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

VOLUME I

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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

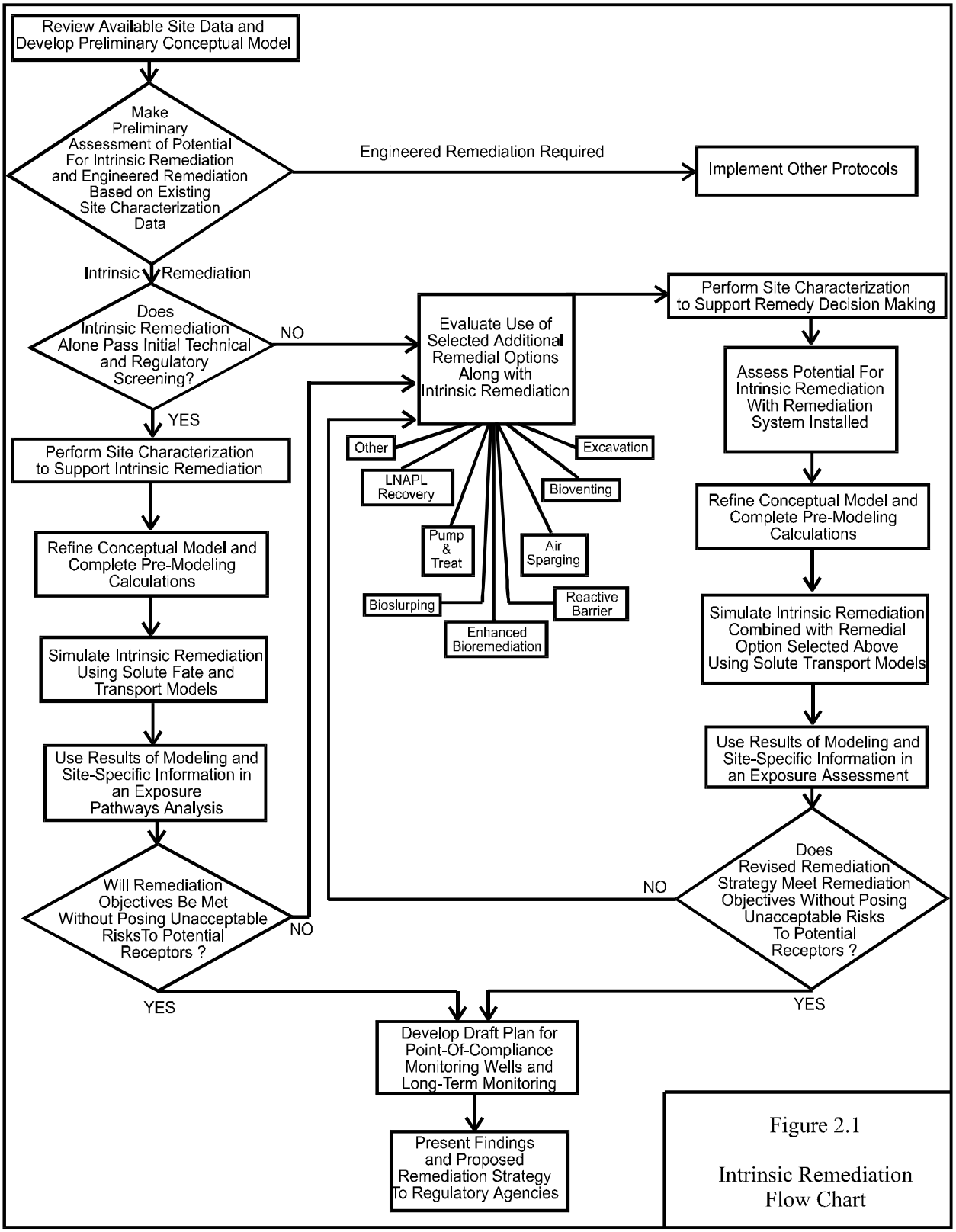


Figure 2.1

Intrinsic Remediation Flow Chart

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; trimethylben-zenes 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_2SO_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 *et al.*, 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_2SO_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	Phenolphtalein 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.

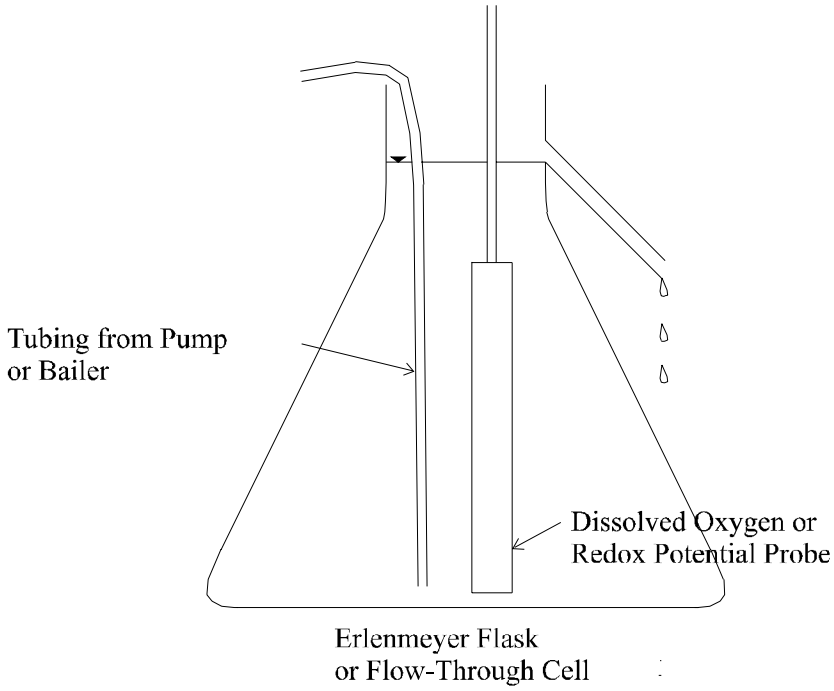


Figure 2.2

Diagram Showing the Suggested Procedure for Dissolved Oxygen and Oxidation-Reduction Potential Sampling

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 CO_2-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

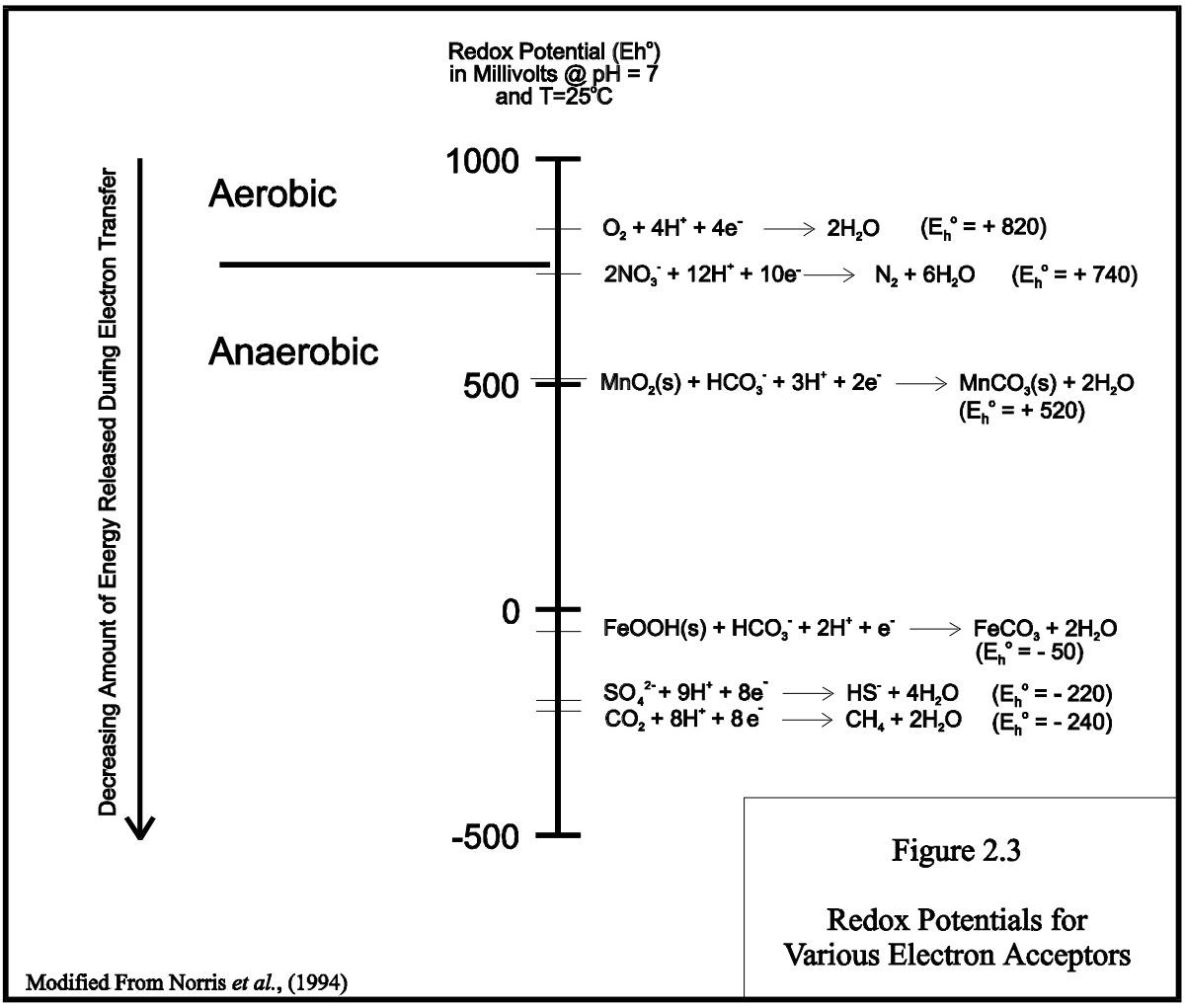
calcium, magnesium, sodium, potassium, or ammonia. These species result from the dissolution of rock (especially carbonate rocks), the transfer of CO_2 from the atmosphere, and respiration of microorganisms. Alkalinity is important in the maintenance of groundwater pH because it buffers the groundwater 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 LNALP 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.

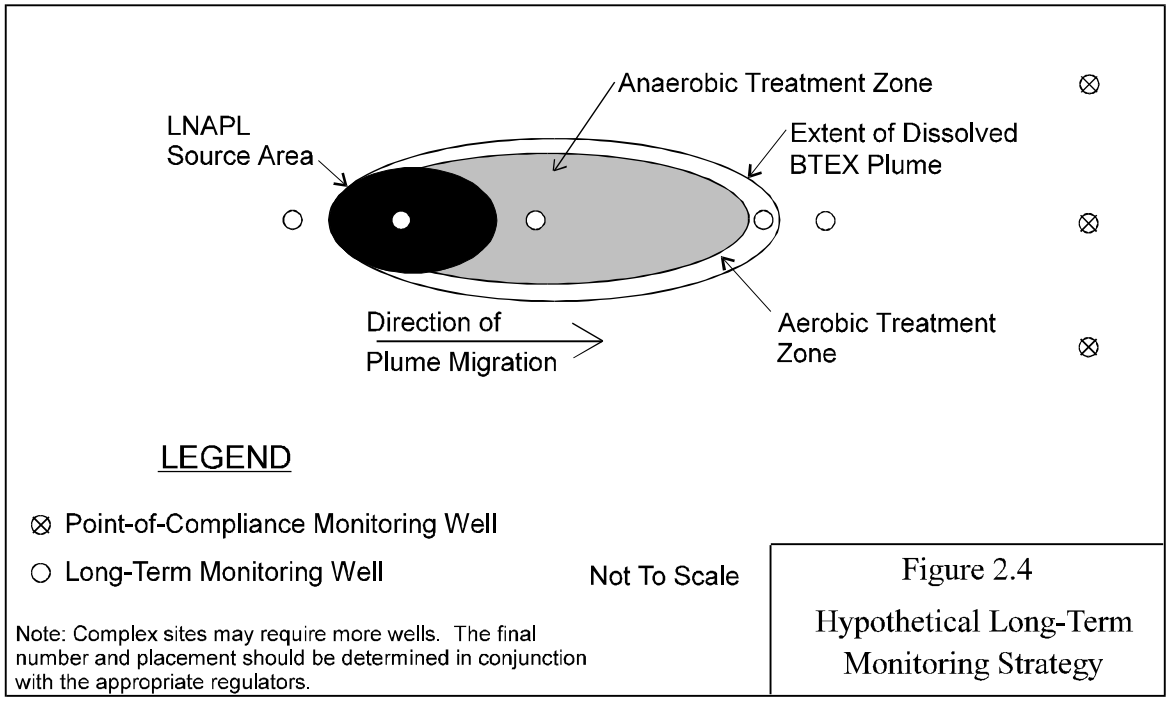


Figure 2.4
Hypothetical Long-Term Monitoring Strategy

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

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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 (^{o}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 No.	Sample Depth (ft)	Sample Type	Penet. Res	PID (ppm)	TLV (ppm)	TOTAL BTEX (ppm)	TPH (ppm)
	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.

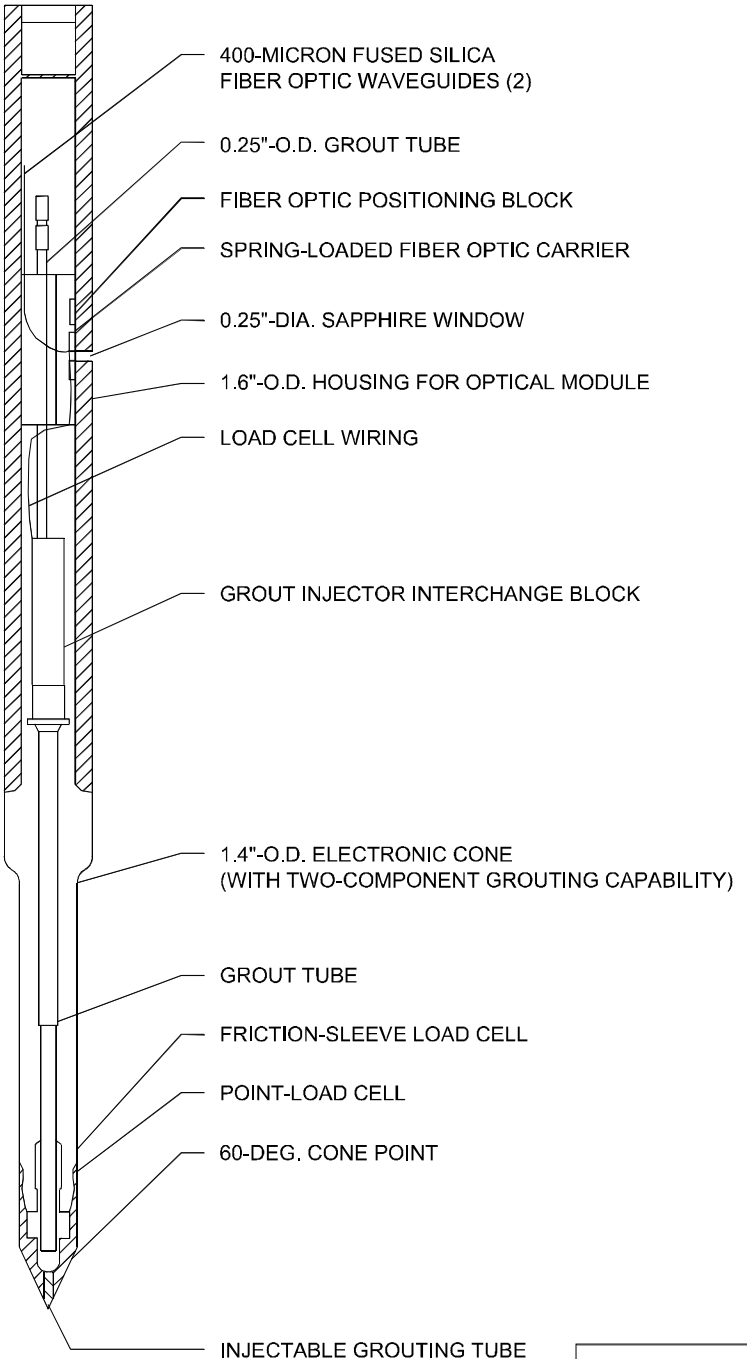

Figure A.3.2

Schematic of
Fiber Optic Fluorometry
Cone Penetrometer

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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 _____

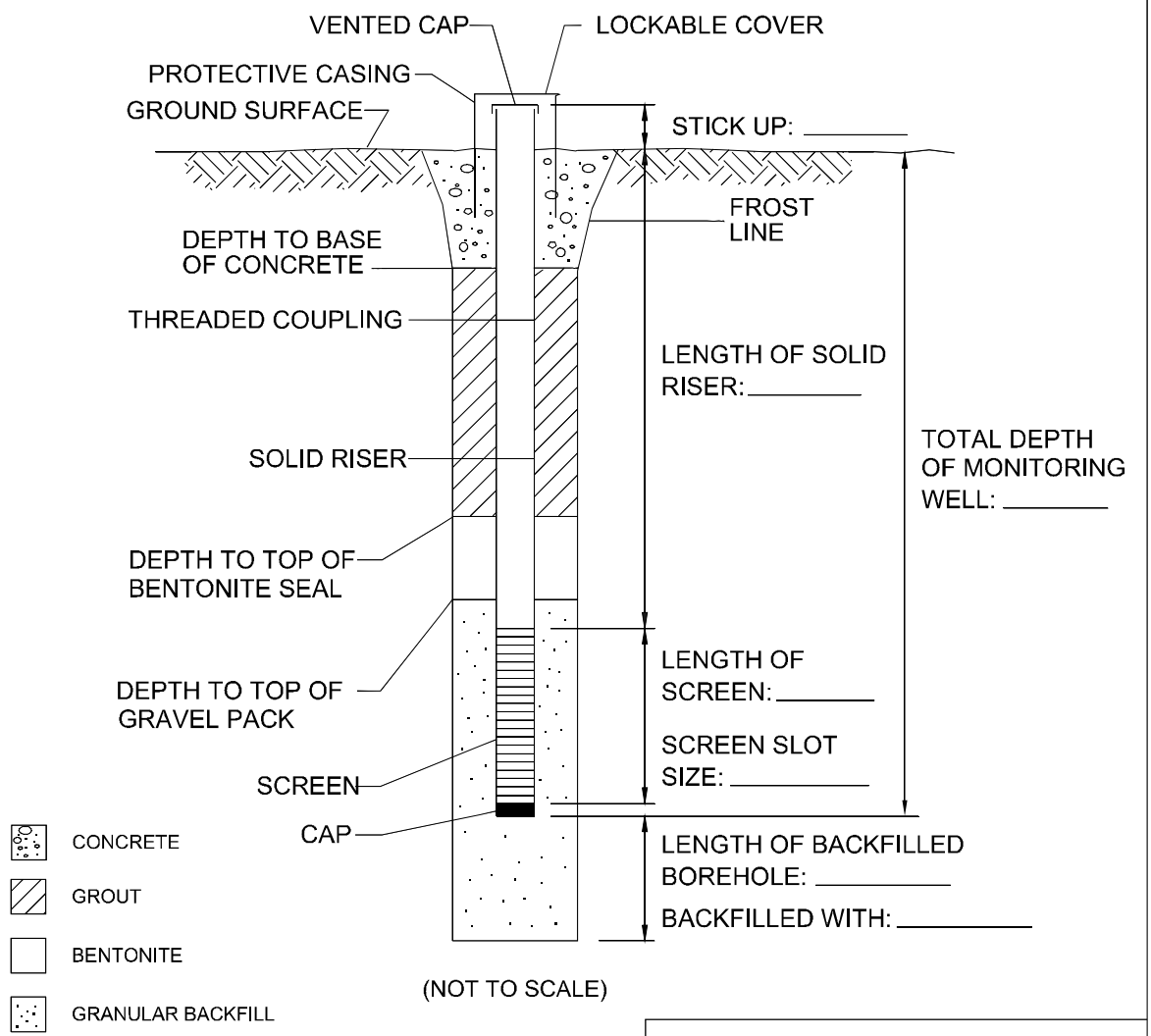
DATUM FOR WATER LEVEL MEASUREMENT _____

SCREEN DIAMETER & MATERIAL _____ SLOT SIZE _____

RISER DIAMETER & MATERIAL _____ BOREHOLE DIAMETER _____

GRANULAR BACKFILL MATERIAL _____ ES REPRESENTATIVE _____

DRILLING METHOD _____ DRILLING CONTRACTOR _____



STABILIZED WATER LEVEL _____ FEET BELOW DATUM.
MEASURED ON _____

Figure A.4.1

Monitoring Well Installation Record

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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(^{o}F ^{o}C) _____
Specific Conductance(µS/cm)_____
Dissolved Oxygen Concentration_____
Oxidation-Reduction Potential_____

Interim Water Characteristics
Gallons Removed: pH:
Temperature (^{O}F ^{O}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(^{O}F ^{O}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.

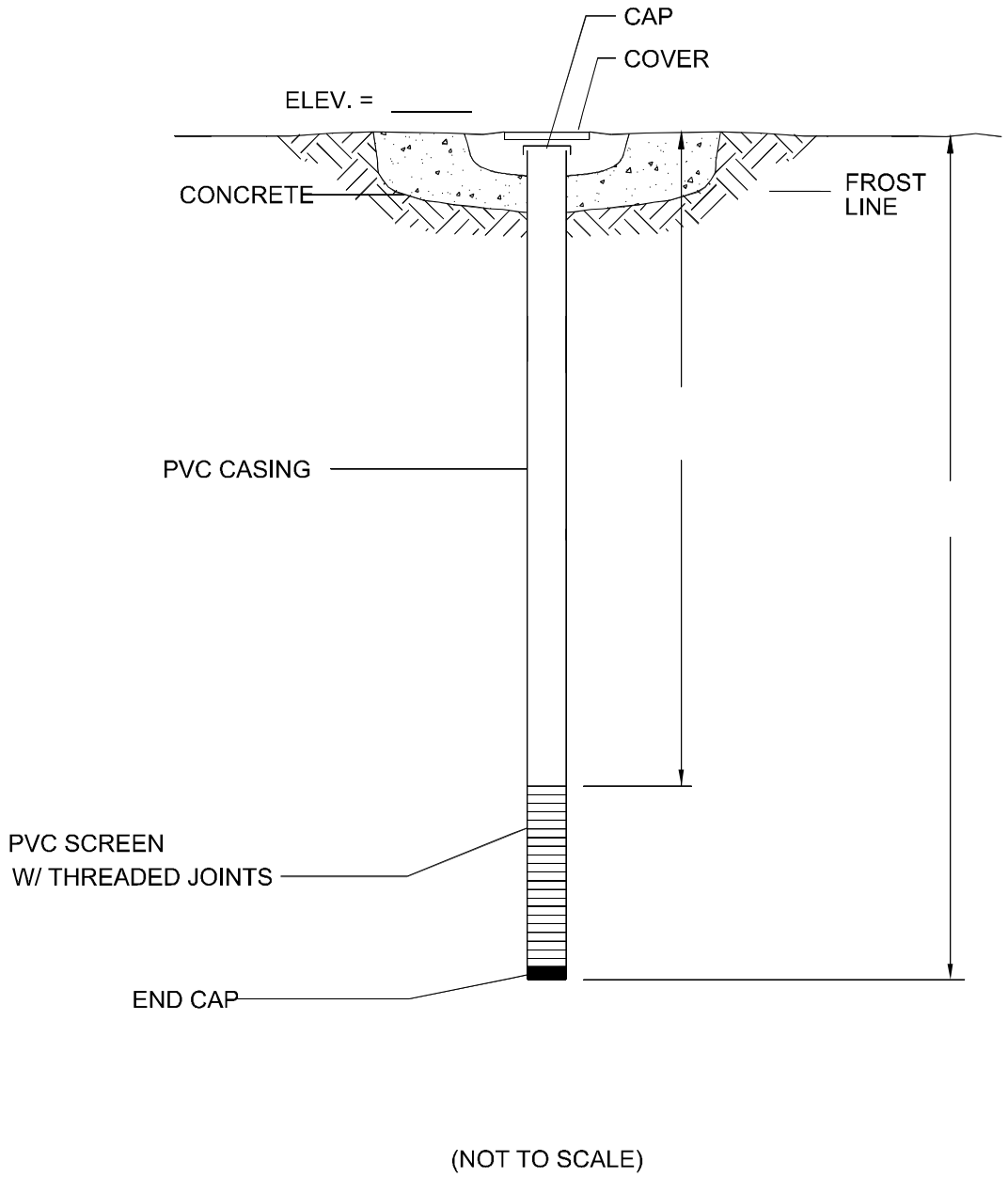

Figure A.4.3

Typical Monitoring Point Completion Diagram

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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 _____

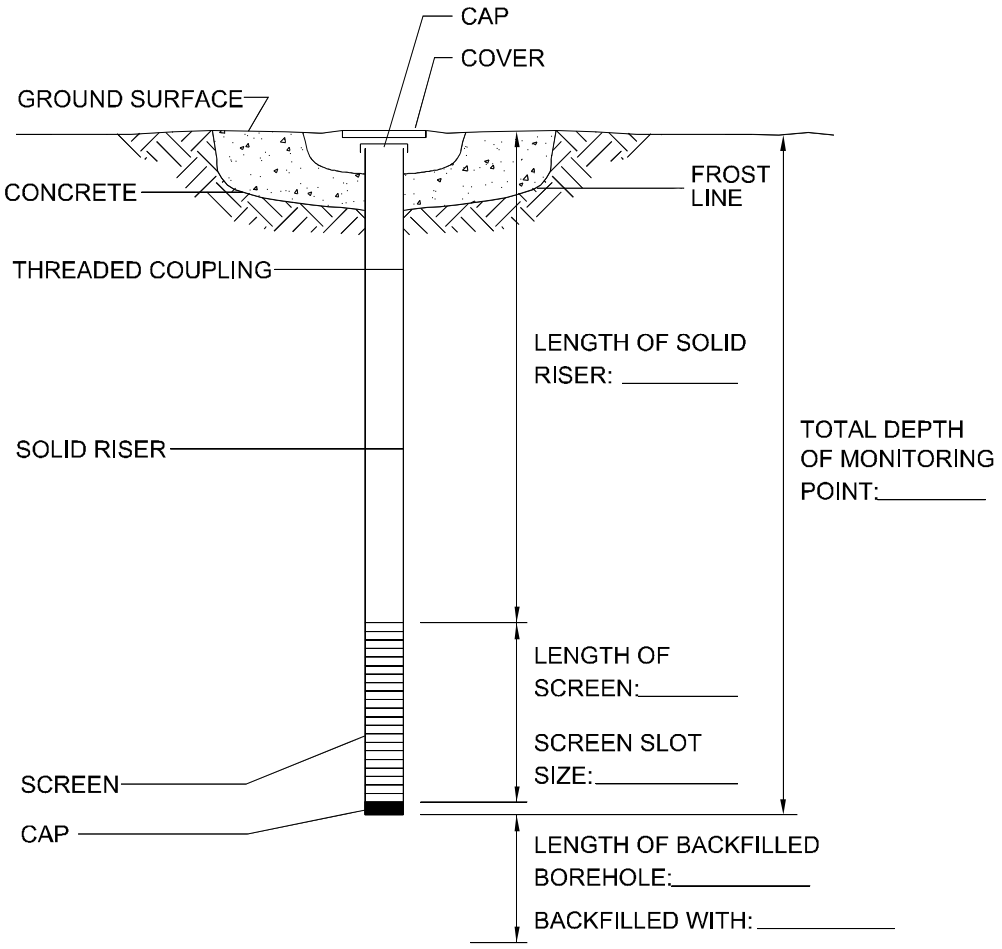
DATUM ELEVATION _____ GROUND SURFACE ELEVATION _____

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

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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 (^{o}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:_____
Method_____	Containers:_____
Method_____	Containers:_____
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.

Figure A.6.1
Slug Test Data Form

Location ____________________ Client: ________________ Well No. __________
Job No. ____________________ Field Scientist ________________ Date __________
Water Level ____________________ Total Well Depth ______________________________
Measuring Datum ____________________ Datum Elevation ______________________________
Weather ____________________ Temp ______________________________
Slug Dimensions and Volume ____
Comments ____

Beginning Time	Ending Time	Initial Head Reading	Ending Head Reading	Test Type (Rise/Fall)	File Name	Comments

- 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:

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

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:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.1.2}$$

Where: C = concentration [M/L^3]
t = time [T]
D_x = hydrodynamic dispersion [L^2/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:

Change in Solute Concentration = Flux In - Flux Out ± Reactions

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

SECTION B-2

ADVECTION

Advective transport is the transport of solutes by the bulk movement of groundwater. Advection is the most important process driving contaminant migration in the subsurface. The linear groundwater velocity in the direction parallel to groundwater flow caused by advection is given by:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} \qquad \text{eq. B.2.1}$$

Where: v_x = average linear velocity [L/T]
K = hydraulic conductivity [L/T]
n_e = effective porosity [L^3/L^3]
dH/dL = hydraulic gradient [L/L]

Solute transport by advection alone yields a sharp solute concentration front. Immediately ahead of the front, the solute concentration is equal to the background concentration (generally zero). Behind the advancing solute front, the concentration is equal to the initial contaminant concentration at the point of release. This is referred to as plug flow and is illustrated in Figures B.2.1, B.2.2, and B.2.3. In reality, the advancing front spreads out due to the processes of dispersion and diffusion, as discussed in Section B-3, and is retarded by sorption and biodegradation, as discussed in Sections B-4 and B-5, respectively.

