	GC/mass spectroscopy method SW8270; high-performance liquid chromatography method SW8310	Analysis needed only when required for regulatory compliance.	PAHs are components of fuel and are typically analyzed for regulatory compliance; data on their concentrations are not used currently in the evaluation of natural attenuation	As required by regulations	Collect 1 L of water in a glass container; cool to 4°C	Fixed-base

Table 2.1. (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Oxygen	Dissolved oxygen meter	Refer to method A4500 for a comparable laboratory procedure.	The oxygen concentration is a data input to the Bioplume model; concentrations less than 1 mg/L generally indicate an anaerobic pathway	Each sampling round	Measure dissolved oxygen on site using a flow-through cell	Field
Water	Nitrate	IC method E300	Method E300 is a Handbook method.	Substrate for microbial respiration if oxygen is depleted	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; add H ₂ SO ₄ to pH less than 2, cool to 4°C	Fixed-base
Water	Iron (II) (Fe ⁺²)	Colorimetric HACH Method # 8146	Filter if turbid.	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese	Each sampling round	Collect 100 mL of water in a glass container	Field
Water	Sulfate (SO ₄ ⁻²)	IC method E300	Method E300 is a Handbook method, if this method is used for sulfate analysis, do not use the field method.	Substrate for anaerobic microbial respiration	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C	Fixed-base
Water	Sulfate (SO ₄ ⁻²)	HACH method # 8051	Colorimetric, if this method is used for sulfate analysis, do not use the fixed-base laboratory method.	Same as above	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C	Field
Water	Methane, ethane, and ethene	Kampbell <i>et al.</i> , 1989	Method published by researchers at the US Environmental Protection Agency.	The presence of CH ₄ suggests BTEX degradation via methanogenesis. Ethane and ethene data are used where chlorinated solvents are suspected of undergoing biological transformation.	Each sampling round	Collect water samples in 50 mL glass serum bottles with butyl gray/Teflon-lined caps; add H ₂ SO ₄ to pH less than 2, cool to 4°C	Fixed-base

Table 2.1. (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Alkalinity	HACH Alkalinity test kit model AL AP MG-L	Phenolphthalein method	General water quality parameter used (1) as a marker to verify that all site samples are obtained from the same groundwater system and (2) to measure the buffering capacity of groundwater	Each sampling round	Collect 100 mL of water in glass container	Field
Water	Oxidation-reduction potential	A2580B	Measurements made with electrodes; results are displayed on a meter; protect samples from exposure to oxygen. Report results against a silver/silver chloride reference electrode	The redox potential of groundwater influences and is influenced by the nature of the biologically mediated degradation of contaminants; the redox potential of groundwater may range from more than 800 mV to less than -400 mV.	Each sampling round	Collect 100–250 mL of water in a glass container, filling container from bottom; analyze immediately	Field
Water	pH	Field probe with direct reading meter.	Field	Aerobic and anaerobic processes are pH-sensitive	Each sampling round	Collect 100–250 mL of water in a glass or plastic container; analyze immediately	Field
Water	Temperature	Field probe with direct reading meter.	Field only	Well development	Each sampling round	Not Applicable	Field
Water	Conductivity	E120.1/SW9050, direct reading meter	Protocols/Handbook methods	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system	Each sampling round	Collect 100–250 mL of water in a glass or plastic container	Field

Table 2.1. (Concluded)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Chloride	Mercuric nitrate titration A4500-Cl ⁻ C	Ion chromatography (IC) method E300 or method SW9050 may also be used	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system	Each sampling round	Collect 250 mL of water in a glass container	Fixed-base
Water	Chloride (optional, see data use)	HACH Chloride test kit model 8-P	Silver nitrate titration	As above, and to guide selection of additional data points in real time while in the field.	Each sampling round	Collect 100mL of water in a glass container	Field

NOTES:

- * Analyses other than those listed in this table may be required for regulatory compliance.
- 1. "HACH" refers to the Hach Company catalog, 1990.
- 2. "A" refers to *Standard Methods for the Examination of Water and Wastewater*, 18th edition, 1992.
- 3. "E" refers to *Methods for Chemical Analysis of Water and Wastes*, USEPA, 1983.
- 4. "Protocols" refers to the AFCEE *Environmental Chemistry Function Installation Restoration Program Analytical Protocols*, 11 June 1992.
- 5. "Handbook" refers to the AFCEE *Handbook to Support the Installation Restoration Program (IRP) Remedial Investigations and Feasibility Studies (RI/FS)*, September 1993.
- 6. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, USEPA, 3rd edition, 1986.
- 7. "ASTM" refers to the *American Society for Testing and Materials*.
- 8. "LUFT" refers to the State of California *Leaking Underground Fuel Tank Field Manual*, 1988 edition.

2.3.2 Groundwater Characterization

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of intrinsic remediation, groundwater samples must be collected and analyzed. Biodegradation of fuel hydrocarbons brings about measurable changes in the chemistry of groundwater in the affected area. By measuring these changes, the proponent of intrinsic remediation can document and quantitatively evaluate the importance of intrinsic remediation at a site.

2.3.2.1 Groundwater Sampling

Groundwater sampling is conducted to determine the concentration and three-dimensional distribution of contaminants and groundwater geochemical parameters. Groundwater samples may be obtained from monitoring wells or point-source sampling devices such as a Geoprobe®, Hydropunch®, or cone penetrometer. All groundwater samples should be collected in accordance with local, state, and federal guidelines. Appendix A contains suggested procedures for groundwater sample collection. These procedures may have to be modified to comply with local, state, and federal regulations.

2.3.2.2 Groundwater Analytical Protocol

The analytical protocol to be used for groundwater sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and aerobic and anaerobic biodegradation. Data obtained from the analysis of groundwater for these analytes is used to scientifically document intrinsic remediation of fuel hydrocarbons and can be used as input into a solute fate and transport model. The following paragraphs describe each groundwater analytical parameter and the use of each analyte in the intrinsic remediation demonstration.

2.3.2.2.1 *Total Volatile and Extractable Hydrocarbons, Aromatic Hydrocarbons, and Polycyclic Aromatic Hydrocarbons*

These analytes are used to determine the type, concentration, and distribution of fuel hydrocarbons in the aquifer. Of the compounds present in most gasolines and jet fuels, the BTEX compounds generally represent the contaminants of regulatory interest. For this reason, these

compounds are generally of significant interest in the fate and transport analysis, as described below and in the appendices. At a minimum, the aromatic hydrocarbon analysis (Method SW8020) must include BTEX and the trimethylbenzene isomers. The combined dissolved concentrations of BTEX and trimethylbenzenes should not be greater than about 30 milligrams per liter (mg/L) for a JP-4 spill (Smith *et al.*, 1981). If these compounds are found in concentrations greater than 30 mg/L, sampling errors such as emulsification of LNAPL in the groundwater sample likely have occurred and should be investigated. The combined dissolved concentrations of BTEX and trimethylbenzenes should not be greater than about 135 mg/L for a gasoline spill (Cline *et al.*, 1991; American Petroleum Institute, 1985). If these compounds are found in concentrations greater than 135 mg/L, then sampling errors such as emulsification of LNAPL in the groundwater sample have likely occurred and should be investigated.

Polycyclic aromatic hydrocarbons (PAHs) are constituents of fuel that also may be of concern. PAHs should be analyzed only if required for regulatory compliance.

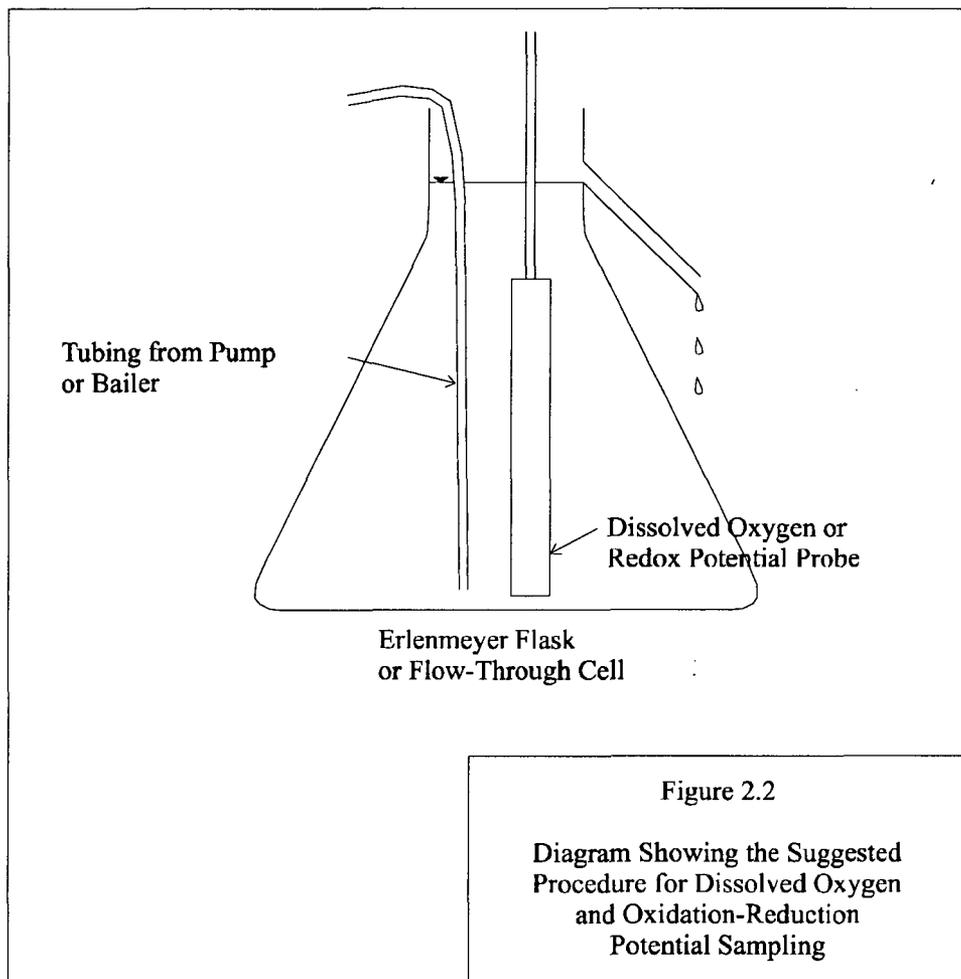
2.3.2.2.2 *Dissolved Oxygen*

Dissolved oxygen is the most thermodynamically favored electron acceptor used in the biodegradation of fuel hydrocarbons. Dissolved oxygen concentrations are used to estimate the mass of contaminant that can be biodegraded by aerobic processes. Each 1.0 mg/L of dissolved oxygen consumed by microbes will destroy approximately 0.32 mg/L of BTEX. During aerobic biodegradation, dissolved oxygen concentrations decrease. Anaerobic bacteria (obligate anaerobes) generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L. The stoichiometry of BTEX biodegradation via aerobic respiration is given in Appendix B.

Dissolved oxygen 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 groundwater samples, it is important to minimize potential aeration by taking the following precautions:

- 1) Use a peristaltic pump to purge the well when possible (depth to groundwater less than approximately 25 feet). To prevent downhole aeration of the sample in wells screened across the water table, well drawdown should not exceed about 5 percent 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 2.2). This will minimize aeration and keep water flowing past the dissolved oxygen probe's sampling membrane. If bubbles are observed in the tubing during purging, the flow rate of the peristaltic pump must be slowed. If bubbles are still apparent, the tubing should be checked for holes and replaced.



- 2) 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 probe beneath the water level in the sampling

container (Figure 2.2). This will minimize aeration and keep water flowing past the dissolved oxygen probe's sampling membrane.

- 3) Downhole dissolved oxygen probes can be used for dissolved oxygen analyses, but such probes must be thoroughly decontaminated between wells. In some cases decontamination procedures can be harmful to the dissolved oxygen probe.

2.3.2.2.3 Nitrate

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation via denitrification. Nitrate concentrations are used to estimate the mass of contaminant that can be biodegraded by denitrification processes. By knowing the volume of contaminated groundwater, the background nitrate concentration, and the concentration of nitrate measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation. Each 1.0 mg/L of ionic nitrate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX. The stoichiometry of BTEX biodegradation via denitrification is given in Appendix B. Example calculations are presented in Appendix C. Nitrate concentrations will be a direct input parameter to the Bioplume III model currently under development by AFCEE.

2.3.2.2.4 Iron (II)

In some cases iron (III) is used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons. During this process, iron (III) is reduced to iron (II), which may be soluble in water. Iron (II) concentrations can thus be used as an indicator of anaerobic degradation of fuel compounds. By knowing the volume of contaminated groundwater, the background iron (II) concentration, and the concentration of iron (II) measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation through iron (III) reduction. The degradation of 1 mg/L of BTEX results in the production of approximately 21.8 mg/L of iron (II) during iron (III) reduction. The stoichiometry of BTEX biodegradation via iron reduction is given in Appendix B. Example calculations are presented in Appendix C. Iron concentrations will be used as a direct input parameter to Bioplume III.

2.3.2.2.5 Sulfate

After dissolved oxygen, nitrate, and bioavailable iron (III) have been depleted in the microbiological treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegradation. This process is termed sulfate reduction and results in the production of sulfide. Sulfate concentrations are used as an indicator of anaerobic degradation of fuel compounds. By knowing the volume of contaminated groundwater, the background sulfate concentration, and the concentration of sulfate measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation through sulfate reduction. Each 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX. The stoichiometry of BTEX biodegradation via sulfate reduction is given in Appendix B. Example calculations are presented in Appendix C. Sulfate concentrations will be used as a direct input parameter for the Bioplume III model.

2.3.2.2.6 Methane

During methanogenesis (an anaerobic biodegradation process), carbon dioxide (or acetate) is used as an electron acceptor, and methane is produced. Methanogenesis generally occurs after oxygen, nitrate, bioavailable iron (III), and sulfate have been depleted in the treatment zone. The presence of methane in groundwater is indicative of strongly reducing conditions. Because methane is not present in fuel, the presence of methane in groundwater above background concentrations in contact with fuels is indicative of microbial degradation of fuel hydrocarbons. Methane concentrations can be used to estimate the amount of BTEX destroyed in an aquifer. By knowing the volume of contaminated groundwater, the background methane concentration, and the concentration of methane measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation via methanogenesis. The degradation of 1 mg/L of BTEX results in the production of approximately 0.78 mg/L of methane during methanogenesis. The stoichiometry of BTEX biodegradation via methanogenesis is given in Appendix B. Example calculations are presented in Appendix C.

2.3.2.2.7 Alkalinity

The total alkalinity of a groundwater system is indicative of a water's capacity to neutralize acid. Alkalinity is defined as *the net concentration of strong base in excess of strong acid with a pure CO₂-water system as the point of reference* (Domenico and Schwartz, 1990). Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of elements such as

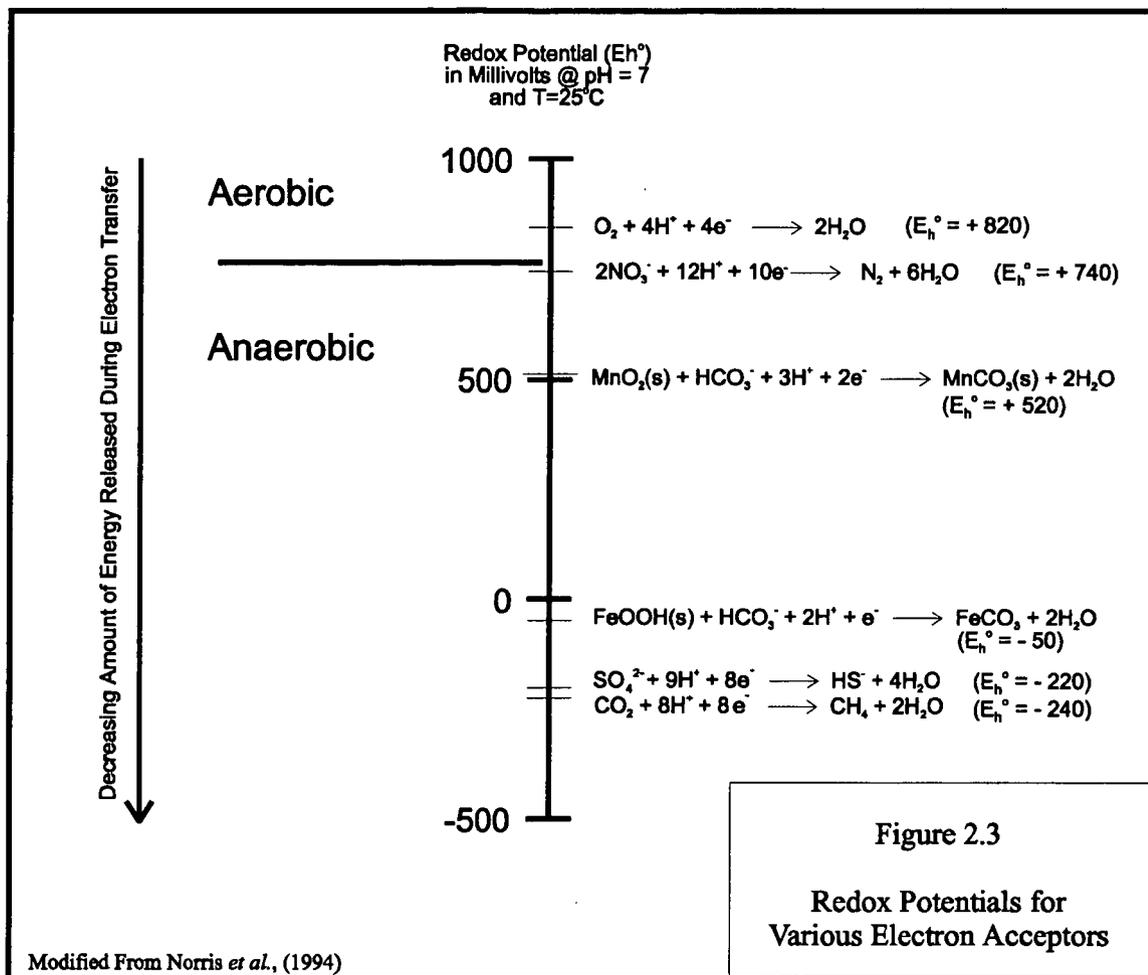
calcium, magnesium, sodium, potassium, or ammonia. These species result from the dissolution of rock (especially carbonate rocks), the transfer of CO₂ from the atmosphere, and respiration of microorganisms. Alkalinity is important in the maintenance of groundwater pH because it buffers the groundwater system against acids generated during both aerobic and anaerobic biodegradation.

In general, areas contaminated by fuel hydrocarbons exhibit a total alkalinity that is higher than that seen in background areas. This is expected because the microbially-mediated reactions causing biodegradation of fuel hydrocarbons cause an increase in the total alkalinity in the system, as discussed in Appendix B. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction, and less pronounced during methanogenesis (Morel and Hering, 1993). In addition, Willey *et al.* (1975) show that short-chain aliphatic acid ions produced during biodegradation of fuel hydrocarbons can contribute to alkalinity in groundwater.

Each 1.0 mg/L of alkalinity produced by microbes results from the destruction of approximately 0.13 mg/L of total BTEX. The stoichiometry of this reaction is given in Appendix B. Example calculations are presented in Appendix C. The production of alkalinity can be used to cross-check calculations of expressed assimilative capacity based on concentrations of electron acceptors.

2.3.2.2.8 Oxidation/Reduction Potential (Eh)

The oxidation/reduction (redox) potential of groundwater (Eh) is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Redox reactions in groundwater contaminated with petroleum hydrocarbons are usually biologically mediated, and therefore, the redox potential of a groundwater system depends upon and influences rates of biodegradation. Knowledge of the redox potential of groundwater also is important because some biological processes operate only within a prescribed range of redox conditions. The redox potential of groundwater generally ranges from -400 millivolts (mV) to 800 mV. Figure 2.3 shows the typical redox conditions for groundwater when different electron acceptors are used.



Redox potential can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Mapping the redox potentials of the groundwater while in the field helps the field scientist to determine the approximate location of the contaminant plume. To map the redox potential of the groundwater while in the field, it is important to have at least one redox measurement (preferably more) from a well located upgradient from the plume. Redox potential 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 groundwater samples (which can affect redox potential measurements), it is important to minimize potential aeration by following the steps outlined in Section 2.3.2.2.2.

2.3.2.2.9 *pH, Temperature, and Conductivity*

Because the pH, temperature, and conductivity of a groundwater sample can change significantly within a short time following sample acquisition, these parameters must be measured in the field in unfiltered, unpreserved, "fresh" water collected by the same technique as the samples taken for dissolved oxygen and redox analyses. 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.

The pH of groundwater has an effect on the presence and activity of microbial populations in groundwater. This is especially true for methanogens. Microbes capable of degrading petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units.

Groundwater temperature directly affects the solubility of oxygen and other geochemical species. The solubility of dissolved oxygen is temperature dependent, being 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-degree Celsius (°C) increase in temperature ("Q"₁₀ rule) over the temperature range between 5 and 25°C. Groundwater temperatures less than about 5°C tend to inhibit biodegradation, and slow rates of biodegradation are generally observed in such waters.

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. Conductivity measurements are used to ensure that groundwater samples collected at a site are representative of the water comprising the saturated zone in which the dissolved contamination is present. If the conductivities of samples taken from different sampling points are radically different, the waters may be from different hydrogeologic zones.

2.3.2.2.10 *Chloride*

Chloride is measured to ensure that groundwater samples collected at a site are representative of the water comprising the saturated zone in which the dissolved contamination is present (i.e., to ensure that all samples are from the same groundwater flow system). If the chloride concentrations of samples taken from different sampling points are radically different, the waters may be from different hydrogeologic zones.

2.3.3 Aquifer Parameter Estimation

2.3.3.1 Hydraulic Conductivity

Hydraulic conductivity is a measure of an aquifer's ability to transmit water, and is perhaps the most important aquifer parameter governing fluid flow in the subsurface. The velocity of groundwater and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential paths for contaminant migration. Estimates of hydraulic conductivity are used to determine residence times for contaminants and tracers, and to determine the seepage velocity of groundwater.

The most common methods used to quantify hydraulic conductivity are aquifer pumping tests and slug tests (Appendix A). Another method that may be used to determine hydraulic conductivity is the borehole dilution test. One drawback to these methods is that they average hydraulic properties over the screened interval. To help alleviate this potential problem, the screened interval of the well should be selected after consideration is given to subsurface stratigraphy. Information about subsurface stratigraphy should come from geologic logs created from continuous cores. An alternate method to delineate zones with high hydraulic conductivity is to use pressure dissipation data from cone penetrometer test logs.

2.3.3.1.1 Pumping Tests

Pumping tests generally give the most reliable information on hydraulic conductivity, but are difficult to conduct in contaminated areas because the water produced during the test generally must be contained and treated. In addition, a minimum 4-inch-diameter well is generally required to complete pumping tests in highly transmissive aquifers because the 2-inch submersible pumps available today are not capable of producing a flow rate large enough for meaningful pumping tests. In areas with fairly uniform aquifer materials, pumping tests can be completed in uncontaminated areas, and the results can be used to estimate hydraulic conductivity in the contaminated area. Pumping tests should be conducted in wells that are screened in the most transmissive zones in the aquifer.

2.3.3.1.2 *Slug Tests*

Slug tests are a commonly used alternative to pumping tests. One commonly cited drawback to slug testing is that this method generally gives hydraulic conductivity information only for the area immediately surrounding the monitoring well. Slug tests do, however, have two distinct advantages over pumping tests: they can be conducted in 2-inch monitoring wells, and they produce no water. If slug tests are going to be relied upon to provide information on the three-dimensional distribution of hydraulic conductivity in an aquifer, multiple slug tests must be performed. It is not advisable to rely on data from one slug test in one monitoring well. Because of this, slug tests should be conducted at several monitoring wells at the site. Like pumping tests, slug tests should be conducted in wells that are narrowly screened in the most transmissive zones in the aquifer.

2.3.3.2 Hydraulic Gradient

The hydraulic gradient is the change in hydraulic head (feet of water) divided by the length of groundwater flow. To accurately determine the hydraulic gradient, it is necessary to measure groundwater levels in all monitoring wells and piezometers at a site. Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific groundwater elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in groundwater flow direction can have a profound influence on contaminant transport. Sites in upland areas are less likely to be affected by seasonal variations in groundwater flow direction than sites situated near surface water bodies such as rivers and lakes.

To determine the effect of seasonal variations in groundwater flow direction on contaminant transport, quarterly groundwater level measurements should be taken over a period of at least 1 year. For many sites, these data may already exist. If hydraulic gradient data over a 1-year period are not available, intrinsic remediation can still be implemented pending an analysis of seasonal variation in groundwater flow direction.

2.3.3.3 Processes Causing an Apparent Reduction in Total Contaminant Mass

Several processes cause a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system. Processes causing an apparent reduction in

contaminant mass include dilution, sorption, and hydrodynamic dispersion. In order to determine the mass of contaminant removed from the system it is necessary to correct observed concentrations for the effects of these processes. This is done by incorporating independent assessments of these processes into the comprehensive solute transport model. The following sections give a brief overview of the processes that result in apparent contaminant reduction. Appendix B describes these processes in detail.

To accurately determine the mass of contaminant transformed to innocuous byproducts, it is important to correct measured BTEX concentrations for those processes that cause an apparent reduction in contaminant mass. This is accomplished by normalizing the measured concentration of each of the BTEX compounds to the concentration of a tracer that is at least as sorptive as BTEX, but that is biologically recalcitrant. Two potential chemicals found in fuel hydrocarbon plumes are trimethylbenzene and tetramethylbenzene (Cozzarelli *et al.*, 1990; Cozzarelli *et al.*, 1994). These compounds are difficult to biologically degrade under anaerobic conditions, and frequently persist in groundwater longer than BTEX. Depending on the composition of the fuel that was released, other tracers are possible. Appendix C (Section C.3.3.4.2.1) contains an example calculation of how to correct for the effects of dilution.

2.3.3.3.1 Dilution

Dilution results in a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system. The two most common causes of dilution are infiltration and monitoring wells screened over large vertical intervals. Infiltration can cause an apparent reduction in contaminant mass by mixing with the contaminant plume, thereby causing dilution. Monitoring wells screened over large vertical distances may dilute groundwater samples by mixing water from clean aquifer zones with contaminated water during sampling. This problem is especially relevant for dissolved BTEX contamination, which may remain near the groundwater table for some distance downgradient from the source. To avoid potential dilution, monitoring wells should be screened over relatively small vertical intervals (less than 5 feet). Nested wells should be used to define the vertical extent of contamination in the saturated zone.

2.3.3.3.2 Sorption (Retardation)

The retardation of organic solutes caused by sorption is an important consideration when simulating intrinsic remediation. Sorption of a contaminant to the aquifer matrix results in an

apparent decrease in contaminant mass because dissolved contamination is removed from the aqueous phase. Dissolved oxygen and other electron acceptors present in the groundwater are not retarded by sorption. Any slowing of the solute relative to the advective transport velocity of the groundwater allows replenishment of electron acceptors into upgradient areas of the plume. The processes of contaminant sorption and retardation are discussed in Appendix B.

2.3.3.3.3 Hydrodynamic Dispersion

The dispersion of organic solutes in an aquifer is another important consideration when simulating intrinsic remediation. The dispersion of a contaminant into relatively pristine portions of the aquifer allows the solute plume to mix with uncontaminated groundwater containing higher concentrations of electron acceptors. Dispersion occurs both downgradient and, more importantly, crossgradient from the direction of groundwater flow.

2.3.4 Optional Confirmation of Biological Activity

Extensive evidence showing that biodegradation of fuel hydrocarbons frequently occurs under natural conditions can be found in the literature. Several of the many available references in support of intrinsic remediation are listed in Section 3 and discussed in Appendix B. The following sections describe three techniques that may be used if it is necessary to show that microorganisms capable of degrading fuel hydrocarbons are present at a site.

2.3.4.1 Field Dehydrogenase Test

The field dehydrogenase test is a qualitative method used to determine if aerobic bacteria are present in an aquifer in quantities capable of biodegrading fuel hydrocarbons. If the test gives a positive result, a sufficient number of microorganisms capable of aerobic metabolism and/or denitrification are present in the aquifer. A negative result for the dehydrogenase test gives no indication of the relative abundance of anaerobic microorganisms capable of utilizing sulfate, iron (III), or carbon dioxide during biodegradation.

2.3.4.2 Microcosm Studies

If additional evidence supporting intrinsic remediation is required, a microcosm study using site-specific aquifer materials and contaminants can be undertaken. Microcosm studies are used

to show that the microorganisms necessary for biodegradation are present and can be used as another line of evidence to support intrinsic remediation.

If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of biodegradation. Such studies are the only "line of evidence" that allows an unequivocal mass balance determination based on the biodegradation of environmental contaminants. If the microcosm study is properly designed, it will be easy for decision makers with nontechnical backgrounds to interpret. 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. Because microcosm studies are time consuming and expensive, they should be undertaken only at sites where there is considerable skepticism concerning the biodegradation of fuel hydrocarbons.

Biodegradation rate constants determined by microcosm studies often are much greater than rates achieved in the field. Microcosms are most appropriate as indicators of the potential for intrinsic bioremediation, and to prove that losses are biological, but it may be inappropriate to use them to generate rate constants. The preferable method of fuel hydrocarbon biodegradation rate-constant determination is by *in situ* field measurement. The collection of material for the microcosm study, the procedures used to set up and analyze the microcosm, and the interpretation of the results of the microcosm study, are presented in Appendix C.

2.3.4.3 Volatile Fatty Acids

During biodegradation of BTEX compounds, volatile fatty acids (VFAs) are produced as metabolic byproducts. The production of these VFAs is a direct indication that biodegradation of BTEX has occurred. This test is a gas chromatography/mass spectrometry method wherein the samples are compared to a standard mixture containing a total of 58 phenols, aliphatic acids, and aromatic acids. Volatile fatty acid analyses are necessary only when there is considerable skepticism about the biodegradation of fuel hydrocarbons at a specific site.

2.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF INTRINSIC REMEDIATION

Site investigation data should first be used to refine the conceptual model and quantify groundwater flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of intrinsic remediation and to help simulate intrinsic remediation over time. Because the burden of proof is on the proponent, all available data must be integrated in such a way that the evidence is sufficient to support the conclusion that intrinsic remediation is occurring.

2.4.1 Conceptual Model Refinement

Conceptual model refinement involves integrating newly gathered site characterization data to refine the preliminary conceptual model that was developed based on previously existing site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. This conceptual model can then be used for contaminant fate and transport modeling. Conceptual model refinement consists of several steps, including preparation of geologic logs, hydrogeologic sections, potentiometric surface/water table maps, contaminant contour (isopleth) maps, and electron acceptor and metabolic byproduct contour (isopleth) maps.

2.4.1.1 Geologic Logs

Geologic logs of all subsurface materials encountered during the soil boring phase of the field work should be constructed. Descriptions of the aquifer matrix should include relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations such as visible fuel or fuel odor. It is also important to correlate the results of volatiles screening using soil sample headspace vapor analysis with depth intervals of geologic materials. The depth of lithologic contacts and/or significant textural changes should be recorded to the nearest 0.1 foot. This resolution is necessary because preferential flow and contaminant transport paths may be limited to thin stratigraphic units.

2.4.1.2 Cone Penetrometer Logs

Cone penetrometer logs express stratigraphic information as the ratio of sleeve friction to tip pressure. Cone penetrometer logs also may contain fluid resistivity data and estimates of aquifer hydraulic conductivity. To provide meaningful data, the cone penetrometer must be capable of providing stratigraphic resolution on the order of 3 inches. To provide accurate stratigraphic information, cone penetrometer logs must be correlated with continuous subsurface cores. At a minimum, there must be one correlation for every hydrostratigraphic unit found at the site. Cone penetrometer logs can be used to complete the hydrogeologic sections discussed in Section 2.4.1.3.

2.4.1.3 Hydrogeologic Sections

Hydrogeologic sections should be prepared from boring logs or CPT data. A minimum of two hydrogeologic sections are required; one parallel to the direction of groundwater flow and one perpendicular to the direction of groundwater flow. Hydraulic head data including potentiometric surface and/or water table elevation data should be plotted on the hydrogeologic section. These sections are useful in locating potential preferential contaminant migration paths and in simulating contaminant transport using solute fate and transport models.

2.4.1.4 Potentiometric Surface or Water Table Map(s)

A potentiometric surface or water table map is a two-dimensional graphic representation of equipotential lines shown in plan view. These maps should be prepared from water level measurements and surveyor's data. Because groundwater flows from areas of high hydraulic head to areas of low hydraulic head, such maps are used to estimate the probable direction of plume migration and to calculate hydraulic gradients. These maps should be prepared using water levels measured in wells screened in the same relative position within the same hydrogeologic unit. To determine vertical hydraulic gradients, separate potentiometric maps should be developed for different horizons in the aquifer to document vertical variations in groundwater flow. Flow nets should also be constructed to document vertical variations in groundwater flow. To document seasonal variations in groundwater flow, separate potentiometric surface or water table maps should be prepared for quarterly water level measurements taken over a period of at least 1 year. In areas with mobile NAPL, a correction must be made for the water table deflection

caused by the NAPL. This correction and potentiometric surface map preparation are discussed in Appendix C.

2.4.1.5 Contaminant Contour Maps

Contaminant contour maps should be prepared for each of the BTEX compounds present and for total BTEX for each discrete sampling event. Such maps allow interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant contour maps are necessary so that contaminant concentrations can be gridded and used for input into a numerical model.

If mobile and residual NAPLs are present at the site, a contour map showing the thickness and vertical and horizontal distribution of each should be prepared. These maps will allow interpretation of the distribution and the relative transport rate of NAPLs in the subsurface. In addition, these maps will aid in partitioning calculations and solute fate and transport model development. It is important to note that, because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of fuel and water, NAPL thickness observations made at monitoring points may not provide an accurate estimate of the actual volume of mobile and residual NAPL in the aquifer. To accurately determine the distribution of NAPLs, it is necessary to take continuous soil cores or to use CPT testing coupled with laser-induced fluorescence. Appendix C discusses the relationship between actual and apparent NAPL thickness.

2.4.1.6 Electron Acceptor, Metabolic Byproduct, and Alkalinity Contour Maps

Contour maps should be prepared for electron acceptors consumed (dissolved oxygen, nitrate, and sulfate) and metabolic byproducts produced [iron (II) and methane] during biodegradation. In addition, a contour map should be prepared for alkalinity. The electron acceptor, metabolic byproduct, and alkalinity contour maps provide evidence of the occurrence of intrinsic remediation at a site.

2.4.1.6.1 *Electron Acceptor Contour Maps*

Contour maps should be prepared for the electron acceptors including dissolved oxygen, nitrate, and sulfate. During aerobic biodegradation, dissolved oxygen concentrations will

decrease to levels below background concentrations. Similarly, during anaerobic degradation, the concentrations of nitrate and sulfate will be seen to decrease to levels below background. The electron acceptor contour maps allow interpretation of data on the distribution of the electron acceptors and the relative transport and degradation rates of contaminants in the subsurface. Thus, electron acceptor contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors. In addition, the dissolved oxygen contour map is used to grid dissolved oxygen concentrations for input into the solute fate and transport model. Bioplume III will allow direct input of all these parameters.

2.4.1.6.2 Metabolic Byproduct Contour Maps

Contour maps should be prepared for the metabolic byproducts iron (II) and methane. During anaerobic degradation, the concentrations of these parameters will be seen to increase to levels above background. These maps allow interpretation of data on the distribution of metabolic byproducts resulting from the microbial degradation of fuel hydrocarbons and the relative transport and degradation rates of contaminants in the subsurface. Thus, metabolic byproduct contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various metabolic byproducts.

2.4.1.6.3 Total Alkalinity Contour Map

A contour map should be prepared for total alkalinity (as CaCO_3). Respiration of dissolved oxygen, nitrate, iron (III), and sulfate tends to increase the total alkalinity of groundwater. Thus, the total alkalinity inside the contaminant plume generally increases to levels above background. This map will allow visual interpretation of alkalinity data by showing the relationship between the contaminant plume and alkalinity.

2.4.2 Pre-Modeling Calculations

Several calculations must be made prior to implementation of the solute fate and transport model. These calculations include sorption and retardation calculations, fuel/water partitioning calculations, groundwater flow velocity calculations, and biodegradation rate-constant calculations. Each of these calculations is discussed in the following sections. The specifics of each calculation are presented in the appendices referenced below.

2.4.2.1 Analysis of Contaminant, Electron Acceptor, Metabolic Byproduct, and Total Alkalinity Data

The extent and distribution (vertical and horizontal) of contamination and electron acceptor and metabolic byproduct concentrations and distributions are of paramount importance in documenting the occurrence of biodegradation of fuel hydrocarbons and in solute fate and transport model implementation.

2.4.2.1.1 *Electron Acceptor and BTEX Data*

Dissolved oxygen concentrations below background in an area with fuel hydrocarbon contamination are indicative of aerobic hydrocarbon biodegradation. Similarly, nitrate and sulfate concentrations below background in an area with fuel hydrocarbon contamination are indicative of anaerobic hydrocarbon biodegradation. If these trends can be documented, it is possible to quantify the relative importance of each biodegradation mechanism, as described in appendices B and C. The contour maps described in Section 2.4.1 can be used to provide visual evidence of these relationships.

Microorganisms generally utilize dissolved oxygen and nitrate in areas with dissolved fuel-hydrocarbon contamination at rates that are instantaneous relative to the average advective transport velocity of groundwater. This results in the consumption of these compounds at a rate approximately equal to the rate at which they are replenished by advective flow processes. For this reason, the use of these compounds as electron acceptors in the biodegradation of dissolved fuel-hydrocarbons is a mass-transport-limited process (Wilson *et al.*, 1985; Borden and Bedient, 1986). The use of models for simulating these processes is discussed in Appendix D.

Microorganisms generally utilize sulfate, iron (III), and carbon dioxide in areas with dissolved fuel-hydrocarbon contamination at rates that are slow relative to rates of dissolved oxygen and nitrate utilization. This results in the consumption of these compounds at a rate that could be slower than the rate at which they are replenished by advective flow processes and plumes of contamination can extend away from the source. The use of these compounds as electron acceptors in the biodegradation of dissolved fuel-hydrocarbons may be a reaction-limited process that is approximated by first-order kinetics. Determination of first-order biodegradation rate constants is discussed in Appendix C.

2.4.2.1.2 *Metabolic Byproduct and BTEX Data*

Elevated concentrations of the metabolic byproducts iron (II) and methane in areas with fuel hydrocarbon contamination are indicative of hydrocarbon biodegradation. If these trends can be documented, it is possible to quantify the relative importance of each biodegradation mechanism, as described in appendices B and C. The contour maps described in Section 2.4.1 can be used to provide visual evidence of these relationships.

2.4.2.1.3 *Total Alkalinity and BTEX Data*

Elevated concentrations of total alkalinity (as CaCO_3) in areas with fuel hydrocarbon contamination are indicative of hydrocarbon biodegradation via aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction. If this trend can be documented, it is possible to estimate the assimilative capacity of the groundwater based on the increase (above background) in total alkalinity in contaminated areas, as described in appendices B and C. The contour maps described in Section 2.4.1 can be used to provide visual evidence of these relationships.

2.4.2.2 Sorption and Retardation Calculations

Contaminant sorption and retardation calculations should be made based on the TOC content of the aquifer matrix and the organic carbon partitioning coefficient (K_{oc}) for each contaminant. The average TOC concentration from the most transmissive zone in the aquifer should be used for retardation calculations. A sensitivity analysis should also be performed during modeling using a range of TOC concentrations, including the lowest TOC concentration measured at the site. At a minimum, sorption and retardation calculations should be completed for BTEX and any tracers. Sorption and retardation calculations are described in Appendix C.

2.4.2.3 Fuel/Water Partitioning Calculations

If NAPL remains at the site, fuel/water partitioning calculations should be made to account for the partitioning from this phase into groundwater. Several models for fuel/water partitioning have been proposed in recent years, including those by Hunt *et al.* (1988), Bruce *et al.* (1991), Cline *et al.* (1991), and Johnson and Pankow (1992). Because the models presented by Cline *et al.* (1991) and Bruce *et al.* (1991) represent equilibrium partitioning, they are the most conservative models.

Equilibrium partitioning is conservative because it predicts the maximum dissolved concentration when LNAPL in contact with water is allowed to reach equilibrium. The results of these equilibrium partitioning calculations can be used in a solute fate and transport model to simulate a continuing source of contamination. The theory behind fuel/water partitioning calculations is presented in Appendix B, and example calculations are presented in Appendix C.

2.4.2.4 Groundwater Flow Velocity Calculations

The average linear groundwater flow velocity of the most transmissive aquifer zone containing contamination should be calculated to check the accuracy of the solute fate and transport model and to allow calculation of first-order biodegradation rate constants. An example of a groundwater flow velocity calculation is given in Appendix C.

2.4.2.5 Biodegradation Rate-Constant Calculations

Biodegradation rate constants are necessary to accurately simulate the fate and transport of BTEX compounds dissolved in groundwater. In many cases, biodegradation of fuel hydrocarbons can be approximated using first-order kinetics. In order to calculate first-order biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution and volatilization. Two methods for determining first-order rate constants are described in Appendix C. One method involves the use of a biologically recalcitrant compound found in the dissolved BTEX plume that can be used as a conservative tracer. The other method, proposed by Buscheck and Alcantar (1995) involves interpretation of a steady-state contaminant plume and is based on the one-dimensional steady-state analytical solution to the advection-dispersion equation presented by Bear (1979).

2.5 SIMULATE INTRINSIC REMEDIATION USING SOLUTE FATE AND TRANSPORT MODELS

Simulating intrinsic remediation allows prediction of the migration and attenuation of the contaminant plume through time. Intrinsic remediation modeling is a tool that allows site-specific data to be used to predict the fate and transport of solutes under governing physical, chemical, and biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that intrinsic remediation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model; therefore, an investment in thorough site

characterization will improve the validity of the modeling results. In some cases, straightforward analytical models of contaminant attenuation are adequate to simulate intrinsic remediation.

Several well documented and widely accepted solute fate and transport models are available for simulating the fate and transport of fuel hydrocarbons under the influence of advection, dispersion, sorption, and biodegradation. One such model that is readily available (nonproprietary) and that is well documented is Bioplume II. The use of solute fate and transport modeling in the intrinsic remediation investigation is described in Appendix D.

The Bioplume II model is based upon the United States Geological Survey (USGS) two-dimensional (2-D) solute transport model (method of characteristics) of Konikow and Bredehoeft (1978). Bioplume II includes an aerobic biodegradation component that is activated by a superimposed plume of dissolved oxygen (Rifai *et al.*, 1988). The model solves the USGS 2-D solute transport equation twice, once for hydrocarbon concentrations in the aquifer and once for a dissolved oxygen plume. The two plumes are combined using superposition at every particle move to simulate the biological reaction between hydrocarbons and oxygen. The model assumes that the hydrocarbons are directly mineralized to carbon dioxide and water through an instantaneous reaction. In recent years many studies have shown that Bioplume II can be used to successfully support the intrinsic remediation option at fuel-hydrocarbon-contaminated sites (Downey and Gier, 1991; Parsons ES, 1994a through 1994d; Parsons ES 1995a through 1995q; Wiedemeier *et al.*, 1993, 1994a, and 1994b).

2.6 CONDUCT AN EXPOSURE PATHWAYS ANALYSIS

After the rates of natural attenuation have been documented, and predictions of the future extent and concentrations of the contaminant plume have been made using the appropriate solute fate and transport model, the proponent of intrinsic remediation should combine all available data and information to negotiate for implementation of this remedial option. Supporting the intrinsic remediation option generally will involve performing an exposure pathways analysis. This analysis includes identifying potential human and ecological receptors at points of exposure under current and future land and groundwater use scenarios. The results of solute fate and transport modeling are central to the exposure pathways analysis. If conservative model input parameters are used, the solute fate and transport model should give conservative estimates of contaminant plume migration. From this information, the potential for impacts on human health and the environment from contamination present at the site can be estimated.

2.7 PREPARE LONG-TERM MONITORING PLAN

Groundwater flow rates at many Air Force sites studied to date are such that many years will be required before contaminated groundwater could potentially reach the Base property boundary. Thus, there frequently is time and space for intrinsic remediation to reduce contaminant concentrations in groundwater to acceptable levels. Experience at 40 Air Force sites studied by AFCEE to date (September 1995) using a draft of this document suggests that many BTEX plumes are relatively stable, or are moving only very slowly with respect to groundwater flow. These examples demonstrate the efficacy of LTM to track plume migration and to validate or refine modeling results.

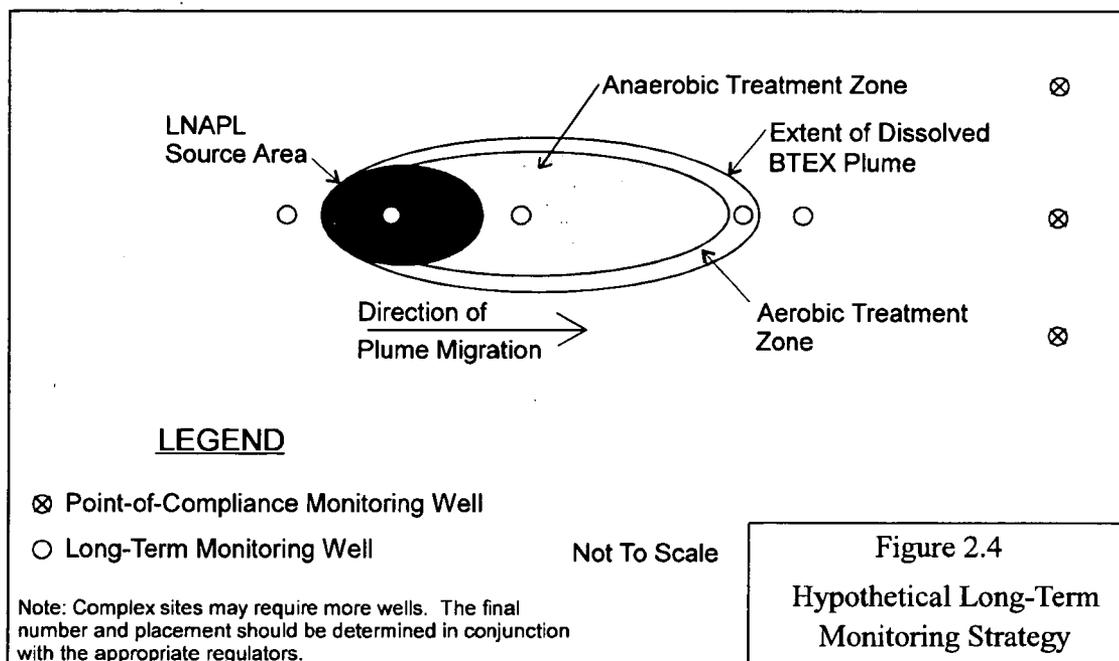
The LTM plan consists of locating groundwater monitoring wells and developing a groundwater sampling and analysis strategy. This plan is used to monitor plume migration over time and to verify that intrinsic remediation is occurring at rates sufficient to protect potential downgradient receptors. The LTM plan should be developed based on site characterization data, the results of solute fate and transport modeling, and the results of the exposure pathways analysis.

The LTM plan includes two types of monitoring wells. Long-term monitoring wells are intended to determine if the behavior of the plume is changing. Point-of-compliance wells are intended to detect movements of the plume outside the negotiated perimeter of containment, and to trigger an action to manage the risk associated with such expansion. Figure 2.4 depicts 1) an upgradient well in unimpacted groundwater, 2) a well in the LNAPL source area, 3) a well downgradient of the LNAPL source area in a zone of anaerobic treatment, 4) a well in the zone of aerobic treatment, along the periphery of the plume, 5) a well located downgradient from the plume where concentrations of petroleum hydrocarbons are below regulatory acceptance levels and soluble electron acceptors are depleted with respect to unimpacted groundwater, and 6) three POC wells.