The one-dimensional advective transport component of the advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.2}$$

Where: v_x = average linear velocity [L/T]
C = contaminant concentration [M/L^3]
t = time [T]
x = distance along flow path [L]

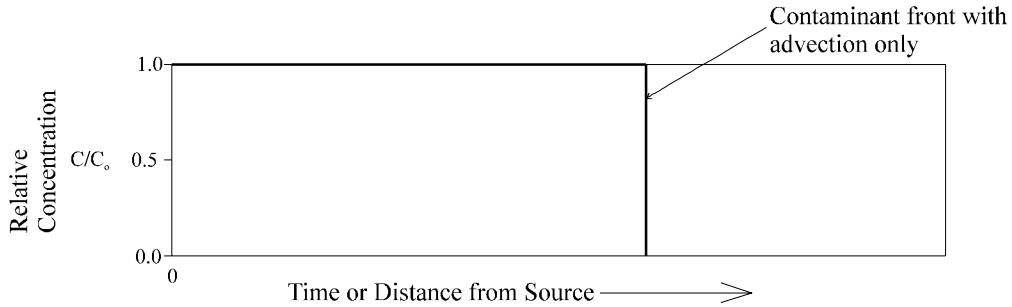

Figure B.2.1 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only.

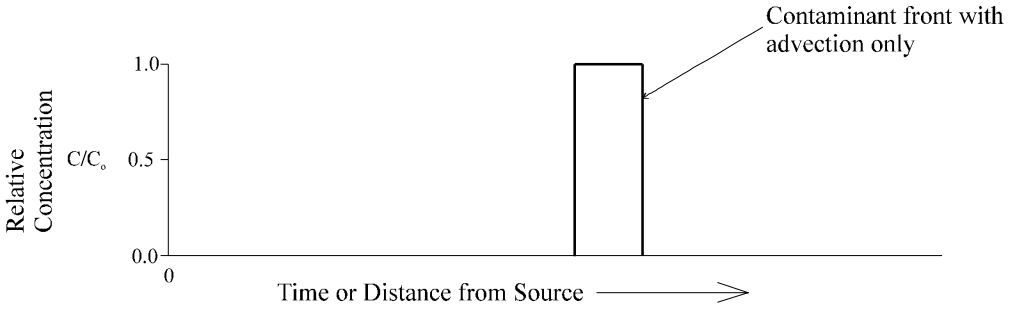

Figure B.2.2 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only.

This equation considers only advective transport of the solute. In some cases this may be a fair approximation for simulating solute migration because advective transport is the main force behind contaminant migration. However, because of dispersion, diffusion, sorption, and biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation (equation B.1.1) to obtain an accurate mathematical description of solute transport.

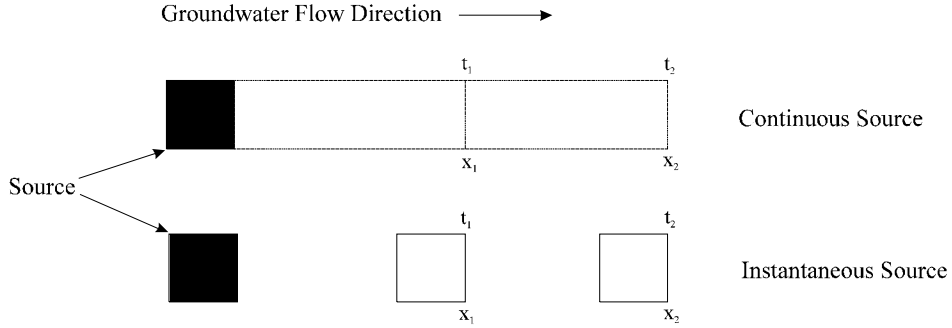

Figure B.2.3 Plume migration in two dimensions (plan view) showing plume migration resulting from advective flow only with continuous and instantaneous sources.

SECTION B-3

HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion, which includes mechanical dispersion and diffusion, is an important process causing dilution of contaminants dissolved in groundwater. The following sections describe these processes and how they are incorporated into the modified advection-dispersion equation (Equation B.1.1). Infiltration, another process that may cause dilution of contaminants, is discussed in Section B-6.

B.3.1 HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion is the process whereby a contaminant plume spreads out in directions that are longitudinal and transverse to the direction of plume migration. There are two components of hydrodynamic dispersion; mechanical dispersion and molecular diffusion. Hydrodynamic dispersion, D, is the sum of mechanical dispersion and molecular diffusion. Mechanical dispersion is the dominant mechanism causing hydrodynamic dispersion at normal groundwater velocities. At extremely low groundwater velocities, molecular diffusion can become the dominant mechanism of hydrodynamic dispersion. Molecular diffusion is generally ignored for most groundwater studies.

B.3.1.1 Mechanical Dispersion

Three processes are responsible for mechanical dispersion (Figure B.3.1). The first process is the variation in flow velocity through pores of various sizes. As groundwater flows through a porous medium, it flows more slowly through large pores than through smaller pores. The second cause of mechanical dispersion is tortuosity, or flow path length. As groundwater flows through a porous medium, some of the groundwater follows less tortuous (shorter) paths, while some of the groundwater takes more tortuous (longer) paths. The longer the flow path, the slower the average linear velocity of the groundwater and the dissolved contaminant. The final process causing mechanical dispersion is variable friction within an individual pore. Groundwater traveling close to the center of a pore experiences less friction than groundwater traveling next to

a mineral grain, and therefore moves faster. These processes cause some of the contaminated groundwater to move faster than the average linear velocity of the groundwater and some to move slower. This variation in average velocity of the solute causes dispersion of the contaminant. As a result of dispersion, the solute front travels at a rate that is faster than would be predicted based solely on the average linear velocity of the groundwater. The overall result of dispersion is spreading and mixing of the contaminant plume with uncontaminated groundwater. Figures B.3.2 and B.3.3 illustrate the effects of hydrodynamic dispersion on an advancing solute front.

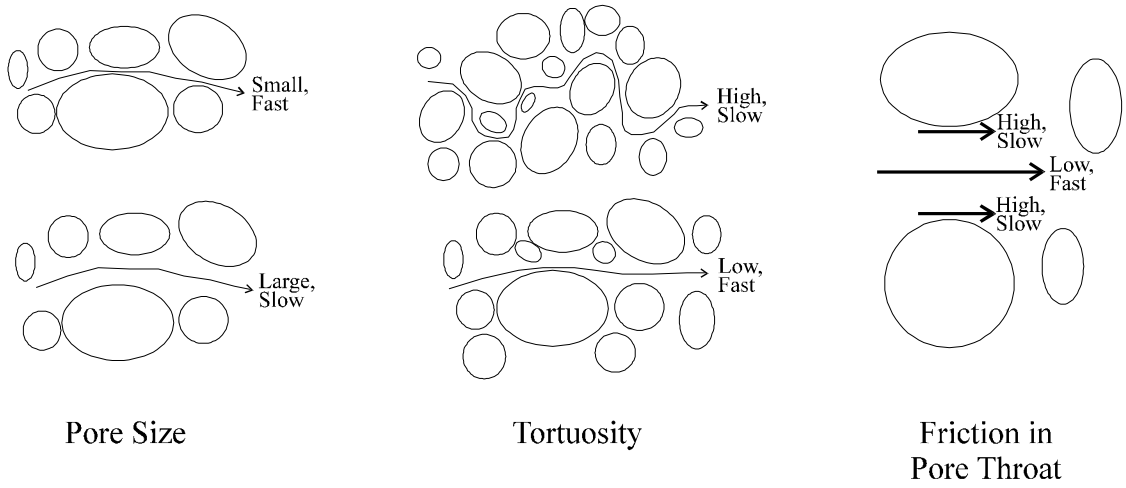

Figure B.3.1 Physical processes causing mechanical dispersion.

The component of hydrodynamic dispersion contributed by mechanical dispersion is given by the relationship:

$$\text{Mechanical Dispersion} = \alpha_x v_x \qquad \text{eq. B.3.1}$$

Where: v_x = average linear groundwater velocity [L/T]
α_x = dispersivity [L]

Mechanical dispersion has two components, longitudinal dispersion and transverse (both horizontal and vertical) dispersion. Longitudinal dispersion is the spreading of a solute in a direction parallel to the direction of groundwater flow. Longitudinal dispersion occurs because of variations in pore size, friction in the pore throat, and tortuosity. Transverse dispersion is the spreading of a solute in directions perpendicular to the direction of groundwater flow. Transverse dispersion is caused by the tortuosity of the porous medium which causes flow paths to branch

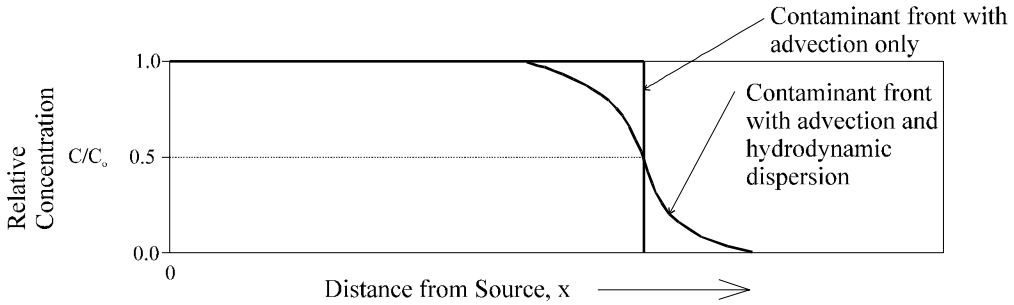

Figure B.3.2 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.

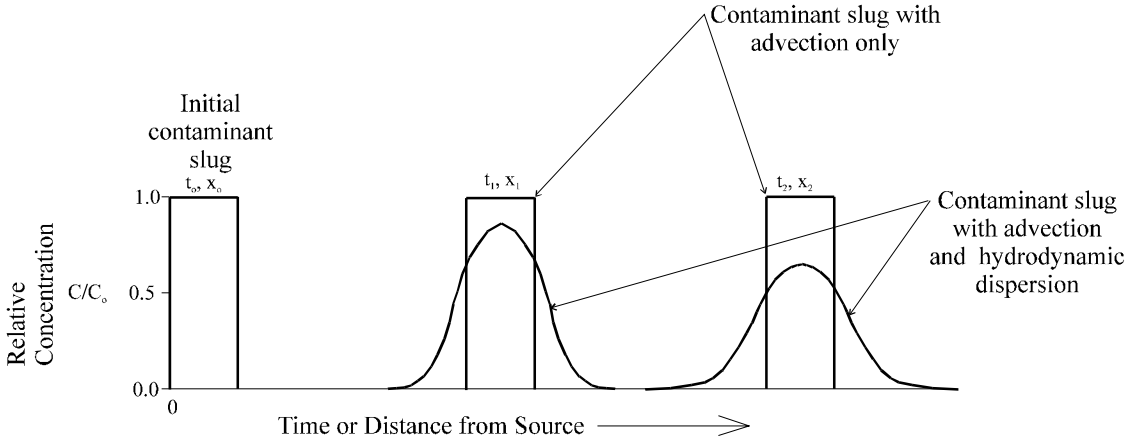

Figure B.3.3 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.

out from the centerline of the contaminant plume. Horizontal transverse dispersion is typically on the order of 10 percent of the longitudinal dispersion. Vertical transverse dispersion is typically on the order of 10 percent of the horizontal transverse dispersion.

B.3.1.2 Molecular Diffusion

Molecular diffusion occurs when concentration gradients cause solutes to migrate from zones of higher concentration to zones of lower concentration, even in the absence of groundwater flow. Molecular diffusion is only important at low groundwater velocities, and therefore can be ignored in areas with high groundwater velocities (Davis *et al.*, 1993).

The molecular diffusion of a solute in groundwater is described by Fick's Laws. Fick's First Law applies to the diffusive flux of a dissolved contaminant under steady-state conditions and, for the one-dimensional case, is given by:

$$F = -D\frac{dC}{dx} \qquad \text{eq. B.3.2}$$

Where: F = mass flux of solute per unit area of time [M/T]
D = diffusion coefficient (L^2/T)
C = solute concentration (M/L^3)
$\frac{dC}{dx}$ = concentration gradient ($M/L^3/L$)

For systems where the dissolved contaminant concentrations are changing with time, Fick's Second Law must be applied. The one-dimensional expression of Fick's Second Law is:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad \text{eq. B.3.3}$$

Where: $\frac{dC}{dt}$ = change in concentration with time [M/T]

The process of diffusion is slower in porous media than in open water because the ions must follow more tortuous flow paths (Fetter, 1988). To account for this, an effective diffusion coefficient, D*, is used.

The effective diffusion coefficient is expressed quantitatively as (Fetter, 1988):

$$D^* = wD \qquad \text{eq. B.3.4}$$

Where: w = empirical coefficient determined by laboratory experiments [dimensionless]

The value of w generally ranges from 0.01 to 0.5 (Fetter, 1988).

B.3.1.3 Equation of Hydrodynamic Dispersion

Hydrodynamic dispersion, D, has two components, mechanical dispersion and molecular diffusion. For one-dimensional flow, hydrodynamic dispersion is represented by the following equation (Freeze and Cherry, 1979):

$$D_x = \alpha_x v_x + D^* \qquad \text{eq. D.3.5}$$

Where: D_x = longitudinal coefficient of hydrodynamic dispersion in the x direction [L^2/T]
α_x = longitudinal dispersivity [L]
v_x = average linear groundwater velocity [L/T]
D* = effective molecular diffusion [L^2/T]

Dispersivity is a parameter that is characteristic of the porous medium through which the contaminant migrates. Dispersivity represents the spreading of a contaminant over a given length of flow, and therefore has units of length. Several approaches can be used to estimate longitudinal dispersivity, α_x. One technique involves conducting a tracer test. Although this is potentially the most reliable method, time and monetary constraints can be prohibitive. Another method commonly used to estimate dispersivity when implementing a solute transport model is to start with a longitudinal dispersivity of 0.1 times the plume length (Lallemand-Barres and Peaudecerf, 1978). Some solute transport modelers will start with an accepted literature value for the types of materials found in the aquifer matrix. After selecting an initial dispersivity, the contaminant transport model is calibrated by adjusting the dispersivity within the range of accepted literature values until the modeled and observed contaminant distribution patterns match (Anderson, 1979). This is a two-step process. The first step is to calibrate the flow model to the hydraulic conditions present at the site. After the groundwater flow model is calibrated to the hydraulics of the system, the contaminant transport model is calibrated by trial and error using various values for dispersivity. There is no unique solution because several parameters, including hydraulic conductivity, effective porosity, and dispersivity, are variable within the flow system (Anderson, 1979; Davis *et al.*, 1993). Table B.3.1 presents commonly accepted literature values for hydrodynamic dispersion.

The dispersion of organic solutes in an aquifer is an important consideration when modeling intrinsic remediation because the dispersion of a contaminant into relatively pristine portions of the aquifer allows the solute to admix with more electron acceptors crossgradient to the direction of groundwater flow.

Table B.3.1

Accepted Literature Values of Dispersivity for Alluvial Sediments (From Walton, 1988)

Aquifer Matrix	Method of Measurement	Longitudinal Dispersivity (m)	Transverse Dispersivity (m)
Alluvial Sediments	Single Well Test	0.03 to 7	0.009 to 1
Alluvial Sediments	Two Well Test	0.1 to 15	
Alluvial Sediments	Areal Model	12 to 61	4 to 30

B.3.2 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION

The advection-dispersion equation is obtained by adding hydrodynamic dispersion to equation B.2.2. In one dimension, the advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.3.6}$$

Where: v_x = average linear velocity [L/T]
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]

This equation considers both advection and hydrodynamic dispersion. Because of sorption and biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation presented as equation B.1.1 to obtain an accurate mathematical description of solute transport.

SECTION B-4

SORPTION

Many organic contaminants, including BTEX, are removed from solution by sorption onto the aquifer matrix. Sorption is the process whereby dissolved contaminants partition from the groundwater and adhere to the particles comprising the aquifer matrix. Sorption of dissolved contamination onto the aquifer matrix results in slowing (retardation) of the contaminant relative to the average advective groundwater flow velocity and a reduction in dissolved BTEX concentrations in groundwater. Sorption can also influence the relative importance of volatilization and biodegradation (Lyman *et al.*, 1992). Figures B.4.1 and B.4.2 illustrate the effects of sorption on an advancing solute front.

This section provides information on how retardation coefficients are determined in the laboratory. It is not the intent of this document to instruct people in how to perform these experiments. This information is provided for informational purposes only. Linear isotherms and previously determined soil sorption coefficients (K_{oc}) are generally used to estimate sorption and retardation.

B.4.1 MECHANISMS OF SORPTION

Sorption of dissolved contaminants is a complex phenomenon caused by several mechanisms, including London-van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange, chemisorption (covalent bonding between chemical and aquifer matrix), dipole-dipole forces, dipole-induced dipole forces, and hydrophobic forces. Because of their nonpolar molecular structure, hydrocarbons most commonly exhibit sorption through the process of hydrophobic bonding. When the surfaces comprising the aquifer matrix are less polar than the water molecule, as is generally the case, there is a strong tendency for the nonpolar contaminant molecules to partition from the groundwater and sorb to the aquifer matrix. This phenomenon is referred to as hydrophobic bonding and is an important factor controlling the fate of many organic pollutants in soils (Devinny *et al.*, 1990). Two components of an aquifer have the greatest effect on sorption:

organic matter and clay minerals. In most aquifers, the organic fraction tends to control the sorption of fuel hydrocarbons.

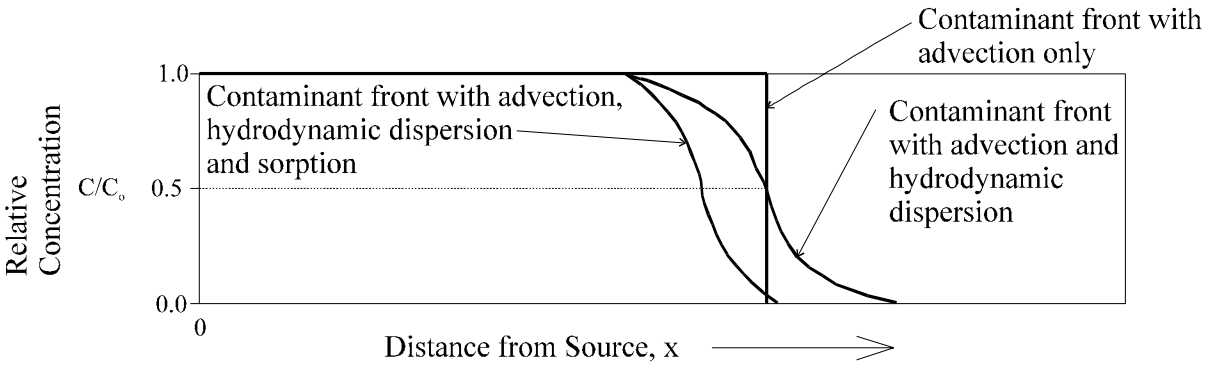

Figure B.4.1 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.

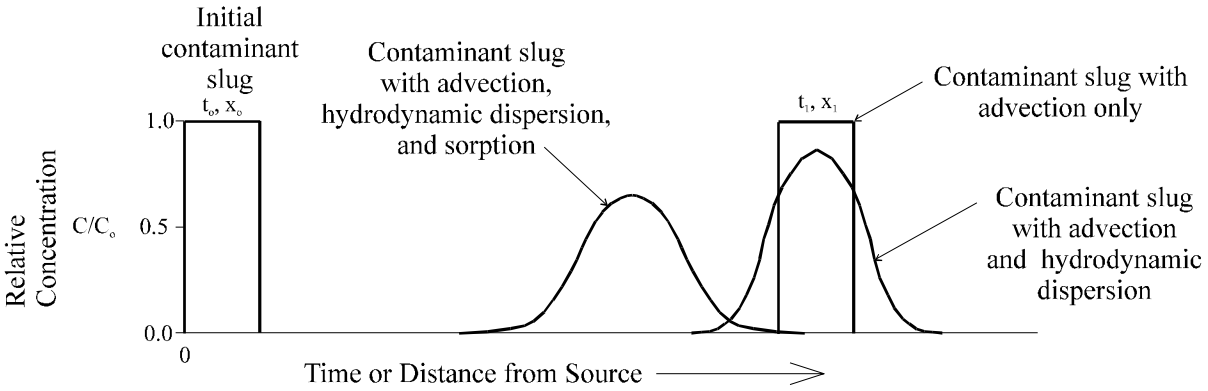

Figure B.4.2 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.

B.4.2 SORPTION MODELS AND ISOTHERMS

Regardless of the sorption mechanism, it is possible to determine the amount of sorption to be expected when a given dissolved contaminant interacts with the materials comprising the aquifer matrix. Bench-scale experiments are performed by mixing water-contaminant solutions of various concentrations with aquifer materials containing various amounts of organic carbon and clay

minerals. The solutions are then sealed with no headspace and left until equilibrium between the various phases is reached. The amount of contaminant left in solution is then measured.

Both environmental conservative isotherms (ECI) and constant soil to solution isotherms (CSI) can be generated. The ECI study uses the same water concentration but changes the soil to water ratio. In CSI isotherm studies the concentration of contaminant in water is varied while the amount of water and sediment is constant. In some instances, actual contaminated water from the site is added. Typically the samples are continually rotated and concentrations measured with time to document equilibrium. True equilibrium may require hundreds of hours of incubation but 80 to 90 percent of equilibrium may be achieved in one or two days.

The results are commonly expressed as a plot of the concentration of chemical sorbed (µg/g) versus the concentration remaining in solution (µg/L). The relationship between the concentration of chemical sorbed (C_a) and the concentration remaining in solution (C_l) at equilibrium is referred to as the sorption isotherm because the experiments are performed at constant temperature.

Sorption isotherms generally exhibit one of three characteristic shapes depending on the sorption mechanism. These isotherms are referred to as the Langmuir isotherm, the Freundlich isotherm, and the linear isotherm (a special case of the Freundlich isotherm). Each of these sorption isotherms, and related equations, are discussed in the following sections.

B.4.2.1 Langmuir Sorption Model

The Langmuir model describes sorption in solute transport systems wherein the sorbed concentration increases linearly with increasing solute concentration at low concentrations and approaches a constant value at high concentrations. The sorbed concentration approaches a constant value because there are a limited number of sites on the aquifer matrix available for contaminant sorption. This relationship is illustrated in Figure B.4.3. The Langmuir equation is described mathematically as (Devinney *et al.*, 1990):

$$C_a = \frac{KC_l b}{1 + KC_l} \qquad \text{eq. B.4.1}$$

Where:
- C_a = sorbed contaminant concentration (mass contaminant/mass soil)
- K = equilibrium constant for the sorption reaction (µg/g)
- C_l = dissolved contaminant concentration (µg/ml)
- b = number of sorption sites (maximum amount of sorbed contaminant)

The Langmuir model is appropriate for highly specific sorption mechanisms where there are a limited number of sorption sites. This model predicts a rapid increase in the amount of sorbed contaminant as contaminant concentrations increase in a previously pristine area. As sorption sites become filled, the amount of sorbed contaminant reaches a maximum level equal to the number of sorption sites, *b*.

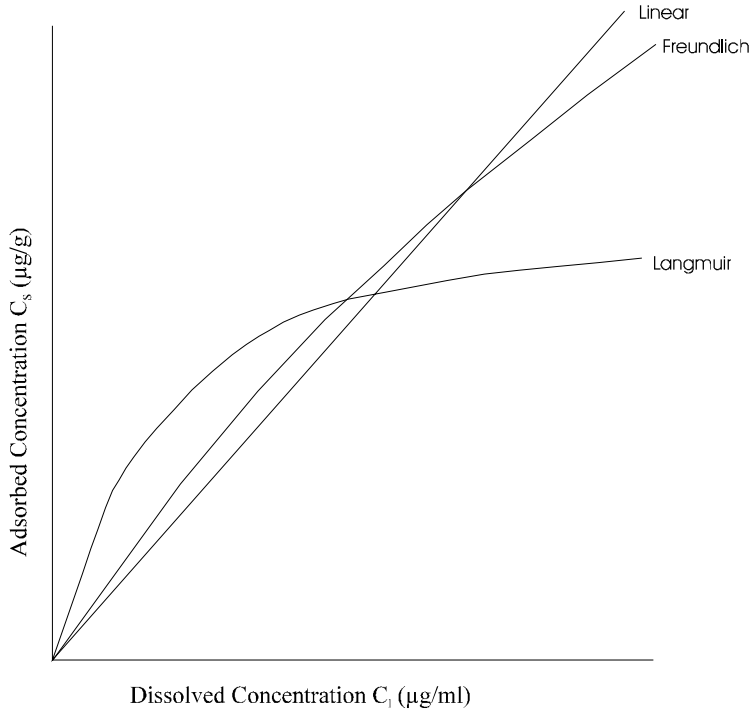

Figure B.4.3 Characteristic adsorption isotherm shapes.

B.4.2.2 Freundlich Sorption Model

The Langmuir isotherm model can be modified if the number of sorption sites is large (assumed infinite) relative to the number of contaminant molecules. This is generally a valid assumption for dilute solutions (e.g., downgradient from a petroleum hydrocarbon spill in the dissolved BTEX plume) where the number of unoccupied sorption sites is large relative to contaminant concentrations. The Freundlich model is expressed mathematically as (Devinny *et al.*, 1990):

$$C_a = K_d C_l^{1/n} \qquad \text{eq. B.4.2}$$

Where: K_d = distribution coefficient
C_a = sorbed contaminant concentration (mass contaminant/mass soil, µg/g)
C_l = dissolved concentration (mass contaminant/volume solution, (µg/ml)
n = chemical-specific coefficient

The value of n in this equation is a chemical-specific quantity that is determined experimentally. Values of 1/n typically range from 0.7 to 1.1, but may be as low as 0.3 and as high as 1.7 (Lyman *et al.* 1992).

The simplest expression of equilibrium sorption is the linear sorption isotherm, a special form of the Freundlich isotherm that occurs when the value of n is 1. The linear isotherm is valid for a dissolved species that is present at a concentration less than one half of its solubility (Lyman *et al.*, 1992). This is a valid assumption for BTEX compounds partitioning from fuel mixtures into groundwater. Dissolved BTEX concentrations resulting from this type of partitioning are significantly less than the pure compound's solubility in pure water. The linear sorption isotherm is expressed as (Jury *et al.*, 1991):

$$C_a = K_d C_l \qquad \text{eq. B.4.3}$$

Where: K_d = distribution coefficient (slope of the isotherm, ml/g).
C_a = sorbed contaminant concentration (mass contaminant/mass soil, µg/g)
C_l = dissolved contaminant concentration (mass contaminant/volume solution, µg/ml)

The slope of the linear isotherm is the distribution coefficient, K_d.

B.4.3 DISTRIBUTION COEFFICIENT

The most commonly used method for expressing the distribution of an organic chemical between the aquifer matrix and the aqueous phase is the distribution coefficient, K_d, which is defined as the ratio of the sorbed contaminant concentration to the dissolved contaminant concentration:

$$K_d = \frac{C_a}{C_l} \qquad \text{eq. B.4.4}$$

Where: K_d = distribution coefficient (slope of the sorption isotherm, ml/g).
C_a = sorbed concentration (mass contaminant/mass soil or µg/g)
C_l = dissolved concentration (mass contaminant/volume solution or µg/ml)

The transport and partitioning of a contaminant is strongly dependent on the chemical's soil/water distribution coefficient and water solubility. The distribution coefficient is a measure of the sorption/desorption potential and characterizes the tendency of an organic compound to be

sorbed to the aquifer matrix. The higher the distribution coefficient, the greater the potential for sorption to the aquifer matrix. The distribution coefficient is the slope of the sorption isotherm at the contaminant concentration of interest. The greater the amount of sorption, the greater the value of K_d. For systems described by a linear isotherm, K_d is a constant. In general terms, the distribution coefficient is controlled by the hydrophobicity of the contaminant and the total surface area of the aquifer matrix available for sorption. Thus, the distribution coefficient for a single compound will vary with the composition of the aquifer matrix. Because of their extremely high specific surface areas (ratio of surface area to volume), the organic carbon and clay mineral fractions of the aquifer matrix generally present the majority of sorption sites in an aquifer.