Although the final number and placement of LTM and POC wells is determined through regulatory negotiation, the following guidance is recommended. Location of LTM wells are based on the behavior of the plume as revealed during the initial site characterization. The final number and location of LTM wells will depend on regulatory considerations. POC wells are placed a distance of 500 feet downgradient from the leading edge of the plume or the distance traveled by the groundwater in 2 years, whichever is greater. If the property line is less than 500

feet downgradient, the POC wells are placed near and upgradient from the property line. The final number and location of POC monitoring wells will depend on regulatory considerations.

The results of a solute fate and transport model can be used to help site the LTM and POC wells. In order to provide a valid monitoring system, all monitoring wells must be screened in the same hydrogeologic unit as the contaminant plume. This generally requires detailed stratigraphic correlation. To facilitate accurate stratigraphic correlation, detailed visual descriptions of all subsurface materials encountered during borehole drilling should be prepared prior to monitoring well installation. The final placement of all monitoring wells should be determined in collaboration with the appropriate regulators.



A groundwater sampling and analysis plan should be prepared in conjunction with POC and LTM well placement. For LTM wells, groundwater analyses should include BTEX, dissolved oxygen, nitrate, iron (II), sulfate, and methane. For POC wells, groundwater analyses should be limited to determining BTEX and dissolved oxygen concentrations. Any state-specific analytical requirements also should be addressed in the sampling and analysis plan to ensure that all data required for regulatory decision making are collected. Water level and NAPL thickness measurements must be made during each sampling event. Quarterly sampling of LTM wells is recommended during the first year to help determine the direction of plume migration and to

determine baseline data. Based on the results of the first year's sampling, the sampling frequency may be reduced to annual sampling in the quarter showing the greatest extent of the plume. Sampling frequency is dependent on the final placement of the POC monitoring wells and groundwater flow velocity. The final sampling frequency should be determined in collaboration with regulators.

2.8 CONDUCT REGULATORY NEGOTIATIONS

The purpose of regulatory negotiations is to provide scientific documentation that supports intrinsic remediation as the most appropriate remedial option for a given site. All available site-specific data and information developed during the site characterization, conceptual model development, pre-modeling calculations, biodegradation rate calculation, groundwater modeling, model documentation, and LTM plan preparation phases of the intrinsic remediation investigation should be presented in a consistent and complementary manner at the regulatory negotiations. Of particular interest to the regulators will be proof that intrinsic remediation is occurring at rates sufficient meet regulatory compliance levels at the POC and to protect human health and the environment. The regulators must be presented with a "weight-of-evidence" argument in support of this remedial option. For this reason, all available evidence in support of intrinsic remediation must be presented at the regulatory negotiations.

A comprehensive LTM and contingency plan also should be presented to demonstrate a commitment to proving the effectiveness of intrinsic remediation as a remedial option. Because LTM and contingency plans are very site specific, they should be addressed in the individual reports generated using this protocol. See Sections 6 and 7 of the two case studies presented in Appendices E and F for examples of such plans.

SECTION 3

REFERENCES

- Abdul, A.S., Kia, S.F., and Gibson, T.L., 1989, Limitations of monitoring wells for the detection and quantification of petroleum products in soils and aquifers: Ground Water Monitoring Review, Spring, 1989, p. 90-99.
- Alvarez, P.J.J., and Vogel, T.M., 1991, Substrate interactions of benzene, toluene, and para-xylene during microbial degradation by pure cultures and mixed culture aquifer slurries: Applied Environmental Microbiology, v. 57, p. 2981-2985.
- American Petroleum Institute, 1985, Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater: American Petroleum Institute, Publication Number 4395
- Anderson, M.P., 1979, Using models to simulate the movement of contaminants through groundwater flow systems: CRC Critical Review in Environmental Control, no. 9, p. 97-156.
- Anderson, M.P., and Woessner, W.W., 1992, Applied Groundwater Modeling - Simulation of Flow and Advective Transport: Academic Press, New York, New York, 381p.
- Arthur D. Little, Inc., 1985, The Installation Restoration Program Toxicology Guide. Volume 1. Prepared for Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, October 1985
- Arthur D. Little, Inc., 1987, The Installation Restoration Program Toxicology Guide. Volume 3. Prepared for Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, June 1987
- Atlas, R. M., 1981, Microbial degradation of petroleum hydrocarbons - an Environmental Perspective; Microbiological Reviews, 45(1):180-209.
- Atlas, R. M., 1984, Petroleum Microbiology: Macmillan Publishing Co., New York.
- Atlas, R.M., 1988, Microbiology - Fundamentals and Applications: Macmillan, New York.
- Avon, L., and Bredehoeft, J.D., 1989, An analysis of trichloroethylene movement in groundwater at Castle Air Force Base, California: Journal of Hydrology, v. 110, p. 23-50.
- Baedecker, M.J., Siegel, D.I., Bennett, P.C., and Cozzarelli, I.M., 1988, The fate and effects of crude oil in a shallow aquifer: I. The distribution of chemical species and geochemical facies, In, G.E. Mallard, and S.E. Ragone, editors, U.S. Geological Survey Toxic Substances Hydrology Program, Proceedings of the Technical Meeting, Phoenix, Arizona,

- September 26-30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-42320, p. 13-20.
- Bailey, G.W., and White, J.L., 1970, Factors influencing the adsorption, desorption, and movement of pesticides in soil, In Residue Reviews, F.A. Gunther and J.D. Gunther, editors: Springer Verlag, p. 29-92.
- Ballestero, T.P., Fiedler, F.R., and Kinner, N.E., 1994, An investigation of the relationship between actual and apparent gasoline thickness in a uniform sand aquifer: *Ground Water*, v. 32, no. 5, p. 708-718.
- Barker, J.F., Patrick, G.C., and Major, D., 1987, Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer: *Ground Water Monitoring Review*, Winter 1987, p. 64-71.
- Barr, K.D., 1993, Enhanced groundwater remediation by bioventing and its simulation by biomodeling: In, R.N. Miller, editor, *Proceedings of the Environmental Restoration Technology Transfer Symposium*, January 26-27, 1993.
- Bartha, R., 1986, Biotechnology of petroleum pollutant biodegradation: *Microbial Ecology*, 12:155-172.
- Battelle, 1995, Test Plan and Technical Protocol for Bioslurping, Rev. 2: US Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.
- Bear, J., 1972, *Dynamics of Fluids in Porous Media*: Dover Publications, Inc., New York, 764 p.
- Bear, J., 1979, *Hydraulics of Groundwater*: McGraw-Hill, Inc., New York, New York, 569.
- Bedient, P.B., Rifai, H.S., and Newell, C.J., 1994, *Groundwater Contamination - Transport and Remediation*: PTR Prentice Hall, New Jersey, 541 p.
- Beller, H.R., Reinhard, M., and Grbic-Galic, D., 1992, Metabolic byproducts of anaerobic toluene degradation by sulfate-reducing enrichment cultures: *Appl. Environ. Microbiol.*, v. 58, p. 3192-3195.
- Beller, H. R., D. Grbic-Galic, and M. Reinhard. 1992b. Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process. *Appl. Environ. Microbiol.* 58:786-793
- Blake, S.B., and Hall, R.A., 1984, Monitoring petroleum spills with wells - some problems and solutions: In, *Proceedings of the Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring*: May 23-25, 1984, p. 305-310.
- Borden, R.C. and Bedient, P.B., 1986, Transport of dissolved hydrocarbons influenced by oxygen limited biodegradation - theoretical development: *Water Resources Research*, v. 22, no. 13, p. 1973-1982.
- Borden, R. C., Gomez, C.A., and Becker, M. T., 1994, Natural Bioremediation of a gasoline spill. In R.E. Hinchee, B.C. Alleman, R. E. Hoeppe and R. N. Miller (Eds.). *Hydrocarbon Bioremediation*. 290-295. Lewis Publishers.
- Borden, R. C., Gomez, C.A., and Becker, M. T., 1995, Geochemical indicators of natural bioremediation. *Ground Water*. (in press).

- Bouwer, E.J., 1992, Bioremediation of Subsurface Contaminants, In R. Mitchell, editor, Environmental Microbiology: Wiley-Liss, New York, p. 287-318.
- Bouwer, H., and Rice, R.C., 1976, A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers With Completely or Partially Penetrating Wells: Water Resources Research, v. 12, no. 3, p. 423-428.
- Bouwer, H., 1989, The Bouwer and Rice slug test - an update: Ground Water, v. 27, no. 3, p. 304-309.
- Bredehoeft, J.D., and Konikow, L.F., 1993, Ground-water models - validate or invalidate: Ground Water, v. 31, no. 2, p. 178-179.
- Brown, D.S. and Flagg, E.W., 1981, Empirical prediction of organic pollutant sorption in natural sediments: Journal of Environmental Quality, v. 10, no. 3, p. 382-386.
- Briggs, G.G., 1981, Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor: Journal of Agriculture and Food Chemistry, v. 29, p. 1050-1059.
- Bruce, L., Miller, T., and Hockman, B., 1991, Solubility versus equilibrium saturation of gasoline compounds - a method to estimate fuel/water partition coefficient using solubility or K_{oc} , In, A. Stanley, editor, NWWA/API Conference on Petroleum Hydrocarbons in Ground Water: NWWA/API, p. 571-582.
- Buscheck, T.E. and Alcantar, C.M., 1995, "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." In, Proceedings of the 1995 Battelle International Conference on In-Situ and On Site Bioreclamation, April 1995
- Cerniglia, C. E. 1984. Microbial transformation of aromatic hydrocarbons, In Petroleum Microbiology. R. M. Atlas editor: Macmillan Publishing Co., New York., p. 99-128.
- Chapelle, F.H., 1993, Ground-Water Microbiology and Geochemistry: John Wily & Sons, Inc., New York, 424 p.
- Chiang, C.Y., Salanitro, J.P., Chai, E.Y., Colthart, J.D., and Klein, C.L., 1989, Aerobic biodegradation of benzene, toluene, and xylene in a sandy aquifer - data analysis and computer modeling, Ground Water, v. 27, no. 6, p. 823-834.
- Chiou, C.T., Porter, P.E., and Schmedding, D.W., 1983, Partition equilibria of nonionic organic compounds between soil organic matter and water: Environmental Science and Technology: v. 17, no. 4, p. 227-231.
- Ciccioli, P., Cooper, W.T., Hammer, P.M., and Hayes, J.M., 1980, Organic solute-mineral surface interactions; a new method for the determination of groundwater velocities: Water Resources Research, v. 16, no. 1, p. 217-223.
- Cline, P.V., Delfino, J.J., and Rao, P.S.C., 1991, Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures: Environmental Science and Technology, v. 25, p. 914-920.
- Concawe, 1979, Protection of groundwater from oil pollution; Den Haag, Report No. 3/79.

- Cozzarelli, I. M., Eganhouse, R.P., and Baedecker, M.J., 1990, Transformation of monoaromatic hydrocarbons to organic acids in anoxic groundwater environment: *Environ. Geol. Water Science*, 16.
- Cozzarelli, I.M., Baedecker, M.J., Eganhouse, R.P., and Goerlitz, D.F., 1994, The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in groundwater: *Geochimica et Cosmochimica Acta*, v. 58, no. 2, p. 863-877.
- CRC, 1956, *Handbook of Chemistry and Physics*: CRC Press
- Cripps, R. E., and Watkinson, R.J., 1978, Polycyclic aromatic hydrocarbon metabolism and environmental aspects, In J. R. Watkinson, editor, *Developments in Biodegradation of Hydrocarbons - 1*, Applied Science Publishers, Ltd., London, p. 133-134.
- Curtis, C. D. 1985. Clay mineral precipitation and transformation during burial diagenesis. *Phil. Trans. R. Soc. London*.315: 91-105
- Dalton, H., and Stirling, D.E., Co-metabolism: *Philos Trans R Soc Lond*, 297:481-496.
- Davies, J. S. and Westlake, D.W.S., 1979. Crude oil utilization by fungi: *Canadian Journal of Microbiology*, 25:146-156.
- Davis, R.K., Pederson, D.T., Blum, D.A., and Carr, J.D., 1993, Atrazine in a stream-aquifer system - estimation of aquifer properties from atrazine concentration profiles: *Ground Water Monitoring Review*, Spring, 1993, p. 134-141
- Davis, J.W., Klier, N.J., and Carpenter, 1994a, Natural biological attenuation of benzene in groundwater beneath a manufacturing facility: *Ground Water*, v. 32, no. 2, p. 215-226.
- Davis, A., Campbell, J., Gilbert, C., Ruby, M.V., Bennett, M., and Tobin, S., 1994b, Attenuation and biodegradation of chlorophenols in groundwater at a former wood treating facility: *Ground Water*, v. 32, no. 2, p. 248-257.
- Dawson K.J. and Istok, J.D., 1991, *Aquifer Testing - Design and analysis of pumping and slug tests*: Lewis Publishers, Chelsea, Michigan, 344 p.
- Dean, J. A., 1972, *Lange's Handbook of Chemistry*, 13th ed.: McGraw-Hill, New York
- de Pastrovich, T.L., Baradat, Y., Barthel, R., Chiarelli, A., and Fussell, D.R., 1979, Protection of groundwater from oil pollution: CONCAWE, The Hague, 61 p.
- Deviny J.S. Everett L.G., Lu J.C.S. and Stollar R.L., 1990, *Subsurface Migration of Hazardous Wastes*: Van Nostrand Reinhold 387 p.
- Domenico, P.A., 1987, An analytical model for multidimensional transport of a decaying contaminant species: *Journal of Hydrology*, 91, p. 49-58.
- Domenico, P.A., and Schwartz, F.W., 1990, *Physical and Chemical Hydrogeology*: John Wiley and Sons, New York, New York, 824 p.
- Donaghue, N. A., Griffin, M., Norris, D.G., and Trudgill, P.W., 1976, The microbial metabolism of cyclohexane and related compounds, In J.M. Sharpley and A. M. Kaplan editors,

Proceedings of the Third International Biodegradation Symposium: Applied Science Publishers, Ltd., London, p. 43-56.

- Downey, D.C. and Gier, M.J., 1991, Supporting the no action alternative at a hydrocarbon spill site: In Proceedings USAF Environmental Restoration Technology Symposium, 7-8 May, San Antonio, Texas, Section U, p. 1-11.
- Dragun, J., 1988, The Soil Chemistry of Hazardous Materials: Hazardous Materials Control Research Institute, Silver Spring Maryland, 458 p.
- Dunlap, W. J., J. F. McNabb, M. R. Scalf, and R. L. Cosby. 1977. Sampling for organic chemicals and microorganisms in the subsurface. EPA-600/2-77-176, U.S. Environmental Protection Agency, Ada OK.
- Edwards, E.A., and Grbic-Galic, D., 1992, Complete mineralization of benzene by aquifer microorganisms under strictly anaerobic conditions: *Appl. Environ. Microbiol.*, v. 58, p. 2663-2666.
- Edwards, E. A., and D. Grbic-Galic. 1994. Anaerobic degradation of toluene and o-xylene by a methanogenic consortium. *Appl. Environ. Microbiol.* 60:313-322
- Edwards, E.A., Wells, L.E., Reinhard, M., and Grbic-Galic, D., 1992, Anaerobic degradation of toluene and xylene by aquifer microorganisms under sulfate-reducing conditions: *Appl. Environ. Microbiol.*, v. 58, p. 794-800.
- Evans, P.J., Mang, D.T., and Young, L.Y., 1991a, Degradation of toluene and m-xylene and transformation of o-xylene by denitrifying enrichment cultures: *Appl. Environ. Microbiol.*, v. 57, p. 450-454.
- Evans, P.J., Mang, D.T., Kim, K.S., and Young, L.Y., 1991b, Anaerobic degradation of toluene by a denitrifying bacterium: *Appl. Environ. Microbiol.*, v. 57, p. 1139-1145.
- Evans, P. J., D. T. Mang, and L. Y. Young. 1991. Degradation of toluene and m-xylene and transformation of o-xylene by denitrifying enrichment cultures. *57*: 450-454
- Farr, A.M., Houghtalen, R.J., and McWhorter, D.B., 1990, Volume estimation of light nonaqueous phase liquids in porous media: *Ground Water*, v. 28, no. 1, p. 48-56.
- Fetter C.W., 1988, *Applied Hydrogeology*: Merrill Publishing Company Columbus Ohio 592 p.
- Fetter, C.W., 1993, *Contaminant Hydrogeology*: MacMillan, New York, New York, 458 p.
- Franke O.L., Reilly T.E., and Bennett, G.D., 1987, Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems - an introduction: United States Geological Survey Techniques of Water-Resources Investigations Book 3 Chapter B5 15 p.
- Freeze, R.A., and Cherry, J.A., 1979, *Groundwater*: Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 604p.
- Gibbs, C. R. 1976. Characterization and application of ferrozine iron reagent as a ferrous iron indicator. *Anal. Chem.* 48:1197-1200

- Gibson, D.J., 1971, The microbial oxidation of aromatic hydrocarbons: *Critical Reviews in Microbiology*, 1:199-223.
- Gibson, D.T., and Subramanian, V., 1984, Microbial degradation of aromatic hydrocarbons, In, D.T. Gibson, editor, *Microbial Degradation of Organic Compounds*: Marcel-Dekker, New York, p. 181-252.
- Godsy, E.M., Goerlitz, D.F., and Grbic-Galic, D., 1992a, Methanogenic biodegradation of creosote contaminants in natural and simulated ground-water ecosystems: *Ground Water*, v. 30, no. 2, p. 232-242.
- Godsy, E.M., Goerlitz, D.F., and Grbic-Galic, D., 1992b, Methanogenic degradation kinetics of phenolic compounds in aquifer-derived microcosms: In Press.
- Goldstein, R. M., Mallory, L.M., and Alexander, M., 1985, Reasons for possible failure of inoculation to enhance biodegradation: *Applied Environmental Microbiology*, 50(4):977-983.
- Grbic-Galic, D., and Vogel, T.M., 1987, Transformation of toluene and benzene by mixed methanogenic cultures: *Applied and Environmental Microbiology*, v. 53, p. 254-260.
- Grbic-Galic, D., 1990, Anaerobic microbial transformation of nonoxygenated aromatic and alicyclic compounds in soil, subsurface, and freshwater sediments: In, J.M. Bollag and G. Stotzky, editors, *Soil Biochemistry*: Marcel Dekker, Inc., New York, p. 117-189.
- Hall, R.A., Blake, S.B., and Champlin, S.C. Jr., 1984, Determination of hydrocarbon thicknesses in sediments using borehole data: In, *Proceedings of the Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring*: May 23-25, 1984, p. 300-304.
- Hampton, D.R., and Miller, P.D.G., 1988, Laboratory investigation of the relationship between actual and apparent product thickness in sands:
- Harlan R.L., Kolm, K.E., and Gutentag, E.D., 1989, *Water-Well Design and Construction*, *Developments in Geotechnical Engineering*, Number 60: Elsevier, 205 p.
- Hassett, J.J., Means, J.C., Banwart, W.L., and Wood, S.G., 1980, *Sorption Properties of Sediments and Energy-Related Pollutants*: EPA/600/3-80-041, U.S. Environmental Protection Agency, Washington, D.C.
- Hassett, J.J., Banwart, W.L., and Griffin, R.A., 1983, Correlation of compound properties with sorption characteristics of nonpolar compounds by soils and sediments; concepts and limitations, In, C.W. Francis and S.I. Auerbach, editors, *Environment and Solid Wastes*: Butterworths, Boston, p. 161-178.
- Hem, J.D., 1989, *Study and Interpretation of the Chemical Characteristics of Natural Water*: United States Geological Survey Water Supply Paper 2254, 264 p.
- Heron, G., C. Crouzet, A. C. M. Bourg, and T. H. Christensen. 1994. Speciation of Fe (II) and Fe(III) in contaminated aquifer sediment using chemical extraction techniques. *Environ. Sci. Technol.* 28: 1698-1705

- Higgins, I.J., and Gilbert, P.D., 1978, The biodegradation of hydrocarbons, In, K.W.A. Chator and H.J. Somerville, editors, *The Oil Industry and Microbial Ecosystems*: Heyden and Sons, London, p. 80-114.
- Hinchee, R.E., Ong, S.K., Miller, R.N., Downey, D.C., and Frandt, R., 1992, Test Plan and Technical Protocol for a Field Treatability Test for Bioventing, Rev. 2: US Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.
- Hopper, D. J., 1978, Incorporation of [^{18}O] water in the formation of p-hydroxybenzyl alcohol by the p-cresol methylhydroxylase from *Pseudomonas putida*: *Biochem. J.*, 175:345-347.
- Hubbert, M.K., 1940, The theory of groundwater motion: *Journal of Geology* v. 48 p. 785-944.
- Hughes, J.P., Sullivan, C.R., and Zinner, R.E., 1988, Two techniques for determining the true hydrocarbon thickness in an unconfined sandy aquifer: *In Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference: NWWA/API*, p. 291 -314.
- Hunt, J.R., Sitar, N., and Udell, K.S., 1988, Nonaqueous phase liquid transport and cleanup, 1. Analysis of mechanisms: *Water Resources Research*, v. 24, no. 8, p. 1247-1258.
- Hunt, M.J., Beckman, M.A., Borlaz, M.A., and Borden, R.C., 1995, Anaerobic BTEX Biodegradation in Laboratory Microcosms and In-Situ Columns: *Proceedings of the Third International Symposium on In Situ and On-Site Bioreclamation*, April 24-27, 1995, San Diego, CA.
- Huntley, D., Hawk, R.N., and Corley, H.P., 1994a, Nonaqueous phase hydrocarbon in a fine-grained sandstone - 1. Comparison between measured and predicted saturations and mobility: *Ground Water*, v. 32, no. 4, p. 626-634.
- Huntley, D., Wallace, J.W., and Hawk, R.N., 1994b, Nonaqueous phase hydrocarbon in a fine-grained sandstone - 2. Effect of local sediment variability on the estimation of hydrocarbon volumes: *Ground Water*, v. 32, no. 5, p. 778-783.
- Hutchins, S.R., 1991, Biodegradation of monoaromatic hydrocarbons by aquifer microorganisms using oxygen, nitrate, or nitrous oxide as the terminal electron acceptor: *Appl. Environ. Microbiol.*, v. 57, p. 2403-2407.
- Hutchins, S.R., Sewell, G.W., Sewell, D.A., Kovacs, D.A., and Smith, G.A., 1991, Biodegradation of aromatic hydrocarbons by aquifer microorganisms under denitrifying conditions: *Environmental Science and Technology*, v. 25, p. 68-76.
- Hvorslev M.J., 1951, Time lag and soil permeability in ground-water observations: *United States Corps of Engineers Waterways Experiment Station Bulletin 36 Vicksburg Mississippi 50 p.*
- Jamison, V.W., Raymond, R.L., and Hudson, J.O. Jr., 1975, Biodegradation of high-octane gasoline in groundwater: *Developments in Industrial Microbiology*, v. 16.
- Jeng, C.Y., Chen, D.H., and Yaws, C.L., 1992, Data compilation for soil sorption coefficient: *Pollution Engineering*, June 15, 1992