Based on the research efforts of Ciccioli *et al*. (1980), Rodgers *et al*. (1980), Karikhoff *et al*. (1979), and Shwarzenbach and Westall (1981), it appears that the primary adsorptive surface for organic chemicals is the organic fraction of the aquifer matrix. However, there is a "critical level of organic matter" below which sorption onto mineral surfaces is the dominant sorption mechanism (McCarty *et al*., 1981). The critical level of organic matter, below which sorption appears to be dominated by mineral-solute interactions, and above which sorption is dominated by organic carbon-solute interactions, is given by (McCarty *et al*., 1981)

$$f_{oc_c} = \frac{A_s}{200}\frac{1}{K_{ow}^{0.84}} \qquad \text{eq. B.4.5}$$

Where: f_{oc_c} = critical level of organic matter (mass fraction)

A_s = surface area of mineralogical component of the aquifer matrix

K_{ow} = octanol-water partitioning coefficient

From this relationship it is apparent that the total organic carbon content of the aquifer matrix is less important for solutes with low octanol-water partitioning coefficients (K_{ow}). Also apparent is the fact that the critical level of organic matter increases as the surface area of the mineralogic fraction of the aquifer matrix increases. The surface area of the mineralogic component of the aquifer matrix is most strongly influenced by the amount of clay. For compounds with low K_{ow} values in materials with a high clay content, sorption to mineral surfaces could be an important factor causing retardation of the chemical.

For benzene, $f_{oc_c} = 0.001$ (0.1 percent organic carbon), if A_s is assumed to be $13 m^2/g$ (Lyman *et al*., 1992). Because ethylbenzene, toluene, and the xylenes have higher K_{ow} values than benzene, an even smaller fraction of organic carbon is required for carbon-based sorption to be important for BTEX.

Several researchers have found that if the distribution coefficient is normalized relative to the aquifer matrix total organic carbon content, much of the variation in observed K_d values between different soils is eliminated (Dragun, 1988). Distribution coefficients normalized to total organic carbon content are expressed as K_{oc}. The following equation gives the expression relating K_d to K_{oc}:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{eq. B.4.6}$$

Where: K_{oc} = soil sorption coefficient normalized for total organic carbon content
K_d = distribution coefficient
f_{oc} = fraction total organic carbon (mg organic carbon/mg soil)

In areas with high clay concentrations and low total organic carbon concentrations, the clay minerals become the dominant sorption sites. Under these conditions, the use of K_{oc} to compute K_d might result in underestimating the importance of sorption in retardation calculations, a source of error that will make retardation calculations based on the total organic carbon content of the aquifer matrix more conservative. In fact, aquifers that have a high enough hydraulic conductivity to spread hydrocarbon contamination generally have low clay content. In these cases, the contribution of sorption to mineral surfaces is generally trivial.

Earlier investigations reported distribution coefficients normalized to total organic matter content (K_{om}). The relationship between f_{om} and f_{oc} is nearly constant and, assuming that the organic matter contains approximately 58 percent carbon (Lyman *et al.*, 1992):

$$K_{oc} = 1.724 K_{om} \qquad \text{eq. B.4.7}$$

B.4.4 COEFFICIENT OF RETARDATION

As mentioned earlier, sorption tends to slow the transport velocity of contaminants dissolved in groundwater. The coefficient of retardation, R, is used to estimate the retarded contaminant velocity. The coefficient of retardation for linear sorption is determined from the distribution coefficient using the relationship:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. B.4.8}$$

Where: R = coefficient of retardation [dimensionless]

ρ_b = bulk density of aquifer [M/L^3]
K_d = distribution coefficient [L^3/M]
n = porosity [L^3/L^3]

The retarded contaminant transport velocity, v_c, is given by:

$$v_c = \frac{v_x}{R} \qquad \text{eq. B.4.9}$$

Where: v_c = retarded contaminant transport velocity [L/T]
v_x = advective groundwater velocity [L/T]
R = coefficient of retardation [dimensionless]

Two methods used to quantify the distribution coefficient and amount of sorption (and thus retardation) for a given aquifer/contaminant system are presented below. The first method involves estimating the distribution coefficient by using K_{oc} for the contaminants and the fraction of organic carbon comprising the aquifer matrix. The second method involves conducting batch or column tests to determine the distribution coefficient. Because numerous authors have conducted experiments to determine K_{oc} values for common contaminants, literature values are reliable, and it generally is not necessary to conduct laboratory tests.

B.4.4.1 Determining the Coefficient of Retardation using K_{oc}

Batch and column tests have been performed for a wide range of contaminant types and concentrations and aquifer conditions. Numerous studies have been performed using the results of these tests to determine if relationships exist that are capable of predicting the sorption characteristics of a chemical based on easily measured parameters. The results of these studies indicate that the amount of sorption is strongly dependent on the amount of organic carbon present in the aquifer matrix and the degree of hydrophobicity exhibited by the contaminant (Bailey and White, 1970; Karickhoff *et al*., 1979; Kenaga and Goring, 1980; Brown and Flagg, 1981; Schwarzenbach and Westall, 1981; Hassett *et al*., 1983; Chiou *et al*., 1983). These researchers observed that the distribution coefficient, K_d, was proportional to the organic carbon fraction of the aquifer times a proportionality constant. This proportionality constant, K_{oc}, is defined as given by equation B.4.6. In effect, equation B.4.6 normalizes the distribution coefficient to the amount of organic carbon in the aquifer matrix. Because it is normalized to organic carbon, values of K_{oc} are dependent only on the properties of the compound (not on the type of soil). Values of K_{oc} have been determined for a wide range of chemicals. Table B.4.1 lists K_{oc} values for BTEX and trimethylbenzene.

Table B.4.1
Values of Aqueous Solubility and K_{oc} for the BTEX compounds

Compound	Solubility (mg/L)	K_{oc} (L/Kg)
Benzene	1750[a]	87.1[a]
Benzene		83[b]
Benzene	1780[c]	190[c,d,f]
Benzene	1780[c]	62[c,e,f]
Benzene	1780[h]	72[h,i]
Benzene*	1780[h]	79[h,j,*]
Benzene	1780[c,h]	89[k]
Toluene	515[a]	151[a]
Toluene		303[b]
Toluene	537[c]	380[c,d,f]
Toluene	537[c]	110[c,e,f]
Toluene*	537[c]	190[k,*]
Ethylbenzene	152[a]	158.5[a]
Ethylbenzene		519[b]
Ethylbenzene	167[c]	680[c,d,f]
Ethylbenzene	167[c]	200[c,e,f]
Ethylbenzene	140[h]	501[h,i]
Ethylbenzene*	140[h]	468[h,j]
Ethylbenzene	167[c]	398[k]
o-xylene	152[a]	128.8[a]
o-xylene		519[b]
o-xylene*	152[a]	422[k,*]
m-xylene	158[a]	
m-xylene		519[b]
m-xylene	162[c]	720[c,d,f]
m-xylene	162[c]	210[c,e,f]
m-xylene*	162[c]	405.37[k,*]
p-xylene	198[a]	204[a]
p-xylene		519[b]
p-xylene*	198[a]	357[k,*]
1,2,3-trimethylbenzene*	75	884[b,*]
1,2,4-trimethylbenzene	59[l]	884[b]
1,2,4-trimethylbenzene*	59[l]	772[k,*]
1,3,5-trimethylbenzene*	72.60[g]	676[k,*]

[a] From Knox *et al.*, 1993
[b] From Jeng *et al.*, 1992; Temperature = 20°C
[c] From Lyman *et al.*, 1992; Temperature = 25°C
[d] Estimated from K_{ow}
[e] Estimated from solubility
[f] Estimate from solubility generally considered more reliable
[g] From Lyman *et al.*, 1992; Temperature = 20°C
[h] From Fetter, 1993
[I] Average of 12 equations used to estimate K_{oc} from K_{ow} or K_{om}
[j] Average of 5 equations used to estimate K_{oc} from Solubility
[k] Average using equations from Kanaga and Goring (1980), Means *et al.* (1980), and Hassett *et al.* (1983) to estimate K_{oc} from solubility
[l] From Sutton and Calder (1975)
* Recommended value

By knowing the value of K_{oc} for a contaminant and the fraction of organic carbon present in the aquifer, the distribution coefficient can be determined by using the relationship:

$$K_d = K_{oc} f_{oc} \qquad \text{eq. B.4.10}$$

When using the method presented in this section to predict sorption of the BTEX compounds, total organic carbon concentrations obtained from the most transmissive aquifer zone should be averaged and used for predicting sorption. This is because the majority of dissolved contaminant transport occurs in the most transmissive portions of the aquifer. In addition, because the most transmissive aquifer zones generally have the lowest total organic carbon concentrations, the use of this value will give a conservative prediction of contaminant sorption and retardation.

B.4.4.2 Determining the Coefficient of Retardation using Laboratory Tests

The distribution coefficient may be quantified in the laboratory using batch or column tests. Batch tests are easier to perform than column tests. Although more difficult to perform, column tests generally produce a more accurate representation of field conditions than batch tests because continuous flow is involved. Knox *et al*. (1993) suggest using batch tests as a preliminary screening tool, followed by column studies to confirm the results of batch testing. The authors of this document feel that batch tests, if conducted properly, will yield sufficiently accurate results for fate and transport modeling purposes provided that sensitivity analyses for retardation are conducted during the modeling.

Batch testing involves adding uncontaminated aquifer material to a number of vessels, adding solutions prepared using uncontaminated groundwater from the site mixed with various amounts of contaminants to produce varying solute concentrations, sealing the vessel and shaking it until equilibrium is reached, analyzing the solute concentration remaining in solution, and calculating the amount of contaminant sorbed to the aquifer matrix using mass balance calculations. A plot of the concentration of contaminant sorbed versus dissolved equilibrium concentration is then made using the data for each reaction vessel. The slope of the line formed by connecting each data point is the distribution coefficient. The temperature should be held constant during the batch test, and should approximate that of the aquifer system through which solute transport is taking place.

Table B.4.2 contains data from a hypothetical batch test. These data are plotted (Figure B.4.4) to obtain an isotherm unique to the aquifer conditions at the site. A regression analysis can then

be performed on these data to determine the distribution coefficient. For linear isotherms, the distribution coefficient is simply the slope of the isotherm. In this example, K_d = 0.0146 L/g. Batch-testing procedures are described in detail by Roy *et al.* (1992).

Table B.4.2

Data from Hypothetical Batch Test Experiment

Initial Concentration (μg/L)	Equilibrium Concentration (μg/L)	Weight of Solid Matrix (g)	Sorbed Concentration* (μg/g)
250	77.3	20.42	1.69
500	150.57	20.42	3.42
1000	297.04	20.42	6.89
1500	510.1	20.42	9.70
2000	603.05	20.42	13.68
3800	1198.7	20.42	25.48
6000	2300.5	20.42	36.23
9000	3560.7	20.42	53.27

*Adsorbed Concentration = ((Initial Concentration-Equilibrium Concentration)*Volume of Solution)/Weight of Solid Matrix

Column testing involves placing uncontaminated aquifer matrix material in a laboratory column and passing solutions through the column. Solutions are prepared by mixing uncontaminated groundwater from the site with the contaminants of interest and a conservative tracer. Flow rate and time are accounted for and samples are periodically taken from the effluent end of the column and analyzed to determine contaminant and tracer concentrations. Breakthrough curves are prepared for the contaminants by plotting chemical concentration versus time (or relative concentration versus number of pore volumes). The simplest way to determine the coefficient of retardation (or the distribution coefficient) from the breakthrough curves is to determine the time required for the effluent concentration to equal 0.5 of the influent concentration. This value can be used to determine average velocity of the center of mass of the contaminant. The retardation factor is determined by dividing the average flow velocity through the column by the velocity of the center of mass of the contaminant. The value thus obtained is the retardation factor. The coefficient of retardation also can be determined by curve fitting using the CXTFIT model of Parker and van Genuchten (1984). Breakthrough curves also can be made for the conservative tracer. These curves can be used to determine the coefficient of dispersion by curve fitting using the model of Parker and van Genuchten (1984).

When using the method presented in this section to predict sorption of the BTEX compounds, aquifer samples should be obtained from the most transmissive aquifer zone. This is because the majority of dissolved contaminant transport occurs in the most transmissive portions of the aquifer. In addition, because the most transmissive aquifer zones generally have the lowest

organic carbon concentrations, the use of these materials will give a conservative prediction of contaminant sorption and retardation.

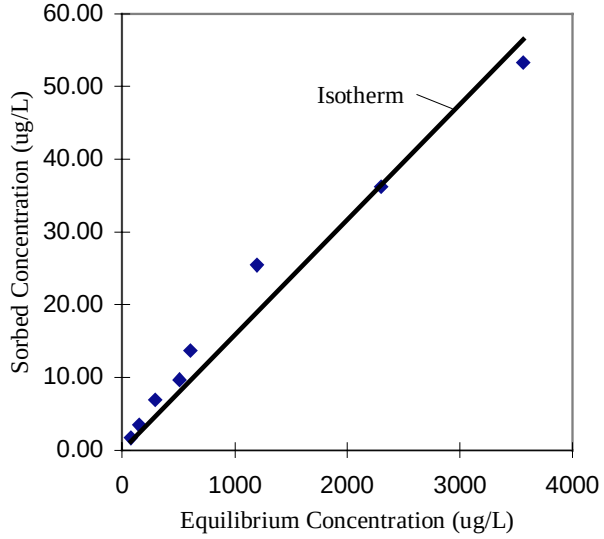

Figure B.4.4 Plot of sorbed concentration vs. equilibrium concentration.

B.4.5 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION WITH RETARDATION

The advection-dispersion equation is obtained by adding hydrodynamic dispersion to equation B.2.2. In one dimension, the advection-dispersion equation is given by:

$$R\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.4.11}$$

Where: v_x = average linear velocity groundwater velocity [L/T]
R = coefficient of retardation [dimensionless]
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]

This equation considers advection, hydrodynamic dispersion, and sorption (retardation). Because of biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation, presented as equation B.1.1, to obtain an accurate mathematical description of solute transport.

SECTION B-5

BIODEGRADATION

Many organic contaminants can be biodegraded by microorganisms indigenous to the subsurface environment. During biodegradation, dissolved BTEX is ultimately transformed into carbon dioxide, methane, and water. Biodegradation of BTEX dissolved in groundwater results in a reduction in contaminant concentration (and mass) and slowing (retardation) of the contaminant relative to the average advective groundwater flow velocity. Figures B.5.1 and B.5.2 illustrate the effects of biodegradation on an advancing solute front.

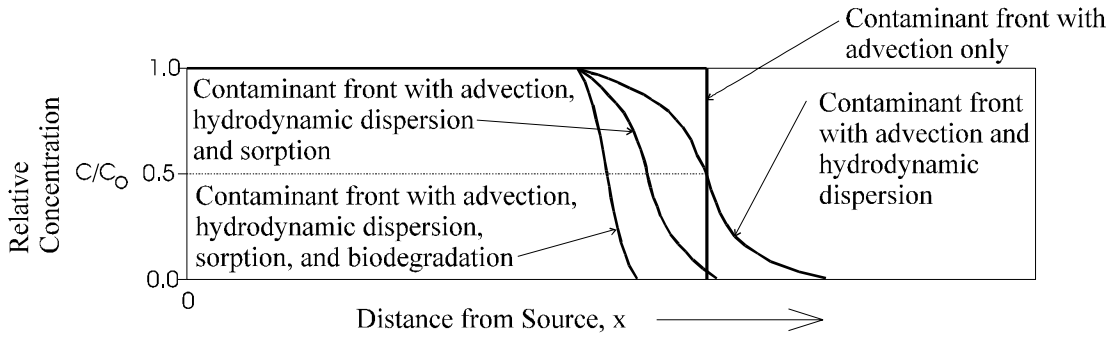

Figure B.5.1 Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; the combined processes of advection, hydrodynamic dispersion, and sorption; and the combined processes of advection, hydrodynamic dispersion, sorption, and biodegradation.

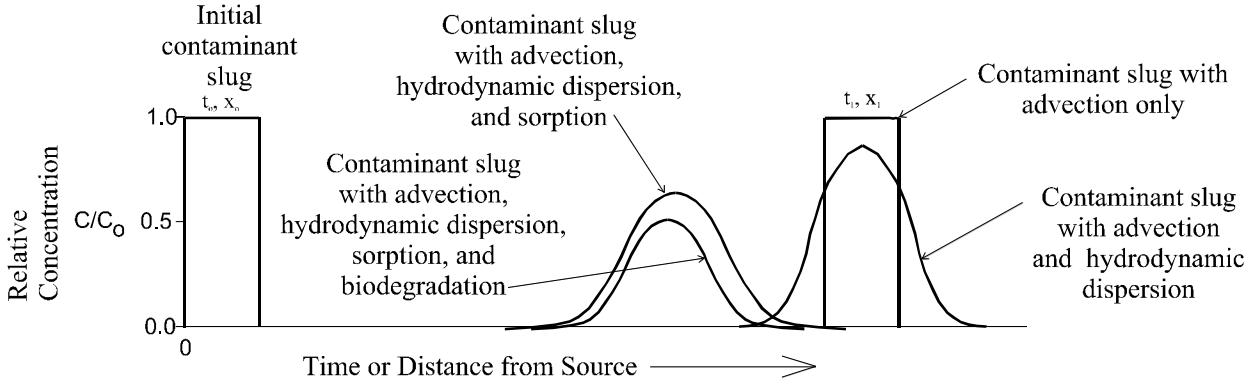

Figure B.5.2 Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; the combined processes of advection, hydrodynamic dispersion, and sorption; and the combined processes of advection, hydrodynamic dispersion, sorption, and biodegradation.

B.5.1 OVERVIEW OF BIODEGRADATION

Over the past two decades, numerous laboratory and field studies have shown that microorganisms indigenous to the subsurface environment can degrade a variety of hydrocarbons, including components of gasoline, kerosene, diesel, and jet fuel (Jamison *et al.*, 1975; Atlas, 1981, 1984, and 1988; Young, 1984; Bartha, 1986; B. H. Wilson *et al.*, 1986 and 1990; Barker *et al.*, 1987; Baedecker *et al.*, 1988; Lee, 1988; Chiang *et al.*, 1989; Cozzarelli *et al.*, 1990; Leahy and Colewell, 1990; Alvarez and Vogel, 1991; Evans *et al.*, 1991a and 1991b; Edwards *et al.*, 1992; Edwards and Grbic-Galic, 1992; Thierrin *et al.*, 1992; Malone *et al.*, 1993; Davis *et al.*, 1994a and 1994b; Lovley *et al.*, 1995). In fact, almost all petroleum hydrocarbons are biodegradable. Under ideal conditions, the biodegradation rates of the low- to moderate-weight aliphatic, alicyclic, and aromatic compounds can be very high. As the molecular weight of the compound increases, so does the resistance to biodegradation (Atlas, 1988; Malone *et al.*, 1993). Table B.5.1 presents a partial list of the many microorganisms known to degrade petroleum hydrocarbons. In reality, if this list were to include all microorganisms capable of biodegrading fuel contaminants, it would be much more extensive.

Table B.5.1
Some Microorganisms Capable of Degrading Various Hydrocarbons
(Modified from Riser-Roberts, 1992).

Contaminant	Microorganisms	Comments/ Biodegradability
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa, Acinetobacter sp., Methylosinus trichosporium OB3b, Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichosporium OB3b, Bacillus sp., Pseudomonas putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, Pseudomonas aeruginosa, Pseudomonas sp., Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylenes	*Pseudomonas putida, methanogens, anaerobes*	High
Jet Fuels	*Cladosporium, Hormodendrum*	High
Kerosene	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Candidaparapsilosis, C. guilliermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae*	High

During biodegradation, microorganisms transform available nutrients into forms useful for energy and cell reproduction by facilitating the transfer of electrons from donors to acceptors. This results in oxidation of the electron donor and reduction of the electron acceptor. Electron donors include natural organic material and fuel hydrocarbons. Electron acceptors are elements

or compounds that occur in relatively oxidized states. The more important electron acceptors in groundwater include dissolved oxygen, nitrate, iron (III), sulfate, and carbon dioxide. In addition, Manganese (IV) can act as an electron acceptor in some groundwater environments. Biodegradation of organic pollutants occurs when microbially mediated redox reactions cause a pollutant to be oxidized. The total number of electrons is conserved during a biochemical reaction. When the metabolite has carbon atoms in a higher oxidation state because of loss of electrons, the reaction product must be present in a reduced state with more electrons/carbon atoms.

When fuel hydrocarbons are utilized as the primary electron donor for microbial metabolism, they typically are completely degraded or detoxified (Bouwer, 1992). When fuel hydrocarbons are not present in sufficient quantities to act as the primary metabolic substrate, they cannot support microbial growth as the only electron donors. In this case, the fuel hydrocarbon can still be degraded, but the microorganisms will obtain the majority of their energy from alternative substrates in the aqueous environment. This type of metabolic degradation of fuel hydrocarbons is referred to as secondary utilization because the fuel hydrocarbon contributes only a small fraction of the energy and carbon needed for cell production and maintenance (Bouwer, 1992). Subsurface bacteria typically are smaller than their terrestrial counterparts, giving rise to a larger surface area to volume ratio. This allows them to efficiently utilize nutrients from dilute solutions (Bouwer, 1992). Bacteria that degrade fuel hydrocarbons have been known to withstand fluid pressures of hundreds of bars, pH conditions ranging from 1 to 10 standard units, temperatures from 0 to 75 degrees Celsius, and salinities greater than those of normal sea water (Freeze and Cherry, 1979).

Biodegradation causes measurable changes in groundwater geochemistry. During aerobic respiration, oxygen is reduced to water, and dissolved oxygen concentrations decrease. In anaerobic systems where nitrate is the electron acceptor, the nitrate is reduced to NO_2^-, N_2O, NO, NH^{4+}, or N_2, and nitrate concentrations decrease. In anaerobic systems where iron (III) is the electron acceptor, it is reduced to iron (II), and iron (II) concentrations increase. In anaerobic systems where sulfate is the electron acceptor, it is reduced to H_2S, and sulfate concentrations decrease. In anaerobic systems where CO_2 is used as an electron acceptor, it is reduced by methanogenic bacteria, and CH_4 is produced. During aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction, total alkalinity will increase. If methanogenesis is the dominant TEAP, alkalinity will remain fairly constant. Table B.5.2 summarizes these trends. Changes in dissolved oxygen, nitrate, iron (II), sulfate, and methane concentrations can be used to ascertain the dominant terminal electron-accepting process (TEAP). Lovley *et al.* (1994) suggest using

dihydrogen (H_2) concentrations to determine the dominant TEAP. However, at this time, measurement of H_2 concentrations in groundwater is not common practice.

Table B.5.2

Trends in Contaminant, Electron Acceptor, Metabolic Byproduct and Total Alkalinity Concentrations During Biodegradation

Analyte	Terminal Electron Accepting Process	Trend in Analyte Concentration During Biodegradation
BTEX	---	Decreases
Dissolved Oxygen	Aerobic Respiration	Decreases
Nitrate	Denitrification	Decreases
Iron (II)	Iron (III) Reduction	Increases
Sulfate	Sulfate Reduction	Decreases
Methane	Methanogenesis	Increases
Alkalinity	Aerobic Respiration, Denitrification, Iron (III) Reduction, and Sulfate Reduction	Increases

Fuel hydrocarbons biodegrade naturally when an indigenous population of hydrocarbon-degrading microorganisms is present in the aquifer and sufficient concentrations of electron acceptors and nutrients are available to these organisms. In most subsurface environments, both aerobic and anaerobic degradation of fuel hydrocarbons can occur, often simultaneously in different parts of the plume. For thermodynamic reasons (as discussed later), microorganisms preferentially utilize those electron acceptors that provide the greatest amount of free energy during respiration (Bouwer, 1992). The rate of natural biodegradation generally is limited by a lack of electron acceptors rather than by a lack of nutrients such as ammonia, nitrate, or, phosphate. Studies at a jet-fuel-contaminated site noted little difference in biodegradation rates in areas with or without nutrient additions (Miller, 1990). These researchers concluded that nitrogen, phosphorus, and other trace nutrients were efficiently recycled by microorganisms at this site.

The driving force of BTEX degradation is the transfer of electrons from an electron donor (BTEX) to an electron acceptor. The energy produced by these reactions is quantified by the Gibb's free energy of the reaction (ΔG_r). The ΔG_r defines the maximum useful energy change for a chemical reaction at a constant temperature and pressure. The state of a redox reaction relative to equilibrium is defined by the sign of ΔG_r. Negative values indicate that the reaction is exothermic (energy producing) and will proceed from left to right (i.e., reactants will be transformed into products and energy will be produced). Positive values indicate that the reaction

is endothermic and in order for the reaction to proceed from left to right, energy must be put into the system. The value of ΔG_r estimates how much free energy is consumed or can be yielded to the system during the reaction.

Like all living organisms, microorganisms are constrained by the laws of thermodynamics. They can facilitate only those redox reactions that are thermodynamically possible (Chapelle, 1993). That is, microorganisms will facilitate only those redox reactions that will *yield* some energy (i.e., $\Delta G_r < 0$). Microorganisms will not invest more energy into the system than can be released. Table B.5.3 presents electron acceptor and electron donor (BTEX) half-cell reactions. This table also gives the calculated ΔG_r values for each of the half-cell reactions. Table B.5.4 gives the Gibbs free energy of formation (ΔG_f) for species used in the half-cell reactions presented in Table B.5.3. The positive calculated ΔG_r values for the oxidation of BTEX (electron donor half-cell reactions) presented in Table B.5.3 indicate that these oxidation reactions are endothermic (i.e., energy-consuming). The negative calculated ΔG_r values for the reduction of the electron acceptors (electron acceptor half-cell reactions) presented in Table B.5.3 indicate that these reduction reactions are exothermic (i.e., energy-producing). In order to derive energy for cell maintenance and production from BTEX, the microorganisms must couple an endothermic reaction (electron donor oxidation) with an exothermic reaction (electron acceptor reduction). Most of the reactions involved in BTEX oxidation cannot proceed abiotically, even though they are thermodynamically favorable. These reactions require microorganisms to proceed. The microorganisms facilitate these redox reactions by providing the necessary activation energy. The requirement of this initial energy input is what prevents these redox reactions from spontaneously occurring in groundwater.

Microorganisms are able to utilize electron transport systems and chemiosmosis to combine energetically favorable and unfavorable reactions with the net result of producing energy for life processes. Table B.5.5 shows how microorganisms combine endothermic and exothermic reactions to release useful energy for cell maintenance and reproduction. By coupling the oxidation of BTEX to the reduction of electron acceptors, the overall reaction becomes energy-yielding, as indicated by the negative ΔG_r values. For example, the oxidation of 1 mole of benzene via oxygen reduction produces 765.34 kilocalories of free energy that is available to the microorganisms. Thus, microorganisms derive a significant source of energy by facilitating this coupled reaction.