- Johnson, R.L., and Pankow, J.F., 1992, Dissolution of dense chlorinated solvents in groundwater, 2. Source functions for pools of solvents: *Environmental Science and Technology*, v. 26, no. 5, p. 896-901.
- Johnson, R.L., Palmer, C.D., and Fish, W., 1989, Subsurface chemical processes, In *Fate and Transport of Contaminants in the Subsurface*, EPA/625/4-89/019: Environmental Protection Agency, Cincinnati, OH and Ada, OK, p. 41-56.
- Jones, J. G. and Eddington, M.A., 1968, An ecological survey of hydrocarbon-oxidizing microorganisms: *J. Gen. Microbiology*, 52:381-390.
- Jury, W.A., Gardner, W.R., and Gardner, W.H., 1991, *Soil Physics*: John Wiley & Sons, New York, New York, 328 p.
- Kampbell, D.H., Wilson, J.T., and Vandegrift, S.A., 1989, Dissolved oxygen and methane in water by a GC headspace equilibrium technique: *Intern. J. Environ. Ana. Chem.*, v. 36, p. 249-257.
- Karickhoff, S.W., Brown, D.S., and Scott, T.A., 1979, Sorption of hydrophobic pollutants on natural sediments: *Water Resources Research*, v. 13, p. 241-248.
- Karickhoff, S.W., 1981, Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils: *Chemosphere*, v. 10, p. 833-846.
- Kemblowski, M.W., and Chiang, C.Y., 1990, Hydrocarbon thickness fluctuations in monitoring wells: *Ground Water* v. 28, no. 2, p. 244-252.
- Kennedy, L.G. and Hutchins, S.R., 1992, Applied geologic, microbiologic, and engineering constraints of in-situ BTEX bioremediation: *Remediation*, p. 83-107.
- Kenaga, E.E., and Goring, C.A.I., 1980, ASTM Special Technical Publication 707: American Society for Testing Materials, Washington, D.C.
- Klein, C., and S. C. Hurlbut Jr. 1985. *Manual of mineralogy*. John Wiley & Sons, New York. 596 p.
- Knox, R.C., Sabatini, D.A., and Canter, L.W., 1993, *Subsurface Transport and Fate Processes*: Lewis Publishers, Boca Raton, Florida, 430 p.
- Konikow, L.F., 1978, Calibration of ground-water models, In *Verification of Mathematical and Physical Models in Hydraulic Engineering*: American Society of Civil Engineers, New York, p. 87-93.
- Konikow, L.F., and Bredehoeft, J.D., 1978, Computer model of two-dimensional solute transport and dispersion in groundwater: United States Geological Survey, *Techniques of Water Resources Investigations of the United States Geological Survey*, Book 7, Chapter C2, 90 p.
- Kruseman, G.P. and de Ridder N.A., 1991, *Analysis and Evaluation of Pumping Test Data*: International Institute for Land Reclamation and Improvement, The Netherlands, 377 p.
- Kuhn, E.P., Colberg, P.J., Schnoor, J.L., Wanner, O., Zehnder, A.J.B., and Schwarzenbach, R.P., 1985, Microbial transformations of substituted benzenes during infiltration of river water to

- groundwater: laboratory column studies: *Environmental Science and Technology*, v. 19, p. 961-968.
- Kuhn, E.P., Zeyer, J., Eicher, P., and Schwarzenbach, R.P., 1988, Anaerobic degradation of alkylated benzenes in denitrifying laboratory aquifer columns: *Applied and Environmental Microbiology*, v. 54, p. 490-496.
- Kukor, J.J., and Olsen, R.H., 1989, Diversity of toluene degradation following long-term exposure to BTEX in situ: *Biotechnology and Biodegradation*, Portfolio Publishing, The Woodlands, Texas, p. 405-421.
- Lallemand-Barres, P., and P. Peaudecerf. 1978. Recherche des relations entre la valeur de la dispersivite macroscopique d'un milieu aquifere, ses autres caracteristiques et les conditions de mesure, etude bibliographique Bulletin, Bureau de Recherches Geologiques et Minieres. Sec. 3/4:277-287.
- Langmuir, D. and Whittemore, D. O., 1971, Variations in the stability of precipitated ferric oxyhydroxides, *In* J. D. Hem (ed.), *Nonequilibrium Systems in Natural Water Chemistry*, Advances in Chemistry Series 106: Am. Chem. Soc., Washington, D.C..
- Larson, R.A., and Weber, E.J., 1994, *Reaction Mechanisms in Environmental Organic Chemistry*: Lewis Publishers, Boca Raton, Florida, 433p.
- Leahy, J. G., and Colewell, R.R., 1990, Microbial degradation of hydrocarbons in the environment: *Microbiological Reviews*, 53(3):305-315.
- Lee, M.D. 1988. Biorestitution of Aquifers Contaminated with Organic Compounds. *CRC Critical Reviews in Environmental Control*. v. 18. p. 29-89.
- Lenhard, R.J., and Parker, J.C., 1990, Estimation of free hydrocarbon volume from fluid levels in monitoring wells: *Ground Water*, v. 28, no. 1, p. 57-67.
- Lovley, D. R. 1987. Organic matter mineralization with the reduction of ferric iron: A review. *Geomicrobiol. J.* 5:375-399
- Lovley, D.R., 1991, Dissimilatory Fe(III) and Mn(IV) reduction: *Microbiological Reviews*, June 1991, p. 259-287.
- Lovley, D. R., and E. J. P. Phillips. 1986. Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac River. *Appl. Environ. Microbiol.* 52:751-757
- Lovley, D. R., and E. J. P. Phillips. 1987. Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments. *Appl. Environ. Microbiol.* 53:2636-2641.
- Lovley, D.R., Baedeker, M.J., Lonergan, D.J., Cozzarelli, I.M., Phillips, E.J.P., and Siegel, D.I., 1989, Oxidation of aromatic contaminants coupled to microbial iron reduction: *Nature*, v. 339, p. 297-299.

- Lovley, D.R., F.H. Chapelle, and J.C. Woodward. 1994. Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Environmental Science & Technology*, v. 28, no. 7., p. 1205-1210.
- Lovley, D.R., J.D. Coates, J.C. Woodward, and E.J.P. Phillips. 1995. Benzene oxidation coupled to sulfate reduction: *Applied and Environmental Microbiology*, v. 61, no. 3., p. 953-958.
- Lyman, W.J., 1982, Adsorption coefficient for soils and sediment, In, W.J. Lyman *et al.*, editors, *Handbook of Chemical Property Estimation Methods*: McGraw-Hill, New York, 4.1-4.33.
- Lyman, W.J., Reidy, P.J., and Levy, B., 1992, *Mobility and Degradation of Organic Contaminants in Subsurface Environments*: C.K. Smoley, Inc., Chelsea, Michigan, 395 p.
- MacIntyre, W.G., Boggs, M., Antworth, C.P., and Stauffer, T.B., 1993, Degradation kinetics of aromatic organic solutes introduced into a heterogeneous aquifer: *Water Resources Research*, v. 29, no. 12, p. 4045-4051.
- Mackenzie, F. T., R. M. Garrels, O. P. Bricker, and F. Bickley. 1967. Silica in sea-water: control by silica minerals. *Science* 155:1404-1405
- Major, D.W., Mayfield, C.I., and Barker, J.F., 1988, Biotransformation of benzene by denitrification in aquifer sand: *Ground Water*, v. 26, p. 8-14.
- Malone, D.R., Kao, C.M., and Borden, R.C., 1993, Dissolution and bioremediation of nonaqueous phase hydrocarbons - model development and laboratory evaluation: *Water Resources Research*, v. 29, no. 7, p. 2203-2213.
- Martel, 1987, *Military Jet Fuels 1944-1987*: AF Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.
- McCarty, P.L., 1972, Energetics of organic matter degradation, In R. Mitchell, *Water Pollution Microbiology*: Wiley-Interscience, p. 91-118.
- McCarty, P.L., Reinhard, M., and Rittmann, B.E., 1981, Trace organics in groundwater: *Environmental Science and Technology*, p. 40-51
- McCall, P.J., Swann, R.L., and Laskowski, 1983, Partition models for equilibrium distribution of chemicals in environmental compartments, In, R.L. Swann and A. Eschenroder, editors, *Fate of Chemicals in the Environment*: American Chemical Society, p. 105-123.
- Mckenna, E. J., and Kallio, R.E., 1964, Hydrocarbon structure - its effect on bacterial utilization of alkanes, In H. Heukelian and W.C Dondero editors: *Principals and Applications in Aquatic Microbiology*: John Wiley & Sons, Inc., New York, p. 1-14.
- Means, J.C., Wood, S.G., Hassett, J.J., and Banwart, W.L., 1980, Sorption of polynuclear aromatic hydrocarbons by sediments and soils: *Environmental Science and Technology*, v. 14, no., 12, p. 1524-1528.
- Mercer, J.W. and Faust C.R., 1981, *Ground-water modeling*: National Water Well Association, 60 p.

- Mercer, J.W., and Cohen, R.M., 1990, A review of immiscible fluids in the subsurface - properties, models, characterization and remediation: *Journal of Contaminant Hydrology*, v.6, p. 107-163.
- Miller, R.N. 1990, A Field-Scale Investigation of Enhanced Petroleum Hydrocarbon Biodegradation in the Vadose Zone at Tyndall Air Force Base, Florida, *In Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference: NWWA/API*, p. 339 -351.
- Monod, J., 1942, *Recherches sur la Croissance des Cultures Bacteriennes*: Herman & Cie, Paris.
- Morel, F.M.M. and Hering, J.G., 1993, *Principles and Applications of Aquatic Chemistry*: John Wiley & Sons, Inc., New York
- National Research Council, 1993, *In Situ Bioremediation, When Does it Work?: National Academy Press, Washington, D.C., 207 p.*
- Naumov, G. B., Ryzhenko, B. N. and Khodakovskiy, I. L., 1974, *Handbook of Thermodynamic Data*. (translated fm. the Russian): U.S. Geol. Survey, USGS-WRD-74-001.
- Newman, W.A., and Kimball, G., 1991, Dissolved oxygen mapping; A powerful tool for site assessments and groundwater monitoring: *Proceedings of the Fifth National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring, and Geophysical Methods, Number 5*, p. 103-117.
- Norris, R.D., Hincbee, R.E., Brown, R., McCarty, P.L, Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bouwer, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and Ward, C.H., 1994, *Handbook of Bioremediation*: Lewis Publishers, Inc., 257 p.
- Parker, J.C., and van Genuchten, 1984, Determining transport parameters from laboratory and field tracer experiments: *Virginia Agricultural Experiment Station, Bulletin*, 84-3.
- Parsons ES, Inc., 1994a, *Intrinsic Remediation Engineering Evaluation/Cost Analysis*, Plattsburgh AFB, New York.
- Parsons ES, Inc., 1994b, *Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis*, Dover AFB, Delaware.
- Parsons ES, Inc., 1994c, *Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis*, Site ST-41, Elmendorf AFB, Alaska.
- Parsons ES, Inc., 1994d, *Intrinsic Remediation Treatability Study for the Hangar 10 Site*, Elmendorf AFB, Alaska.
- Parsons ES, Inc., 1995a, *Intrinsic Remediation Engineering Evaluation/Cost Analysis*, Hill AFB, Utah.
- Parsons ES, Inc., 1995b *Intrinsic Remediation Treatability Study*, Patrick AFB, Florida.
- Parsons ES, Inc., 1995c, *Draft Intrinsic Remediation Treatability Study*, Eglin AFB, Florida.
- Parsons ES, Inc., 1995d, *Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis*, Bolling AFB, D.C.

- Parsons ES, Inc., 1995e, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis, Madison ANGB, Wisconsin.
- Parsons ES, Inc., 1995f, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis, Battle Creek ANGB, Michigan.
- Parsons ES, Inc., 1995g, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis, Upper Naknek Site, King Salmon AFB, Alaska.
- Parsons ES, Inc., 1995h, Intrinsic Remediation Treatability Study for the Gasoline Station, MacDill AFB, Florida.
- Parsons ES, Inc., 1995i, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis, Myrtle Beach, South Carolina.
- Parsons ES, Inc., 1995j, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis for FT-003, Offutt AFB, Nebraska.
- Parsons ES, Inc., 1995k, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis for FT-001, Westover AFRES, Massachusetts.
- Parsons ES, Inc., 1995l, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis for FT-003, Westover AFRES, Massachusetts.
- Parsons ES, Inc., 1995m, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis Seymour Johnson AFB, North Carolina.
- Parsons ES, Inc., 1995n, Draft Intrinsic Remediation Engineering Evaluation/Cost Analysis Pope AFB, North Carolina.
- Parsons ES, Inc., 1995o, Intrinsic Remediation Treatability Study for Site ST-57, MacDill AFB, Florida.
- Parsons ES, Inc., 1995p, Intrinsic Remediation Treatability Study for Site OT-24, MacDill AFB, Florida.
- Parsons ES, Inc., 1995q, Intrinsic Remediation Treatability Study, Langley AFB, Virginia.
- Payne, W.J., 1981, The status of nitric oxide and nitrous oxide as intermediates in denitrification: In, C.C. Delwiche, editor, Denitrification, Nitrification, and Atmospheric Nitrous Oxide: Wiley-Interscience, New York, New York, p. 85-103.
- Perry, J. J, 1984, Microbial metabolism of cyclic alkanes, In, Petroleum Microbiology. R. M. Atlas, editor, Macmillan Publishing Co., New York, p. 61-67.
- Postgate, J. R. 1984. The sulfate-reducing bacteria. Cambridge University Press, New York.
- Rao, P.S.C., and Davidson, J.M., 1980, Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models, In, M.R. Overcash and J.M. Davidson, editors, Environmental Impact of Nonpoint Source Pollution: Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p. 23-67.

- Reinhard, M., Goodman, N.L., and Barker, J.F., 1984, Occurrence and distribution of organic chemicals in two landfill leachate plumes: *Environmental Science and Technology*, 18:953-961.
- Rifai, H.S., Bedient, P.B., Wilson, J.T., Miller, K.M., and Armstrong, J.M., 1988, Biodegradation modeling at aviation fuel spill site: *Journal of Environmental Engineering*, v. 114, no. 5, p. 1007-1029.
- Riser-Roberts, E., 1992, *Bioremediation of Petroleum Contaminated Sites*: C.K. Smoley, Boca Raton, Florida, 461 p.
- Roy, W.R., Krapac, I.G., Chou, S.F.J., and Griffin, R.A., 1992, Batch-type procedures for estimating soil adsorption of chemicals: United States Environmental Protection Agency Technical Resource Document EPA/530-SW-87-006-F, 100 p.
- Segol, 1994, *Classic Groundwater Simulations*:
- Sellers, K.L., and Schreiber, R.P., 1992, Air sparging model for predicting groundwater clean up rate: Proceedings of the 1992 NGWA Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Prevention, Detection, and Restoration Conference, November, 1992.
- Shwarzenbach, R.P. and Westall, J., 1981, Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies: *Environmental Science and Technology*, p. 1360-1367.
- Shwarzenbach, R.P., W. Giger, E. Hoehn, and J. K. Schneider. 1983. Behavior of organic compounds during infiltration of river water to groundwater. Field studies. *Environmental Science and Technology*, 17:472-479.
- Shwarzenbach, R.P., and Westall, J., 1985, Sorption of hydrophobic trace organic compounds in groundwater systems: *Water Science Technology*, v. 17, p. 39-55.
- Singer, M. E., and Finnerty, W.R., 1984, Microbial metabolism of straight-chain and branched alkanes, In R.M. Atlas, editor, *Petroleum Microbiology*: Macmillan Publishing Co., New York, p. 1-59.
- Smith, J.H., Harper, J.C., and Jaber, H., 1981, Analysis and environmental fate of Air Force distillate and high density fuels: Report No. ESL-TR-81-54, Tyndall Air Force Base, Florida, Engineering and Services Laboratory.
- Smith, M. R., 1990, The biodegradation of aromatic hydrocarbons by bacteria: *Biodegradation*, 1:191-206.
- Srinivasan, P., and Mercer, J.W., 1988, Simulation of biodegradation and sorption processes in groundwater: *Ground Water*, v. 26, no. 4, p. 475-487.
- Starr, R.C. and Gillham, R.W., 1993, Denitrification and organic carbon availability in two aquifers: *Ground Water*, v. 31, no. 6, p. 934-947
- Stauffer, T.B., T.B. Antworth, J.M. Boggs, and W.G. MacIntyre. 1994. "A Natural Gradient Tracer Experiment in a Heterogeneous Aquifer with Measured In Situ Biodegradation Rates: A Case for Natural Attenuation." In Proceedings of the Symposium on Intrinsic

- Bioremediation of Groundwater, August 30 - September 1, 1994. US Environmental Protection Agency, p. 73 - 84.
- Stotzky, G., 1974, Activity, ecology, and population dynamics of microorganisms in soil, In A. Laskin and H. Lechevalier editors, *Microbial ecology*: CRC Press, Cleveland, p. 57-135.
- Stookey, L. L. 1970. Ferrozine-A new spectrophotometric reagent for iron. *Anal. Chem.* 42:779-781
- Stucki, J. W., P. Komadel, and H. T. Wilkinson. 1987. Microbial reduction of structural iron (III) in smectites. *Soil Science Society of America Journal.* 51: 1663-1665
- Stucki, J. W. P. F. Low, C. B. Roth, and D. C. Golden. 1984. Effects of oxidation state of octahedral iron on clay swelling. *Clays and Clay Minerals.* 32:357-362
- Stumm, W., and Morgan, J. J., 1981, *Aquatic Chemistry*: John Wiley & Sons, New York.
- Sutton, C., and Calder, J.A., 1975, Solubility of higher-molecular weight n-paraffins in distilled water and seawater: *J. Chem. Eng. Data*, v. 20, p. 320-322.
- Swindoll, M.C., Aelion, C.M., and Pfaender, F.K., 1988, Influence of inorganic and organic nutrients on aerobic biodegradation and on the adaptation response of subsurface microbial communities: *Applied and Environmental Microbiology*, 54(1):221-217.
- Testa, S.M., and Paczkowski, M.T., 1989, Volume determination and recoverability of free hydrocarbon: *Ground Water Monitoring Review*, Winter, 1989, p. 120-128.
- Thierrin, J., Davis, G.B., Barber, C., Patterson, B.M., Pribac, F., Power, T.R., and Lambert, M., 1992, Natural degradation rates of BTEX compounds and naphthalene in a sulfate reducing groundwater environment, In *In-Situ Bioremediation Symposium "92"*, Niagara-on-the-Lake, Ontario, Canada, September 20-24, 1992: In Press.
- Trudgill, P. W., 1984, Microbial degradation of the alicyclic ring: structural relationships and metabolic pathways, In D.T. Gibson, editor, *Microbial Degradation of Organic Compounds*: Marcel Dekker, Inc. New York, p. 131-180.
- US Environmental Protection Agency, 1987, *A Compendium of Superfund Field Methods*. EPA/540/P-87/001A. OSWER Directive 9355.0-14.
- US Environmental Protection Agency, 1990, *Groundwater - Volume 1: Groundwater and Contamination*: EPA/625/6-90/016A.
- US Environmental Protection Agency, 1991a, *Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells*: EPA/600/4-89/034, 221 pp.
- US Environmental Protection Agency, 1992b. *Contract Laboratory Program Statement of Work for Inorganics Analyses, Multi-Media, Multi-Concentration*. Document Number ILM03.0.
- van Genuchten, M. Th. and Alves, W.J., 1982, *Analytical Solutions of the One-Dimensional Convective-Dispersive Solute Transport Equation*: U.S. Department of Agriculture, Technical Bulletin Number 1661, 151 p.

- von Gunten, U., and Zobrist, J., 1993, Biogeochemical changes in groundwater-infiltration systems - Column Studies: *Geochim. Cosmochim. Acta*, v.57, p. 3895-3906.
- Vogel, T. M., and Grbic-Galic, D., 1986, Incorporation of Oxygen from Water into Toluene and Benzene During Anaerobic Fermentative Transformation: *Applied and Environmental Microbiology*, 52:200-202.
- Vroblesky, D.A., and Chapelle, F.H., 1994, Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation: *Water Resources Research*, v. 30, no. 5, p. 1561-1570.
- Walton, W.C., 1988, *Practical Aspects of Groundwater Modeling*: National Water Well Association, Worthington, Ohio, 587 p.
- Walton, W.C., 1991, *Principles of Groundwater Engineering*: Lewis Publishers, Chelsea, Michigan, 546 p.
- Wexler, E.J. 1992. Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow: United States Geological Survey, *Techniques of Water-Resources Investigations of the United States Geological Survey*, Book 3, Chapter B7, 190 p.
- Wiedemeier, T.H., Guest, P.R., Henry, R.L., and Keith, C.B., 1993, The use of Bioplume to support regulatory negotiations at a fuel spill site near Denver, Colorado, *In Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference*: NWWA/API, p. 445 -459.
- Wiedemeier, T.H., Miller, R.N., Wilson, J.T., and Kampbell, D.H., 1994a, Proposed Air Force guidelines for successfully supporting the intrinsic remediation (natural attenuation) option at fuel hydrocarbon contaminated sites: Accepted for presentation at the 1994 NWWA/API Outdoor Action Conference.
- Wiedemeier, T.H., Blicher, B., and Guest, P.R., 1994b, Risk-based approach to bioremediation of fuel hydrocarbons at a major airport: *Federal Environmental Restoration III & Waste Minimization Conference & Exhibition*.
- Wiedemeier, T.H., Swanson, M.A., Herrington, R.T., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1995a, Comparison of two methods for determining biodegradation rate constants at the field scale: Submitted to *Ground Water Monitoring and Remediation*.
- Wiedemeier, T.H., Swanson, M.A., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1995b, Patterns of Intrinsic Bioremediation at Two United States Air Force Bases: *In Proceedings of the 1995 Conference on Bioremediation*
- Wiedemeier, T.H., Wilson, J.T., and Miller, R.N., 1995c, Significance of Anaerobic Processes for the Intrinsic Bioremediation of Fuel Hydrocarbons: *In Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference*: NWWA/API.

- Willey, L.M., Kharaka, Y.K., Presser, T.S., Rapp, J.B., and Barnes, Ivan, 1975 Short chain aliphatic acid anions in oil field waters and their contribution to the measured alkalinity: *Geochimica et Cosmochimica Acta*, v. 39. p. 1707-1711.
- Wilson, B. H., Smith, G.B., and Rees, J.F., 1986, Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material - A microcosm study: *Environmental Science and Technology*, 20:997-1002.
- Wilson, B.H., Bledsoe, B., and Kampbell, D., 1987, Biological processes occurring at an aviation gasoline spill site, In R. C. Averett and D. M. Mcknight editors, *Chemical Quality of Water and the Hydrologic Cycle*: Lewis Publishers, Chelsea, Michigan, p. 125-137.
- Wilson, B.H., Wilson, J.T., Kampbell, D.H., Bledsoe, B.E., and Armstrong, J.M., 1990, Biotransformation of monoaromatic and chlorinated hydrocarbons at an aviation gasoline spill site: *Geomicrobiology Journal*, v. 8, p. 225-240.
- Wilson, J.L., and Miller, P.J., 1978, Two-dimensional plume in uniform ground-water flow: *American Society of Civil Engineers, Journal of Hydraulic Division*, v. 104, no. HY4, p. 503-514.
- Wilson, J.T., McNabb, J.F., Cochran, J.W., Wang, T.H., Tomson, M.B., and Bedient, P.B., 1985, Influence of microbial adaptation on the fate of organic pollutants in groundwater: *Environmental Toxicology and Chemistry*, v. 4, p. 721-726.
- Wilson, J.T., Leach, L.E., Henson, M., and Jones, J.N., 1986, In Situ bioremediation as a groundwater remediation technique: *Ground Water Monitoring Review*, Fall 1986, p. 56-64.
- Wilson, J.T., Kampbell, D.H., and Armstrong, J., 1993, Natural bioreclamation of alkylbenzenes (BTEX) from a gasoline spill in methanogenic groundwater: *Proceedings of the Environmental Restoration Technology Transfer Symposium, San Antonio, Texas*
- Wilson, J.T., Pfeffer, F.M., Weaver, J.W., Kampbell, D.H., Wiedemeier, T.H., Hansen, J.E., and Miller, R.N., 1994, Intrinsic bioremediation of JP-4 jet fuel: *United States Environmental Protection Agency, Symposium on Intrinsic Bioremediation of Groundwater, EPA/540/R-94/515*, p. 60-72.
- Wu, J., C. B. Roth, and P. F. Low. 1988. Biological reduction of structural iron in sodium-nontronite. *Soil Science Society of America Journal*. 52: 295-296
- Young, L.Y., 1984, Anaerobic degradation of aromatic compounds, In, D.R. Gibson, editor, *Microbial Degradation of Aromatic Compounds*: Marcel-Dekker, New York.
- Zehnder, A. J. B., 1978, Ecology of Methane Formation, In, R. Mitchell editor, *Water Pollution Microbiology*: Wiley, New York, p. 349-376.
- Zeyer, J., Kuhn, E.P., and Schwarzenbach, R.P., 1986, Rapid microbial mineralization of toluene and 1,3 dimethylbenzene in the absence of molecular oxygen: *Applied & Environmental Microbiology*, v. 52, p. 944-947.