Table B.5.3

Electron Donor and Electron Acceptor Half-Cell Reactions

HALF-CELL REACTIONS	ΔG°_r (kcal/ equiv)*	ΔG°_r (kJ/ equiv)*	E° (mV)	Eh (mV)	pE	Conditions for Eh and pE §
ELECTRON-ACCEPTOR (REDUCTION) HALF-CELL REACTIONS						
$5e^- + 6H^+ + NO_3^- \Rightarrow 0.5N_2 + 3H_2O$ **Error! Switch argument not specified.** *Denitrification*	-28.7	-120.	+1.24	+0.712	+12.0	pH = 7 $\Sigma[N]=10^{-3}$
$4e^- + 4H^+ + O_2 \Rightarrow 2H_2O$ **Error! Switch argument not specified.** *Aerobic Respiration*	-28.3	-119.	+1.23	+0.805	+13.6	pH = 7 P_{O_2} **Error! Switch argument not specified.**=0.21 atm
$2e^- + 4H^+ + \underline{MnO_2} \Rightarrow Mn^{2+} + 2H_2O$ **Error! Switch argument not specified.** *Pyrolusite Dissolution/Reduction*	-28.3	-119	+1.23	+0.550	+9.27	pH = 7 $\Sigma[Mn]=10^{-5}$
$e^- + H^+ + CO_2 + \underline{MnOOH} \Rightarrow \underline{MnCO_3} + H_2O$ **Error! Switch argument not specified.** *a Manganite Carbonation/Reduction*	-23.1	-96.8	+1.00	+0.412	+6.96	pH = 8 P_{CO_2} **Error! Switch argument not specified.**=10^{-2}
$e^- + H^+ + \underline{MnO_2} \Rightarrow \underline{MnOOH}$ **Error! Switch argument not specified.** *Pyrolusite Hydrolysis/Reduction*	-22.1	-92.5	+0.959	+0.545	+9.21	pH = 7
$e^- + 3H^+ + \underline{Fe(OH)_{3,amph.}} \Rightarrow Fe^{2+} + 3H_2O$ **Error! Switch argument not specified.** *Amorphous "Goethite" Dissolution/Reduction*	-21.5	-89.9	+0.932	+0.163	+2.75	pH = 6
$8e^- + 10H^+ + NO_3^- \Rightarrow NH_4^+ + 3H_2O$ **Error! Switch argument not specified.** *Nitrate Reduction*	-20.3	-84.9	+0.879	+0.362	+6.12	pH = 6 Σ[Fe]=10^{-5}
$2e^- + 2H^+ + NO_3^- \Rightarrow NO_2^- + H_2O$ **Error! Switch argument not specified.** *Nitrate Reduction*	-18.9	-78.9	+0.819	+0.404	+6.82	pH = 7
$1e^- + 3H^+ + \underline{FeOOH} \Rightarrow Fe^{2+} + 2H_2O$ **Error! Switch argument not specified.** *"iron (III) oxyhydroxide" Dissolution/Reduction*	-15.0	-62.9	+0.652	-0.118	-1.99	pH = 6 Σ[Fe]=10^{-5}
$e^- + 3H^+ + \underline{Fe(OH)_{3,xline.}} \Rightarrow Fe^{2+} + 3H_2O$ **Error! Switch argument not specified.** *Crystallized "Goethite" Dissolution/Reduction*	-11.8	-49.2	+0.510	-0.259	-4.38	pH = 6 Σ[Fe]=10^{-5}
$e^- + H^+ + CO_{2,g} + \underline{Fe(OH)_{3,amph.}} \Rightarrow \underline{FeCO_3} + 2H_2O$ **Error! Switch argument not specified.** *Amorphous "Goethite" Carbonation/Reduction*	-11.0	-46.2	+0.479	-0.113	-1.90	pH = 8 P_{CO_2} **Error! Switch argument not specified.**=10^{-2} atm
$8e^- + 9H^+ + SO_4^{2-} \Rightarrow HS^- + 4H_2O$ **Error! Switch argument not specified.** *Sulfate Reduction*	-5.81	-24.3	+0.252	-0.281	-4.74	pH = 8
$8e^- + 10H^+ + SO_4^{2-} \Rightarrow H_2S^o + 4H_2O$ **Error! Switch argument not specified.** *Sulfate Reduction*	-6.93	-28.9	+0.301	-0.143	-2.42	pH = 6
$8e^- + 8H^+ + CO_{2,g} \Rightarrow CH_{4,g} + 2H_2O$ **Error! Switch argument not specified.** *Methanogenesis*	-3.91	-16.4	+0.169	-0.259	-4.39	pH = 7 P_{CO_2} **Error! Switch argument not specified.**=10^{-2}

HALF-CELL REACTIONS	$\Delta G°_r$ (kcal/equiv)*	$\Delta G°_r$ (kJ/equiv)*	E° (mV)	Eh (mV)	pE	Conditions for Eh and pE §
						P_{CH_4}**Error! Switch argument not specified.**$=10^0$
ELECTRON-DONOR (OXIDATION) HALF-CELL REACTIONS						
$12\,H_2O + C_6H_6 \Rightarrow 6\,CO_2 + 30\,H^+ + 30\,e^-$ **Error! Switch argument not specified.** *Benzene Oxidation*	+2.83	+11.8	+0.122	-0.316	-5.34	pH = 7 P_{CO_2}**Error! Switch argument not specified.**$=10^{-2}$
$14\,H_2O + C_6H_5CH_3 \Rightarrow 7\,CO_2 + 36\,H^+ + 36\,e^-$ **Error! Switch argument not specified.** *Toluene Oxidation*	+2.96	+12.4	+0.128	-0.309	-5.22	pH = 7 P_{CO_2}**Error! Switch argument not specified.**$=10^{-2}$
$16\,H_2O + C_6H_5C_2H_5 \Rightarrow 8\,CO_2 + 42\,H^+ + 42e^-$ **Error! Switch argument not specified.** *Ethylbenzene Oxidation*	+2.95	+12.4	+0.128	-0.308	-5.21	pH = 7 P_{CO_2}**Error! Switch argument not specified.**$=10^{-2}$
$16\,H_2O + C_6H_4(CH_3)_2 \Rightarrow 8\,CO_2 + 42\,H^+ + 42e^-$ **Error! Switch argument not specified.** *m-Xylene Oxidation*	+3.02	+12.7	+0.131	-0.305	-5.88	pH = 7 P_{CO_2}**Error! Switch argument not specified.**$=10^{-2}$

NOTES:

* = $DG°_r$ for half-cell reaction as shown divided by the number of electrons involved in reaction.

§ = Conditions assumed for the calculation of Eh and pE (pE = Eh/0.05916). Where two dissolved species are involved, other than those mentioned in this column, their activities are taken as equal. Note, this does not affect the free energy values listed.

Table B.5.4

Gibbs Free Energy of Formation for Species used in Half Cell Reactions and Coupled Oxidation-Reduction Reactions

Species	State	$\Delta G^{o}_{f,298.15}$ (kcal/mole)	Source*
e^-	i	0	Std
H^+	i	0	Std
O_2	g	0	Std
H_2O	l	-56.687	Dean (1972)
Carbon Species			
CO_2	g	-94.26	Dean (1972)
CH_2O, formalydehyde	aq	-31.02	Dean (1972)
C_6H_6, benzene	l	+29.72	Dean (1972)
CH_4, methane	g	-12.15	Dean (1972)
$C_6H_5CH_3$, toluene	l	+27.19	Dean (1972)
$C_6H_5C_2H_5$, ethylbenzene	l	+28.61	Dean (1972)
$C_6H_4(CH_3)_2$, o-xylene	l	+26.37	Dean (1972)
$C_6H_4(CH_3)_2$, m-xylene	l	+25.73	Dean (1972)
$C_6H_4(CH_3)_2$, p-xylene	l	+26.31	Dean (1972)
Nitrogen Species			
NO_3^-	i	-26.61	Dean (1972)
N_2	g	0	Std
NO_2^-	i	-7.7	Dean (1972)
NH_4^+	i	-18.82	Dean (1972)
Sulfur Species			
SO_4^{2-}	i	-177.97	Dean (1972)
H_2S	aq	-6.66	Dean (1972)
H_2S	g	-7.9	Dean (1972)
HS^-	i	+2.88	Dean (1972)
Iron Species			
Fe^{2+}	i	-18.85	Dean (1972)
Fe^{3+}	i	-1.1	Dean (1972)
♋Fe_2O_3, hematite	c	-177.4	Dean (1972)
♋FeOOH, iron (III) oxyhydroxide	c	-117.2	Naumov *et al.* (1974)
$Fe(OH)_3$, goethite	a	-167.416	Langmuir and Whittemore (1971)
$Fe(OH)_3$, goethite	c	-177.148	Langmuir and Whittemore (1971)
$FeCO_3$, siderite	c	-159.35	Dean (1972)
Manganese Species			
Mn^{2+}	i	-54.5	Dean (1972)
MnO_2, pyrolusite	c	-111.18	Stumm and Morgan (1981)
MnOOH, manganite	c	-133.29	Stumm and Morgan (1981)
$MnCO_3$, rhodochrosite	p	-194	Dean (1972)

NOTES:
c = crystallized solid
a = amorphous solid (may be partially crystallized - dependent on methods of preparation)
p = freshly precipitated solid
i = dissociated, aqueous ionic species (concentration = 1 m)
aq = undissociated aqueous species
g = gaseous
l = liquid
std = accepted by convention
Wherever possible, multiple sources were consulted to eliminate the possibility of typographical error.

Table B.5.5

Coupled BTEX Oxidation-Reduction Reactions

Coupled Benzene Oxidation-Reduction Reactions	$\Delta G°_r$ (kcal/mole Benzene)	$\Delta G°_r$ (kJ/mole Benzene)	Stoichiometric Mass Ratio of Electron Acceptor to BTEX Compound	Stoichiometric Mass Ratio of Metabolic Byproduct to BTEX Compound	Mass of Compound Degraded per unit mass of Electron Acceptor Utilized (mg)	Mass of Compound Degraded per unit mass of Metabolic Byproduct Produced (mg)
$7.5O_2 + C_6H_6 \Rightarrow 6CO_{2,g} + 3H_2O$ **Error! Switch argument not specified.** *Benzene oxidation /aerobic respiration*	-765.34	-3202	3.07:1	---	0.33	---
$6NO_3^- + 6H^+ + C_6H_6 \Rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g}$ **Error! Switch argument not specified.** *Benzene oxidation / denitrification*	-775.75	-3245	4.77:1	---	0.21	---
$30H^+ + 15\underline{MnO_2} + C_6H_6 \Rightarrow 6CO_{2,g} + 15Mn^{2+} + 18H_2O$ **Error! Switch argument not specified.** *Benzene oxidation / manganese reduction*	-765.45	-3202	16.7:1	10.56:1	0.06	0.09
$60H^+ + 30\underline{Fe(OH)_{3,a}} + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$ **Error! Switch argument not specified.** *Benzene oxidation / iron reduction*	-560.10	-2343	41:1	21.5:1	0.024	0.047
$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6CO_{2,g} + 3.75H_2S^o + 3H_2O$ **Error! Switch argument not specified.** *Benzene oxidation / sulfate reduction*	-122.93	-514.3	4.61:1	---	0.22	---
$4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2,g} + 3.75CH_4$ **Error! Switch argument not specified.** *Benzene oxidation / methanogenesis*	-32.40	-135.6	---	0.77:1 a/	---	1.30

Table B.5.5 (Continued)

Coupled BTEX Oxidation-Reduction Reactions

Coupled Toluene Oxidation-Reduction Reactions	ΔG°_r (kcal/mole Toluene)	ΔG°_r (kJ/mole Toluene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound	Stoichiometric Mass Ratio of Metabolic Byproduct to BTEX Compound	Mass of Compound Degraded per unit mass of Electron Acceptor Utilized (mg)	Mass of Compound Degraded per unit mass of Metabolic Byproduct Produced (mg)
$9O_2 + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 4H_2O$ **Error! Switch argument not specified.** *Toluene oxidation / aerobic respiration*	-913.76	-3823	3.13:1	---	0.32	---
$7.2NO_3^- + 7.2H^+ + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 7.6H_2O + 3.6N_{2,g}$ **Error! Switch argument not specified.** *Toluene oxidation / denitrification*	-926.31	-3875	4.85:1	---	0.21	---
$36H^+ + 18\underline{MnO_2} + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 18Mn^{2+} + 22H_2O$ **Error! Switch argument not specified.** *Toluene oxidation / manganese reduction*	-913.89	-3824	17.01:1	10.75:1	0.06	0.09
$72H^+ + 36\underline{Fe(OH)_{3,a}} + C_6H_5CH_3 \Rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$ **Error! Switch argument not specified.** *Toluene oxidation / iron reduction*	-667.21	-2792	42:1	21.86:1	0.02	0.046
$9H^+ + 4.5SO_4^{2-} + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 4.5H_2S^o + 4H_2O$ **Error! Switch argument not specified.** *Toluene oxidation / sulfate reduction*	-142.86	-597.7	4.7:1	---	0.21	---
$5H_2O + C_6H_5CH_3 \Rightarrow 2.5CO_{2,g} + 4.5CH_4$ **Error! Switch argument not specified.** *Toluene oxidation / methanogenesis*	-34.08	-142.6	---	0.78:1	---	1.28

Table B.5.5 (Continued)

Coupled BTEX Oxidation-Reduction Reactions

Coupled Ethylbenzene Oxidation-Reduction Reactions	ΔG°_r (kcal/mole Ethylbenzene)	ΔG°_r (kJ/mole Ethylbenzene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound	Stoichiometric Mass Ratio of Metabolic Byproduct to BTEX Compound	Mass of Compound Degraded per unit mass of Electron Acceptor Utilized (mg)	Mass of Compound Degraded per unit mass of Metabolic Byproduct Produced (mg)
$10.5 O_2 + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,g} + 5 H_2O$ **Error! Switch argument not specified.** *Ethylbenzene oxidation /aerobic respiration*	-1066.13	-4461	3.17:1	---	0.32	---
$8.4 NO_3^- + 8.4 H^+ + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,g} + 9.2 H_2O + 4.2 N_{2,g}$ **Error! Switch argument not specified.** *Ethylbenzene oxidation / denitrification*	-1080.76	-4522	4.92:1	---	0.20	---
$46 H^+ + 22\underline{MnO_2} + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,g} + 22 Mn^{2+} + 28 H_2O$ **Error! Switch argument not specified.** *Ethylbenzene oxidation / manganese reduction*	-1066.27	-4461	18.01	11.38:1	0.06	0.09
$84 H^+ + 42\underline{Fe(OH)_{3,a}} + C_6H_5C_2H_5 \Rightarrow 8 CO_2 + 42 Fe^{2+} + 110 H_2O$ **Error! Switch argument not specified.** *Ethylbenzene oxidation / iron reduction*	-778.48	-3257	42.3:1	22:1	0.024	0.045
$10.5 H^+ + 5.25 SO_4^{2-} + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,g} + 5.25 H_2S^o + 5 H_2O$ **Error! Switch argument not specified.** *Ethylbenzene oxidation / sulfate reduction*	-166.75	-697.7	4.75:1	---	0.21	---
$5.5 H_2O + C_6H_5C_2H_5 \Rightarrow 2.75 CO_{2,g} + 5.25 CH_4$ **Error! Switch argument not specified.** *Ethylbenzene oxidation / methanogenesis*	-39.83	-166.7	---	0.79:1	---	1.27

Table B.5.5 (Concluded)

Coupled BTEX Oxidation-Reduction Reactions

Coupled m-Xylene Oxidation-Reduction Reactions	ΔG°_r (kcal/mole *m*-xylene)	ΔG°_r (kJ/mole *m*-xylene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound	Stoichiometric Mass Ratio of Metabolic Byproduct to BTEX Compound	Mass of Compound Degraded per unit mass of Electron Acceptor Utilized (mg)	Mass of Compound Degraded per unit mass of Metabolic Byproduct Produced (mg)
$10.5\,O_2 + C_6H_4(CH_3)_2 \Rightarrow 8\,CO_{2,g} + 5\,H_2O$ **Error! Switch argument not specified.** *m-Xylene oxidation / aerobic respiration*	-1063.25	-4448	3.17:1	---	0.32	---
$8.4\,NO_3^- + 8.4\,H^+ + C_6H_4(CH_3)_2 \Rightarrow 8\,CO_{2,g} + 9.2\,H_2O + 4.2\,N_{2,g}$ **Error! Switch argument not specified.** *m-Xylene oxidation / denitrification*	-1077.81	-4509	4.92:1	---	0.20	---
$46\,H^+ + 22\underline{MnO_2} + C_6H_4(CH_3)_2 \Rightarrow 8\,CO_{2,g} + 22\,Mn^{2+} + 28\,H_2O$ **Error! Switch argument not specified.** *m-Xylene oxidation / manganese reduction*	-1063.39	-4449	18.01	11.38:1	0.06	0.09
$84\,H^+ + 42\underline{Fe(OH)_{3,a}} + C_6H_4(CH_3)_2 \Rightarrow 8\,CO_2 + 42\,Fe^{2+} + 110\,H_2O$ **Error! Switch argument not specified.** *m-Xylene oxidation / iron reduction*	-775.61	-3245	42.3:1	22:1	0.024	0.045
$10.5\,H^+ + 5.25\,SO_4^{2-} + C_6H_4(CH_3)_2 \Rightarrow 8\,CO_{2,g} + 5.25\,H_2S^o + 5\,H_2O$ **Error! Switch argument not specified.** *m-Xylene oxidation / sulfate reduction*	-163.87	-685.6	4.75:1	---	0.21	---
$5.5\,H_2O + C_6H_4(CH_3)_2 \Rightarrow 2.75\,CO_{2,g} + 5.25\,CH_4$ **Error! Switch argument not specified.** *m-Xylene oxidation / methanogenesis*	-36.95	-154.6	---	0.79:1	---	1.27

a/ Mass of methane produced during microbial respiration.

Coupled redox reactions would be expected to occur in order of their thermodynamic energy yield assuming that there are organisms capable of facilitating each reaction and that there is an adequate supply of BTEX and electron acceptors (Stumm and Morgan, 1981; Chapelle, 1993). Figure B.5.3 illustrates the expected sequence of microbially mediated redox reactions. In general, reactions that yield the most energy tend to take precedence over those reactions that yield less energy (Stumm and Morgan, 1981; Godsey, 1994). Although denitrification yields slightly more energy than aerobic respiration, free dissolved oxygen is toxic to obligate anaerobic bacteria in concentrations in excess of about 0.5 mg/L. Therefore, dissolved oxygen must be removed from the groundwater before denitrification can occur. This being the case, aerobic respiration is the first reaction to occur in an aerobic environment that contains microorganisms capable of aerobic respiration (i.e., obligate aerobes or facultative anaerobes) (Bouwer, 1992; Chapelle, 1993). Once the available dissolved oxygen is depleted and anaerobic conditions dominate the interior regions of the BTEX plume, facultative or obligate anaerobic microorganisms can utilize other electron acceptors in the following order of preference: nitrate, manganese, iron (III), sulfate, and finally carbon dioxide. As each electron acceptor being utilized for biodegradation becomes depleted, the next most preferable electron acceptor is utilized. Each successive redox couple provides less energy to the microorganism.

The expected sequence of redox processes is also a function of the oxidizing potential of the groundwater which is a measure of the relative tendency of a solution or chemical reaction to accept or transfer electrons. As each subsequent electron acceptor is utilized, the groundwater becomes more reducing and the redox potential of the water decreases. The main force driving this change in redox potential is microbially mediated redox reactions. Redox potential can be used as a crude indicator of which redox reactions may be operating at a site. The redox potential determined in the field using a probe is termed Eh. Eh can be expressed as pE, which is the hypothetical measure of the electron activity associated with a specific Eh. High pE means that the solution or redox couple has a relatively high oxidizing potential. Figures 2.3 and B.5.4 show the relationship between the dominant TEAP and the redox potential of the groundwater.

The reduction of highly oxidized species results in an overall decrease in the oxidizing potential of the groundwater. As shown in Figures B.5.3 and B.5.4, the reduction of oxygen and nitrate will reduce the oxidizing potential to levels at which iron (III) reduction can occur. As each chemical species that can be used to oxidize BTEX is exhausted, the microorganisms are forced to use electron acceptors with a lower oxidizing capacity. When sufficiently negative pE levels

have been developed by these redox reactions, sulfate reduction and methane fermentation can occur.

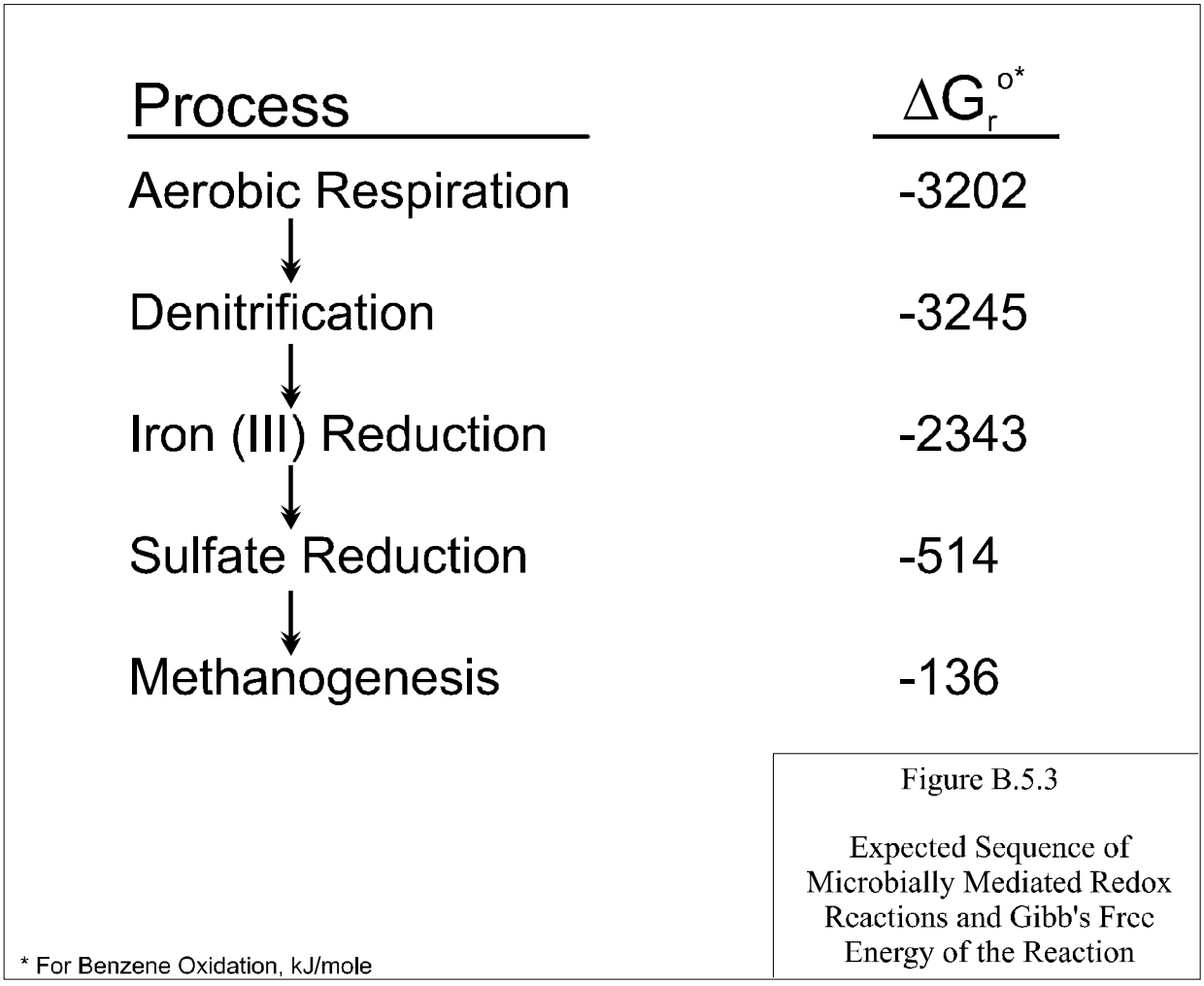

Figure B.5.3

Expected Sequence of Microbially Mediated Redox Reactions and Gibb's Free Energy of the Reaction

Microorganisms can facilitate the oxidation of BTEX using only compounds or redox couples that have a higher oxidizing potential than BTEX. Table B.5.3 presents the calculated pE values for each of the oxidation (BTEX) and reduction (electron acceptor) half-cell reactions. This table shows that the processes of aerobic respiration, denitrification, iron (III) reduction, sulfate reduction, and methanogenesis all have a higher oxidizing potential than BTEX oxidation. Thus, these electron acceptors can be used to oxidize BTEX.

The preferred order of electron acceptor utilization noted above is not purely the result of thermodynamics or the oxidation-reduction potential of the groundwater. Denitrification (the

reduction of nitrate or nitrite to nitrogen gas) will not occur in the presence of free dissolved oxygen (McCarty, 1972). Thus, nitrate cannot be used as an electron acceptor until the

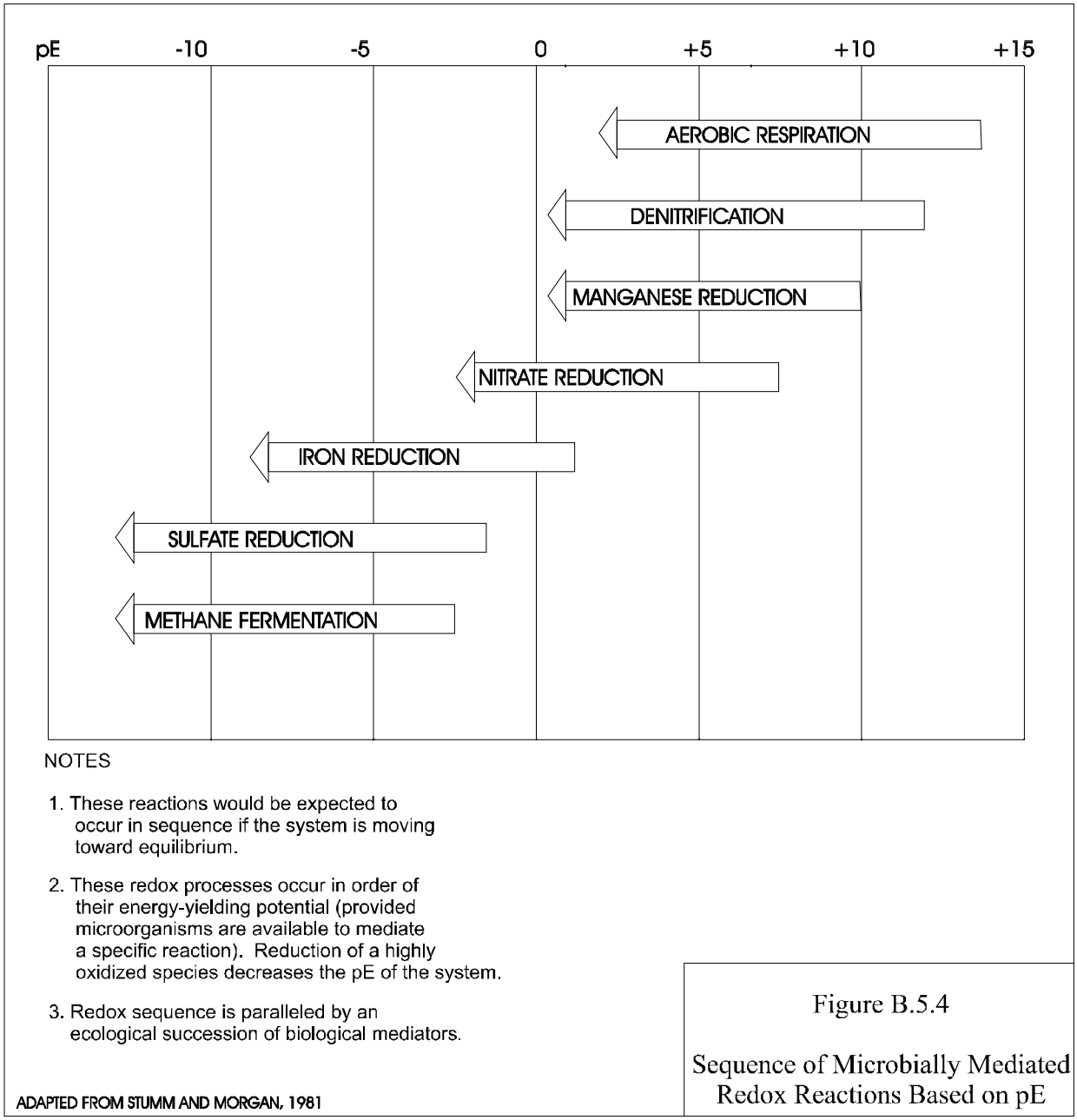

Figure B.5.4

Sequence of Microbially Mediated Redox Reactions Based on pE

concentration of dissolved oxygen falls below about 0.5 mg/L. In addition, because oxygen and nitrate (if present at high concentrations) are toxic to sulfate-reducing organisms, sulfate cannot be used as an electron acceptor in the presence of either oxygen or high concentrations of nitrate (McCarty, 1972). During anaerobic biodegradation, aerobic degradation can still be occurring near the margins of the plume where dispersion helps spread the plume out into more oxygenated regions of the aquifer. Because there is unequivocal evidence that microbial processes degrade fuel hydrocarbons, the most important things to ascertain during the intrinsic remediation

demonstration are which mechanisms of biodegradation are most important and the rate at which biodegradation is occurring. Biodegradation rates can be limited by substrate availability or by the availability of electron acceptors.

B.5.2 AEROBIC BIODEGRADATION

Biodegradation of fuel hydrocarbons is often an aerobic process that occurs when indigenous populations of hydrocarbon-degrading microorganisms are supplied with the oxygen and nutrients necessary to utilize fuel hydrocarbons as an energy source. Hydrocarbon-degrading microorganisms are ubiquitous, and as many as 28 hydrocarbon-degrading isolates (bacteria and fungi) have been discovered in different subsurface environments (Davies and Westlake, 1977; Jones and Eddington, 1968). Because indigenous microorganisms are well adapted to the physical and chemical conditions of the subsurface environment in which they reside, they have a distinct advantage over microorganisms injected into the subsurface to enhance biodegradation. Therefore, attempts to enhance biodegradation have often met with less-than-anticipated success (Goldstein *et al.*, 1985).

Almost all types of fuel hydrocarbons can be biodegraded under aerobic conditions (Borden *at al.*, 1994). Mineralization of fuel hydrocarbons to carbon dioxide and water under aerobic conditions involves the use of oxygen as a cosubstrate during the initial stages of metabolism and as a terminal electron acceptor during the later stages of metabolism for energy production (Higgins and Gilbert, 1978; Gibson and Subramanian, 1984; Young, 1984). As shown earlier, the O_2-H_2O redox couple has a high oxidizing potential and, when coupled with endothermic reactions involving BTEX, can be used by microorganisms to release a large amount of free energy (Tables B.5.3 and B.5.5). In fact, reduction of molecular oxygen is one of the most energetically favorable of the redox reactions involved in BTEX degradation.