APPENDIX A

SITE CHARACTERIZATION IN SUPPORT OF INTRINSIC REMEDIATION

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SECTION A-1

INTRODUCTION

Detailed site characterization is an important aspect of the intrinsic remediation demonstration. A review of existing site characterization data is particularly useful before initiating supplemental site characterization activities. Such a review allows development of a preliminary conceptual hydrogeologic model and facilitates effective placement of additional data collection points. Because the burden of proof for intrinsic remediation is on the proponent, very detailed site-specific characterization is required to support this remedial option.

To help quantify rates of intrinsic remediation and to help successfully implement this remedial option, the following site-specific physical and chemical hydrogeologic parameters should be determined:

Physical hydrogeologic characteristics to be determined include:

- Depth from measurement datum to the groundwater surface (and to mobile light nonaqueous-phase liquid [LNAPL], if present).
- Depths from measurement datum to the top and base of the shallow saturated zone (where feasible).
- Hydraulic conductivity through slug or pumping tests, as required.
- Estimate of dispersivity (accepted literature values are generally used).
- Estimate of effective porosity (accepted literature values are generally used).
- Stratigraphic analysis of subsurface media.
- Interaction between groundwater and surface water and rates of infiltration/recharge.
- Preferential flow paths for contaminant transport.
- Patterns of aquifer use.
- Location of potential receptors, including groundwater recharge and discharge areas.

- Groundwater well locations, including municipal supply wells and well fields, private domestic wells, agricultural supply wells, industrial production wells, and any other groundwater production wells
- Groundwater discharge points downgradient of site.

Chemical hydrogeologic characteristics to be determined include:

- Three-dimensional distribution of residual, mobile, and dissolved contaminants. The distribution of residual and mobile contaminants will be used to define the dissolved plume source area.
- Groundwater quality and geochemical data, including
 - Alkalinity
 - Aromatic hydrocarbons (including the trimethylbenzene isomers)
 - Total petroleum hydrocarbons (total volatile hydrocarbons [TVH] and total extractable hydrocarbons [TEH])
 - Dissolved oxygen
 - Iron (II)
 - Methane
 - Nitrate
 - Sulfate
 - Temperature
 - Chloride
 - Conductivity
 - pH
 - Oxidation/reduction (redox) potential
 - Any other analyses required for regulatory compliance
- Soil quality and geochemical data, including
 - Total petroleum hydrocarbons
 - Benzene, toluene, ethylbenzene, and xylenes (BTEX)
 - Total organic carbon (TOC)
 - Moisture
 - Any other analyses required for regulatory compliance
- Chemical analysis of mobile LNAPL to determine mass fraction of BTEX.

Several soil, groundwater, and LNAPL sampling techniques may be used to gather these data, including conventional soil borings, cone penetrometer testing (CPT), monitoring well installation and sampling, Geoprobe® or Hydropunch® sampling, and soil gas sampling. Regardless of the techniques used, groundwater, soil, and LNAPL samples must be obtained for laboratory analyses. At sites where surface water bodies are affected (or potentially affected) by contamination, surface water and sediment sample collection and analysis may be useful. Laboratory analyses should be performed on as many soil and groundwater samples as is necessary to define the horizontal and vertical extent of contamination. The final number and locations of samples should be based on regulatory considerations. The analytical protocols to be used for soil and groundwater samples are discussed in Section 2 of the protocol document. If LNAPL is present at the site, a sample of it should be analyzed for mass fraction of BTEX so that equilibrium dissolved concentrations can be determined.

This appendix consists of six sections, including this introduction. Section A-2 discusses preliminary conceptual model development and selection of sites for additional data collection. Section A-3 discusses soil characterization methodologies. Section A-4 discusses groundwater characterization methodologies. Section A-5 discusses soil and groundwater handling procedures. Section A-6 discusses aquifer characterization methodologies.

SECTION A-2

PRELIMINARY CONCEPTUAL MODEL DEVELOPMENT AND LOCATION OF ADDITIONAL DATA POINTS

After reviewing existing site characterization data, a preliminary conceptual model should be developed and an assessment of the potential for intrinsic remediation made. Successful conceptual model development involves integrating site-specific data into a coherent representation of the groundwater flow and contaminant transport system. A conceptual model is a three-dimensional representation of the groundwater flow and contaminant transport system based on available geological, hydrological, climatological, and analytical data for the site. After development, the preliminary conceptual model will be used to determine optimal placement of additional data collection points and to help develop the numerical groundwater flow and contaminant transport model for the site.

Successful conceptual model development involves:

- Definition of the problem to be solved (generally the unknown nature and extent of existing and future contamination).
- Integration of available data including:
 - Local geologic and topographic maps
 - Hydraulic data
 - Biological data
 - Geochemical data
 - Site stratigraphy
 - Contaminant concentration and distribution data (isopleth maps).
- Determination of additional data requirements, including:
 - Borehole locations and monitoring well spacing
 - An approved sampling and analysis plan.

Ancillary data that are necessary for conducting an exposure pathways analysis also should be determined concurrently with development of the conceptual model. These data can include the following:

- Determination of preferential groundwater flow pathways and points of groundwater discharge at which receptors may be exposed.
- Research to compile sociocultural data (e.g., surrounding land uses and well surveys) to establish potential receptors and receptor exposure points.
- Determination of applicable regulatory standards for groundwater, and soil if appropriate.
- Determination of likely future land use scenarios.

These data will help establish regulatory point-of-compliance (POC) goals and aid in the selection of locations for POC wells to ensure that human health and the environment are not adversely impacted by site-related contamination.

SECTION A-3

SOIL CHARACTERIZATION METHODOLOGIES

Several techniques are available for collection of soil samples for lithologic description and laboratory analysis. Regardless of the lithologic logging technique chosen, it is imperative that continuous samples be collected so that stratigraphic relationships and the vertical extent of soil contamination can be determined. Conventional soil borings are generally the most common method used for soil sample collection. Newer technologies, such as CPT allow a much larger area to be covered in a given time, but are somewhat limited in their ability to collect soil samples. Lithologic logs and soil analytical results from previous investigations may be available to supplement or eliminate soil characterization activities in support of intrinsic remediation. Regardless of the source of information or the method chosen, sufficient soil samples must be collected to adequately define the horizontal and vertical extent of contamination and those soil characteristics that would affect the migration (transport) and distribution of contaminants.

In order to increase investigation efficiency, all necessary digging, drilling, and groundwater monitoring well installation permits should be obtained prior to mobilizing to the field. In addition, proposed drilling locations must be cleared for utilities and other infrastructure prior to any drilling activities. Frequently, results obtained during field investigations indicate that an alternate sampling strategy might provide more appropriate information than the one originally proposed. Therefore, it is useful to have all utility lines located and marked prior to initiation of field activities to allow for investigation flexibility.

In general, water to be used in drilling, equipment cleaning, or grouting should be obtained from a potable water supply. Water use approval should be verified by contacting the appropriate facility personnel. The field scientist should make the final determination of the suitability of the water to be used for these activities.

A.3.1 SOIL BORINGS

Soil boring locations should be selected to provide sufficient data for successful implementation of the intrinsic remediation option. Soil boring data will be used to refine the preliminary conceptual model and as input into a numerical model, such as Bioplume II®. The biggest advantages of soil borings are that a large sample volume can be generated and US Environmental Protection Agency (USEPA) approved monitoring wells can be installed in such borings. Some disadvantages of soil borings are that they are time consuming and they generate large volumes of potentially contaminated soil that must be properly managed.

A.3.1.1 Equipment Decontamination Procedures

In order to prevent sample cross contamination, equipment decontamination must be performed. At a minimum, decontamination procedures should include the use of a high-pressure, steam/hot water wash. Some projects, states, or USEPA Regions may require additional decontamination procedures. Upon arrival at the site, and between each borehole, the augers, drilling rods, bits, casing, samplers, tools, and other downhole equipment should be decontaminated. The drill rig also should be decontaminated upon arrival at the site. Only water from an approved source should be used for decontamination.

All sampling tools must be cleaned onsite, prior to use and between each sampling event, with a clean water/phosphate-free detergent mix and a clean water rinse. Materials that cannot be cleaned to the satisfaction of the field scientist should not be used. All decontamination activities must be conducted in a manner so that the excess water will be controlled and not allowed to flow into any open borehole. Some projects, states, or USEPA Regions may require containment of the decontamination fluids

A.3.1.2 Drilling and Soil Sampling

Drilling in unconsolidated soils is generally accomplished using the hollow-stem auger method. If subsurface conditions are such that the planned drilling technique does not produce acceptable results (e.g., unstable borehole walls or poor soil sample recovery), another technique deemed more appropriate for the type of soils present should be used. Any alternate soil sampling procedure used must be approved by the field scientist and should be appropriate for the subsurface lithologies present at the site.

Continuous soil samples should be obtained using a CME[®] split-barrel, continuous sampling device or another similar method judged acceptable by the field scientist. Samples must be collected continuously over the full depth of the soil borehole. Direct collection of soil samples into liners within the split-spoon sampler will better preserve volatile organic compounds (VOCs). The soil samples should be split and removed from the continuous sampler. A portion of the sample should immediately be transferred to sample vials for laboratory analysis. A representative portion of the soil sample should be screened for VOCs using photoionization detector (PID) headspace measurements. Soil samples collected for the headspace procedure should correlate with samples placed in laboratory sample vials and should be quickly transferred to clean glass jars, sealed with aluminum foil, and held for 15 minutes at an ambient temperature of 68 degrees Fahrenheit (°F) or greater. The field scientist should record both the hold time and ambient temperature in the field log book. Semiquantitative measurements of VOC concentrations are made by puncturing the aluminum foil seal with the PID probe and reading the concentration of the headspace gases. The PID relates the concentration of total VOCs in the sample to an isobutylene calibration standard. Headspace measurements should be performed on all samples collected during drilling operations. Soil samples with the highest PID readings should be submitted to the laboratory for analysis. Actual sampling procedures should be in accordance with local, state, and federal requirements.

The field scientist should observe all drilling and sample collection activities, maintain a detailed descriptive log of subsurface materials recovered, photograph representative samples, and properly label and store soil samples. An example of a geologic boring log form is presented in Figure A.3.1. This example should be adequate for most sites. If there is significant vertical variability, the scale should be adjusted accordingly. The descriptive log must contain, at a minimum:

- Sample interval (top and bottom depths);
- Sample recovery;
- Presence or absence of contamination (based on PID, visual, or olfactory evidence);
- Water level during drilling, the water level at the completion of drilling, and the overnight or 24-hour water level if the borehole remains open;
- Sediment or rock description, including relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations;

GEOLOGIC BORING LOG

Sheet 1 of 1

BORING NO.: _____ CONTRACTOR: _____ DATE SPUD: _____
 CLIENT: _____ RIG TYPE: _____ DATE CMPL.: _____
 JOB NO.: _____ DRLG METHOD: _____ ELEVATION: _____
 LOCATION: _____ BORING DIA: _____ TEMP: _____
 GEOLOGIST: _____ DRLG FLUID: _____ WEATHER: _____
 COMENTS: _____

Elev. (ft)	Depth (ft)	Profile	USCS	Geologic Description	Sample		Penet. Res	PID (ppm)	TLV (ppm)	TOTAL BTEX (ppm)	TPH (ppm)
					No.	Depth (ft)					
	1										
	5										
	10										
	15										
	20										
	25										
	30										
	35										

Water Level During Drilling _____
 Water Level @ Completion of Drilling _____
 Water Level After 24 Hours (if borehole left open) _____

NOTES
 bgs - Below Ground Surface
 GS - Ground Surface
 TOC - Top of Casing
 NS - Not Sampled
 SAA - Same As Above

SAMPLE TYPE
 D - DRIVE
 C - CORE
 G - GRAB

Figure A.3.1
Example Geologic Boring Log

- Unified soil classification system classification of sediments;
- Blow counts, and any additional drilling or soil sampler information (cable tool blows, Shelby tube time/pressure, etc.); and
- Lithologic contacts: the depth of lithologic contacts and/or significant textural changes should be measured and recorded to the nearest 0.1 foot (1 inch).

Soils exhibiting petroleum hydrocarbon contamination based on PID screening should be handled in accordance with local regulations. Upon completion of the drilling activities, samples from the contaminated soils should be collected and analyzed by the appropriate USEPA-approved methods for waste disposal characterization. Some projects, states, or USEPA Regions may require containment and sampling of all investigation-derived soils.

If contaminated soils are encountered during drilling (based on visual, olfactory, or PID indications), and the potential for cross-contamination is anticipated, drilling should be stopped, and modified drilling procedures should be implemented to prevent the transfer of contaminants to deeper water-bearing strata.

Surface runoff such as miscellaneous spills and leaks, precipitation, and spilled drilling fluid must not be allowed to enter any borehole or well either during or after borehole drilling/well construction. To prevent this from happening, starter casing, recirculation tanks, berms around the borehole, or surficial bentonite packs, as appropriate, should be used.

A.3.1.3 Borehole Abandonment

In general, any borehole should be completed as a monitoring well, bioventing well, or bioventing monitoring point. Completing all boreholes in this manner usually saves money in the long run. For example, if a borehole is completed in the unsaturated zone in a contaminated area, it is possible that bioventing may be required at a later date. If the borehole is abandoned, it may be necessary to install a bioventing well at a later date. If a bioventing well is initially installed in the borehole, such duplication of effort is not necessary. As another example, if a borehole is completed in the unsaturated zone in an uncontaminated area, it is possible that bioventing may be required in the area at a later date and this location can be used as a bioventing or background monitoring point, thereby avoiding unnecessary duplication of effort.

If for some reason, a borehole is not completed as a monitoring well, bioventing well, or bioventing monitoring point, it must be abandoned according to state or federal protocol.

Borehole abandonment is generally accomplished by backfilling the hole with bentonite chips or a Portland cement/sodium bentonite grout mixture to within approximately 3 feet of ground surface. If Portland cement/sodium bentonite grout is used, the bentonite content of the grout generally should not exceed 5 percent by dry weight. If standing water is present in the boring, the grout mixture should be placed using a tremie pipe inserted below the static water level near the bottom of the boring. The grout mixture should be pumped through the tremie pipe until undiluted grout is present near ground surface in the boring.

Twenty-four hours after abandonment, the field scientist should check the abandoned site for grout settlement and specify additional grout, or backfill the hole to ground surface with clean native soil, or concrete, as necessary. Boreholes drilled through asphalt or concrete paving should be finished with a like material blended to the surrounding pavement.

A.3.2 CONE PENETROMETER TESTING

CPT is increasingly being used for successful site characterization. CPT is accomplished using a cone penetrometer truck, which consists of an instrumented probe that is forced into the ground using a hydraulic load frame mounted on a heavy truck, with the weight of the truck providing the necessary reaction mass. The penetrometer equipment is generally mounted inside an 18-foot van body attached to a 10-wheel truck chassis with a turbo-charged diesel engine. Ballast in the form of metal weights and a steel water tank that can hold approximately 5,000 pounds of water, are added to the truck to achieve an overall push capability of approximately 45,000 pounds. This push capacity may be limited in tight soils by the structural bending capacity of the 1.405-inch outside-diameter (OD) push rods, rather than by the weight of the truck. Penetration force is supplied by a pair of large hydraulic cylinders bolted to the truck frame.

The penetrometer probe generally has a 1.405-inch-OD, 60-degree conical tip, and a 1.405-inch-OD by 5.27-inch-long friction sleeve. Inside the probe, two load cells independently measure the vertical resistance against the conical tip and the side friction along the sleeve. Each load cell is a cylinder of uniform cross section inside the probe which is instrumented with four strain gauges in a full-bridge circuit. Forces are sensed by the load cells, and the data are transmitted from the probe assembly via a cable running through the push tubes. The analog data are digitized, recorded, and plotted by computer in the penetrometer truck. Penetration, dissipation, and resistivity data are used to determine site stratigraphy.

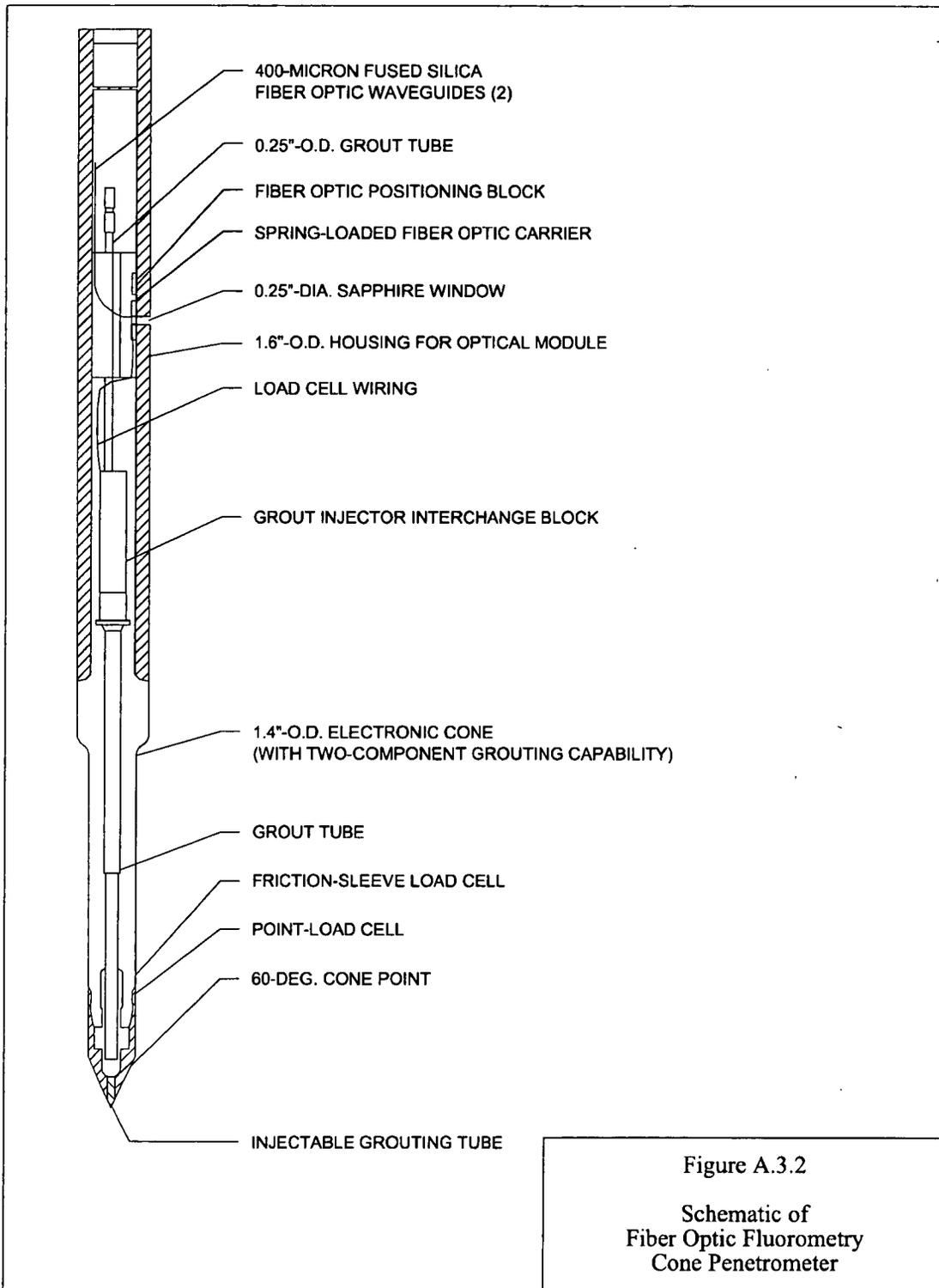
In some cases, the CPT tool can be coupled with a laser-induced fluorescence (LIF) device that is used to delineate the areal extent of a contaminant plume. The LIF/CPT probe is designed to measure tip and sleeve stress, pore pressure, and LIF simultaneously. A fiber optic cable connected to the laser spectrometer, and a 6-pair electrical conductor connected to the CPT data acquisition system, are routed through the interior of the push tubes to the CPT probe. Two load cells measure vertical resistance beneath the tip and frictional resistance on the side of the probe, respectively. A pressure gauge located above the cone tip monitors the pore water pressure. Figure A.3.2 is a schematic of the CPT tip that incorporates LIF.

The basic laser system components of the LIF-CPT are a Nd:YAG[®] pump laser, two separate and independent dye lasers, frequency-doubling crystals to convert the visible dye laser output to ultraviolet, a fiber optic probe, a monochromator for wavelength resolution of the return fluorescence, a photomultiplier tube to convert photons into an electrical signal, a digital oscilloscope for waveform capture, and a control computer. The fiber optic probe for the cone penetrometer consists of a delivery and a collection fiber, a protective sheath, a fiber optic mount within the cone, and a sapphire window. The uphole portion of the system is adaptable to either groundwater monitoring fiber optic probes or an optical cone penetrometer probe. Optimal wavelengths to be used during a continuous CPT push are determined from initial data. Wavelength is selected to give the strongest fluorescence signal, which can be attributed to the presence of contamination. Past experience suggests that a short wavelength of less than 275 nanometers (nm) may be appropriate for the fluorescence of BTEX.

A.3.2.2 Soil Core Sampling and Analysis

The purpose of the soil corings is to verify/validate the LIF/CPT data. All necessary digging permits should be obtained prior to mobilizing to the field. In addition, all utility lines should be located and all proposed CPT locations cleared prior to any CPT pushing activities.

Soil cores collected for CPT confirmation/calibration can be collected using standard HSA techniques, Geoprobe sampling apparatus, or in some cases, CPT sampling apparatus. Enough cores must be collected to allow confirmation/calibration of the CPT readings. The actual number of soil cores will depend on site conditions. The determination of the number of soil cores required to confirm/calibrate the CPT data should be made by the field geologist in conjunction with the CPT operator. Soil samples should be collected continuously over the full depth of the CPT penetration. Procedures should be modified, as necessary, to ensure good sample recovery.



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Direct collection of soil samples into liners within the sampler will better preserve VOCs. The soil samples should be split and removed from the continuous sampler. A portion of the sample should immediately be transferred to sample vials for laboratory analysis. A representative portion of the soil sample should be analyzed for VOCs using PID headspace measurements, as described in Section A.3.1.2.

The field scientist should observe all drilling and sample collection activities, maintain a detailed descriptive log of subsurface materials recovered, photograph representative samples, and properly label and store soil samples. An example of a geologic boring log form is presented in Figure A.3.1. This example should be adequate for most sites. If there is a large amount of vertical variability then the scale should be adjusted accordingly. The contents of the descriptive log are listed in Section A.3.1.2.

Although soil cuttings should be very minimal with the CPT technology, any soil cuttings exhibiting petroleum hydrocarbon contamination based on PID screening should be handled in accordance with local regulations.

A.3.2.3 CPT Hole Grouting Procedure

Cone penetrometer testing can create holes that may provide potential contamination pathways into groundwater. To prevent cross contamination, the test holes should be grouted to seal the hole and eliminate the contaminant migration pathway. The instrumented cone assembly and any other retrievable portion of the assembly will be completely removed from the penetration hole. Grout is generally prepared by mixing up to 5 percent (by dry weight) bentonite with Portland cement. Some CPT trucks are capable of injecting grout into the hole as the pushrods are removed.

A.3.2.4 Decontamination Procedures

Generally, the CPT push rods are cleaned with a steam-cleaning system as the rods are withdrawn from the ground. Most cone penetrometer trucks have a vacuum system that recovers nearly 100 percent of the steam-cleaning rinseate. Rinseate is generated only as the rods move past the cleaner, thereby minimizing liquid waste generation. Care should be taken not to apply the pressurized steam to the LIF module. Rinseate generally should be collected for proper disposal.

Potable water should be used for CPT equipment cleaning, decontamination, and grouting. Precautions should be taken to minimize any impact to the surrounding area that might result from decontamination operations. Fuel, lubricants, and other similar substances are to be handled in a manner consistent with accepted safety procedures and standard operating practices.

A.3.3 BORING AND CONE PENETROMETER TEST LOCATION SURVEY

The horizontal location of all boring and CPT locations should be measured relative to established coordinates. Horizontal coordinates should be measured to the nearest 0.1 foot. The elevation of the ground surface and the measurement datum should be measured relative to mean sea level. The ground surface elevation should be measured to the nearest 0.1 foot, and the measurement datum to the nearest 0.01 foot.

A.3.4 SOIL ANALYTICAL PROTOCOL

The analytical protocol to be used for soil sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and both aerobic and anaerobic biodegradation of fuel hydrocarbons. Section 2.3.1.2 of the protocol document describes each soil analytical parameter and the use of each analyte in the intrinsic remediation demonstration.

SECTION A-4

GROUNDWATER CHARACTERIZATION METHODOLOGIES

This section describes the scope of work required to collect groundwater quality samples to support the intrinsic remediation demonstration. In order to maintain a high degree of quality control during groundwater sampling, the procedures described in the following sections should be followed.

Groundwater sampling should be conducted only by qualified scientists and technicians trained in the conduct of well sampling, sampling documentation, and chain-of-custody procedures. In addition, sampling personnel should thoroughly review this protocol document and the site-specific work plan prior to sample acquisition and have a copy of the work plan available onsite for reference. Detailed groundwater sampling and sample handling procedures are presented in following sections. Samples should be collected in accordance with local, state, and federal requirements.

Rapid and inexpensive survey techniques such as Geoprobe or CPT are appropriate for the initial site characterization and plume definition of the intrinsic remediation demonstration. Conventional monitoring wells will be required for long-term monitoring (LTM) and point-of-compliance (POC) groundwater sampling.

A.4.1 MONITORING WELL INSTALLATION AND SAMPLING

A.4.1.1 Monitoring Well Installation

Groundwater monitoring wells should be located based on the distribution of contaminants in each plume. At a minimum, one monitoring well should be placed upgradient of the contaminant plume, two wells should be placed within the plume, and three wells should be placed various distances downgradient of the plume. The number of wells should be related to site conditions and the size of the spill. To define the three-dimensional extent of contamination and to determine the three-dimensional hydraulic relationships within the saturated zone, it is best to use nested wells with a maximum screened interval of 5 feet. Screening a larger area of the saturated

zone will result in averaging of contaminant concentrations and hydraulic properties. To ensure well integrity, nested well pairs generally should be completed in separate boreholes. Detailed well installation procedures are described in the following paragraphs. Of course, local protocols, regulations, and site conditions should dictate actual well completion details.

A.4.1.1.1 Well Materials Decontamination

Well completion materials should be inspected by the field scientist to ensure that they are clean and acceptable for monitoring purposes prior to use. If not factory sealed, casing, screen, and casing plugs and caps should be cleaned with a high-pressure, steam/hot-water cleaner using approved water prior to use. Prepackaged sand, bentonite, and Portland cement should be used in well construction, and the bags should be inspected for possible external contamination before use. Materials that cannot be cleaned to the satisfaction of the field scientist should not be used.

A.4.1.1.2 Well Casing

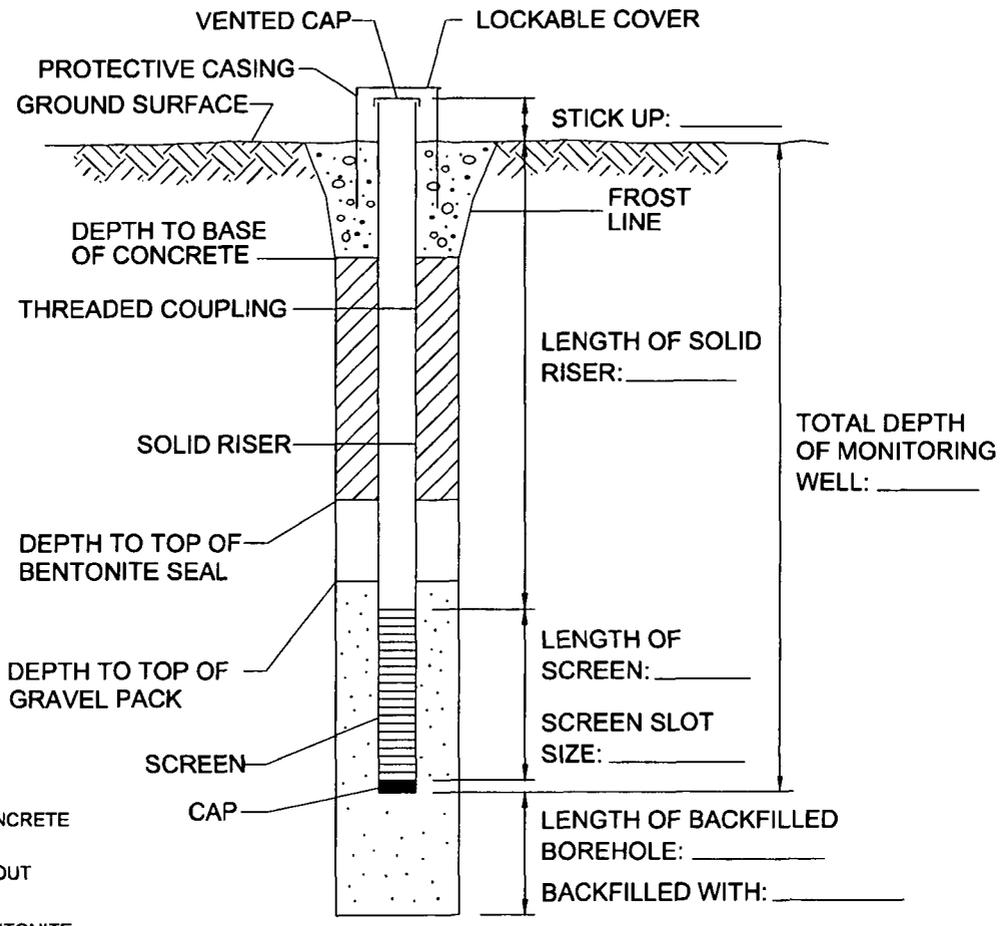
Upon completion of drilling to the proper boring termination depth, the monitoring well casing can be installed. Well construction details should be noted on a Monitoring Well Installation Record form (Figure A.4.1). This information will become part of the permanent field record for the site.

Blank well casing should be constructed of Schedule 40 polyvinyl chloride (PVC) with an inside diameter (ID) of 2 inches when installing wells in boreholes, and Schedule 40 PVC with an ID of 0.5 or 1.5 inches when installing wells in CPT holes. All well casing sections should be flush-threaded; glued joints should not be used. The casing at each well should be fitted with a threaded bottom plug and a top cap constructed of the same type of material as the well casing. The top should be vented to maintain ambient atmospheric pressure within the well casing. Site conditions and local, state, and federal requirements should ultimately dictate well completion details and materials.

The field scientist should verify and record the boring depth, the lengths of all casing and screen sections, and the depth to the top of all well completion materials placed in the annulus between the casing and borehole wall. All lengths and depths should be measured to the nearest 0.1 foot.

MONITORING WELL INSTALLATION RECORD

JOB NAME _____ WELL NUMBER _____
 JOB NUMBER _____ INSTALLATION DATE _____ LOCATION _____
 DATUM ELEVATION _____ GROUND SURFACE ELEVATION _____
 DATUM FOR WATER LEVEL MEASUREMENT _____
 SCREEN DIAMETER & MATERIAL _____ SLOT SIZE _____
 RISER DIAMETER & MATERIAL _____ BOREHOLE DIAMETER _____
 GRANULAR BACKFILL MATERIAL _____ ES REPRESENTATIVE _____
 DRILLING METHOD _____ DRILLING CONTRACTOR _____



-  CONCRETE
-  GROUT
-  BENTONITE
-  GRANULAR BACKFILL

(NOT TO SCALE)

STABILIZED WATER LEVEL _____ FEET
 BELOW DATUM.
 MEASURED ON _____

Figure A.4.1

Monitoring Well
 Installation Record

A.4.1.1.3 Well Screen

Well screens should be constructed of Schedule 40 PVC with an ID of 2 inches when installing wells in boreholes, and Schedule 40 PVC with an ID of 0.5 or 1.5 inches when installing wells in CPT holes. The screens should be factory slotted with 0.010-inch openings. Wells generally should be installed in nested pairs with a maximum 5-foot screened interval. Screening a larger section of the saturated zone will result in averaging of contaminant concentrations and hydraulic properties. It is usually desirable to screen at least one well so that seasonal fluctuations of the water table can be measured. The positioning of well screens should be selected by the field scientist after consideration is given to the geometry and hydraulic characteristics of the stratum in which the well will be screened. Wells should be screened so that the vertical distribution of contaminants and hydraulic gradients can be delineated. To ensure well integrity, nested well pairs generally should be completed in separate boreholes. Site conditions and local, state, and federal requirements should ultimately dictate well completion details and materials.

A.4.1.1.4 Sand Filter Pack

When monitoring wells are completed in boreholes, a graded sand filter should be placed around the screened interval and should extend approximately 2 feet above the top of the screen. Design of the sand filter should be based on the grain size distribution of the aquifer matrix as described in Harlan *et al.* (1989), but generally will consist of 10-20 silica sand. When monitoring points are completed in CPT holes, the annulus will generally be too small to allow filter pack construction. In such cases, native aquifer materials will be allowed to collapse around the well. Because of the absence of a filter pack, monitoring points in very silty or clayey materials may yield water that is too turbid for analysis.

A.4.1.1.5 Annular Sealant

An annular seal of sodium bentonite pellets must be placed above the filter pack. The pellet seal should be a minimum of 2 feet thick. When installed above the water table, the bentonite seal should be hydrated in place in 6-inch lifts using potable water. The pellet seal must be overlain by a Portland cement/sodium bentonite grout that will extend from the top of the pellet seal to below the maximum frost line in the region. The Portland cement/sodium bentonite grout should consist of one 94-pound sack of cement and about 5 pounds of bentonite for each 7 gallons of water used. The bentonite content of the cement/bentonite mix should not exceed 5 percent by dry weight. The grout should be overlain by concrete extending to the ground surface. To reduce

heaving of the newly installed monitoring well caused by freeze-thaw processes, it is imperative that the uppermost concrete seal extend below the maximum frost line for the area. In some cases, use of bentonite grout without cement can be used to minimize frost heave damage. USEPA Region 4 has found that in some cases the potable water supply has been chemically treated to the extent that water and soil analyses can be significantly altered. In these cases, an alternate water supply should be used, especially for drilling fluid, water used to prepare grout, and bentonite hydration water.

A.4.1.1.6 Protective Well Cover

To provide protection for the PVC well casing, each monitoring well should be completed with an above-grade or an at-grade protective cover. The choice of installing an above-grade protective well cover versus an at-grade protective well cover will depend mainly on aesthetics and logistical considerations. The facility point-of-contact should be consulted prior to work plan development so the appropriate well cover can be specified. In general, above-grade well covers are better because they are easily located and the problem of standing water in the annulus at the well head is minimized.

A.4.1.1.6.1 Above-Grade Cover

In areas where pavement is present, the above-grade cover should be cemented in place using concrete blended to the existing pavement. In areas where pavement is not already present, a 6-inch-thick, 2-foot-diameter concrete pad should be constructed around the protective cover. In either case, the concrete immediately surrounding the well cover should be sloped gently away from the protective casing to facilitate runoff during precipitation events.

A.4.1.1.6.2 At-Grade Cover

In areas where pavement is present, the at-grade cover should be cemented in place using concrete blended to the existing pavement. In areas where pavement is not already present, a 6-inch-thick, 2-foot-diameter concrete pad will be constructed around the protective cover. In either case, the concrete immediately surrounding the well cover should be sloped gently away from the protective casing to facilitate runoff during precipitation events. The seal of the cap to the well should be water tight.

A.4.1.2 Well Development

Before any new well can be used for monitoring water levels or taking water samples, it must be developed. Development removes sediment from inside the well casing and flushes fines, cuttings, and drilling fluids from the sand pack and the portion of the formation adjacent to the well screen. The water samples are intended for analysis of soluble electron acceptors and petroleum hydrocarbons. A small amount of turbidity does not interfere with these analyses. Turbidity criteria for drinking water are not relevant. Well development should be accomplished in a manner that is consistent with local, state, and federal requirements.

If the depth to water allows, well development can be accomplished using a bailer, peristaltic pump with dedicated Teflon[®]-lined polyethylene tubing, or a submersible pump. The bailer or pump must be regularly lowered to the bottom of the well so that fines that have accumulated in the bottom are agitated and removed from the well in the development water.

Development should be continued until a minimum of 10 casing volumes of water have been removed from the well and the water pH, temperature, specific conductivity, dissolved oxygen concentration, and redox potential have stabilized (i.e., three readings are taken with less than 10 percent difference). If the development water is still turbid after removal of 10 casing volumes, development should be continued until the water becomes clear or the turbidity of the water produced is stable after the removal of several additional casing volumes.

The development procedure specifies that 10 casing volumes of water be removed from the well. However, some wells completed in marginal aquifers will be evacuated dry during well development prior to the recovery of 10 casing volumes. In these low-productivity wells, development activity will have to be staged over a period of time to allow water to refill the well bore. In the event that 10 casing volumes of water cannot be recovered, the water volume recovered should be noted in the development records noting this deficiency.

Clean development waters should be discharged at the drilling site in a manner that will control excessive ponding. Visibly or PID-indicated contaminated waters must be collected in contained and transported to the facility storage area for storage or to the facility water treatment plant for treatment and disposal. The facility point-of-contact should be consulted to determine the final disposition of purge waters. Some projects, states, or USEPA Regions require the containment of all development water produced at potentially contaminated sites.

A record of well development should be maintained for each well. The well development record should be maintained in a bound field notebook or on monitoring well development forms

by the field scientist. Figure A.4.2 is an example of a monitoring well/point development record. A summary well development record form should be prepared for each well. Development records must include:

- Well number;
- Date and time of development;
- Development method;
- Pre-development water level and well depth;
- Volume of water produced;
- Description of water produced;
- Post-development water level and well depth; and
- Field analytical measurements, including pH, temperature, dissolved oxygen concentration, redox potential, and specific conductivity.

A.4.1.3 Groundwater Monitoring Well Sampling

All equipment to be used for sampling should be assembled and properly cleaned and calibrated (if required) prior to arriving in the field. In addition, all record-keeping materials should be gathered prior to leaving the office.

A.4.1.3.1 Preparation for Sampling

Prior to starting the sampling procedure, the area around the well should be cleared of foreign materials, such as brush, rocks, and debris. These procedures will prevent sampling equipment from inadvertently contacting debris around the monitoring well.

A.4.1.3.2 Equipment Cleaning and Calibration

All portions of sampling and test equipment that will contact the sample matrix must be thoroughly cleaned before use. This includes the water-level probe and cable, bailer (unless a dedicated disposable bailer is used), bailer lifting line, test equipment for onsite use, and other equipment or portions thereof that will contact the samples. Based on the types of sample analyses to be conducted, a cleaning protocol similar to the following should be used:

**Figure A.4.2
Example Monitoring Well/Point Development Record**

MONITORING WELL/POINT DEVELOPMENT RECORD

Page__ of__

Job Number _____ Job Name _____
 Location _____ By _____ Date _____
 Well Number _____ Measurement Datum _____

Pre-Development Information

Time (Start): _____

Water Level: _____

Total Depth of Well: _____

Water Characteristics

Color _____ Clear Cloudy
 Odor: None Weak Moderate Strong
 Any Films or Immiscible Material _____
 pH _____ Temperature(°F °C) _____
 Specific Conductance(μS/cm) _____
 Dissolved Oxygen Concentration _____
 Oxidation-Reduction Potential _____

Interim Water Characteristics

Gallons Removed: _____ pH: _____
 Temperature (°F °C): _____ Specific Conductance(μS/cm): _____
 Dissolved Oxygen Concentration: _____ Oxidation-Reduction Potential: _____

Post-Development Information

Time (Finish): _____

Water Level: _____

Total Depth of Well/Point: _____

Approximate Volume Removed: _____

Equipment Used for Development: _____

Pumping Rate and Period (if a pump is used): _____

Water Characteristics

Color _____ Clear Cloudy
 Odor: None Weak Moderate Strong
 Any Films or Immiscible Material _____
 pH _____ Temperature(°F °C) _____
 Specific Conductance(μS/cm) _____
 Dissolved Oxygen Concentration _____
 Oxidation-Reduction Potential _____

Comments:

- Clean with potable water and phosphate-free laboratory detergent such as Alconox®;
- Rinse with potable water;
- Rinse with distilled or deionized water;
- Rinse with reagent-grade methanol or similar;
- Rinse with distilled or deionized water;
- Air dry the equipment prior to use.

Final selection of cleaning procedures should be based on project, state, and USEPA Region requirements and anticipated site contaminants. Any deviations from established cleaning procedures should be documented in the field scientist's field notebook and on the groundwater sampling form.

If pre-cleaned dedicated sampling equipment is used, the cleaning protocol specified above is not required. Laboratory-supplied sample containers will be cleaned, sealed, and certified by the laboratory, and therefore do not need to be cleaned in the field. The type of container provided and the method of container decontamination will be documented in the permanent record of the sampling event.

As required, field analytical equipment should be calibrated according to the manufacturer's specifications immediately prior to use in the field. This applies to equipment used for onsite measurements of pH, electrical conductivity, temperature, dissolved oxygen, and redox potential.

A.4.1.3.3 Water Level and Total Depth Measurements

Prior to removing any water from the well the static water level should be measured. An electric water level probe should be used to measure the depth to groundwater below the datum to the nearest 0.01 foot. After measuring the static water level, the water level probe should be slowly lowered to the bottom of the well, and the total well depth should be measured to the nearest 0.01 foot. Based on these measurements the volume of water to be purged from the well can be calculated. If mobile LNAPL is encountered, the LNAPL thickness should be determined, and attempts should be made to sample both the groundwater below the LNAPL layer and the fluid making up the LNAPL.

A.4.1.3.4 Mobile LNAPL Thickness Measurements

At sites where phase-separated hydrocarbons are present in the groundwater system, it is important to accurately measure the thickness of floating hydrocarbons. Accurate measurement of hydrocarbon thickness allows for estimation of the amount and distribution of the hydrocarbon and correction of measured groundwater elevations.

There are three methods that can be used to determine the thickness of mobile LNAPL in a well, including use of an interface probe, a bailer, or tape and paste. Interface probes generally operate on either tight refraction sensors or density float switches to detect hydrocarbons and the hydrocarbon/water interface. The depth to mobile LNAPL and depth to water should be measured to the nearest 0.01 foot. The thickness of phase-separated hydrocarbons should also be measured to the nearest 0.01 foot. Three consecutive measurements should be made to ensure the accuracy of the measuring instrument. A clear bailer can be slowly lowered into the well until it intersects the fluid but is not totally immersed. The bailer is then retrieved, and the floating LNAPL can be visually observed and measured with an engineer's tape. The third method for measurement of floating hydrocarbon thickness is hydrocarbon paste and an engineer's tape. The paste, when applied to the tape, changes color when it intersects the hydrocarbon and the hydrocarbon/water interface. Measurements of the mobile LNAPL thickness can be made directly from the engineer's tape. It is extremely important to remember to thoroughly decontaminate all equipment between well measurement events to prevent cross contamination of wells.

Measurements of mobile LNAPL thickness made in monitoring wells provide only an estimate of the actual thickness of NAPL at that location. Actual mobile and residual LNAPL thicknesses can only be obtained from continuous soil cores. Correcting apparent mobile LNAPL thickness as measured in monitoring wells to true thickness is discussed in Appendix C.

A.4.1.3.5 Well Bore Purging

The volume of water contained within the well casing at the time of sampling should be calculated, and three times the calculated volume removed from the well prior to the collection of samples for analysis. All purge water should be placed in 55-gallon drums pending final disposition. To prevent cross contamination between wells, dedicated disposable bailers, or peristaltic pumps with dedicated Teflon[®]-lined polyethylene tubing should be used for well evacuation. Additional methods for well purging include use of bladder pumps, WaTerra[®] pumps, or down hole positive-displacement pumps such as the Grundfos[®] pump. All wells should be purged in accordance with local, state, or federal requirements.

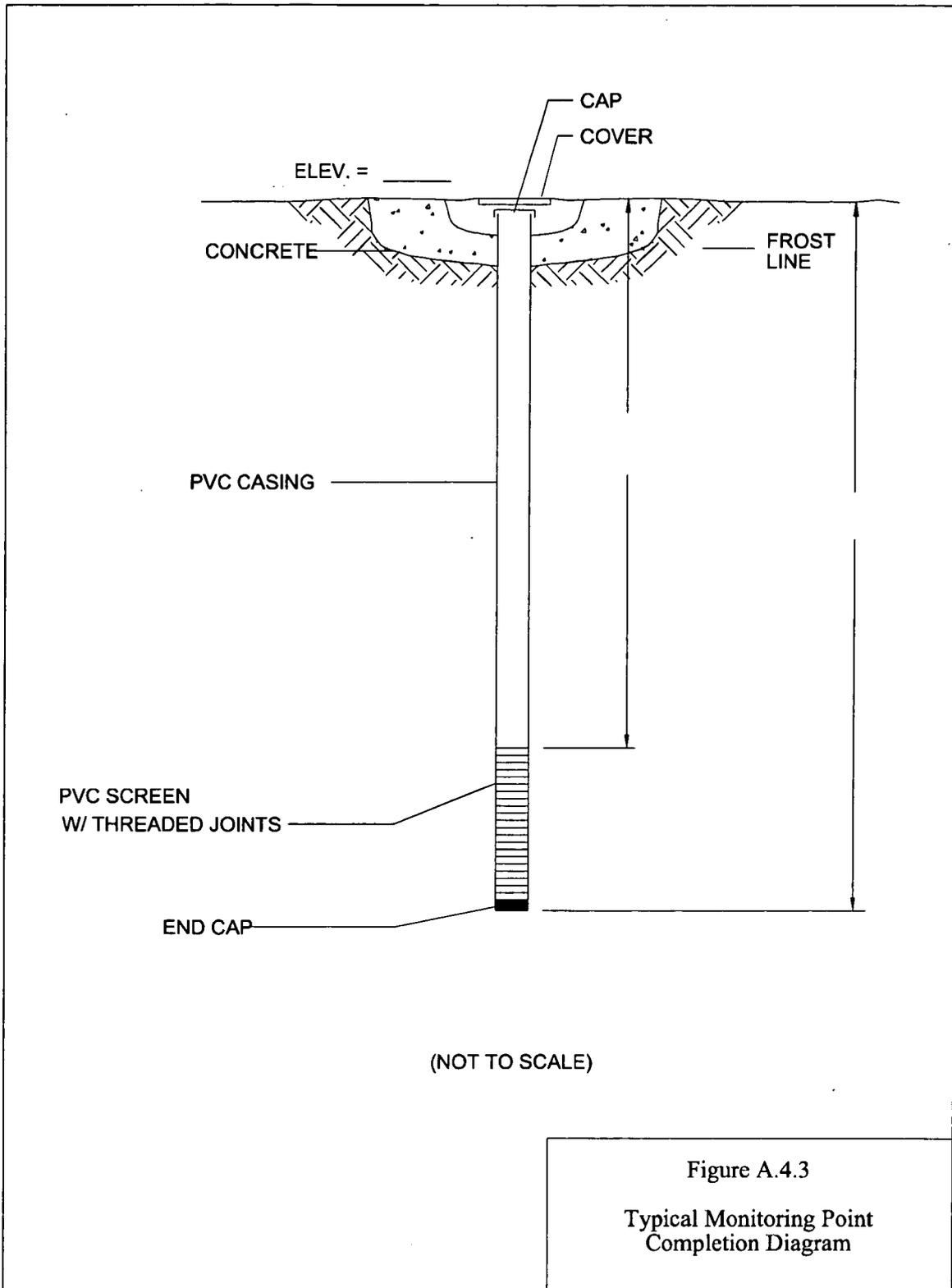
If a well is evacuated to a dry state during purging, the well should be allowed to recharge, and the sample should be collected as soon as sufficient water is present in the well to obtain the necessary sample quantity. Sample compositing, or sampling over a lengthy period by accumulating small volumes of water at different times to eventually obtain a sample of sufficient volume, is not allowable.