An important consideration in evaluating long-term risks at a site is an accurate estimate of the potential for natural biodegradation BTEX in the groundwater. A reduction in dissolved oxygen concentrations within an existing BTEX plume is a strong indication that indigenous bacteria are already established and actively biodegrading fuel contamination via aerobic respiration. In general, dissolved oxygen concentrations will be lower than background levels in groundwater that contains BTEX.

Aerobic attack on petroleum hydrocarbons requires the action of oxygenases and, therefore, the presence of free dissolved oxygen. Subsurface environments can quickly become devoid of oxygen, especially if high concentrations of organic contaminants are present. When this is the

case, the rate of aerobic biodegradation will typically be limited by oxygen supply rather than by nutrient concentration (Borden and Bedient, 1986). Although nutrients such as nitrogen and phosphorus are essential for biodegradation of organic contaminants by bacteria, the influence of inorganic and organic nutrients on *in situ* biodegradation varies substantially, and in some cases, the addition of nutrients into the subsurface environment has been shown to have little or no effect on biodegradation rates of hydrocarbons (Swindoll *et al.*, 1988; Miller, 1990). In any event, biodegradation of fuel hydrocarbons occurs in most subsurface environments without the addition of supplemental nutrients.

Low-molecular-weight aromatic hydrocarbons such as BTEX are easily biodegraded in the concentrations found dissolved in groundwater. Aromatic biodegradation involves the formation of a diol, followed by cleavage and formation of a diacid, followed by *ortho*- or *meta*-cleavage of the ring structure (Cerniglia, 1984; Smith, 1990). Extensive methyl substitution can inhibit initial oxidation (Cripps and Watkinson, 1978), and chain lengths longer than butyl groups will be preferentially degraded before *ortho*- or *meta*- cleavage of the aromatic ring occurs.

N-alkanes between C10 and C22 are perceived as the most readily degradable hydrocarbon constituents (Atlas, 1981). The common type of attack by microorganisms is through terminal or subterminal attack of the saturated chain, causing formation of a primary or secondary alcohol. Oxidation then continues to aldehydes and fatty acids for primary attack, and ketones and esters for secondary attack. Branched alkanes pose a problem for bacteria because methyl- or higher-chained groups on subterminal carbons block the β-oxidation pathway (Mckenna and Kallio, 1964; Singer and Finnerty, 1984). Sufficiently branched isoalkanes are extremely biologically recalcitrant, and the isoalkanes pristane and phytane are commonly used as biomarkers in crude oils. Cycloaliphatic compounds are difficult to biodegrade because the oxidases required for initial oxidation and subsequent ring cleavage are seldom found in the same bacteria (Donaghue *et al.*, 1976). There have been several reports of cycloaliphatic oxidation through cometabolic pathways (Perry, 1984; Trudgill, 1984). For instance, biodegradation of cyclohexane can proceed by conversion to cyclohexanol by one bacterial species, followed by lactonization to hexanoic acid by another. Alkylated cycloaliphatics are considered more easily biodegraded because β-oxidation of the methyl group gives bacteria leverage to break the rings by initial formation of para-alcohols or para-ketones. Once the ring is broken, biodegradation proceeds through *n*-alkane biodegradation mechanisms. Because of their low solubility in groundwater, however, these compounds generally are not very mobile in the subsurface environment, and therefore represent only a very localized problem.

Petroleum hydrocarbons mixtures, such as JP-4 jet fuel, with its multitude of potential primary substrates will undergo simultaneous degradation of the aliphatic, aromatic, and alicyclic hydrocarbons. Mixed hydrocarbon-degrader populations often contain microorganisms that produce enzymes with a broad specificity for substrates that can result in the degradation of hydrocarbon mixtures through co-metabolic pathways (Perry, 1984). Early evidence of this was presented by Jamison *et al.* (1975), who reported that individual hydrocarbon mineralization rates were not the same as in hydrocarbon mixtures. Biodegradation rates for each of the constituents may certainly vary however, depending on site-specific environmental and biological factors.

The detailed mineralization of aromatic hydrocarbons to carbon dioxide and water under aerobic conditions involves the use of oxygen as a cosubstrate during the initial stages of hydrocarbon metabolism, and the later use of oxygen as the terminal electron acceptor for energy production (Young, 1984; Higgins and Gilbert, 1978; Gibson and Subramanian, 1984).

The following equations describe the overall stoichiometry of aromatic hydrocarbon biodegradation. In the absence of microbial cell production, the oxidation (mineralization) of benzene to carbon dioxide and water is given by:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

Therefore, 7.5 moles of oxygen are required to metabolize 1 mole of benzene. On a mass basis, the ratio of oxygen to benzene is given by:

Molecular weights:	Benzene	6(12) + 6(1) = 78 gm
	Oxygen	7.5(32) = 240 gm

Mass Ratio of Oxygen to Benzene = 240:78 = 3.08:1

Therefore, in the absence of microbial cell production, 3.08 mg of oxygen are required to completely metabolize 1 mg of benzene. Similar calculations can be made for toluene, ethylbenzene, and xylene. The results of these calculations are shown in Table B.5.5. Table B.5.6 summarizes the mass of total BTEX degraded per mg of dissolved oxygen utilized. This table was prepared by averaging the values for BTEX presented in Table B.5.5.

Based on the stoichiometry presented in Table B.5.5, the ultimate metabolic byproducts of aerobic respiration are carbon dioxide and water. However, this stoichiometry presents the final products of aerobic respiration only. In reality, several intermediate products are produced from the BTEX before the end result is achieved.

Table B.5.6
Mass Ratio of Electron Acceptors Removed or Metabolic Byproducts Produced to Total BTEX Degraded.

Terminal Electron Accepting Process	Average Mass Ratio of Electron Acceptor to Total BTEX[a/]	Average Mass Ratio of Metabolic Byproduct to Total BTEX [a/]	Mass of BTEX Degraded per unit mass of Electron Acceptor Utilized (mg) [a/]	Mass of BTEX Degraded per unit mass of Metabolic Byproduct Produced (mg) [a/]
aerobic respiration	3.14:1	-----	0.32	-----
denitrification	4.9:1	-----	0.21	-----
iron (III) reduction	-----	21.8:1	-----	0.05
sulfate reduction	4.7:1	-----	0.21	-----
methanogenesis	-----	0.78:1	-----	1.28

a/ Simple average of all BTEX compounds based on individual compound stoichiometry.

Actual oxygen requirements may vary from those predicted by the stoichiometric relationships presented above because they are dependent upon the bacterial yield coefficient (Y_m) that describes the amount of biomass produced per unit mass of substrate biodegraded. Yields of microbial biomass vary depending on the thermodynamics of substrate biodegradation and on the availability of oxygen, nutrients, and substrate concentration (McCarty, 1978). Energy for cell maintenance is also needed, and this energy need is not reflected in the stoichiometric relationships presented above. The culmination of these few additional factors suggests that the actual oxygen demand will range from approximately 1 to 3 mg of oxygen per 1 mg of benzene removed through biodegradation. Because cell production rates generally are not measured at a site, and to be conservative, an oxygen to total BTEX ratio of 3.1:1 should be used when modeling the aerobic component of intrinsic remediation.

B.5.3 ANAEROBIC BIODEGRADATION

Soon after fuel hydrocarbon contamination enters the groundwater system, rapid depletion of dissolved oxygen caused by increased levels of microbial respiration results in the establishment of anaerobic conditions within the dissolved contaminant plume. Certain requirements must be met in order for anaerobic (anoxic) bacteria to degrade fuel hydrocarbons including: absence of dissolved oxygen; availability of carbon sources (BTEX), electron acceptors, and essential nutrients; and proper ranges of pH, temperature, salinity, and redox potential. When oxygen is absent, nitrate, sulfate, iron (III), and carbon dioxide can serve as terminal electron acceptors.

It is now known with a high degree of certainty that aromatic organic compounds such as BTEX, some of the simple polynuclear aromatic compounds, and some nitrogen heterocyclic organic compounds can be degraded in anaerobic groundwater (Grbic´-Galic´ and Vogel, 1987; Lovley *et al.*, 1989; Hutchins, 1991; Grbic´-Galic´, 1990; Beller *et al.*, 1992a and 1992b; Edwards *et al.*, 1992; Edwards and Grbic´-Galic´,1992; Lovley *et al.*, 1995).

During anaerobic degradation, the aromatic compounds are first oxidized to phenols or organic acids, then transformed to long-chain volatile fatty acids that are finally metabolized to carbon dioxide and possibly to methane. Destruction of the more hazardous compounds, such as BTEX, is associated with accumulation of fatty acids, production of methane, solubilization of iron, and reduction of nitrate and sulfate (Cozzarelli, *et al.*, 1990; Wilson *et al.*, 1990). Figure B.5.5 shows some of these oxidized intermediates.

Depending on the type of electron acceptor present [nitrate, iron (III), sulfate, or carbon dioxide], pH conditions, and redox potential, anaerobic biodegradation can occur by denitrification, iron (III) reduction, sulfate reduction, or methanogenesis. Other, less common anaerobic degradation mechanisms such as manganese reduction may dominate if the physical and chemical conditions in the subsurface favor use of these electron acceptors. Environmental conditions and microbial competition ultimately will determine which processes will dominate, but in a typical aquifer denitrification typically occurs first, followed by iron (III) reduction, sulfate reduction, and finally by methanogenesis. Vroblesky and Chapelle (1994) show that the dominant terminal electron accepting process can vary both temporally and spatially in an aquifer with fuel hydrocarbon contamination. For example, a given area within an aquifer may switch among iron (III) reduction, sulfate reduction, and methanogenesis depending on seasonal recharge of dissolved oxygen and sulfate recharge.

Initial oxidation of petroleum hydrocarbons under anaerobic conditions largely depends on the chemical structure of the compound. Cozzarelli *et al.* (1990) found that monoaromatic compounds with alkyl substituents longer than an ethyl group were highly recalcitrant to biodegradation under anaerobic conditions. Examples of such compounds include diethylbenzene, methylpropylbenzene, and n-butyl-benzene. The actual pathways used by anaerobic bacteria to biodegrade petroleum hydrocarbons is less understood than aerobic pathways. It is certain that monoaromatics are susceptible to anaerobic biodegradation, and oxygen is derived from water molecules under many circumstances. Vogel and Grbic-Galic (1986) used ^{18}O-labeled water to show that water was the source of oxygen for toluene and benzene biodegradation under methane fermentative conditions. In this case, ^{18}O-labeled p-cresol was the first intermediate detected. It

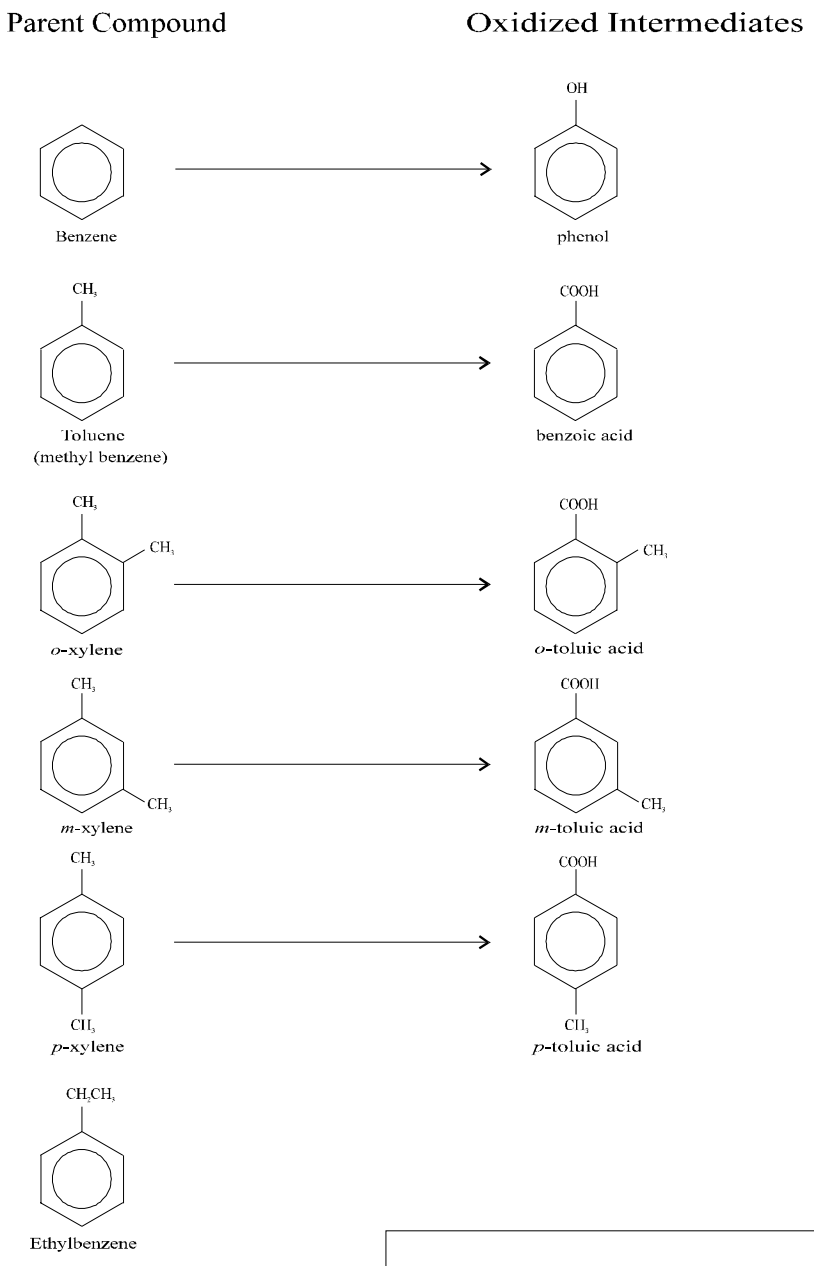

Figure B.5.5

Some Oxidized Intermediates Produced During Anaerobic Biodegradation

Modified from Cozzarelli et al. (1990)

has been suggested that denitrifying bacteria also incorporate oxygen from water in the initial oxidation of aromatic compounds (Hopper, 1978), forming aromatic alcohols. As biodegradation proceeds, alicyclic and aromatic rings are cleaved by incorporation of oxygen, derived from water, to form various aliphatic acids. Complete mineralization of BTEX during anaerobic biodegradation results in the formation of carbon dioxide, methane, and water.

B.5.3.1 Denitrification

After almost all free dissolved oxygen has been removed from the aquifer and anaerobic conditions prevail, nitrate can be used as an electron acceptor by facultative anaerobic microorganisms to mineralize BTEX via denitrification. Denitrification ultimately results in the formation of carbon dioxide, water, and dinitrogen gas (N_2). In areas where denitrification is occurring, there will be a strong correlation between areas with elevated dissolved BTEX concentrations and depleted nitrate concentrations relative to measured background concentrations. The absence of nitrate in contaminated groundwater suggests that nitrate may be functioning as an electron acceptor.

The oxidation of BTEX via denitrification is thermodynamically more favorable than aerobic respiration (Table B.5.5). However, nitrate can only function as an electron acceptor in microbially facilitated BTEX degradation reactions if the groundwater system has been depleted of dissolved oxygen (i.e., the groundwater must be functionally anaerobic). Oxygen is toxic to the enzyme systems used for electron transfer and energy production of nitrate-reducing microorganisms (McCarty, 1972). Many species of bacteria are capable of reducing nitrate to produce respirative energy (McCarty, 1972; Chapelle, 1993; Riser-Roberts, 1992). Denitrification occurs in the following sequence (Payne, 1981; von Gunten and Zobrist, 1993):

$$NO_3^- \Rightarrow NO_2^- \Rightarrow NO \Rightarrow N_2O \Rightarrow NH_4^+ \Rightarrow N_2$$

Each reaction in this sequence is catalyzed by different microorganisms (Chapelle, 1993). Denitrification occurs only under anaerobic conditions; under aerobic conditions, the process is reversed and nitrification occurs (if the necessary conditions are met). Denitrification is favored under pH conditions ranging from 6.2 to 10.2 standard units and results in corresponding redox potentials (Eh) of 665 mV and -200 mV, respectively (Stotzky, 1974).

There are four requirements for denitrification (Starr and Gillham, 1993) including: 1) Nitrate in the aquifer, 2) Organic carbon, 3) Denitrifying bacteria, and 4) Reducing conditions (i.e., low to no dissolved oxygen).

The following equations describe the overall stoichiometry of denitrification caused by anaerobic microbial biodegradation. In the absence of microbial cell production, the mineralization of benzene to carbon dioxide and water is given by:

$$6NO_3^- + 6H^+ + C_6H_6 \rightarrow 6CO_{2(g)} + 6H_2O + 3N_{2(g)}$$

Therefore, 6 moles of nitrate are required to metabolize 1 mole of benzene. On a mass basis, the ratio of nitrate to benzene is given by:

Molecular weights:	Benzene	6(12) + 6(1) = 78 gm
	Nitrate	6(62) = 372 gm

Mass ratio of nitrate to benzene = 372:78 = 4.77:1

Therefore, 4.77 mg of nitrate are required to completely metabolize 1 mg of benzene. Similar calculations can be made for toluene, ethylbenzene, and xylene. The results of these calculations are shown in Table B.5.5. Based on these calculations, the average ratio of nitrate consumed per mole of BTEX degraded is 4.87:1. Table B.5.6 summarizes the mass of total BTEX degraded per mg of nitrate utilized during denitrification.

Plumes of dissolved fuel hydrocarbons generally do not contain nitrate, indicating that adaptation of the necessary bacterial populations is rapid, and ambient concentrations of nitrate are quickly consumed. This is similar to the relationship observed between dissolved oxygen and BTEX in contaminant plumes, and suggests that nitrate availability, and not microbial processes, may be the limiting factor during denitrification. This is an important observation and is consistent with observations at 40 Air Force sites studied to date.

Work conducted by several authors suggests that the biodegradation of BTEX under denitrifying conditions occurs in the following order: toluene, p-xylene, m-xylene, ethylbenzene, and finally o-xylene (Norris *et al.*, 1994). The work by Kuhn *et al.* (1988), Evans *et al.* (1991a and 1991b) and Hutchins *et al.* (1991b) suggests that benzene is biologically recalcitrant under denitrifying conditions. However, Major *et al.* (1988) report degradation of benzene under conditions thought to be denitrifying. Kukor and Olsen (1989) also note biodegradation of benzene under denitrifying conditions.

Kuhn *et al.* (1985) used aquifer material taken from the water-sediment interface of a river in a microcosm study of anaerobic, hydrocarbon biodegradation. The indigenous microorganisms were supplied with nitrate. Biodegradation of *p*-xylene and *m*-xylene occurred after 3 months. Biodegradation of *o*-xylene occurred only after removal of both *p*-xylene and *m*-xylene. The

degradation of the xylenes in this experiment was clearly linked to nitrate respiration. In related experiments, *m*-xylene was completely biodegraded under denitrifying conditions in a similar laboratory microcosm, and 80 percent of ^{14}C radiolabeled *m*-xylene and 75 percent of ^{14}C radiolabeled toluene were mineralized after 8 days (Zeyer *et al.*, 1986).

B.5.3.2 Iron (III) Reduction

Once the available dissolved oxygen and nitrate in the aquifer have been depleted, iron (III) can be used as an electron acceptor. The reduction of insoluble iron [Fe^{3+}, ferric iron, or iron (III)] to the soluble form [Fe^{2+}, ferrous iron, or iron (II)] through microbially mediated oxidation of organic matter (or organic pollutants) in groundwater is a common occurrence. In fact, Lovley *et al*. (1989) identified an organism (GS-15) that anaerobically degrades toluene under iron-reducing conditions. Aquifer sediments can contain large amounts of iron (III). According to Lovley (1991) and Norris *et al.* (1994), the best forms of iron (III) for microbiological reduction are poorly crystalline iron (III) oxides and iron (III) oxyhydroxides.

Iron (III) may be present in large amounts within certain systems, thus providing a large reservoir of potential electron acceptors to facilitate BTEX degradation. Interestingly, studies with iron-reducing isolates show that these microorganisms must be in direct contact with the iron (III) to facilitate its reduction (Lovley *et al.*, 1991).

To determine if iron (III) is being used as an electron acceptor at a site, iron (II) concentrations in groundwater are measured. If areas with high BTEX concentrations coincide with areas of high iron (II) relative to measured background concentrations, BTEX biodegradation via iron reduction is likely occurring. Iron (III) concentrations are not measured, because without knowing the degree of crystallinity of the iron, it is not possible to determine how much of the iron is available to microorganisms.

The following equations describe the overall stoichiometry of benzene oxidation by iron reduction caused by anaerobic microbial biodegradation. In the absence of microbial cell production, the mineralization of benzene is given by:

$$60H^+ + 30Fe(OH)_{3,\,a} + C_6H_6 \rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$$

Therefore, 30 moles of $Fe(OH)_3$ are required to metabolize 1 mole of benzene. On a mass basis, the ratio of $Fe(OH)_3$ to benzene is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm

$Fe(OH)_3$ 30(106.85) = 3205.41gm

Mass ratio of $Fe(OH)_3$ to benzene = 3205.41:78 = 41.1:1

Therefore, 41.1 mg of $Fe(OH)_3$ are required to completely metabolize 1 mg of benzene. Alternatively, the mass ratio of iron (II) produced during respiration to benzene degraded can be calculated and is given by:

Molecular weights:	Benzene	6(12) + 6(1) = 78 gm
	Fe^{2+}	30(55.85) = 1675.5 gm

Mass ratio of Fe^{2+} to benzene = 1675.5:78 = 21.5:1

Therefore, 21.5 mg of Fe^{2+} are produced during mineralization of 1 mg of benzene. Similar calculations can be made for toluene, ethylbenzene, and xylene. The results of these calculations are shown in Table B.5.5. Based on these calculations, the average ratio of iron (II) produced per mole of BTEX degraded is 21.8:1. The average ratio of $Fe(OH)_3$ consumed per mole of BTEX degraded is 41.9:1. Table B.5.6 summarizes the mass of total BTEX degraded per mg of iron (II) produced.

The oxidation BTEX coupled with the reduction of iron (III) may result in high concentrations of iron (II) in groundwater within and near the contaminant plume. Lovley (1991) points out that high concentrations of iron (II) are generally observed in aquifers contaminated with organic compounds. Although not completely understood, this evidence suggests that iron (III) reduction to iron (II) coupled with BTEX oxidation is an important anaerobic BTEX degradation process. Most of the iron (III) that is reduced to iron (II) is subsequently reprecipitated when the groundwater mixes with oxygenated groundwater downgradient of the plume.

Although relatively little is known about the anaerobic metabolic pathways involving the reduction of iron (III), this exothermic process has been shown to be a major metabolic pathway for some microorganisms (Lovley and Phillips, 1987; Chapelle, 1993). High concentrations of dissolved iron (II) were once attributed to the spontaneous and reversible reduction of iron (III) oxyhydroxides, which are thermodynamically unstable in the presence of organic compounds such as BTEX. Yet recent evidence suggests that the reduction of iron (III) cannot occur without microbial mediation (Lovley and Phillips, 1987; Lovley *et al.*, 1991; Chapelle, 1993). None of the common organic compounds found in low-temperature, neutral, reducing groundwater could reduce iron (III) oxyhydroxides to iron (II) under sterile laboratory conditions (Lovley *et al.*, 1991).

B.5.3.3 Sulfate Reduction

Once the available oxygen and nitrate in the groundwater system have been depleted, sulfate-reducing bacteria can begin degrading fuel hydrocarbons. Decreases in Eh, along with dissolved oxygen and nitrate depletion, will favor sulfate-reducing bacteria at a redox potential of -200 mV and a pH of 7 standard units (Postgate, 1984).

Sulfate is reduced to sulfide during the oxidation of BTEX. The presence of decreased concentrations of sulfate and increased concentrations of sulfide relative to background concentrations indicates that sulfate may be participating in BTEX oxidation reactions at a site. In general, the extent and significance of BTEX biodegradation via sulfate reduction is not well understood (Norris *et al.,* 1994). Although oxidation of benzene by sulfate reduction is thermodynamically favorable (see Table B.5.3), it is not as favorable as aerobic respiration, denitrification, or iron reduction. Additionally, sulfate-reducing microorganisms typically are sensitive to environmental conditions, including temperature, inorganic nutrients, and pH (Zehnder, 1978). An imbalance in suitable environmental conditions could severely limit the significance of BTEX degradation via sulfate reduction.

According to Hem (1985), low sulfate concentrations commonly result from the bacterial reduction of sulfate. In waters containing dissolved BTEX, sulfate concentrations are further reduced, and these microbes utilize BTEX as the oxidant. Lovley *et al*. (1995) show that under sulfate-reducing conditions, benzene is mineralized to carbon dioxide and water with no intermediate products such as phenol, benzoate, p-hydroxybenzoate, cyclohexane, and acetate. Furthermore, the results of their work show that benzene can be biodegraded in the absence of dissolved oxygen. Thierrin *et al.* (1992) described the biodegradation of a BTEX plume from a gasoline spill in Perth, Western Australia, under sulfate-reducing conditions. Edwards *et al.* (1992) give an example where toluene and the xylenes are degraded by indigenous microorganisms under sulfate-reducing conditions. Beller *et al.* (1992a) describe the metabolic byproducts of toluene biodegradation under sulfate-reducing conditions.

The following equations describe the overall stoichiometry of BTEX oxidation by sulfate reduction caused by anaerobic microbial biodegradation. In the absence of microbial cell production, the mineralization of benzene is given by:

$$7.5H^{+} + 3.75SO_4^{2-} + C_6H_6 \rightarrow 6CO_{2(g)} + 3.75H_2S^{o} + 3H_2O$$

Therefore, 3.75 moles of sulfate are required to metabolize 1 mole of benzene. On a mass basis, the ratio of sulfate to benzene is given by:

Molecular weights:	Benzene	6(12) + 6(1) = 78 gm
	Sulfate	3.75(96) = 360 gm

Mass ratio of sulfate to benzene = 360:78 = 4.6:1

Therefore, 4.6 mg of sulfate are required to completely metabolize 1 mg of benzene. Similar calculations can be made for toluene, ethylbenzene, and xylene. The results of these calculations are shown in Table B.5.5. Based on these calculations, the average ratio of sulfate consumed per mole of BTEX degraded is 4.7:1. Table B.5.6 summarizes the mass of total BTEX degraded per mg of sulfate utilized during sulfate reduction.

B.5.3.4 Methanogenesis

Based on the free energy yield and the oxidizing potential, the CO_2-CH_4 redox couple also can be used to oxidize BTEX to carbon dioxide and water once the groundwater is sufficiently reducing. To attain necessary reducing conditions, other highly oxidizing chemical species such as oxygen, nitrate, and manganese must first be reduced. This redox reaction is called methanogenesis or methane fermentation. Methane fermentation yields less free energy to the system than the other chemical species (Figure B.5.3 and Table B.5.3). The presence of methane in groundwater at concentrations elevated relative to background concentrations is a good indicator of methane fermentation because it is the only organic compound in the carbon cycle that is thermodynamically stable. Elevated concentrations of methane correlated with elevated concentrations of total BTEX suggest that methanogenesis is working to biodegrade BTEX.

The following equations describe the overall stoichiometry of benzene oxidation by methanogenesis. In the absence of microbial cell production, the mineralization of benzene is given by:

$$C_6H_6 + 4.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4$$

The mass ratio of methane produced during respiration to benzene degraded can be calculated and is given by:

Molecular weights:	Benzene	6(12) + 6(1) = 78 gm
	CH_4	3.75(16) = 60 gm

Mass ratio of CH_4 to benzene = 60:78 = 0.77:1

Therefore, 0.77 mg of CH_4 are produced during mineralization of 1 mg of benzene. Similar calculations can be made for toluene, ethylbenzene, and xylene. The results of these calculations are shown in Table B.5.5. Based on these calculations, the average ratio of methane produced

per mole of BTEX degraded is 0.78:1. Table B.5.6 summarizes the mass of total BTEX degraded per mg of methane produced.

This reaction is accomplished in at least four steps (Chapelle, 1993). In each step hydrogen reacts with carbon. During the final step of methanogenesis, a methyl-coenzyme M methylreductase ($CoM\text{-}CH_3$) complex is formed and the carbon is reduced to methane (Chapelle, 1993).

Because of the relatively small amounts of free energy produced by these reactions, methanogenesis is generally not the thermodynamically-favored reaction in the anaerobic environment but will proceed in environments that lack other electron acceptors or after these other electron acceptors (e.g., nitrate, sulfate) have been depleted. Methanogenic bacteria are active after sulfate reduction ceases and methanogenesis begins. Methanogenesis causes the redox potential to fall below -200 mV for a pH of 7 (Zehnder, 1978).