A.4.1.3.6 Sample Extraction

Sample extraction should be done in accordance with local, state, and federal requirements. If a peristaltic pump is used, the sample should be collected directly from the discharge end of the tubing. If a dedicated, disposable, polyethylene bailer is used, it should be lowered into the water gently to prevent splashing and extracted gently to prevent creation of an excessive vacuum in the well. The sample should be transferred directly into the appropriate sample container. If a bailer is used, the water sample must be transferred to the sample container by discharging the sample from the bottom of the bailer. In any case, the water should be carefully poured down the inner walls of the sample bottle to minimize aeration of the sample. Unless other instructions are given by the analytical laboratory, sample containers should be completely filled so that no air space remains in the container.

A.4.2 MONITORING POINT INSTALLATION AND SAMPLING

Groundwater monitoring points are similar to monitoring wells in that they consist of Schedule 40 PVC slotted screen and solid riser. Groundwater monitoring points differ from monitoring wells in that they are completed in holes created using CPT (or Geoprobe[®]) equipment. Because of the extremely small to nonexistent annular space between the PVC monitoring point completion materials and the hole created using the CPT, common monitoring well completion components including the gravel pack, bentonite seal, and Portland cement/sodium bentonite seal are not used. Because these components are missing, groundwater monitoring points should be installed only in shallow aquifers where installation of such devices will not result in the cross-contamination of adjacent water-bearing strata. Groundwater monitoring points are best utilized in shallow unconfined aquifers where such contamination is not a potential problem. Figure A.4.3 shows a typical monitoring point completion.



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A.4.2.1 Monitoring Point Locations and Completion Intervals

Groundwater monitoring points should be located based on the distribution of contaminants in each plume. At a minimum, one monitoring point should be placed upgradient of the contaminant plume, two points should be placed within the plume, and three points should be placed various distances downgradient of the plume. The number of points should be related to site conditions and the size of the spill. Each monitoring point should consist of a pair of nested monitoring points: a shallow point intended to sample the shallow portion of the aquifer and a deep point intended to sample the groundwater at some depth below the water table. The shallow screened interval generally should extend from 1 foot above the water table to no more than 5 feet below the water table. The deep screened interval should have between 3 and 6 feet of screen. The deep points should be placed based on contaminant distribution. Such short screened intervals, with between 3 and 6 feet of screen each, help mitigate the dilution of water samples from potential vertical mixing of contaminated and uncontaminated groundwater in the monitoring point casing. In addition, short screened intervals used in nested pairs give important information on the nature of vertical hydraulic gradients in the area.

A.4.2.2 Monitoring Point Installation

A.4.2.2.1 Preplacement Activities

All necessary digging, coring, drilling, and groundwater monitoring point installation permits should be obtained prior to mobilizing to the field. In addition, all utility lines should be located and proposed drilling locations cleared prior to any intrusive activities.

Water to be used in monitoring point installation and equipment cleaning should be obtained from a potable water supply. The field hydrogeologist should make the final determination as to the suitability of water for these activities. It is recommended that the source water utilized for decontamination activities be tested for the same parameters as the analytical samples from the specific site.

A.4.2.2.2 Monitoring Point Materials Decontamination

Monitoring point completion materials should be inspected by the field hydrogeologist and determined to be clean and acceptable prior to use. If not factory sealed, casing, screen, and casing plugs and caps should be cleaned with a high-pressure, steam/hot-water cleaner using

approved water prior to use. Materials that cannot be cleaned to the satisfaction of the field hydrogeologist should not be used.

A.4.2.2.3 Monitoring Point Screen and Casing

Groundwater monitoring points are installed by pushing 0.5-inch ID PVC through the inside of the CPT pushrods. As the pushrod descends, new PVC casing is continuously attached until the desired depth is reached and a fully cased monitoring point is created.

Monitoring point construction details should be noted on a Monitoring Point Installation Record form (Figure A.4.4). This information becomes part of the permanent field record for the site.

Monitoring point screens are constructed of flush-threaded, Schedule 40 PVC with an ID of 0.5 inch. The screens should be factory slotted with 0.01-inch openings. The positions of the screens should be selected by the field hydrogeologist after consideration is given to the geometry and hydraulic characteristics of the stratum in which the monitoring point will be screened.

Blank monitoring point casing should be constructed of Schedule 40 PVC with an ID of 0.5 inch. All monitoring point casing sections should be flush-threaded; glued joints should not be used. The casing at each monitoring point should be fitted with a bottom cap and a top cap constructed of PVC. The top cap should be vented to maintain ambient atmospheric pressure within the monitoring point casing.

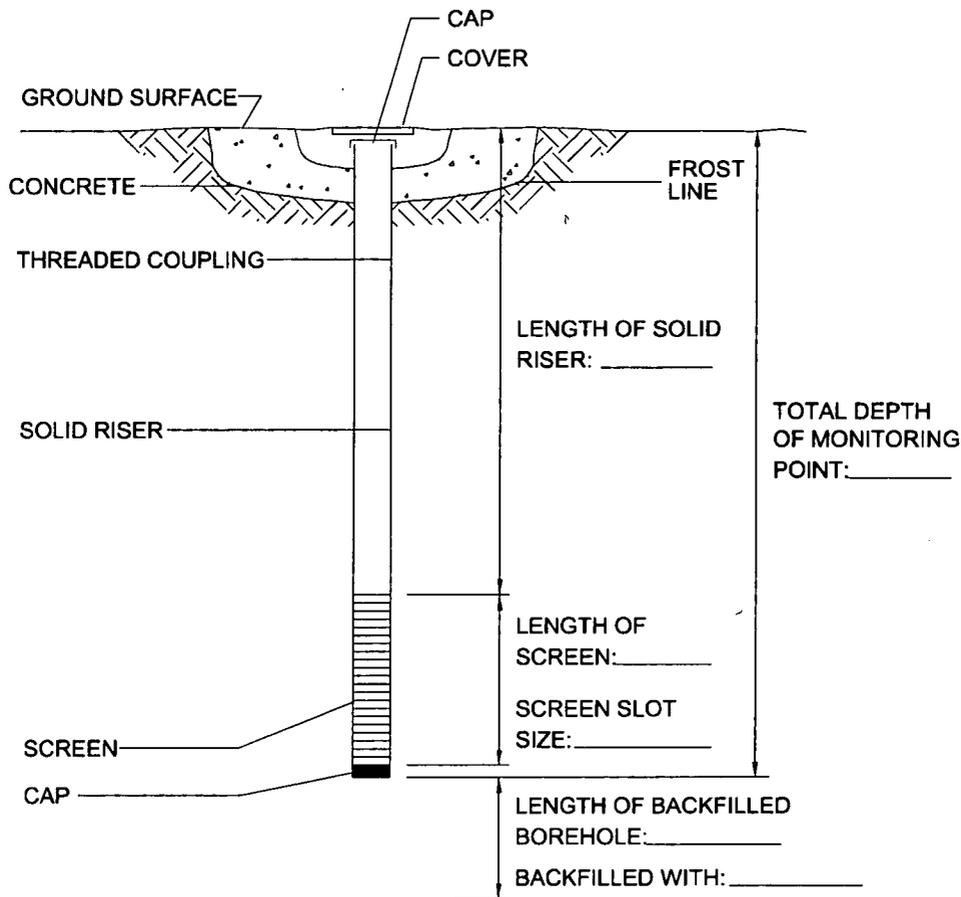
The field hydrogeologist should verify and record the total depth of the monitoring point, the lengths of all casing sections, and the depth to the top of all monitoring point completion materials. All lengths and depths are to be measured to the nearest 0.1 foot.

A.4.2.2.4 Protective Cover

To provide protection for the PVC well casing, each monitoring point will be completed with either an at-grade, or an above-grade protective cover. In either case, the concrete immediately surrounding the monitoring point will be sloped gently away from the protective casing to facilitate runoff during precipitation events. Protective cover installation procedures are described in Section A.4.1.1.6.

MONITORING POINT INSTALLATION RECORD

JOB NAME _____ MONITORING POINT NUMBER _____
 JOB NUMBER _____ INSTALLATION DATE _____ LOCATION _____
 DATUM ELEVATION _____ GROUND SURFACE ELEVATION _____
 DATUM FOR WATER LEVEL MEASUREMENT _____
 SCREEN DIAMETER & MATERIAL _____ SLOT SIZE _____
 RISER DIAMETER & MATERIAL _____ BOREHOLE DIAMETER _____
 CONE PENETROMETER CONTRACTOR _____ ES REPRESENTATIVE _____



(NOT TO SCALE)

STABILIZED WATER LEVEL _____ FEET
 BELOW DATUM.
 TOTAL MONITORING POINT DEPTH _____ FEET
 BELOW DATUM.
 GROUND SURFACE _____ FEET

Figure A.4.4
Example Monitoring Point
Installation Record

A.4.2.3 Monitoring Point Development

New monitoring points must be developed prior to sampling. Development removes sediment from inside the monitoring point casing and flushes fines from the portion of the formation adjacent to the monitoring point screen. Monitoring point development can be accomplished using either a small, custom-made bailer or a peristaltic pump. The bailer or pump tubing should be regularly lowered to the bottom of the monitoring point so that fines that have accumulated in the bottom are agitated and removed from the monitoring point in the development water.

Development should be continued until a minimum of 10 casing volumes of water has been removed from the monitoring point and until pH, temperature, specific conductivity, dissolved oxygen concentration, and redox potential have stabilized. If the water remains turbid after removing 10 casing volumes of water, monitoring point development should continue until the turbidity of the water produced is constant.

A monitoring point development record shall be maintained for each point. The monitoring point development record will be completed in the field by the field hydrogeologist. Figure A.4.2 is an example of the monitoring well/point development record. Development records will include:

- Monitoring point number;
- Date and time of development;
- Development method;
- Pre-development water level and monitoring point depth;
- Volume of water produced;
- Description of water produced;
- Post-development water level and monitoring point depth; and
- Field analytical measurements, including pH, temperature, dissolved oxygen concentration, redox potential, and specific conductivity.

A.4.2.4 Monitoring Point Location and Datum Survey

The location and elevation of the new monitoring points should be surveyed soon after completion. The horizontal location should be measured relative to established coordinates. Horizontal coordinates are to be measured to the nearest 0.1 foot. The elevation of the ground surface adjacent to the monitoring point casing and the measurement datum elevation (top of PVC casing) is to be measured relative to a mean sea level datum. The ground surface elevation

is to be measured to the nearest 0.1 foot, and the measurement datum, outer casing, and surveyor's pin (if present) elevation should be measured to the nearest 0.01 foot.

A.4.2.5 Monitoring Point Sampling

Monitoring point sampling should be accomplished in accordance with the procedures described in Section A.4.1.3.

A.4.3 HYDROPUNCH® SAMPLING

The HydroPunch II® sampling device is designed to be pushed or driven to the desired sample depth, either from the ground surface or from the bottom of a drilled borehole. The HydroPunch® utilizes an air-tight and water-tight sealed intake screen and sample chamber that is isolated from the surrounding environment as the tool is advanced. The surface of the HydroPunch® is designed to prevent the downward transport of contamination as the tool is advanced; it cleans itself as the soil particles are displaced to the side. The tight seal created as the soil is displaced and compacted allows the collection of a discrete sample from a specific depth.

The HydroPunch® can be used to sample both groundwater and floating LNAPL. Groundwater samples should be collected from the groundwater table to below visibly impacted groundwater at 5-foot intervals using the HydroPunch® sampling apparatus. When performing a groundwater investigation exclusively with the HydroPunch® sampling device, samples should be taken in an upgradient (background) area, within the defined mobile LNAPL plume, in the area immediately downgradient of the mobile LNAPL plume, within the dissolved BTEX plume, and immediately downgradient of the dissolved BTEX plume. HydroPunch® provides up to 1.2 liters of sample volume. This should be sufficient for the water quality analyses detailed in Table 2.1. Should the sample volume prove to be insufficient, the analytical protocol should be modified based on sample yield at each depth interval.

All equipment to be used for sampling should be assembled and properly cleaned and calibrated (if required) prior to arriving in the field. In addition, all record-keeping materials must be gathered prior to leaving the office.

A.4.3.1 Preparation for Sampling

Prior to starting the sampling procedure, the area around the HydroPunch[®] sampling location must be cleared of foreign materials, such as brush, rocks, and debris. These procedures will prevent sampling equipment from inadvertently contacting surface debris.

A.4.3.2 Equipment Cleaning and Calibration

All portions of sampling and testing equipment that will contact the sample matrix must be thoroughly cleaned before. This includes the HydroPunch[®] tool, water-level probe and cable, lifting line, test equipment for onsite use, and other equipment or portions thereof that will contact the samples. The cleaning protocol to be used is described in Section A.4.1.3.2.

A.4.3.3 Water Level and Total Depth Measurements

Prior to removing any water from the HydroPunch[®] sampling device, the static water should be measured. Hollow, high-density polyethylene (HDPE) tubing connected to a manometer will be inserted into the hollow HydroPunch[®] until the manometer indicates that groundwater has been reached. The HDPE attached to the manometer will then be marked at the level of the ground surface and removed. The depth to water will be determined by placing a tape measure next to the HDPE tubing and measuring the length from the base of the tubing to the ground level mark to the nearest 0.01 foot. The sampling depth is measured (to the nearest 0.1 foot) by noting the depth to which the HydroPunch[®] tool was driven.

A.4.3.4 Sample Acquisition

Samples should be collected in accordance with local, state, and federal requirements. Special care should be taken to prevent contamination of the groundwater and extracted samples. The two primary ways that sample contamination can occur are through contact with improperly cleaned equipment and by cross contamination through insufficient cleaning of equipment between wells. To prevent such contamination, new HDPE tubing must be used for each water level measurement. If the water level probe and cable are used to determine static water levels and well total depths, they should be thoroughly cleaned between uses at different sampling locations. In addition to the use of properly cleaned equipment, a clean pair of new, disposable nitrile gloves will be worn each time a different well is sampled.

The following paragraphs present the procedures to be followed for groundwater (or LNAPL) sample collection from the HydroPunch[®]. These activities should be performed in the order

presented below. Exceptions to this procedure should be noted in the field scientist's field notebook.

The sampling depth and interval generally should be specified prior to driving the HydroPunch[®] into the ground. The field scientist should verify the sampling depth by measuring the length of each HydroPunch[®] sampling rod prior to insertion into the ground. After insertion, the drive rods or hammer are retracted to pull the cone out of the body of the HydroPunch[®] device, permitting groundwater to enter. A minimum of 6 inches of the body of the device must be in the driven hole to provide a good annular seal.

After allowing for adequate fill time, the HydroPunch[®] sampling device is pulled to the surface, unthreaded from the upper subassembly, and replaced with the thread retainer. The sample is then transferred directly into the analyte-appropriate sample container. The water should be carefully poured down the inner walls of the sample bottle to minimize aeration of the sample. Unless other instructions are given by the analytical laboratory, sample containers should be completely filled so that no air space remains in the container.

A.4.4 GEOPROBE[®] SAMPLING

This section describes the scope of work required for collecting groundwater quality samples using the Geoprobe[®] sampling apparatus. In order to maintain a high degree of quality control during the sampling event, the procedures described in the following sections should be followed.

The sampling depth and interval should be determined prior to driving the Geoprobe[®] sampling rods into the ground. The field scientist should verify the sampling depth by measuring the length of each Geoprobe[®] sampling rod prior to insertion into the ground. A disposable drive tip will be placed at the tip of the Geoprobe[®] sampling rods. This tip is threaded on the uphole end to allow attachment of dedicated 3/8-inch, HDPE tubing. After reaching the desired depth, the 3/8-inch HDPE tubing is threaded through the center of the hollow Geoprobe[®] sampling rods and secured to the drive point. The polyethylene tubing is perforated at the downhole end using a 1/16-inch drill bit at 1/4-inch intervals alternately offset at 90-degree angles. The Geoprobe[®] sampling rods are then pulled back approximately 1 foot to allow groundwater to enter the perforated end of the polyethylene tubing. When the rod is pulled up, the sampling tip remains at the probe termination depth, and the 1-foot perforated interval of the polyethylene tubing is exposed to groundwater. The groundwater sample is then acquired using a peristaltic pump.

Groundwater sampling will be conducted by qualified scientists and technicians trained in the conduct of Geoprobe® sampling, records documentation, and chain-of-custody procedures. In addition, sampling personnel should thoroughly review this plan prior to sample acquisition and must have a copy of the plan available onsite for reference.

Detailed groundwater sampling and sample handling procedures are presented in following sections.

A.4.4.1 Preparation for Sampling

All equipment to be used for sampling is to be assembled and properly cleaned and calibrated (if required) prior to arriving in the field. In addition, all record-keeping materials should be gathered prior to leaving the office.

A.4.4.2 Equipment Cleaning and Calibration

All portions of sampling and test equipment that will contact the sample must be thoroughly cleaned before use. This includes water-level probe and cable, lifting line, test equipment for onsite use, and other equipment or portions thereof that will contact the samples. A cleaning protocol similar to that described in Section A.4.1.3.2 should be used.

A.4.4.3 Water Level and Total Depth Measurements

Prior to removing any water from the Geoprobe® sampling device, the static water should be measured. Several commercially available water-level probes are capable of recording water levels through the center of the hollow Geoprobe® rods. The depth to water should be determined to the nearest 0.1 foot. The sampling depth also should be measured (to the nearest 0.1 foot) by noting the depth to which the Geoprobe® tool was driven.

A.4.4.5 Purging

The Geoprobe® sampling point should be purged prior to sample acquisition. Groundwater should be pumped through the same dedicated Teflon®-lined polyethylene tubing that will be used for sample acquisition. The sampling point should be purged until pH, temperature, specific conductivity, dissolved oxygen, and redox potential readings have stabilized. Additional details on purging are specified in Section 4.1.3.5.

A.4.4.6 Sample Acquisition

Samples should be collected in accordance with local, state, and federal requirements. Special care must be taken to prevent contamination of the groundwater and extracted samples. The two primary ways that sample contamination can occur are through contact with improperly cleaned equipment and by cross contamination through insufficient cleaning of equipment between sampling locations. To prevent such contamination, the HDPE used to determine static water levels and sample depth should not be reused. In addition to the use of properly cleaned equipment, a clean pair of new, disposable nitrile gloves will be worn each time a different Geoprobe® location is sampled.

The following paragraphs present the procedures that comprise groundwater sample acquisition from the Geoprobe®. These activities should be performed in the order presented below. Exceptions to this procedure should be noted in the field scientist's field notebook.

A peristaltic pump should be used to extract groundwater samples from the Geoprobe® sampling point. Prior to sample collection, groundwater should be purged until dissolved oxygen, temperature, pH, specific conductivity, and redox readings have stabilized. The sample is collected at the discharge end of the HDPE tubing directly into the appropriate sample container. The water should be carefully directed down the inner walls of the sample bottle to minimize aeration of the sample.

Unless other instructions are given by the analytical laboratory, sample containers should be completely filled so that no air space remains in the container. Excess water collected during sampling should be handled in accordance with local regulations.

SECTION A-5

SOIL AND GROUNDWATER SAMPLE HANDLING

This section describes the handling of soil and groundwater samples from the time of sampling until the samples arrive at the laboratory.

A.5.1 SAMPLE PRESERVATION, CONTAINERS, AND LABELS

The analytical laboratory should add any necessary chemical preservatives prior to shipping the containers to the site. Samples should be properly prepared for transportation to the analytical laboratory by placing the samples in a cooler containing ice to maintain a shipping temperature of approximately 4 degrees centigrade (°C).

Sample containers and appropriate container lids should be provided by the analytical laboratory. The sample containers should be filled in accordance with accepted procedures for the sample matrix and the type of analysis to be conducted. Container lids should be tightly closed. The sample label should be firmly attached to the container side, and the following information legibly and indelibly written on the label:

- Facility name;
- Sample identification;
- Sample type (groundwater, surface water, etc.);
- Sampling date;
- Sampling time;
- Preservatives added; and
- Sample collector's initials.

A.5.2 SAMPLE SHIPMENT

After the samples are sealed and labeled, they should be packaged for transport to the analytical laboratory. The packaged samples should be delivered to the analytical laboratory shortly after sample acquisition using an overnight delivery service. The following packaging and labeling procedures are to be followed:

- Abide by all US Department of Transportation (DOT) shipping regulations;
- Package samples so that they will not leak, spill, or vaporize from their containers;
- Label shipping container with
 - Sample collector's name, address, and telephone number;
 - Laboratory's name, address, and telephone number;
 - Description of sample;
 - Quantity of sample; and
 - Date of shipment.

A.5.3 CHAIN-OF-CUSTODY CONTROL

After the samples are collected, chain-of-custody procedures must be followed to establish a written record of sample handling and movement between the sampling site and the analytical laboratory. Each shipping container should have a chain-of-custody form completed in triplicate by the sampling personnel. One copy of this form should be kept by the sampling contractor after sample delivery to the analytical laboratory; the other two copies should be retained at the laboratory. One of the laboratory copies will become a part of the permanent record for the sample and will be returned with the sample analytical results. The chain-of-custody form should contain the following information:

- Unique sample identification number;
- Sample collector's printed name and signature;
- Date and time of collection;
- Sample location;
- Sample matrix;
- Sample size and container;
- Chemical preservatives added;
- Analyses requested;
- Signatures of individuals involved in the chain of possession; and
- Inclusive dates of possession.

The chain-of-custody documentation should be placed inside the shipping container so that it will be immediately apparent to the laboratory personnel receiving the container, but cannot be damaged or lost during transport. The shipping container is to be sealed so that it will be obvious if the seal has been tampered with or broken.

A.5.4 SAMPLING RECORDS

In order to provide complete documentation of the sampling event, detailed records are to be maintained by the field scientist. Figure A.5.1 is an example groundwater sampling form. At a minimum, these records must include the following information:

- Sample location (facility name);
- Sample identification;
- Sample location map or detailed sketch;
- Date and time of sampling;
- Sampling method;
- Field observations of
 - Sample appearance,
 - Sample odor;
- Weather conditions;
- Water level prior to purging (groundwater samples);
- Total well depth (groundwater samples);
- Purge volume (groundwater samples);
- Water level after purging (groundwater samples);
- Well condition (groundwater samples);
- Sample depth;
- Sampler's identification;
- Field measurements of pH, temperature, specific conductivity, dissolved oxygen concentration, and redox potential (groundwater samples); and
- Any other relevant information.

A.5.5 GROUNDWATER AND SOIL ANALYTICAL PROTOCOL

Laboratory analyses should be performed on all soil and groundwater samples using the analytical procedures listed in Table 2.1. Prior to sampling, arrangements should be made with the analytical laboratory to provide a sufficient number of appropriate sample containers for the samples to be collected. All containers, preservatives, and shipping requirements should be consistent with the analytical protocol. The field scientist must specify the necessary quality control samples and notify the laboratory so that they can prepare these bottles. For samples requiring chemical preservation, preservatives should be added to containers by the laboratory prior to shipping. Shipping containers, ice chests with adequate padding, and cooling media should be sent by the laboratory to the site.