When the pH of groundwater is buffered by the presence of carbonate in the aquifer, the metabolic activity of the microorganisms becomes the rate-limiting step. The rate of reaction is controlled by the density of the active organisms and by the concentration of metabolizable compounds. B.H. Wilson *et al.* (1986) used a microcosm to show that BTEX was biodegraded under methanogenic conditions. Grbic´-Galic´ and Vogel (1987) show the potential for the complete degradation of benzene and toluene to carbon dioxide and methane by methanogenic bacteria in laboratory studies. Wilson *et al.* (1987 and 1990) described the methanogenic degradation of benzene, toluene, and xylenes in groundwater contaminated by an aviation gasoline spill. Cozzarelli *et al.* (1990) reported the anaerobic biodegradation of alkylbenzenes in a contaminant plume originating from a spill of crude oil in Minnesota. The groundwater was actively methanogenic and accumulated long-chain volatile fatty acids. Wilson *et al.* (1993) studied biodegradation of aromatic hydrocarbons in a plume produced from a gasoline spill from a leaking underground storage tank. The water was methanogenic and accumulated acetate. The rates of anaerobic biodegradation in this plume were very similar to the rates in the crude oil spill studied by Cozzarelli *et al.* (1990) and the aviation gasoline spill studied by Wilson *et al.* (1990).

B.5.4 NEUTRALIZATION OF BIOGENIC CARBON DIOXIDE

In general, as the amount of total dissolved BTEX that is being oxidized increases, the total alkalinity increases. This is expected because the microbially-mediated reactions causing biodegradation of fuel hydrocarbons produce carbon dioxide. 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 which can be produced during biodegradation of fuel hydrocarbons as intermediates can contribute to alkalinity in groundwater.

Carbon dioxide is produced during the respiration of petroleum hydrocarbons. In aquifers that have carbonate minerals as part of the matrix, the carbon dioxide forms carbonic acid which dissolves these minerals, increasing the alkalinity of the groundwater. An increase in alkalinity (measured as $CaCO_3$) in an area with BTEX concentrations elevated over background conditions can be used to infer the amount of petroleum hydrocarbon destroyed through aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction. Assuming complete mineralization, these reactions follow the generalized stoichiometry:

$$CH \rightarrow CO_2 + H_2O \rightarrow H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

The mass ratio of alkalinity produced during oxidation of BTEX can be calculated. The molar ratio of alkalinity (as $CaCO_3$) produced during benzene oxidation via aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction is given by:

$$C_6H_6 \rightarrow 6CO_2 \rightarrow 6CaCO_3$$

Therefore, 6 moles of $CaCO_3$ are produced during the metabolism of 1 mole of benzene. On a mass basis, the ratio of alkalinity to benzene is given by:

Molecular weights:	Benzene	6(12)+6(1) = 78 gm
	Alkalinity (as $CaCO_3$)	6(40)+6(12)+18(16) = 600 gm
	Mass ratio of alkalinity to benzene = 600:78 = 7.69:1	

Therefore, 7.69 mg of alkalinity (as $CaCO_3$) are produced during the metabolism of 1 mg of benzene. This means that for every 1 mg of alkalinity produced, 0.13 mg of BTEX is destroyed. Similar calculations can be made for toluene, ethylbenzene, and xylene. Table B.5.7 summarizes the results of these calculations for all of the BTEX compounds during aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction. Methanogenesis does not cause significant changes in alkalinity.

Table B.5.7

Mass Ratio of Alkalinity (as $CaCO_3$) Produced to BTEX Degraded During Aerobic Respiration, Denitrification, Iron (III) Reduction, and Sulfate Reduction

Alkalinity Production Reaction	Stoichiometric Mass Ratio of Alkalinity Produced to BTEX Degraded	Mass of Compound Degraded (mg) per unit mass of Alkalinity Produced (mg)
$C_6H_6 \rightarrow 6CO_2 \rightarrow 6CaCO_3$ **Error! Switch argument not specified.** *Benzene Oxidation*	600:78	0.13
$C_7H_8 \rightarrow 7CO_2 \rightarrow 7CaCO_3$ **Error! Switch argument not specified.** *Toluene Oxidation*	700:92	0.13
$C_8H_{10} \rightarrow 8CO_2 \rightarrow 8CaCO_3$ **Error! Switch argument not specified.** *Ethylbenzene Oxidation*	800:104	0.13
$C_8H_{10} \rightarrow 8CO_2 \rightarrow 8CaCO_3$ **Error! Switch argument not specified.** *Xylene Oxidation*	800:104	0.13

B.5.5 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION WITH RETARDATION AND BIODEGRADATION

The advection-dispersion equation is obtained by adding a biodegradation term to equation B.4.11. In one dimension, this is expressed as:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.5.1}$$

Where: v_x = average linear groundwater velocity [L/T]
R = coefficient of retardation
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]
λ = first-order biodegradation decay rate [T^{-1}]

This equation considers advection, hydrodynamic dispersion, sorption (retardation), and biodegradation. First-order rate constants are appropriate for iron (III)-reducing, sulfate-reducing, and methanogenic conditions. They are not appropriate under aerobic or denitrifying conditions.

SECTION B-6

VOLATILIZATION AND INFILTRATION

B.6.1 VOLATILIZATION

While not a destructive attenuation mechanism, volatilization does remove contaminants from the groundwater system. Partitioning of a contaminant between the liquid phase and the gaseous phase is governed by Henry's Law. Thus, the Henry's Law constant of a chemical determines the tendency of a contaminant to volatilize from groundwater into the soil gas. Henry's Law states that the concentration of a contaminant in the gaseous phase is directly proportional to the compound's concentration in the liquid phase and is a constant characteristic of the compound. Stated mathematically, Henry's Law is given by (Lyman *et al.*, 1992):

$$C_a = HC_l$$

Where: H = Henry's Law Constant (atm m^3/mol)
C_a = concentration in air (atm)
C_l = concentration in water (mol/m^3)

Henry's Law constants for hydrocarbons range over three orders of magnitude, with the light aromatics having the lowest volatility (e.g., BTEX). Henry's Law constants for the saturated aliphatics range from 1 to 10 atm m^3/mol @ 25ºC, for the unsaturated and cyclo-aliphatics H range from 0.1 to 1 atm m^3/mol @ 25ºC, and for the light aromatics H ranges from 0.007 to 0.02 atm m^3/mol @ 25ºC (Lyman *et al.*, 1992). Values of Henry's Law constants for the BTEX compounds are given in Table B.6.1. The solubility and relative volatility of the BTEX compounds lead to a very strong enrichment of these compounds in the dissolved-phase in groundwater relative to the other constituents of hydrocarbon fuels (Lyman *et al.*, 1992).

Table B.6.1
Henry's Law Constants and Vapor Pressures for
Common Fuel Hydrocarbon Compounds

Compound	Vapor Pressure (mmHg @ 25°C)	Henry's Law Constant ($atm\text{-}m^3/mol$)
Benzene	95	0.0054
Ethylbenzene	10	0.0066
Toluene		0.0067
o-Xylene	10	0.00527
m-Xylene	10	0.007
p-Xylene	10	0.0071
1,2,3-Trimethylbenzene		0.00318
1,2,4-Trimethylbenzene		0.007
1,3,5-Trimethylbenzene		0.006
1,2,4,5-Tetramethylbenzene		0.0249

The physiochemical properties of the BTEX compounds give them low Henry's Law constants. Because of the small surface area of the groundwater flow system exposed to soil gas, volatilization of the BTEX compounds from groundwater is a relatively slow process that, in the interest of being conservative, generally can be neglected when modeling biodegradation. Chiang *et al.* (1989) demonstrated that less than 5 percent of the mass of dissolved BTEX is lost to volatilization in the saturated groundwater environment. Because of this, the impact of volatilization on dissolved contaminant reduction can generally be neglected. Factors affecting the volatilization of contaminants from groundwater into soil gas include the contaminant concentration, the change in contaminant concentration with depth, the Henry's Law constant and diffusion coefficient of the compound, mass transport coefficients for the contaminant in both water and soil gas, sorption, and the temperature of the water (Larson and Weber, 1994)

B.6.2 INFILTRATION

Infiltration of water into a water table aquifer has two effects on the natural attenuation of fuel hydrocarbons. Perhaps the most obvious effect is dilution. The second effect is reaeration. This tends to increase the overall electron-accepting capacity within the contaminant plume. For example, iron (II) will be oxidized back to iron (III). Vroblesky and Chapelle (1994) present data from a site where a major rainfall event introduced sufficient dissolved oxygen into the contaminated zone to cause reprecipitation of iron (III) onto mineral grains. This reprecipitation made iron (III) available for reduction by microorganisms, thus resulting in a shift from methanogenesis back to iron (III) reduction (Vroblesky and Chapelle, 1994).

SECTION C-3

INTRINSIC REMEDIATION CALCULATIONS

Several calculations using site-specific data must be made in order to document the occurrence of natural attenuation and successfully implement the intrinsic remediation alternative. The following sections describe these calculations.

C.3.1 CALCULATING HYDRAULIC PARAMETERS

Hydraulic parameters necessary for adequate site characterization and model implementation include hydraulic conductivity, transmissivity, hydraulic gradient, linear groundwater flow velocity, hydrodynamic dispersion, and retarded solute transport velocity. Calculations for these parameters are discussed in the following sections.

C.3.1.1 Hydraulic Conductivity

Hydraulic conductivity, K, is a measure of an aquifer's ability to transmit water and is perhaps the most important variable governing fluid flow in the subsurface. Hydraulic conductivity has the units of length over time [L/T]. Observed values of hydraulic conductivity range over 12 orders of magnitude, from $3x10^{-12}$ to 3 cm/sec ($3x10^{-9}$ to $3x10^{3}$ m/day) (Table C.3.1). In general terms, the hydraulic conductivity for unconsolidated sediments tends to increase with increasing grain size and sorting. The velocity of groundwater and dissolved contaminants is directly related to the hydraulic conductivity of the saturated zone. Subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential pathways for contaminant migration. The most common methods used to quantify hydraulic conductivity in the subsurface are aquifer pumping tests and slug tests. The quantitative analysis of pumping and slug test data is beyond the scope of this document. For information on the quantitative analysis of these data, the reader is referred to the works of Kruseman and de Ridder (1991) and Dawson and Istok (1991).

Table C.3.1

Representative Values of Hydraulic Conductivity for Various Sediments and Rocks
(From Domenico and Schwartz, 1990)

Material	Hydraulic Conductivity (m/day)	Hydraulic Conductivity (cm/sec)
UNCONSOLIDATED SEDIMENT		
Glacial till	$9x10^{-8}$ - $2x10^{-1}$	$1x10^{-10}$ - $2x10^{-4}$
Clay	$9x10^{-7}$ - $4x10^{-4}$	$1x10^{-9}$ - $5x10^{-7}$
Silt	$9x10^{-5}$ - 2	$1x10^{-7}$ - $2x10^{-3}$
Fine sand	$2x10^{-2}$ - $2x10^{1}$	$2x10^{-5}$ - $2x10^{-2}$
Medium sand	$8x10^{-2}$ - $5x10^{1}$	$9x10^{-5}$ - $6x10^{-2}$
Coarse sand	$8x10^{-2}$ - $5x10^{2}$	$9x10^{-5}$ - $6x10^{-1}$
Gravel	$3x10^{1}$ - $3x10^{3}$	$3x10^{-2}$ - 3
SEDIMENTARY ROCK		
Karstic limestone	$9x10^{-2}$ - $2x10^{3}$	$1x10^{-4}$ - 2
Limestone and dolomite	$9x10^{-5}$ - $5x10^{-1}$	$1x10^{-7}$ - $6x10^{-4}$
Sandstone	$3x10^{-5}$ - $5x10^{-1}$	$3x10^{-8}$ - $6x10^{-4}$
Siltstone	$9x10^{-7}$ - $1x10^{-3}$	$1x10^{-9}$ - $1x10^{-6}$
Shale	$9x10^{-9}$ - $2x10^{-4}$	$1x10^{-11}$ - $2x10^{-7}$
CRYSTALLINE ROCK		
Vesicular basalt	$3x10^{-2}$ - $2x10^{3}$	$4x10^{-5}$ - 2
Basalt	$2x10^{-6}$ - $3x10^{-2}$	$2x10^{-9}$ - $4x10^{-5}$
Fractured igneous and metamorphic	$7x10^{-4}$ - $3x10^{1}$	$8x10^{-7}$ - $3x10^{-2}$
Unfractured igneous and metamorphic	$3x10^{-9}$ - $2x10^{-5}$	$3x10^{-12}$ - $2x10^{-8}$

C.3.1.1.1 Hydraulic Conductivity from Pumping Tests

Pumping tests generally provide the most reliable information about aquifer hydraulic conductivity. Pumping test data for geohydraulic characteristics are most commonly interpreted by graphic techniques. The analytical method used for interpretation of the data will depend upon the physical characteristics of the aquifer and test wells. The assumptions inherent in the analytical method used to calculate aquifer characteristics should be evaluated to ensure acceptance of the method for the subsurface conditions present at the site under investigation.

The interpretation of aquifer pumping test data is not unique. Similar sets of data can be obtained from various combinations of geologic conditions. Field data of drawdown *vs.* time and/or distance are plotted on graph paper either by hand or using programs such as AQTESOLV® or a spreadsheet program. There are numerous methods of interpreting pumping test data. The method to be used for each pumping test should be selected based on site-specific

conditions (aquifer conditions, test conditions, assumptions made, etc.). Most hydrogeology text books contain pumping test evaluation techniques. Two publications dealing with pump test analysis are recommended (Kruseman and de Ridder, 1991 and Dawson and Istok, 1991).

C.3.1.1.2 Hydraulic Conductivity from Slug Tests

Slug tests are a commonly used alternative to pumping tests that are relatively easy to conduct. The biggest advantage of slug tests is that no contaminated water is produced during the test. During pumping tests at fuel-hydrocarbon-contaminated sites, large volumes of contaminated water that must be treated typically are produced. 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. 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, both within the same well and at several monitoring wells at the site. It is not advisable to rely on data from one slug test in a single monitoring well. Data obtained during slug testing are generally analyzed using the method of Hvorslev (1951) for confined aquifers or the method of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions.

C.3.1.2 Transmissivity

The transmissivity, T, of an aquifer is the product of the aquifer's hydraulic conductivity, K, and the saturated thickness, b:

$$T = Kb \qquad \text{eq. C.3.1}$$

For a confined aquifer, b is the thickness of the aquifer between confining units. For unconfined aquifers, b is the saturated thickness of the aquifer measured from the water table to the underlying confining layer. Transmissivity has the units of length squared over time [L^2/T].

C.3.1.3 Hydraulic Head and Gradient

Determining the magnitude of hydraulic gradients is important because gradients influence the direction and rate of contaminant migration. Hydraulic head, H, and specifically, variations in hydraulic head within an aquifer, is the driving force behind groundwater movement and solute migration. The total hydraulic head at one location in a system is the sum of the elevation head, pressure head, and velocity head (Figure C.3.1):

$$H = h_z + h_p + h_v \qquad \text{eq. C.3.2}$$

Where: H = total hydraulic head [L]
h_z = elevation head = z = elevation relative to the reference plane [L]
h_p = pressure head [L]
h_v = velocity head [L]

Pressure head is given by:

$$h_p = \frac{p}{\rho g}$$

Where: p = fluid pressure
ρ = density
g = acceleration due to gravity

Velocity head is given by:

$$h_v = \frac{v^2}{2g}$$

Where: v = groundwater velocity
g = acceleration due to gravity

Because h_v is generally assumed to be zero for most groundwater flow, the relationship for total head is generally written:

$$H = z + \frac{p}{\rho g} \qquad \text{eq. C.3.3}$$

Thus, the total hydraulic head at a point measured by a piezometer is the sum of the elevation at the base of the piezometer plus the length of the water column in the piezometer. The total hydraulic head in a piezometer is determined by measuring the depth from a surveyed reference point (datum) to the surface of the standing water. The elevation of the water surface is the total hydraulic head in the piezometer. This total head is the total head at the base of the piezometer, not the water table elevation, unless the piezometer terminates immediately below the water table

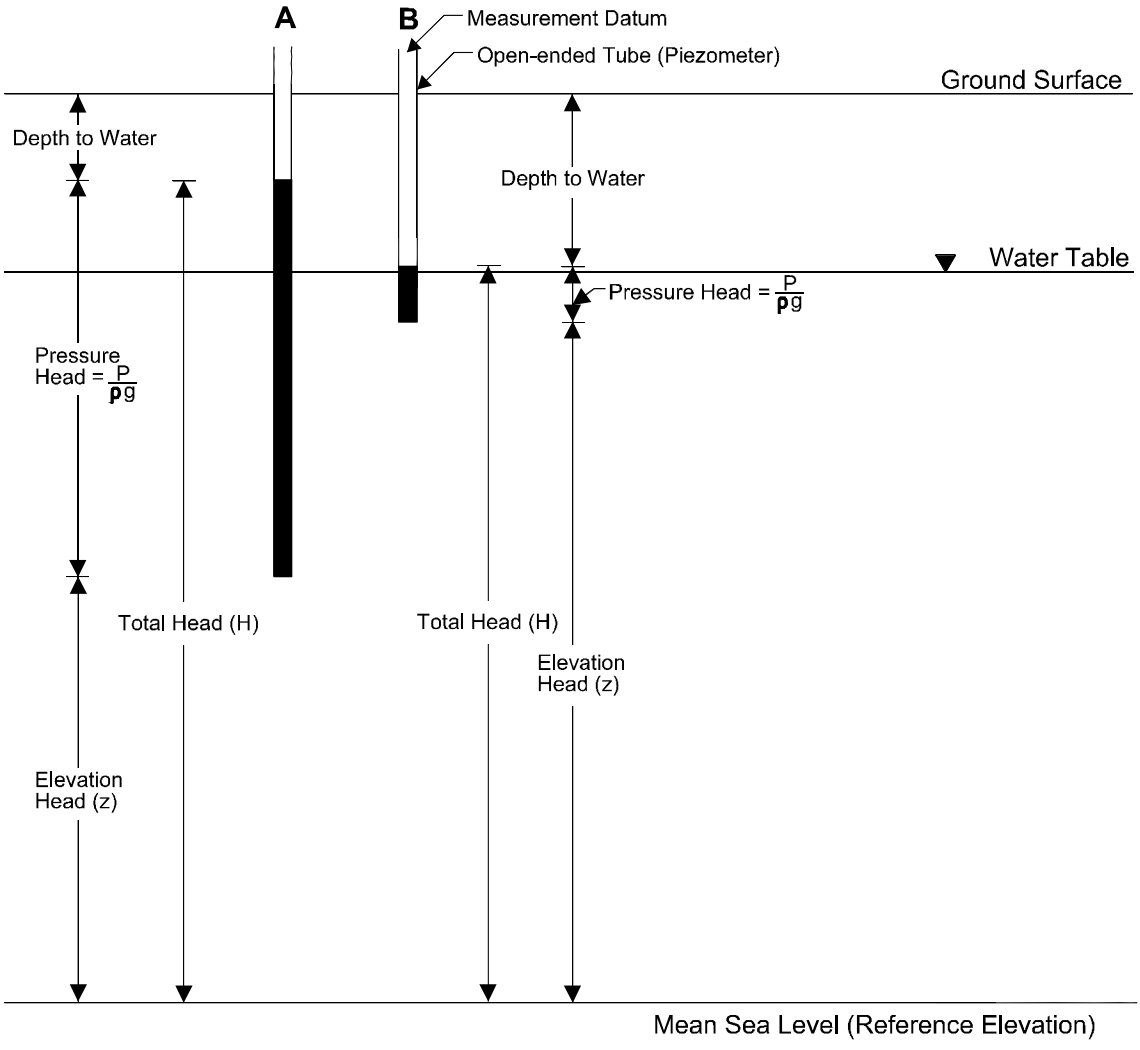

Figure C.3.1

Hydraulic Head

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C3-5

or is a well screened across the water table. Figure C.3.1 shows a pair of nested piezometers that illustrate the relationships between total hydraulic head, pressure head, and elevation head. Because groundwater flows from areas with high total head (point A, Figure C.3.1) to areas with lower total head (point B), this figure depicts a water table aquifer with a strong upward vertical gradient. This figure illustrates how nested piezometers (or wells) are used to determine the importance of vertical gradients at a site. This figure also illustrates the importance of using wells screened in the same portion of the aquifer (preferably across the water table) when preparing potentiometric surface maps.

The hydraulic gradient (dH/dL) is a dimensionless number that is the change in hydraulic head (dH) between two points divided by the length of groundwater flow between these same two points, parallel to the direction of groundwater flow, and is given by:

$$\text{Hydraulic Gradient} = \frac{dH}{dL} \qquad \text{eq. C.3.4}$$

Where: dH = change in total hydraulic head between two points [L]
dL = distance between the two points used for head measurement [L]

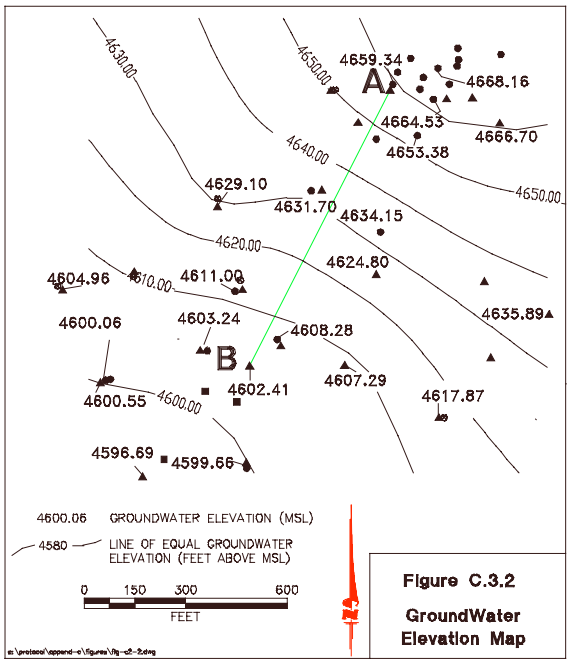
In a system where flow is not occurring, the total hydraulic head, H, is the same everywhere in the system and the hydraulic gradient is zero. To accurately determine the hydraulic gradient, it is necessary to measure groundwater levels in all monitoring wells at the site. Because hydraulic gradients 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. 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.

The hydraulic gradient must be determined parallel to the direction of groundwater flow. Unless two monitoring wells screened in the same relative location within the same hydrogeologic unit are located along a line parallel to the direction of groundwater flow, the potentiometric surface map is generally used to determine the hydraulic gradient. To determine the hydraulic gradient, an engineer's scale is used to draw a line perpendicular to the equal-potential lines on the potentiometric surface map (i.e., parallel to the direction of groundwater flow). Measure the distance between the two equal-potential lines, making note of the groundwater potential at each equal-potential line. Subtract the larger potential from the smaller potential, and divide this number by the distance between the two equal potential lines, being sure to use consistent units.

The number generated will be a negative number because water flows from areas of higher potential to areas of lower potential.

Example C.3.1: Hydraulic Gradient Calculation

Given the water table elevation map shown in Figure C.3.2, calculate the hydraulic gradient between points A and B. Assume that all wells are screened across the water table.



Solution:

The hydraulic gradient is given by dH/dL. The line connecting points A and B is parallel to the direction of groundwater flow. The water table elevation is 4659.34 ft msl at point A and 4602.41 ft msl at point B. Therefore, because groundwater flows from areas of high head to areas of lower head:

$$dH = 4602.41 - 4659.34 = -56.93\,feet$$

The distance between the two points A and B is 936 feet. Therefore:

$$dL = 936\,feet$$

$$\text{and } \frac{dH}{dL} = \frac{-56.93\,ft}{936\,ft} = -0.06\,\frac{ft}{ft} = -0.06\,\frac{m}{m}$$

C.3.1.4 Total Porosity (n) and Effective Porosity (n_e)

Total porosity (n) is the volume of voids in a unit volume of aquifer. Specific retention is the amount of water (volumetric) that is retained against the force of gravity after a unit volume of an unconfined aquifer is drained. Storativity is defined as the volume of water that a confined aquifer takes into or releases from storage per unit surface area of the aquifer per unit change in total hydraulic head. Effective porosity, n_e, is the total porosity of the aquifer minus the specific retention (unconfined) or storativity (confined) of the aquifer:

$$n_e = n - S \qquad \text{eq. C.3.5}$$

Where: n_e = effective porosity [dimensionless]
n = total porosity [dimensionless]
S = specific retention (unconfined) or storativity (confined) [dimensionless]

Effective porosity can be estimated using the results of a tracer test. Although this is potentially the most accurate method, time and monetary constraints can be prohibitive. For this reason, the most common technique is to use an accepted literature value for the types of materials making up the aquifer matrix, and then to calibrate a contaminant transport model by adjusting the value of effective porosity (in conjunction with other input parameters such as transmissivity) within the range of accepted literature values until the modeled and observed contaminant distribution patterns match. Because aquifer materials can have a range of effective porosity, sensitivity analyses should be performed to determine the effect of varying the effective porosity on numerical model results. Values of effective porosity chosen for the sensitivity analyses should vary over the accepted range for the aquifer matrix material. Table C.3.2 presents accepted literature values for total porosity and effective porosity. Contaminant transport model sensitivity analysis is discussed in Appendix D.

Table C.3.2

Representative Values of Dry Bulk Density, Total Porosity, and Effective Porosity for Common Aquifer Matrix Materials (After Walton, 1988 and Domenico and Schwartz, 1990))

Aquifer Matrix	Dry Bulk Density (gm/cm^3)	Total Porosity	Effective Porosity
Clay	1.00-2.40	0.34-0.60	0.01-0.2
Peat	---	---	0.3-0.5
Glacial Sediments	1.15-2.10	---	0.05-0.2
Sandy Clay	---	---	0.03-0.2
Silt	---	0.34-0.61	0.01-0.3
Loess	0.75-1.60	---	0.15-0.35
Fine Sand	1.37-1.81	0.26-0.53	0.1-0.3
Medium Sand	1.37-1.81	---	0.15-0.3
Coarse Sand	1.37-1.81	0.31-0.46	0.2-0.35
Gravely Sand	1.37-1.81	---	0.2-0.35
Fine Gravel	1.36-2.19	0.25-0.38	0.2-0.35
Medium Gravel	1.36-2.19	---	0.15-0.25
Coarse Gravel	1.36-2.19	0.24-0.36	0.1-0.25
Sandstone	1.60-2.68	0.05-0.30	0.1-0.4
Siltstone	---	0.21-0.41	0.01-0.35
Shale	1.54-3.17	0.0-0.10	---
Limestone	1.74-2.79	0.0-50	0.01-0.24
Granite	2.24-2.46	---	---
Basalt	2.00-2.70	0.03-0.35	---
Volcanic Tuff	---	---	0.02-0.35

C.3.1.5 Linear Groundwater Flow Velocity (Seepage or Advective Velocity)

The average linear groundwater flow velocity (seepage velocity) in one dimension in the direction parallel to groundwater flow in a saturated porous medium is given by:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} \qquad \text{eq. C.3.6}$$

Where: v_x= average linear groundwater velocity parallel to groundwater flow direction (seepage velocity) [L/T]

K = hydraulic conductivity [L/T]

n_e = effective porosity [L^3/L^3]

$\frac{dH}{dL}$ = hydraulic gradient [L/L]

The average linear groundwater flow velocity should be calculated to estimate groundwater flow and solute transport velocity, to check the accuracy of groundwater models, and to calculate first-order biodegradation rate constants.

Example C.3.2: Linear Groundwater Flow Velocity Calculation

Calculate the linear groundwater flow velocity in a medium-grained sandy aquifer. The hydraulic gradient as determined from the potentiometric surface map in the previous example is -0.06 m/m. The hydraulic conductivity is 1.7×10^{-1} m/day as determined by pumping tests.

Solution:

Because the effective porosity of this sediment is not known, it is necessary to estimate this parameter. From Table C.3.2, the effective porosity for a medium-grained sand is approximately 23 percent.