**Figure A.5.1
Groundwater Sampling Record**

SAMPLING LOCATION _____
 SAMPLING DATE(S) _____

GROUNDWATER SAMPLING RECORD - MONITORING WELL/POINT _____
 (number)

REASON FOR SAMPLING: Regular Sampling; Special Sampling;
 DATE AND TIME OF SAMPLING: _____, 19____ a.m./p.m.
 SAMPLE COLLECTED BY: _____ of _____

WEATHER: _____
 DATUM FOR WATER DEPTH MEASUREMENT (Describe): _____

MONITORING WELL CONDITION:

LOCKED: UNLOCKED

WELL NUMBER (IS - IS NOT) APPARENT _____

STEEL CASING CONDITION IS: _____

INNER PVC CASING CONDITION IS: _____

WATER DEPTH MEASUREMENT DATUM (IS - IS NOT) APPARENT _____

DEFICIENCIES CORRECTED BY SAMPLE COLLECTOR

MONITORING WELL REQUIRED REPAIR (describe): _____

Check-off

1 EQUIPMENT CLEANED BEFORE USE WITH _____
 Items Cleaned (List): _____

2 LNAPL DEPTH _____ FT. BELOW DATUM

Measured with: _____

WATER DEPTH _____ FT. BELOW DATUM

Measured with: _____

3 WATER-CONDITION BEFORE WELL EVACUATION (Describe):

Appearance: _____

Odor: _____

Other Comments: _____

4 WELL EVACUATION:

Method: _____

Volume Removed: _____

Observations: Water (slightly - very) cloudy

Water level (rose - fell - no change)

Water odors: _____

Other comments: _____

Figure A.5.1 (Continued)

5 [] SAMPLE EXTRACTION METHOD:

- Bailer made of: _____
- Pump, type: _____
- Other, describe: _____

Sample obtained is GRAB; COMPOSITE SAMPLE

6 [] ON-SITE MEASUREMENTS:

- | | |
|-------------------------|----------------------|
| Temp: _____ ° _____ | Measured with: _____ |
| pH: _____ | Measured with: _____ |
| Conductivity: _____ | Measured with: _____ |
| Dissolved Oxygen: _____ | Measured with: _____ |
| Redox Potential: _____ | Measured with: _____ |
| Salinity: _____ | Measured with: _____ |
| Nitrate: _____ | Measured with: _____ |
| Sulfate: _____ | Measured with: _____ |
| Ferrous Iron: _____ | Measured with: _____ |
| Other: _____ | |

7 [] SAMPLE CONTAINERS (material, number, size): _____

8 [] ON-SITE SAMPLE TREATMENT:

- Filtration: Method _____ Containers: _____
- Method _____ Containers: _____
- Method _____ Containers: _____

- Preservatives added:
- Method _____ Containers: _____

9 [] CONTAINER HANDLING:

- Container Sides Labeled
- Container Lids Taped
- Containers Placed in Ice Chest

10 [] OTHER COMMENTS: _____

SECTION A-6

AQUIFER CHARACTERIZATION METHODOLOGIES

Adequate characterization of the groundwater flow and contaminant transport system is an important component of the intrinsic remediation demonstration. The following sections describe the methodologies that should be used to characterize the hydrogeologic system.

A.6.1 HYDRAULIC CONDUCTIVITY

Hydraulic conductivity is perhaps the most important aquifer parameter governing groundwater flow and contaminant transport in the subsurface. Typical methods for determining hydraulic conductivity in the field include pumping tests and slug tests, both of which are described below.

A.6.1.1 Definitions

- **Hydraulic Conductivity (K).** A quantitative measure of the ability of porous material to transmit water; defined as the volume of water that will flow through a unit cross-sectional area of porous or fractured material per unit time under a unit hydraulic gradient.
- **Transmissivity (T).** A quantitative measure of the ability of an aquifer to transmit water. It is the product of the hydraulic conductivity and the saturated thickness.
- **Slug Test.** Two types of testing are possible; a rising head or falling head test. A slug test consists of adding (or removing) a solid cylinder of known volume to (or from) the well to be tested and measuring the rate of recovery of the water level inside the well.
- **Rising Head Test.** A test used in an individual well within the saturated zone to estimate the hydraulic conductivity of the surrounding formation by lowering the water level in the well and measuring the rate of recovery of the water level. The water level is lowered by removing a submerged solid cylinder (slug) from the well.
- **Falling Head Test.** A test used in an individual well to estimate the hydraulic conductivity of the surrounding formation by raising the water level in the well by insertion of a slug, and then measuring the rate of drop in the water level.

- **Storage Coefficient (S).** Volume of water that an aquifer releases from or takes into storage per unit area of aquifer, per unit of change in head. The storage coefficient is dimensionless.
- **Specific Yield (S_y).** The volume of water that a saturated soil will yield per unit volume of aquifer, under the influence of gravity.
- **Specific Capacity (C_s).** Rate of yield per unit of drawdown in a pumping well.
- **Drawdown (s).** Difference between the elevation of the nonpumping potentiometric surface and the water level elevation, at some position during pumping.
- **Discharges (Q).** Volume of water removed per unit of time.
- **Unconfined (Water Table) Aquifer.** An aquifer in which the water table forms the upper boundary.
- **Confined Aquifer.** An aquifer confined between two low permeability layers where the water level in a well completed in the aquifer rises to some level (i.e., potentiometric surface) above the top of the aquifer.

A.6.1.2 Slug Tests

Slug tests should be conducted to estimate the hydraulic conductivity of the shallow saturated zone if it is not possible to conduct pumping tests. A slug test is a single-well hydraulic test used to determine the hydraulic conductivity of an aquifer in the immediate vicinity of the well. Slug tests can be used for both confined and unconfined aquifers that have a transmissivity of less than 7,000 square feet per day (ft^2/day). Slug testing can be performed using either a rising head or a falling head test; in the method presented herein both methods are used in sequence. Slug tests should be conducted in all wells present at a site. The analysis of slug test data is discussed in Appendix C.

A.6.1.2.1 Equipment

The following equipment is needed to conduct a slug test:

- Teflon®, PVC , or metal slugs
- Nylon or polypropylene rope
- Electric water level indicator
- Pressure transducer/sensor
- Field logbook/forms
- Automatic data recording instrument (such as the Hermit Environmental Data Logger®, In-Situ, Inc. Model SE1000B or equal)

A.6.1.2.2 General Test Methods

Slug tests are accomplished by removal of a solid slug (rising head) or introduction of a solid slug (falling head), and then allowing the water level to stabilize while taking water level measurements at closely spaced time intervals.

Prior to testing, the monitoring well must be thoroughly developed as described in Section A.4.1.2, and water levels should be allowed to stabilize. Slug testing should proceed only after water level measurements show that static water level equilibrium has been achieved. During the slug test, the water level change should be influenced only by the introduction (or subtraction) of the slug volume. Other factors, such as inadequate well development, extended pumping, etc., may lead to inaccurate results. It is up to the field scientist to decide when static equilibrium has been reached in the well. The pressure transducer, slugs, and any other down-hole equipment must be decontaminated prior to and immediately after the performance of the slug test.

A.6.1.2.3 Falling Head Test

The falling head test is the first step in the two-step slug-testing procedure. The following steps describe the procedure to be followed to perform the falling head test.

1. Decontaminate all downhole equipment prior to initiating the test.
2. Open the well. Where wells are located within a 100-year flood plain, and equipped with water tight caps, the well should be unsealed at least 24 hours prior to testing to allow the water level to stabilize. The protective casing will remain locked during this time to prevent vandalism.
3. Prepare the Slug Test Data form (Figure A.6.1) with entries for:
 - Borehole/well number.
 - Project number.
 - Project name.
 - Aquifer testing team.
 - Climatic data.
 - Ground surface elevation.
 - Top of well casing elevation.

- Identification of measuring equipment being used.
 - Page number.
 - Static water level.
 - Date.
4. Measure the static water level in the well to the nearest 0.01 foot.
 5. Lower the decontaminated pressure transducer into the well and allow the displaced water to return to its static level. This can be determined by making periodic water level measurements until the static water level in the well is within 0.01 foot of the original static water level.
 6. Lower the decontaminated slug into the well to just above the water level in the well.
 7. Turn on the data logger and quickly lower the slug below the water table being careful not to disturb the pressure transducer. Follow the owner's manual for proper operation of the data logger.
 8. Terminate data recording when the water level stabilizes in the well. Remove the slug from the well and continue with the rising head test.

Hard copies of the data logger output (drawdown vs. time) should be printed on field printers before transporting the logger back to the office.

A.6.1.2.4 Rising Head Test

Immediately following completion of the falling head test, the rising head test is performed. The following steps describe the rising head slug test procedure.

1. Measure the static water level in the well to the nearest 0.01 foot to ensure that it has returned to the static water level.
2. Initiate data recording and quickly withdraw the slug from the well. Follow the owner's manual for proper operation of the data logger.
3. Terminate data recording when the water level stabilizes in the well. Remove the pressure transducer from the well and decontaminate it.

A.6.1.3 Pumping Tests

This section outlines the methods for determining aquifer hydraulic characteristics from pumping tests. For a more detailed discussion of how to conduct a pumping test, the reader is referred to the work of Dawson and Istok (1991) and Kruseman and de Ridder (1991). The methods described in this section may be used for both unconfined and confined aquifers. Values obtained are representative of the conditions of the aquifer over a large area. The interpretation of aquifer pumping test data is not unique. Similar sets of data can be obtained from various combinations of geologic conditions. The interpretation of pumping test data is discussed in Appendix C of this protocol document.

The pumping test procedure consists of pumping a well at a constant rate for a specified length of time, and measuring the rate of drawdown of the water table or potentiometric surface in the surrounding aquifer. Periodic water level measurements are taken in both the pumped well and any nearby observation wells. Field personnel must have a basic familiarity with pumping tests, and should be trained to assist in conducting the test and gathering data.

A.6.1.3.1 Equipment

The equipment needed to perform aquifer tests includes:

- Pumps
- Gate valve
- Electrical generator
- Flow meter with totalizer
- Water level indicators
- Pressure gauge
- Field logbook/forms
- Pressure transducers and data recorder
- Engineer's tape calibrated to 0.01 ft
- 5-gallon pail
- Conductivity meter, pH meter, and thermometer
- Barometer
- Semi-log and log-log graph paper
- Portable computer
- Field printer for data
- Type matching curves
- Meter and stopwatch for discharge measurement
- Hose or pipe for transfer of water
- Adequately sized tank for storing contaminated water

A.6.1.3.2 Procedure

The location of an aquifer test is determined to a great extent by the size of the area, the uniformity and homogeneity of the aquifer, and known or suspected recharge or barrier boundary conditions. The hydrogeological conditions of the site should not change over short distances, and should be representative of the area under study.

As much information as possible should be collected and evaluated before performing an aquifer pumping test. Such data should include groundwater flow direction, hydraulic gradients, well characteristics, regional water level trends, the existence of other pumping wells in the vicinity of the test area, the anticipated groundwater quality and quantity of the discharge water need to determine type/volume of storage container(s), and the expected specific capacity of the pumped well.

Pumping equipment should conform to the size of the well. Drilling logs, data associated with well construction, and performance characteristics of other wells in the area should be considered. Transmissivities may be estimated from the boring logs, laboratory permeability tests, and slug tests. Any number of observation wells may be used. The number chosen is contingent upon both cost and the need to obtain the maximum amount of accurate and reliable data. If three or more observation wells are to be installed, and there is a known boundary condition, the wells should be placed along a radial line extending from the pumping well toward the boundary. One well should be placed perpendicular to the line of observation wells to determine whether radial anisotropy exists within the aquifer. If two observation wells are to be installed, they should be placed in a triangular pattern, non-equidistant from the pumping well. Observation wells should be located at distances and depths appropriate for the planned method for analysis of the aquifer test data. Observation well spacing should be determined based upon expected drawdown conditions that are the result of the geohydraulic properties studies, pumping test duration, and the pumping rate proposed. Preliminary pumping results should also be used (if available). Not all projects can afford the luxury of preliminary testing and pump testing.

If testing a confined aquifer that is relatively thin, the pumping well should be screened for the entire thickness of the aquifer. For a confined aquifer, the water level in the pumping well should not be allowed, if possible, to fall below the bottom of the upper confining stratum during a pumping test. For an unconfined aquifer, the wells should be screened in the bottom one-third or two-thirds of the saturated zone.

A.6.1.3.2.1 Preparation for Testing

For at least 24 hours prior to performing a pumping test, water levels in the test well and observation wells and barometric pressure should be measured hourly to determine whether there is a measurable fluctuation and trend in water levels. If pressure transducers and a data logger are used, water levels should be recorded hourly. If a trend is apparent, a curve of the change in depth versus time should be prepared and used to correct the water levels observed during the test.

Test wells should undergo preliminary pumping or step drawdown tests prior to the actual test. This will enable fines to be flushed from the adjacent formation near the well and a steady flow rate to be established. The preliminary pumping should determine the maximum drawdown in the well and the proper pumping rate should be determined by step drawdown testing. The aquifer should then be given time to recover before the actual pumping test begins (as a rule-of-thumb, one day).

Barometric changes may affect water levels in wells, particularly in semiconfined and confined aquifers. A change in barometric pressure may cause a change in the water level. The field barometer should be calibrated prior to use. Any change in barometric pressure during the test should be recorded, to allow corrections in water level measurements taken during the pumping test.

A record should be maintained in the field logbook of the times of pumping and discharge of other wells in the area, and if their radii of influence intersect the cone of depression of the test well. All measurements and observations should be recorded in a field notebook or on an Aquifer Test Data Form. If data loggers with transducers are used, field measurements should be performed in case of data logger malfunction.

In areas of severe winter climates, where the frost line may extend to depths of several feet, pumping tests should be avoided during cold weather months where the water table is less than 12 feet from the surface. Under certain conditions, the frozen soil acts as a confining stratum, and combined with leaky aquifer and delayed storage characteristics, test results may be unreliable.

A.6.1.3.2.2 Conducting the Pumping Test

Immediately prior to starting the pump, the water levels should be measured in all wells to determine the static water levels upon which all drawdowns will be based. These data and the times of measurement should be recorded on the Aquifer Test Data Form. Data loggers should be reset for each well to a starting water level of 0.0 foot.

Water pumped from an unconfined aquifer during a pumping test should be disposed of in such a manner as not to allow the aquifer to be recharged by infiltration during the test. This means that the water must be piped well away from the well and associated observation wells. Recharge could adversely affect the results obtained. Also, if contaminated water is pumped during the test, the water must be stored and treated or disposed of according to the project work plan for the study. The discharge water may be temporarily stored in drums, a lined, bermed area, or tanks. If necessary, it should be transported and staged in a designated secure area.

The discharge rate should be measured frequently throughout the test and controlled to maintain it as constant as possible, after the initial excess discharge has been stabilized. This can be achieved by using a control valve.

The pitch or rhythm of the pump engine or generators provides a check on performance. If there is a sudden change in pitch, the discharge should be checked immediately and proper adjustments to the control valve or the engine speed should be made, if necessary. Do not allow the pump to break suction during the test. Allow for maximum drawdown of the well during the step drawdown test. If done properly, the flow control valve can be pre-set for the test and will not have to be adjusted during pumping. If the pump does shut down during the test, make necessary adjustments and restart the test after the well has stabilized.

At least 10 measurements of drawdown for each log cycle of time should be made both in the test well and the observation wells. Data loggers can be set to record in log time, which is very useful for data analysis. A suggested schedule for recording water level measurements made by hand is as follows:

- 0 to 10 minutes - 0.5, 1.0, 2.5, 2.0, 2.5, 3.0, 4.5, 6.5, 8, and 10 minutes. It is important in the early part of the test to record with maximum accuracy the time at which readings are taken.
- 10 to 100 minutes - 10, 15, 20, 25, 30, 40, 50, 65, 80 and 100 minutes.

- Then, at 1-hour intervals from 100 minutes to 1,440 minutes (one day) and every 2 hours after 1 day completion.

Initially, there should be sufficient field personnel to station one person at each well used in the pumping test (unless an automatic water-level recording system has been installed). After the first 2 hours of pumping, two people are usually sufficient to complete the test. A third person is needed when treatment of the pumped water is required prior to discharge.

Field personnel should be aware that electronic equipment sometimes fails in the field. Some field crews have experienced complete loss of data due to failure of a logger or transducer. It is a good idea to record data in the field logbook or on a manual form as the data are produced. That way, the data are not lost should the equipment fail.

The discharge or pumping rate should be measured with a flow meter that also has a totalizer. When the pumping is complete, the total gallons pumped are divided by the time of pumping to obtain the average discharge rate for the test. Periodic checking and recording of the pumping rate during the test also should be performed.

The total pumping time for a test depends on the type of aquifer and degree of accuracy desired. Economizing on the duration of pumping is not recommended. More reliable results are obtained if pumping continues until the cone of depression achieves a stabilized condition. The cone of depression will continue to expand at a slower rate until recharge of the aquifer equals the pumping rate, and a steady-state condition is established. The time required for steady-state flow to occur may vary from a few hours to years.

Under normal conditions, it is a good practice to continue a pumping test in a confined aquifer for at least 24 hours, and in an unconfined aquifer for a minimum of 72 hours. A longer duration of pumping may reveal the presence of boundary conditions or delayed yield. Use of portable computers allows time/drawdown plots to be made in the field. If data loggers are used to monitor water levels, hard copies of the data printed on field printers should be obtained before transporting the logger back to the office for downloading.

A.6.2 HYDRAULIC GRADIENT

In order to determine the hydraulic gradient and groundwater flow direction, it is necessary to take water level measurements. To adequately determine the flow direction of a solute plume, it is desirable to have a minimum of quarterly water level measurements over a period of 1 year.

A.6.2.1 Water Level Measurements

Water levels at all monitoring wells and piezometers should be measured within a short time interval so that the water level data are comparable. Water levels measured in wells should not be used for gradient calculations and potentiometric surface maps until the wells are developed and the water levels have stabilized. The depth to water below the measurement datum is made using an electric water level probe, and measurements should be made to the nearest 0.01 ft.

A.6.2.2 Well Location and Datum Survey

The location and elevation of all wells at the site should be surveyed by a registered surveyor. The horizontal location should be measured relative to established facility coordinates. Horizontal coordinates should be measured to the nearest 0.1 foot. Vertical location of the ground surface adjacent to the well casing, the measurement datum (top of the interior casing), and the top of the outer well casing should be measured relative to a mean sea level datum. The ground surface elevation should be measured to the nearest 0.1 foot, and the measurement datum, outer casing, and surveyor's pin (if present) elevations should be measured to the nearest 0.01 foot.

APPENDIX B

IMPORTANT PROCESSES AFFECTING THE FATE AND TRANSPORT OF FUEL HYDROCARBONS IN THE SUBSURFACE

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SECTION B-1

INTRODUCTION

B.1.1 FATE AND TRANSPORT MECHANISMS

This appendix presents an overview of the important processes affecting the fate and transport of benzene, toluene, ethylbenzene, and xylene (BTEX) dissolved in groundwater. Processes discussed include advection, hydrodynamic dispersion (mechanical dispersion and diffusion), sorption, biodegradation, infiltration, and volatilization. Table B.1.1 summarizes these processes. The environmental fate and transport of a contaminant is controlled by the compound's physical and chemical properties and the nature of the subsurface media through which the compound is migrating. Important properties include:

- Soil/water distribution coefficient (K_d);
- Organic carbon/water partition coefficient (K_{oc});
- Octanol/water partition coefficient (K_{ow});
- Water solubility;
- Vapor pressure;
- Henry's Law constant (air/water partition coefficient, H);
- Indigenous bacterial population;
- Hydraulic conductivity;
- Porosity;
- Total organic carbon content;
- Bulk density;
- Grain size distribution; and
- Ambient groundwater geochemistry.

Table B.1.1
Summary of Important Processes Acting on BTEX in the Subsurface

Process	Description	Dependencies	Effect
Advection	Movement of solute by bulk groundwater movement.	Dependent on aquifer properties, mainly hydraulic conductivity and effective porosity, and hydraulic gradient. Independent of contaminant properties.	Main mechanism driving contaminant movement in the subsurface.
Dispersion	Fluid mixing due to groundwater movement and aquifer heterogeneities.	Dependent on aquifer properties and scale of observation. Independent of contaminant.	Causes longitudinal, transverse, and vertical spreading of the plume. Reduces solute concentration.
Diffusion	Spreading and dilution of contaminant due to molecular diffusion.	Dependent on contaminant properties and concentration gradients. Described by Fick's Laws.	Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration. Generally unimportant at most groundwater flow velocities.
Sorption	Reaction between aquifer matrix and solute whereby the relatively hydrophobic BTEX compounds become sorbed to organic carbon or clay minerals.	Dependent on aquifer matrix properties (organic carbon and clay mineral content, bulk density, specific surface area, and porosity) and contaminant properties (solubility, hydrophobicity, octanol-water partitioning coefficient).	Tends to reduce solute transport rate and remove solutes from the groundwater via sorption to the aquifer matrix.
Infiltration (Simple Dilution)	Infiltration of water from the surface into the subsurface.	Dependent on aquifer matrix properties, depth to groundwater and climate.	Causes dilution of the contaminant plume and replenishes electron acceptor concentrations, especially dissolved oxygen.
Volatilization	Volatilization of BTEX from the aqueous phase in groundwater into the vapor phase in soil gas.	Dependent on the chemical's vapor pressure and Henry's Law constant.	Causes removal of BTEX from the groundwater.
Biodegradation	Microbially mediated oxidation-reduction reactions that transform BTEX to carbon dioxide and water.	Dependent on groundwater geochemistry, microbial population and contaminant properties. BTEX is biodegradable under aerobic and anaerobic conditions.	Results in complete mineralization of BTEX to carbon dioxide and water. Most important process in contaminant mass reduction.
Partitioning from LNAPL	Partitioning from LNAPL into groundwater. LNAPL plumes tend to act as a continuing source of groundwater contamination.	Dependent on aquifer matrix (relative permeability, capillary pressure, and residual saturation) and contaminant properties (solubility, mass fraction, volatility, density, interfacial tension).	Dissolution of BTEX from LNAPL represents the primary source of dissolved BTEX in groundwater.

Intrinsic remediation results from the integration of several subsurface attenuation mechanisms, both nondestructive and destructive. Several processes are known to cause a reduction in the concentration and/or mass of a contaminant dissolved in groundwater. Those processes that result only in the reduction of a contaminant's concentration but not of the total contaminant mass in the system are termed nondestructive and include hydrodynamic dispersion, sorption, volatilization, and dilution via infiltration. Nondestructive attenuation mechanisms are discussed in Sections B-2, B-3, B-4, and B-6. Those processes that result in a reduction in the total mass of contaminant in the system are referred to as destructive. Biodegradation is the dominant destructive attenuation mechanism acting on the BTEX compounds. Biodegradation is discussed in Section B-5.

It is important to separate nondestructive from destructive attenuation mechanisms during the intrinsic remediation demonstration. The methods for correcting apparent attenuation caused by nondestructive attenuation mechanisms are discussed in Appendix C.

B.1.2 MATHEMATICAL DESCRIPTION OF SOLUTE FATE AND TRANSPORT

The partial differential equation describing BTEX migration and attenuation in the saturated zone includes terms for advection, dispersion, sorption, and biodegradation. In one dimension, the partial differential equation describing solute transport in the saturated zone is:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} \pm Q_s \quad \text{eq. B.1.1}$$

Where: C = solute concentration [M]

t = time [T]

D_x = hydrodynamic dispersion [L^2/T]

R = coefficient of retardation [dimensionless]

x = distance along flow path [L]

v_x = transport velocity in x direction [L/T]

Q_s = general source or sink term for reactions involving the production or loss of solute (e.g., biodegradation) [$M/L^3/T$]

The biodegradation of BTEX compounds commonly can be approximated using first-order kinetics. In one dimension, the partial differential equation describing solute transport with first-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} - \lambda C$$

eq. B.1.2

Where: C = concentration [M/L³]

t = time [T]

D_x = hydrodynamic dispersion [L²/T]

x = distance along flow path [L]

R = coefficient of retardation [dimensionless]

v_x = transport velocity in x direction [L/T]

λ = first-order decay rate [T⁻¹]

These equations serve to illustrate how the processes of advection, dispersion, sorption, and biodegradation are integrated to describe the fate and transport of solutes in the saturated zone. These relationships were derived using the continuity (conservation of mass) equation, which states that the rate of change of contaminant mass within a unit volume of porous media is equal to the flux of contaminant into the unit volume minus the flux out of the unit volume (Freeze and Cherry, 1979). Processes governing flux into the unit volume include advection and hydrodynamic dispersion (including mechanical dispersion and diffusion). Processes governing flux out of the unit volume include advection, hydrodynamic dispersion, sorption, and chemical reactions (most notably biodegradation for BTEX). Stated mathematically, the change in solute concentration is:

$$\text{Change in Solute Concentration} = \text{Flux In} - \text{Flux Out} \pm \text{Reactions}$$

The following sections describe each of the processes affecting the fate and transport of the BTEX compounds.