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} = -\frac{(0.17\frac{m}{day})(-0.06\frac{m}{m})}{0.23} = 0.044\frac{m}{day}$$

C.3.1.6 Coefficient of Retardation and Retarded Contaminant Transport Velocity

When the average linear velocity of a dissolved contaminant is less than the average linear velocity of the groundwater, the contaminant is said to be “retarded.” The difference between the

velocity of the groundwater and that of the contaminant is caused by sorption and is described by the coefficient of retardation, R, which is defined as:

$$R = \frac{v_x}{v_c} \qquad \text{eq. C.3.7}$$

Where: R = coefficient of retardation
v_x = average linear groundwater velocity parallel to groundwater flow
v_c = average velocity of contaminant parallel to groundwater flow

The ratio v_x/v_c describes the relative velocity between the groundwater and the dissolved contaminant. When $K_d = 0$ (no sorption), the transport velocities of the groundwater and the solute are equal ($v_x = v_c$). If it can be assumed that sorption is adequately described by the distribution coefficient (valid when $f_{oc} > 0.001$), the coefficient of retardation for a dissolved contaminant (for saturated flow) is given by:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. C.3.8}$$

Where: R = coefficient of retardation
ρ_b = bulk density (Section C.3.1.6.1)
K_d = distribution coefficient (Section C.3.1.6.2)
n = total porosity

This relationship expresses the coefficient of retardation in terms of the bulk density and effective porosity of the aquifer matrix and the distribution coefficient for the contaminant. Substitution of this equation into equation C.3.7 gives:

$$\frac{v_x}{v_c} = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. C.3.9}$$

Solving for the contaminant velocity, v_c, gives:

$$v_c = \frac{v_x}{1 + \frac{\rho_b K_d}{n}} \qquad \text{eq. C.3.10}$$

Retardation of a contaminant relative to the advective transport velocity of the groundwater flow system has important implications for intrinsic remediation. If retardation is occurring, dissolved oxygen and other electron acceptors traveling at the advective transport velocity of the groundwater sweep over the contaminant plume from the upgradient margin. This results in

greater availability of electron acceptors within the plume for biodegradation of fuel hydrocarbons. In addition, adsorption of a contaminant to the aquifer matrix results in dilution of the dissolved BTEX plume.

C.3.1.6.1 Bulk Density

The bulk density of a soil, ρ_b, as used in most groundwater models, expresses the ratio of the mass of dried soil to its total volume (solids and pores together).

$$\rho_b = \frac{M_s}{V_T} = \frac{M_s}{(V_s + V_a + V_w)} \qquad \text{eq. C.3.11}$$

Where: ρ_b = bulk density
M_s = mass of solid in the system
V_T = total volume in the system
V_s = volume of solid in the system
V_a = volume of air (or gas) in the system
V_w = volume of water (or liquid) in the system

Bulk density is related to particle density by:

$$\rho_b = (1 - n)\rho_s \qquad \text{eq. C.3.12}$$

Where: ρ_b = bulk density
n = total porosity
ρ_s = density of grains comprising the aquifer

The bulk density is always less than the particle density, ρ_s; for example, if pores constitute half the volume, then ρ_b is half of ρ_s. The bulk density of a soil is affected by the structure of the soil (looseness and degree of compaction), as well as by its swelling and shrinking characteristics, both of which depend on clay content and soil moisture. Even in extremely compacted soil, the bulk density remains appreciably lower than the particle density. This is because the particles can never interlock perfectly, and the soil remains a porous body, never completely impervious. In sandy soils, ρ_b can be as high as 1.81 gm/cm^3. In aggregated loams and clayey soils, ρ_b can be as low as 1.1 gm/cm^3. Table C.3.2 contains representative values of dry bulk density for common sediments and rocks.

C.3.1.6.2 Distribution Coefficient and Total Organic Carbon Content

The distribution coefficient is described in Section B.4.3. Recall equation B.4.10, which gives the relationship between f_{oc} and K_{oc}:

$$K_d = K_{oc} f_{oc} \qquad \text{eq. C.3.13}$$

Where: K_d = distribution coefficient [L^3/M]
K_{oc} = soil adsorption coefficient for soil organic carbon content [L^3/M]
f_{oc} = fraction soil organic carbon (mg organic carbon/mg soil) [M/M]

Representative K_{OC} values are given in Table B.4.1. The fraction of soil organic carbon must be determined from site-specific data. Representative values of total organic carbon (TOC) in common sediments are given in Table C.3.3. Because most solute transport occurs in the most transmissive aquifer zones, it is imperative that soil samples collected for total organic carbon analyses come from these zones in background areas. To be conservative, the average of all total organic carbon concentrations from sediments in the most transmissive aquifer zone should be used for retardation calculations.

Example C.3.3: Retarded Solute Transport Velocity Calculation

For groundwater flow and solute transport occurring in a shallow, saturated, well-sorted, fine-grained, sandy aquifer, with a total organic carbon content of 0.7 percent, a hydraulic gradient of -0.015 m/m, and an hydraulic conductivity of 25 m/day, calculate the retarded contaminant velocity for benzene.

Solution:

Because the total porosity, effective porosity, and the bulk density are not given, values of these parameters are obtained from Table C.3.2. The median values for total porosity, effective porosity, and bulk density are approximately 0.4, 0.2, and 1.6 kg/L respectively.

The first step is to calculate the average linear groundwater velocity, v_x.

$$v_x = -\frac{\left(25\frac{m}{day}\right)\left(-0.015\frac{m}{m}\right)}{0.2} = 1.9\frac{m}{day}$$

Table C.3.3

Representative Values of Total Organic Carbon for Common Sediments

Texture	Depositional Environment	Fraction Organic Carbon	Site Name
medium sand	fluvial-deltaic	0.00053 - 0.0012	Hill AFB, Utah
fine sand		0.0006 - 0.0015	Bolling AFB, D.C.
fine to coarse sand	back-barrier (marine)	0.00026 - 0.007	Patrick AFB, Florida
organic silt and peat	glacial (lacustrine)	0.10 - 0.25	Elmendorf AFB, Alaska
silty sand	glaciofluvial	0.0007 - 0.008	Elmendorf AFB, Alaska
silt with sand, gravel and clay (glacial till)	glacial moraine	0.0017 - 0.0019	Elmendorf AFB, Alaska
medium sand to gravel	glaciofluvial	0.00125	Elmendorf AFB, Alaska
loess (silt)	eolian	0.00058 - 0.0016	Offutt AFB, Nebraska
fine - medium sand	glaciofluvial or glaciolacustrine	< 0.0006 - 0.0061	Truax Field, Madison Wisconsin
fine to medium sand	glaciofluvial	0.00021 - 0.019	King Salmon AFB, Fire Training Area, Alaska
			Dover AFB, Delaware
fine to coarse sand	glaciofluvial	0.00029 - 0.073	Battle Creek ANGB, Michigan
sand	fluvial	0.0057	Oconee River, Georgia[a/]
coarse silt	fluvial	0.029	Oconee River, Georgia[a/]
medium silt	fluvial	0.020	Oconee River, Georgia[a/]
fine silt	fluvial	0.0226	Oconee River, Georgia[a/]
silt	lacustrine	0.0011	Wildwood, Ontario[b/]
fine sand	glaciofluvial	0.00023 - 0.0012	Various sites in Ontario[b/]
medium sand to gravel	glaciofluvial	0.00017 - 0.00065	Various sites in Ontario[b/]

a/ Karickhoff, 1981
b/ Domenico and Schwartz (1990)

The next step is to determine the distribution coefficient, K_d. Values of K_{oc} for BTEX are obtained from Table B.4.1 and are listed in Table C.3.4.

For benzene K_{oc} = 79 L/kg, and (using equation C.3.13):

$$K_d = \left(79 \frac{L}{kg}\right)(0.007) = 0.553 \frac{L}{kg}$$

The retarded contaminant velocity is given by (equation C.3.10):

$$v_c = \frac{1.9\frac{m}{day}}{1+\frac{\left(1.6\frac{kg}{L}\right)\left(0.553\frac{L}{kg}\right)}{0.4}} = 0.59\frac{m}{day}$$

This example illustrates that contaminant sorption to total organic carbon can have a profound influence on contaminant transport by significantly slowing the rate of dissolved contaminant migration.

Table C.3.4

Example Retardation Calculations for the BTEX Compounds

Compound	K_{oc} L/kg	Fraction Organic Carbon	Distribution Coefficient (L/kg)	Bulk Density (kg/L)	Total Porosity	Coefficient of Retardation	Advective Groundwater Velocity (m/day)	Contaminant Velocity (m/day)
Benzene	79	0.007	0.553	1.60	0.40	3.21	1.90	0.59
Toluene	190	0.007	1.33	1.60	0.40	6.32	1.90	0.30
Ethylbenzene	468	0.007	3.276	1.60	0.40	14.10	1.90	0.13
m-xylene	405	0.007	2.835	1.60	0.40	12.34	1.90	0.15
o-xylene	422	0.007	2.954	1.60	0.40	12.82	1.90	0.15
p-xylene	357	0.007	2.499	1.60	0.40	11.00	1.90	0.17
1,2,3-trimethylbenzene	884	0.007	6.188	1.60	0.40	25.75	1.90	0.07
1,2,4-trimethylbenzene	772	0.007	5.404	1.60	0.40	22.62	1.90	0.08
1,3,5-trimethylbenzene	676	0.007	4.732	1.60	0.40	19.93	1.90	0.10

C.3.2 CONTAMINANT SOURCE TERM CALCULATIONS

NAPLs present in the subsurface can represent a continuing source of groundwater contamination. Sorption of fuel hydrocarbons onto the aquifer matrix occurs when NAPL enters the subsurface. When sufficient quantities of NAPL are present, the unsaturated zone may initially be saturated with NAPL, but after a period of time the NAPL will drain from the pores under the influence of gravity, leaving a thin coating of NAPL. Depending on the surface area of the materials comprising the subsurface, the surface tension of the NAPL, and the porosity and permeability of the subsurface materials, some NAPL also may be held between the grains by capillarity. NAPL adhering to the grains of the aquifer matrix or retained by capillarity is herein referred to as residual NAPL. If the NAPL is mobile within and among the pores of the aquifer matrix, as is generally the case near the water table, the NAPL is referred to as mobile NAPL.

If BTEX concentrations in the residual and mobile LNAPL are not decreasing over time, or if they are decreasing very slowly, extremely long times will be required for natural attenuation of the dissolved contaminant plume. This will likely make intrinsic remediation unattractive to regulators and will reduce the chance of implementation. In order for intrinsic remediation to be a

viable remedial option, the source of continuing groundwater contamination must be decreasing over time (decaying), either by natural weathering processes or via engineered remedial solutions such as mobile LNAPL recovery, bioventing, or bioslurping. Because natural weathering processes can be fairly slow, especially in static systems where the groundwater elevation does not fluctuate significantly, it will generally be necessary to implement engineered remedial solutions to remove the LNAPL. However, in cases where the LNAPL has been in the ground for a long period of time, it may be weathered to the point that it no longer acts as a source of significant groundwater contamination (Section C.3.2.3). Because of their physical and chemical properties, the BTEX compounds are generally the first to be removed from the LNAPL via natural weathering processes. Wiedemeier *et al.* (1993) used mass fraction BTEX analyses from mobile LNAPL at a jet fuel spill site in Colorado to show that the weathered LNAPL was not capable of producing dissolved BTEX concentrations above regulatory groundwater quality standards.

To determine how long it will take for a dissolved contaminant plume to disappear, it is necessary to estimate how fast the contaminant source (LNAPL) is being removed. Source removal rates can be estimated where bioventing is being used to remediate residual LNAPL by collecting soil samples in the source area at the start of remedial activities. After the system has been operating for a period of time, soil samples are collected from approximately the same location(s). Comparison of BTEX concentrations in samples collected from the same location makes it possible to determine when the source area has been remediated. This approach has been used successfully at several Air Force bases where pilot-scale bioventing systems had been installed and where 1-year sampling data were available. Experience with the bioventing initiative shows that at most of the 105 sites where data are available, 99 percent of the BTEX mass in the subsurface vadose zone is remediated in 1 year. In areas with mobile LNAPL it is much more difficult to estimate cleanup times, so conservative estimates should be made based on LNAPL removal rates. Predicting the cleanup time for sites with mobile LNAPL is especially difficult because residual LNAPL will remain after the recoverable mobile LNAPL has been removed. One remedial technology that has shown promise for both residual and mobile LNAPL is bioslurping. Bioslurping removes mobile LNAPL via suction lift. During bioslurping operations, a vacuum is induced in the unsaturated zone. This vacuum draws oxygen from uncontaminated areas into the area contaminated with residual LNAPL and extracts soil gas into which VOCs have volatilized. A properly installed bioslurping system thus acts as a mobile LNAPL recovery system, a bioventing system, and a soil vapor extraction system.

The work of Smith *et al*. (1981) and Cline *et al.* (1991) shows that the aromatic hydrocarbons, and in particular, BTEX, constitute by far the greatest mass of compounds that partition from fuels into groundwater. Smith *et al.* (1981) list 40 compounds that have equilibrium concentrations in a JP-4 jet fuel/water mixture of greater that 0.01 mg/L. The work of Smith *et al*. (1981) shows that the major water-soluble aromatic components (compounds found in concentrations greater than about 1 percent of the total mass of dissolved constituents) of jet fuel are BTEX, the trimethylbenzenes, naphthalene, and the methylnaphthalenes. Table C.3.5 shows the relative concentrations of these compounds in JP-4. In a 1:10 fuel:water mix, BTEX makes up approximately 82 percent, or 22.61 mg/L, of the total dissolved concentration of 27.63 mg/L for the 1:10 fuel to water mixture. The trimethylbenzene isomers have a combined concentration of 0.87 mg/L (approximately 3 percent of total concentration). Smith *et al.* (1981) also used fuel:water ratios of 1:100, 1:1,000, and 1:10,000. As the ratio of water increased, the total dissolved concentration of the 40 water soluble fuel components decreased, to a minimum value of 4.58 mg/L for the 1:10,000 JP-4 to water mixture (Table C.3.5). Based on this information, the highest reasonable concentration of total fuel hydrocarbons dissolved in groundwater in contact with JP-4 should be about 28 mg/L, and the highest equilibrium total BTEX concentration should be about 23 mg/L. If concentrations higher than this are reported by the analytical laboratory, emulsification of LNAPL in the sample should be suspected.

Table C.3.5

Dissolved Concentrations (in Water) of Water-Soluble Components Present in JP-4[a/]

Compound	**Fuel to Water Ratio**			
	1:10	**1:100**	**1:1,000**	**1:10,000**
Benzene (mg/L)	9.82	6.99	1.55	0.07
Toluene (mg/L)	8.49	7.79	3.71	0.70
Ethylbenzene (mg/L)	0.67	0.64	0.59	0.17
Xylenes (mg/L)	3.63	3.49	3.33	0.92
Trimethylbenzenes (mg/L)	0.87	0.79	1.13	0.54
Naphthalene (mg/L)	0.39	0.31	0.41	0.10
Methylnaphthalenes (mg/L)	0.24	0.17	0.32	0.16
All Others (mg/L)	3.52	2.83	2.85	1.92
Total (mg/L)	27.63	23.01	13.89	4.58
Total BTEX (mg/L)	22.61	18.90	9.18	1.86
Percent Total BTEX	82	82	66	41

a/ Modified from Smith *et al.*, 1981

Table C.3.6 summarizes the work conducted by Cline *et al.* (1991) on 31 gasoline samples. The compounds listed in this table represent the major water-soluble components in gasoline (compounds found in concentrations greater than about 1 percent of the total gas chromatography/flame ionization detector peak area for all compounds detected in the aqueous

phase), which are BTEX, n-propylbenzene, 3- and 4-ethyltoluene, and 1,2,3-trimethylbenzene. Based on the information presented in Table C.3.6, the highest reasonable concentration of total fuel hydrocarbons dissolved in groundwater in contact with gasoline should be about 135 mg/L, and the highest equilibrium total BTEX concentration should be about 132 mg/L. If concentrations higher than this are reported by the analytical laboratory, emulsification of LNAPL in the sample should be suspected.

There are two methods that can be used to determine the concentration of contaminants dissolved in groundwater beneath NAPL and thus quantify the contaminant source loading. The first method involves directly measuring the concentration of dissolved contaminants in groundwater beneath the NAPL plume. The second method involves the use of partitioning calculations. The following sections describe each approach.

Table C.3.6

Weight Percent Water-Soluble Components in Gasoline and Their Concentrations in Water in Contact with Gasoline

Compound	Gasoline Composition[a/] (Weight Percent)	Dissolved Concentration[a/] (mg/L)	Gasoline Composition[b/] (Weight Percent)	Dissolved Concentration[b/] (mg/L)
benzene	1.73	42.6	1.94	58.7
toluene	9.51	69.4	4.73	33.4
ethylbenzene	1.61	3.2	2.0	4.3
m- and *p*-xylene	5.95	11.4	--	--
o-xylene	2.33	5.6	2.27	6.9
m-xylene	--	--	5.66	11.0
p-xylene	--	--	1.72	4.4
n-propylbenzene	0.57	0.4	--	--
3-,4-ethyltoluene	2.20	1.7	--	--
1,2,3-trimethylbenzene	0.8	0.7	--	--
1,2,4-trimethylbenzene	--	--	3.26	1.1
Total	24.7	135	21.58	119.8
Total BTEX		132.2		118.7
Percent Total BTEX		98		99

a/ Cline *et al.* (1991)

b/ American Petroleum Institute (1985) average of 24 analyses from nine fuel:water solutions (1:10 fuel:water)

C.3.2.1 Direct Measurement of Dissolved Contaminant Concentrations in Groundwater in Contact with NAPL

Two methods can be used to determine the dissolved concentration of contaminants in groundwater beneath a NAPL plume. The first method involves collecting groundwater samples

from beneath a LNAPL lens in monitoring wells. The second method involves collecting samples of mixed LNAPL and water from monitoring wells.

C.3.2.1.1 Collecting Groundwater Samples From Beneath the LNAPL

This method involves carefully sampling groundwater beneath a floating LNAPL lens. One way of collecting a groundwater sample from beneath a lens of floating LNAPL involves using a peristaltic pump. The depth to the base of the mobile LNAPL is measured, a length of high-density polyethylene (HDPE) tubing that will reach 1 to 2 feet beneath the LNAPL is lowered into the well, and the sample is collected. Another useful technique for obtaining such a sample where the depth to groundwater is too deep to allow use of a peristaltic pump is to use a Grundfos® pump. If a Grundfos® pump is used to collect a water sample from beneath LNAPL, it is imperative that the pump be thoroughly cleaned after each use, and that good sampling logic be used (e.g., sample less contaminated wells first). Also, dedicated bladder pumps that are being used for long-term monitoring (LTM) in wells with LNAPL can be used to collect water samples from beneath the LNAPL.

C.3.2.1.2 Collecting Mixed Groundwater/NAPL Samples

This method involves collecting a sample of groundwater and floating LNAPL from a monitoring well, placing the sample in a sealed container used for volatile organics analysis being careful to ensure there is no headspace, allowing the sample to reach equilibrium, and submitting the water beneath the floating NAPL to a qualified laboratory for analysis. A disposable bailer generally works best for collection of this type of sample. Smith *et al.* (1981) has information on how to conduct such a test. Two or three samples should be collected from different monitoring wells containing LNAPL at the site. This test should only be done when it is not possible to collect a discrete sample from beneath the LNAPL.

C.3.2.2 Partitioning Calculations

LNAPL present at a site represents a continuing source of contamination because BTEX and other aromatic compounds will partition from the LNAPL into the groundwater. In such cases, it is generally necessary to estimate the dissolved concentration of BTEX expected in groundwater near the LNAPL. Partitioning calculations can be performed for sites with NAPL to quantify contaminant loading from the NAPL into the groundwater. Such calculations allow estimation of the impact of continuing sources of contamination on dissolved BTEX concentrations. The

results of partitioning calculations may show that even if the NAPL is allowed to remain in the ground, dissolved contaminant concentrations will remain below regulatory guidelines. This is especially true when weathered NAPLs with initially low BTEX concentrations, such as jet fuels (Jet A, JP-4, *etc.*) are present. Partitioning calculations made by Wiedemeier *et al.* (1993) showed that NAPL present in the subsurface at a fueling facility near Denver, Colorado was incapable of producing dissolved BTEX concentrations in groundwater above regulatory standards. Partitioning calculations should be confirmed with a LTM program.

If partitioning calculations suggest that partitioning from the LNAPL could increase dissolved BTEX concentrations in groundwater to above regulatory guidelines at a point of compliance, then this continuing source of groundwater contamination should be remediated. Residual LNAPL contamination in the unsaturated zone is generally best remediated using bioventing, a technique that introduces air (oxygen) into the subsurface, thus stimulating aerobic biodegradation of fuel hydrocarbons. When found in the saturated zone, residual LNAPL is extremely difficult to remove. Maximum BTEX concentrations resulting from such partitioning will occur when the groundwater and LNAPL reach equilibrium. Assuming that equilibrium is reached gives the most conservative modeling results. Alternate, less conservative models for partitioning from LNAPL into the aqueous phase are given by Hunt *et al.* (1988) and Johnson and Pankow (1992). These models are described below.

C.3.2.2.1 Equilibrium Partitioning of BTEX from Mobile LNAPL into Groundwater

The fuel-water partitioning coefficient, K_{fw}, is defined as the ratio of the concentration of a compound in the fuel to the compound's equilibrium concentration in water in contact with the fuel:

$$K_{fw} = \frac{C_f}{C_w} \qquad \text{eq. C.3.14}$$

Where: K_{fw} = fuel-water partitioning coefficient [dimensionless]
C_f = concentration of the compound in the fuel [M/L^3]
C_w = concentration of the compound dissolved in groundwater [M/L^3]

Table C.3.7 lists values of K_{fw} for BTEX and trimethylbenzenes (TMB) in jet fuel and gasoline. The relationships relating K_{fw} to the aqueous solubility of a pure compound in pure water, S, presented in Table C.3.8 can be used to estimate K_{fw} for compounds not listed in this table.

Table C.3.7

Fuel-Water Partitioning Coefficients (K_{fw}) for Those Compounds Most Commonly found in the Aqueous Phase in Water in Contact with Jet Fuel or Gasoline

Compound	K_{fw} [a/] (JP-4 Jet Fuel)	K_{fw} [b/] (Gasoline)	K_{fw} [c/] (Gasoline)
Benzene	2,455	231	350
Toluene	2,754	895	1,250
Ethylbenzene	4,786	3,411	4,500
o-xylene	7,079	3,162	3,630
m-xylene	3,715	3,539	4,350
p-xylene	7,586	2,961	4,350
1,2,3-Trimethylbenzene	NA	NA	13,800
1,2,4-Trimethylbenzene	8,913	12,270	NA
1,3,5-Trimethylbenzene	NA	6,493	NA

a/ From experiments conducted by Smith *et al.*, 1981 (For JP-4)
b/ Model of Bruce *et al.*, 1991 (for gasoline)
c/ Model of Cline *et al.*, 1991 (for gasoline)
NA = not analyzed

Table C.3.8

Relationships Relating Fuel-Water Partitioning Coefficients (K_{fw}) to Pure Aqueous-Phase Solubility

LNAPL Type	Relationship Relating S to K_{fw} [a/]	Reference
JP-4	$\log K_{fw} = -0.797 \log S + 1.681$	Smith *et al.*, 1981
JP-5	$\log K_{fw} = -0.746 \log S + 1.757$	Smith *et al.*, 1981
JP-8	$\log K_{fw} = -0.864 \log S + 1.508$	Smith *et al.*, 1981
Gasoline	$\log K_{fw} = -1.15 \log S + 6.099$	Bruce *et al.*, 1991
Gasoline	$\log K_{fw} = -1.00 \log S + 0.85$	Cline *et al.*, 1991

a/ Determined using linear regression on data for dissolved compound concentrations in a fuel-water mix.

Using the definition of K_{fw} presented above, the maximum (equilibrium) total dissolved BTEX concentration resulting from the partitioning of BTEX from NAPL into groundwater is given by:

$$C_w = \frac{C_f}{K_{fw}} \qquad \text{eq. C.3.15}$$

This relationship predicts the concentration of dissolved BTEX in the groundwater if the LNAPL is allowed to remain in contact with the groundwater long enough so that equilibrium between the two phases is reached.

To complete partitioning calculations, samples of the mobile LNAPL must be collected and analyzed to determine the type of fuel and the mass fraction of BTEX present in the fuel. From

the mass fraction BTEX data, the concentration of each BTEX compound in the fuel on a volumetric basis, C_f, can be calculated by using the relationship:

$$C_f = F_f \rho_f \qquad \text{eq. C.3.16}$$

Where: ρ_f = Density of fuel (Table C.3.9)
F_f = Mass fraction of compound in the fuel

Using mass fraction BTEX data from the LNAPL analyses, and the fuel-water partitioning coefficients presented in Table C.3.7, the maximum dissolved benzene, toluene, ethylbenzene, and total xylene concentrations expected in groundwater caused by the partitioning of these compounds from the LNAPL can be calculated using equation C.3.15.

Table C.3.9

Density of Common Liquids

Type of Liquid	Density (gm/cm^3)	Density (gm/m^3 = mg/L)
Miscellaneous Liquids:		
Water	1.0	1,000,000
Gasoline	0.68-0.76	680,000 - 760,000
Jet Fuel	0.74-0.85	740,000 - 850,000
JP-4	0.75	750,000
Kerosene	0.78-0.82	780,000 - 820,000
Fuel Oil and Diesel Oil:	0.82-0.95	820,000 - 950,000
BTEX and TMB		
Benzene	0.868	868,000
Toluene	0.8669	866,900
Ethylbenzene	0.8669	866,900
o-xylene	0.8802	880,200
m-xylene	0.8642	864,200
p-xylene	0.8610	861,000
1,2,3-trimethylbenzene	0.88	880,000
1,2,4-trimethylbenzene	0.88	880,000
1,3,5-trimethylbenzene	0.87	870,000
1,2,4,5-tetramethylbenzene	0.84	840,000

Example C.3.4: Equilibrium Partitioning Calculation

Mass fraction BTEX data from a sample of JP-4 LNAPL collected at a site with up to 3 feet of mobile LNAPL floating on the water table indicate that the mass fractions of benzene, toluene, ethylbenzene, and xylene are 0.000001, 0.00002, 0.0047, and 0.0009, respectively. Calculate the concentration of BTEX dissolved in groundwater in contact with the LNAPL that would be expected under equilibrium conditions.

Solution:

The first step is to determine the concentration of each compound in the LNAPL. From Table C.3.9, the density of JP-4 jet fuel is 750,000 mg/L. The concentration of each compound is calculated using equation C.3.16. The results of this calculation are listed in Table C.3.10. The next step is to use the fuel-water partitioning coefficient (Table C.3.7) for each compound and the concentration of each compound in the fuel to determine the equilibrium concentration in the groundwater using equation C.3.15. The results of this calculation are listed in Table C.3.10.

Table C.3.10

Solution to Example C.3.4

Compound	Concentration in LNAPL (C_f, mg/L)	Fuel-Water Partitioning Coefficient (K_{fw})[a/]	Concentration in Water (µg/L)
benzene	0.75	2,455	0.31
toluene	15	2,754	5.45
ethylbenzene	3,525	4,786	736.5
xylene	675	6,126[b/]	110.2

a/ From Table C.3.7.
b/ Average of all isomers.

C.3.2.2.2 Nonequilibrium Partitioning of BTEX from Mobile LNAPL into Groundwater

The steady-state, two-dimensional dissolution of BTEX from a pool of NAPL floating on the water table into groundwater (assumed to be a semi-infinite medium) can be described by the steady-state, two-dimensional, advection-dispersion equation (Hunt *et al.*, 1988):

$$v_x \frac{\partial C}{\partial x} = D_z \frac{\partial^2 C}{\partial z^2} \qquad x,z > 0 \qquad \text{eq. C.3.17}$$

Where: C = contaminant concentration dissolved in water
v_x = average linear groundwater velocity
D_z = vertical dispersion coefficient

If it is assumed that:

- The time required for total NAPL dissolution is exceedingly long in comparison to the contact time between the NAPL pool and the flowing groundwater
- The NAPL pool is wide compared to the horizontal transverse mixing process
- The NAPL pool can be approximated as a rectangle
- The NAPL lens width does not affect the dissolution rate

- The elevation of the NAPL lens is taken as z=0, with z measured positively upward.
- The boundary conditions are:

$C(x, z = \infty) = 0$
$C(x, z = 0) = C_e \qquad 0 \le x \le L$
$C(x = 0, z) = 0$

Where: C = contaminant concentration dissolved in water
C_e = Effective water solubility
L = Horizontal length of NAPL pool,

then the rate of dissolution of constituents from an LNAPL lens into groundwater flowing beneath the lens can be calculated as two-dimensional, steady-state dissolution, and the surface area averaged mass transfer rate, M_a, is calculated as (Johnson and Pankow, 1992; Hunt *et al.*, 1988):

$$M_a = C_e n_e \sqrt{\frac{4 D_z v_x}{\pi L}} \qquad \text{eq. C.3.18}$$

Where: n_e = effective porosity
L = length of NAPL lens parallel to groundwater flow direction
v_x = Average linear groundwater flow velocity
C_e = Effective water solubility (proportional to a compound's pure phase solubility and mole fraction in the NAPL)
D_z = Vertical dispersion coefficient

The vertical dispersion coefficient, D_z, results from a combination of molecular diffusion and mechanical dispersion and is defined as (Johnson and Pankow, 1992):

$$D_z = D_e + v_x \alpha_z \qquad \text{eq. C.3.19}$$

Where: D_e = effective molecular diffusivity (corrected for porosity and tortuosity)
α_z = vertical dispersivity (typically 0.01 of longitudinal dispersivity)
v_x = average linear groundwater flow velocity

A typical value of D_e for a nonpolar organic compound is 1×10^{-5} cm^2/sec (Sellers and Schreiber, 1992).

"At very low flow velocities where molecular diffusion dominates, the average concentration decreases with increasing flow velocity because of decreasing contact time. At higher groundwater flow velocities where dispersion dominates over diffusion, average percent solubility becomes independent of velocity. This is because the transverse dispersion coefficient is proportional to flow velocity, and D_z/v is constant. At typical groundwater flow velocities, an effluent concentration far less than the solubility limit is expected. For example, for a flow

velocity of 1 m/day and $\alpha_z = 10^{-4}$ m, less than 1 percent of solubility is predicted, and considerable pumping would be required to remove the contaminant. The analysis predicts a constant contaminant concentration dissolved in the extracted water as long as the separate phase covers the boundary" (Hunt *et al.*, 1988, pp. 1253 and 1254).

LNAPL dissolution is modeled in Bioplume II simulations using one injection well in each cell containing mobile LNAPL. The injection rate for each well, Q_i, is given by:

$$Q_i = \frac{AM_a}{C_e} \qquad \text{eq. C.3.20}$$

Where: Q_i = injection rate
A = cell area
M_a = average mass transfer rate
C_e = effective water solubility

A similar approach can be used for residual LNAPL. In this case it will be necessary to use BTEX data collected from cores. When this method is used, the mass of residual LNAPL in contact with the groundwater must be determined.

C.3.2.3 Intrinsic Remediation of Contaminant Sources

The concentration of petroleum hydrocarbons in groundwater in contact with fuel spills is controlled by the concentration of the particular hydrocarbon in the oily phase hydrocarbon. Raoult's Law predicts that the equilibrium concentration would be water solubility of that particular hydrocarbon, multiplied by its mole fraction in the oily phase material. When wells that have been installed across LNAPL spills are monitored for several years, frequently the concentrations of BTEX are seen to decline by several orders of magnitude. This is largely due to intrinsic remediation of the LNAPL itself, supported by natural weathering processes, including diffusion of oxygen through the vadose zone. Apparently, BTEX is degraded first, leaving a residual of branched and normal alkanes. As a result, hydrocarbon contamination (i.e., BTEX) disappears from the groundwater, although considerable quantities of total petroleum hydrocarbons (TPH) may remain in the aquifer. The effect is well illustrated in the following case study.

In 1988, at least 1,200 gallons of unleaded gasoline was inadvertently pumped from an underground storage tank onto the land surface at the petroleum, oil, and lubricants (POL) facility at Eglin AFB, Florida. The fuel flowed overland toward a small creek 160 feet from the spill, then infiltrated until it reached the water table. When sampled in 1993, the spill remained as

LNAPL in a smear zone extending from the point of release to the point of discharge of groundwater to a wetland (Figure C.3.3).

Core samples were collected across the water table at (1) the location of the original spill, (2) a location intermediate between the spill and the creek, and (3) the bank of the creek (Figure C.3.3). Core samples were analyzed for TPH and BTEX. Wells were installed in the boreholes used to acquire the cores and were screened across the interval containing TPH.

Cline *et al.* (1991) examined the variation in fuel to water partition coefficients for 31 gasoline samples. Their estimates of K_{fw} for various gasoline components are presented in Table C.3.7. TPH- and BTEX-concentration data in core samples from the spill at Eglin AFB are presented in Table C.3.11. Assuming the specific gravity of gasoline is 0.74, the following relationship was used to estimate C_f for a given BTEX compound (e.g., benzene) in a given core sample.

$$C_f = \frac{Benzene(mg/kg)}{TPH(mg/kg)} x \frac{0.74(kg)TPH}{1.0(l)TPH} x \frac{10^6(mg)TPH}{1.0(kg)TPH}$$

The concentrations of BTEX in groundwater in contact with that particular core material were predicted by dividing C_f by K_{fw} from Table C.3.7. Table C.3.12 compares the predictions to the actual measured concentrations of BTEX in groundwater from monitoring wells screened across the depth interval from which the core samples were acquired.

The gasoline near the receptor, and half way between the source and the receptor, was so weathered that no BTEX was detectable at concentrations greater than 0.01 mg/kg, although considerable quantities of TPH remained (Table C.3.11). Duplicate samples at the TPH maximum near the source were weathered, but appreciable concentrations of BTEX remained, and the pattern of weathering varied between the cores.

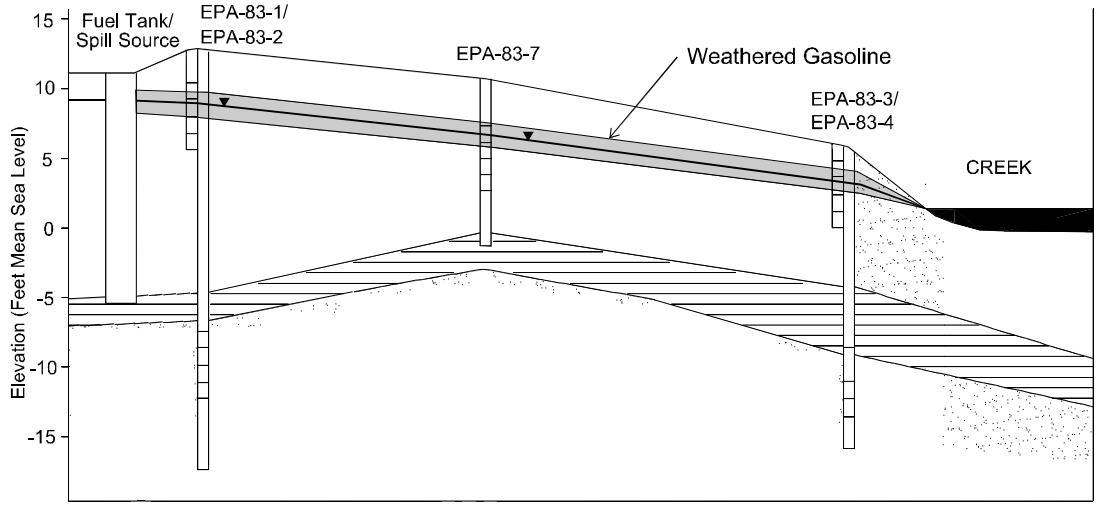


Figure C.3.3

Cross Section of a Gasoline Spill at the POL, Eglin AFB

Table C.3.11

Concentrations of TPH and BTEX in Core Material from a Gasoline Spill

Depth (feet)	TPH	Benzene	Toluene	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene
	----------mg/kg----------						
Adjacent to the Spill (EPA-83-2)							
3.0-3.4	2140	2.66	5.68	4.01	10.6	21.2	17.2
3.0-3.5	1550	0.165	18.2	2.05	41.7	69.1	59.2
On Half of the Way to the Creek (EPA-83-7)							
4.0-5.0	1170	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
6.0-7.0	5310	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Adjacent to the Creek (EPA-83-4)							
1.5-2.0	1210	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2.0-2.5	1970	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2.3-3.0	7090	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Groundwater in contact with the weathered gasoline near the spill contained BTEX concentrations that were either in good agreement with those predicted from analysis of the cores, or were somewhat lower than those predicted by core analysis. A comparison of water sample results from September 1993 and October 1994 suggest that intrinsic remediation is continuing in the spill area. Despite high concentrations of TPH, the residual gasoline was so highly weathered that it could not support groundwater concentrations of BTEX that exceeded regulatory standards downgradient from the spill.

Extrapolation to Other Sites

The sensitivity of this comparison depends on the amount of TPH in the soil, and how extensively the TPH is weathered. To predict benzene concentrations near regulatory standards may require TPH concentrations as high as 5,000 to 10,000 mg/kg. It also depends on the detection limit for benzene in core material. If extracts are analyzed by gas chromatography (GC) using a flame ionization detector, alkanes in the window for BTEX will give false positives at the detection limit required. To avoid false positives in this case study, the concentration of BTEX in core samples were quantified by GC/mass spectral analysis.

Table C.3.12.
Comparison of BTEX in Groundwater to Predictions Based on the BTEX Content of the Weathered Residual Gasoline.

Sample Interval (ft bgs)		Benzene	Toluene	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene
		μg/L					
Well EPA 83-2, Near the Gasoline Spill							
3.0-3.4	prediction	2600	1600	310	840	1700	1600
3.0-3.5	prediction	230	7000	217	4600	7600	7800
	measured 09/93	300	1400	350	540		410
	measured 10/94	46	75	13	93	179	219
Well EPA 83-7, 70 feet Downgradient (One Half of the Distance to the Receptor)							
4.0-5.0	prediction	<18	<5	<1.4	<1.5	<1.5	<1.7
6.0-7.0	prediction	<4	<1	<0.3	<0.3	<0.3	<0.4
	measured 09/93	2.2	4.3	36	36		26
	measured 10/94	1.9	1.0	<1	<1	<1	<1
Well EPA 83-4, 150 feet Downgradient, Adjacent to the Receptor							
1.5-2.0	prediction	<17	<5	<1.4	<1.4	<1.4	<1.7
2.0-2.5	prediction	<11	<3	<0.8	<0.9	<0.9	<1.0
2.3-3.0	prediction	<3	<0.8	<0.2	<0.2	<0.2	<0.3
	measured 09/93	<1	<1	<1	<1	<1	<1
	measured 10/94	<1	1.4	<1	<1	<1	<1

C.3.3 CONFIRMING AND QUANTIFYING BIODEGRADATION

Chemical evidence of two types can be used to document the occurrence of biodegradation. The first type of evidence is graphical and is provided by the electron acceptor and metabolic byproduct maps discussed in Section C-2. The second line of evidence involves using a conservative tracer.

C.3.3.1 Isopleth maps

The extent and distribution of contamination relative to electron acceptors and metabolic byproducts can be used to qualitatively document the occurrence of biodegradation. Depleted dissolved oxygen concentrations in areas with fuel hydrocarbon contamination indicates that an active zone of aerobic hydrocarbon biodegradation is present. Depleted nitrate and sulfate concentrations in areas with fuel hydrocarbon contamination indicate that an active zone of anaerobic hydrocarbon biodegradation is present and that denitrification and sulfate reduction are occurring. Elevated iron (II) and methane concentrations in areas with fuel hydrocarbon contamination indicate that an active zone of anaerobic hydrocarbon biodegradation is present and that iron reduction and methanogenesis are occurring. Isopleth maps of contaminants, electron acceptors, and metabolic byproducts can be used as evidence that biodegradation of fuel

hydrocarbons is occurring. Figures C.2.7 and C.2.8 show how these maps can be used to support the occurrence of biodegradation. Figure C.2.7 shows that areas with depleted dissolved oxygen, nitrate, and sulfate correspond with areas having elevated BTEX concentrations. Figure C.2.8 shows that areas with elevated iron (II) and elevated methane concentrations also coincide with areas having elevated BTEX concentrations. These figures suggest that aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis are all occurring at the example site.

C.3.3.2 Conservative Tracer

In order to ensure that at least a portion of observed decreases in contaminant concentrations over time can be attributed to biodegradation, measured concentrations of BTEX must be corrected for the effects of dispersion, dilution, and sorption. A convenient way of doing this is to use compounds present in the dissolved BTEX plume that have Henry's Law constants and soil sorption coefficients that are similar to those of BTEX and that are biologically recalcitrant under anaerobic conditions. One such compound that is useful in some, but not all, groundwater environments is TMB. The three isomers of this compound (*1,2,3*-TMB, *1,2,4*-TMB, and *1,3,5*-TMB) have Henry's Law constants and soil sorption coefficients that are similar to BTEX (compare Tables B.4.1 and B.6.1). Also, the TMB isomers are generally present in sufficient quantities in fuel mixtures to be readily detectable when dissolved in groundwater and are fairly recalcitrant to biodegradation under anaerobic conditions. The degree of recalcitrance of TMB is site-specific, and the use of this compound as a conservative tracer must be evaluated on a case-by-case basis. Another compound of potential use as a conservative tracer is tetramethylbenzene.

The corrected concentration of a compound is the concentration of the compound that would be expected at one point (B) located downgradient from another point (A) after correcting for the effects of dispersion, dilution, and sorption between points A and B. One relationship that can be used to calculate the corrected contaminant concentration is:

$$C_{B,Corr} = C_B\left(\frac{TMB_A}{TMB_B}\right) \qquad \text{eq. C.3.21}$$

Where $C_{B,Corr}$ = corrected concentration of compound of interest at Point B
C_B = measured concentration of compound of interest at Point B
TMB_A = measured concentration of trimethylbenzene at Point A
TMB_B = measured concentration of trimethylbenzene at Point B

Trimethylbenzene is slightly more hydrophobic than BTEX and therefore has a higher soil sorption coefficient. This causes preferential sorption of TMB. In addition, TMB generally is not entirely recalcitrant under anaerobic conditions, and appears to degrade rapidly under aerobic conditions. The degree of recalcitrance of TMB is site-specific, and the use of this compound must be evaluated on a case-by-case basis. However, if any TMB mass is lost to the processes of biodegradation or preferential sorption, equation C.3.21 becomes more conservative (i.e., lower mass losses due to biodegradation and lower biodegradation rate constants will be calculated).

After correcting measured BTEX concentrations for the effects of dispersion, dilution, and sorption, it is possible to estimate the amount of BTEX removed from the system (converted to carbon dioxide and water) via biodegradation, $\Delta C_{Bio,AB}$, between the two points (A) and (B) using the relationship:

$$\Delta C_{Bio,AB} = C_{A,Obs} - C_{B,Corr} \qquad \text{eq. C.3.22}$$

Where: $\Delta C_{Bio,AB}$ = change in BTEX concentration between points A and B caused by biodegradation
$C_{A,Obs}$ = observed BTEX concentration at point A
$C_{B,Corr}$ = corrected BTEX concentration at point B

The mass of BTEX lost between these two points can be calculated if the volume of water between the two points is known.

The percent of BTEX lost to biodegradation between the two points (A) and (B) can now be calculated, and is given by:

$$\Delta BTEX_{Bio} = \left(\frac{\Delta C_{Bio,AB}}{\Delta C_{Total,AB}} \right) \bullet 100 = \left(\frac{C_{A,Obs} - C_{B,Corr}}{C_{A,Obs} - C_{B,Obs}} \right) \bullet 100 \qquad \text{eq. C.3.23}$$

Where: $\Delta BTEX_{Bio}$ = percent BTEX lost to biodegradation
$C_{B,Corr}$ = TMB-corrected BTEX concentration at point B
$C_{A,Obs}$ = observed BTEX concentration at point A
$C_{B,Obs}$ = observed BTEX concentration at point B
$\Delta C_{Total,AB}$ = observed change in BTEX concentration between points A and B
$\Delta C_{Bio,AB}$ = change in BTEX concentration between points A and B caused by biodegradation

Example C.3.5: BTEX Lost to Biodegradation

Given the observed concentrations of BTEX and TMB at three points (A, B, and C) that form a line parallel to the direction of groundwater flow and that are located in the anaerobic core of the BTEX plume where contaminant concentrations are the highest (Table C.3.13, Figure C.3.4), complete the following:

1) Correct the observed total BTEX concentration for the effects of dispersion, dilution, and sorption.
2) Estimate the change in BTEX concentration due to biodegradation between points A and B and B and C.
3) Calculate the percent of BTEX lost between points A and B and B and C due to biodegradation.

Table C.3.13

Percent BTEX Lost to Biodegradation

Compound	Point A Measured Concentration (µg/L)	Point B Measured Concentration (µg/L)	Point B Corrected Concentration[a/] (µg/L)	Change in Concentration via Biodegradation (µg/L)	Percent Lost to Biodegradation[b/] Between A and B	Point C Measured Concentration (µg/L)	Point C Corrected Concentration[a/] (µg/L)	Change in Concentration via Biodegradation (µg/L)	Percent Lost to Biodegradation Between B and C
benzene	5,600	4,260	4,260	1,340	100	6	7	4,253	100
toluene	5,870	3,910	3,910	1,960	100	18	22	3,888	100
ethylbenzene	955	816	816	139	100	103	126	690	97
xylene	9,050	7,350	7,350	1,700	100	1,555	1,904	5,446	94
total BTEX	21,475	16,336	16,336	5,139	100	1,682	2,059	14,277	97
trimethylbenzene	417	485	417	0	0	396	485	0	0

a/ See text for calculation of corrected concentration.

b/Percent Lost to Biodegradation = $((Measured_A - Corrected_B)/(Measured_A - Measured_B))*100$

Solution:

1) Equation C.3.21 is used to correct the observed total BTEX concentration for the effects of dispersion, dilution, and sorption as follows.

The concentration of TMB goes up between points A and B. This implies that TMB is 100-percent recalcitrant between these points, and therefore suggests that any loss of BTEX is due to biodegradation. Because of this, the corrected BTEX concentration at point B is equal to the measured concentration at point B. The corrected total BTEX concentration at point C is given by:

$$C_{C,Corr} = 1{,}682\frac{\mu g}{L}\left(\frac{485\frac{\mu g}{L}}{396\frac{\mu g}{L}}\right) = 2{,}060\frac{\mu g}{L}$$

If the corrected concentration of a compound at the downgradient location, $C_{B,Corr}$, is greater than the observed concentration of the compound at the upgradient point, C_A, TMB is not a conservative tracer relative to the compound (i.e., the given compound is more biologically recalcitrant between the two points than TMB). This is not the case in this example. At sites where this is the case for total BTEX, TMB cannot be used as a conservative tracer.

2) Equation C.3.22 is used to estimate the amount of BTEX lost to biodegradation between points A and B and B and C.

The amount of BTEX lost to biodegradation between points A and B is:

$$\Delta C_{Bio,AB} = 21{,}475\frac{\mu g}{L} - 16{,}336\frac{\mu g}{L} = 5{,}139\frac{\mu g}{L}$$

The amount of BTEX lost to biodegradation between points B and C is

$$\Delta C_{Bio,BC} = 16{,}336\frac{\mu g}{L} - 2{,}059\frac{\mu g}{L} = 14{,}277\frac{\mu g}{L}$$

In some cases, the corrected concentration of a compound at the downgradient location will be greater than the observed concentration of the compound at the upgradient point. When this is the case, the amount of BTEX lost to biodegradation between two points will be a negative number. This is not the case in this example. When this is the case, TMB is not a conservative tracer relative to the compound (i.e., the given compound is more recalcitrant between the points than TMB). In situations where this is the case for total BTEX, TMB cannot be used as a conservative tracer.

3) Equation C.3.23 is used to calculate the percent of BTEX lost between points A and B and B and C due to biodegradation.

The percent of total BTEX lost to biodegradation between points A and B is:

$$\Delta BTEX_{Bio,AB} = \left(\frac{21{,}475\frac{\mu g}{L} - 16{,}336\frac{\mu g}{L}}{21{,}475\frac{\mu g}{L} - 16{,}336\frac{\mu g}{L}}\right) \bullet 100 = 100\%$$

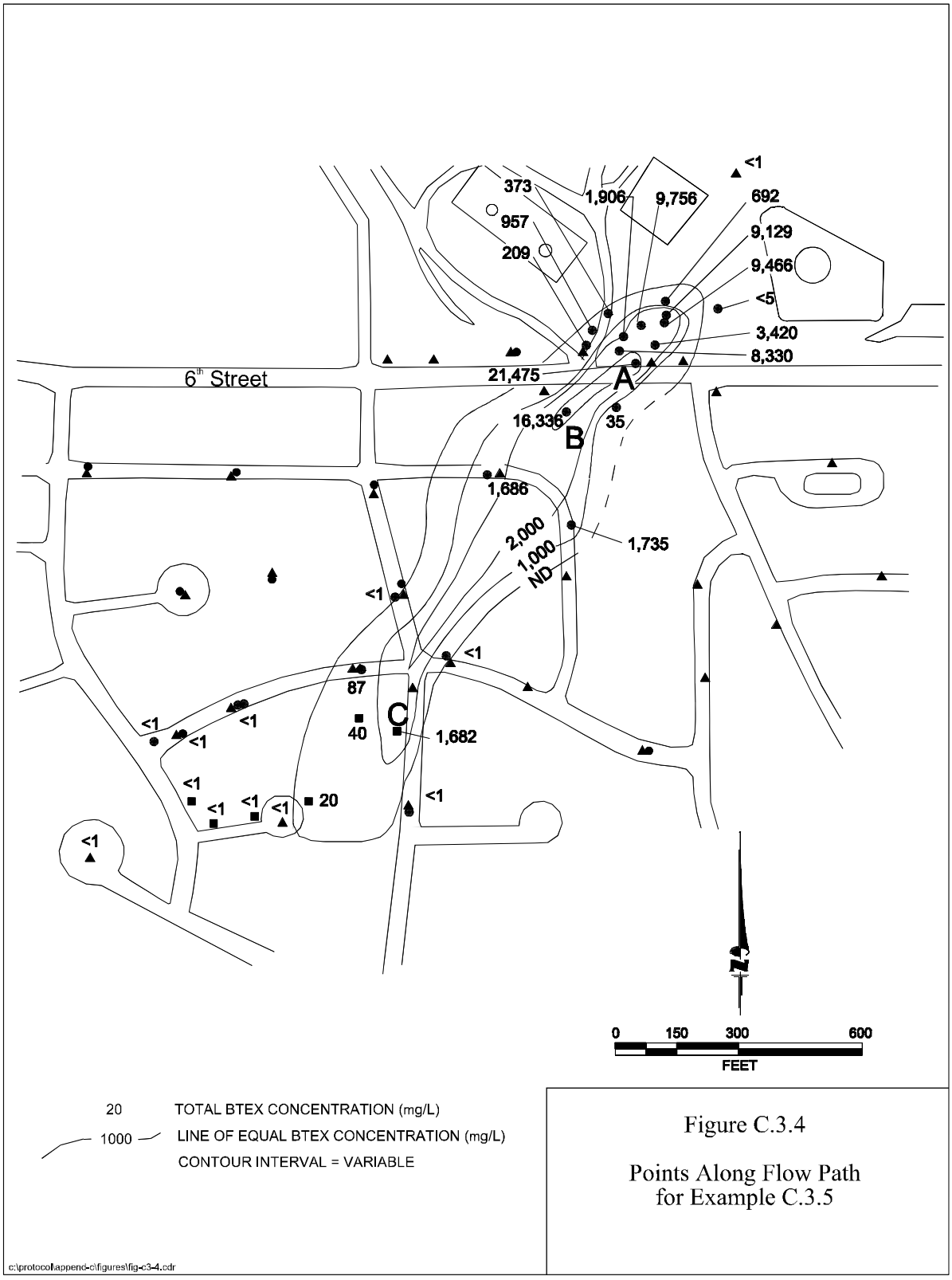


Figure C.3.4

Points Along Flow Path
for Example C.3.5

C3-33

The percent of total BTEX lost to biodegradation between points B and C is:

$$\Delta BTEX_{Bio,BC} = \left(\frac{16{,}336 \frac{\mu g}{L} - 2{,}059 \frac{\mu g}{L}}{16{,}336 \frac{\mu g}{L} - 1{,}682 \frac{\mu g}{L}} \right) \bullet 100 = 97\%$$

In some cases, the corrected concentration of a compound at the downgradient location will be greater than the observed concentration of the compound at the upgradient point. When this is the case, the percentage of BTEX lost to biodegradation between two points will be a negative number. This is not the case in this example. When this is the case, TMB is not a conservative tracer relative to the compound (i.e., the given compound is more recalcitrant between the points than TMB). In situations where this is the case for total BTEX, TMB cannot be used as a conservative tracer.

C.3.3.3 Mass Balance Calculations

Based on the stoichiometric relationships presented in Appendix B, mass balance calculations can be completed for each of the electron acceptors. The results of the mass balance calculations give an indication of the intrinsic capacity of the groundwater to degrade BTEX. The following sections give examples of these mass balance calculations using the data provided in Table C.3.14.

Table C.3.14

Hypothetical Electron Acceptor and Metabolic Byproduct Concentrations

Electron Acceptor or Metabolic Byproduct	Background Concentration (mg/L)	Concentration in Core of Plume (Area with Highest BTEX Concentration) (mg/L)
Dissolved Oxygen	6	0
Nitrate	8	0
Iron (II)	1	51
Sulfate	98	0
Methane	1	12

C.3.3.3.1 Dissolved Oxygen

From a mass balance standpoint, the potential mass of BTEX biodegraded by respiration of dissolved oxygen is given by:

$$BTEX_{Bio,DO} = 0.32(O_B - O_M) \qquad \text{eq. C.3.24}$$

Where: $BTEX_{Bio,DO}$ = reduction in BTEX concentration via aerobic respiration
0.32 = mg/L BTEX degraded per mg/L dissolved oxygen consumed according to the stoichiometry presented in Table B.5.5
O_B = background dissolved oxygen concentration (mg/L)
O_M = lowest measured dissolved oxygen concentration (mg/L)

By knowing the volume of contaminated groundwater, the background dissolved oxygen concentration, and the concentration of dissolved oxygen measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation. For example, groundwater with a background dissolved oxygen concentration of approximately 6.0 mg/L has the capacity to assimilate 1.92 mg/L (1,920 µg/L) of total BTEX.

C.3.3.3.2 Nitrate

From a mass balance standpoint, the potential mass of BTEX biodegraded via denitrification is given by:

$$BTEX_{Bio,N} = 0.21(N_B - N_M) \qquad \text{eq. C.3.25}$$

Where: $BTEX_{Bio,N}$ = reduction in BTEX concentration via denitrification
0.21 = mg/L (average) BTEX degraded per mg/L nitrate consumed according to the stoichiometry presented in Appendix B.
N_B = background nitrate concentration (mg/L)
N_M = measured nitrate concentration (mg/L)

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. For example, groundwater with a background nitrate concentration of approximately 8 mg/L has the capacity to assimilate 1.68 mg/L (1,680 µg/L) of total BTEX during denitrification.

C.3.3.3.3 Iron

From a mass balance standpoint, the potential mass of BTEX biodegraded by iron (III) reduction is given by:

$$BTEX_{Bio,Fe} = 0.05(Fe_M - Fe_B) \qquad \text{eq. C.3.26}$$

Where: $BTEX_{Bio,Fe}$ = reduction in BTEX concentration via iron reduction
0.05 = mg/L (average) BTEX degraded per mg/L iron (II) produced according to the stoichiometry presented in Table B.5.5
Fe_B = background iron (II) concentration (mg/L)
Fe_M = measured iron (II) concentration (mg/L)

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. As an example, consider a site where the groundwater that has a background iron (II) concentration of 1 mg/L. If the highest measured iron (II) concentration within the BTEX plume is 51 mg/L, the groundwater at this site has the capacity to assimilate at least 0.05(51 mg/L - 1 mg/L) = 2.50 mg/L (2,500 µg/L) of total BTEX during iron reduction.

C.3.3.3.4 Sulfate

From a mass balance standpoint, the potential mass of BTEX biodegraded by sulfate reduction is given by:

$$BTEX_{Bio,S} = 0.21(S_B - S_M) \qquad \text{eq. C.3.27}$$

Where: $BTEX_{Bio,S}$ = reduction in BTEX concentration via sulfate reduction
0.21 = mg/L (average) BTEX degraded per mg/L sulfate consumed according to the stoichiometry presented in Table B.5.5
S_B = background sulfate concentration (mg/L)
S_M = measured sulfate concentration (mg/L)

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. For example, if the groundwater at a site has a sulfate concentration of 98 mg/L the potential mass of BTEX that could be degraded by sulfate reduction is 20.6 mg/L (20,600 µg/L).

C.3.3.3.5 Methane

The potential mass of BTEX biodegraded via methanogenesis is given by:

$$BTEX_{Bio,M} = 1.28(M_M - O_B) \qquad \text{eq. C.3.28}$$

Where: $BTEX_{Bio,M}$ = reduction in BTEX concentration via methanogenesis
1.28 = mg/L (average) BTEX degraded per mg/L methane produced according to the stoichiometry presented in Table B.5.5
M_B = background methane concentration (mg/L)
M_M = measured methane concentration (mg/L)

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. As an example, consider a site where the groundwater has a background methane concentration of 1 mg/L. If the highest measured methane concentration within the BTEX plume is 12.0 mg/L, the groundwater at this site has the capacity to assimilate 1.28(12.0 mg/L -1 mg/L) = 14.1 mg/L (14,100 µg/L) of total BTEX during methanogenesis.

C.3.3.3.6 Alkalinity

From a mass balance standpoint, the mass of BTEX biodegraded to produce an increase in alkalinity is given by:

$$BTEX_{Bio,A} = 0.13(A_P - A_B) \qquad \text{eq. C.3.29}$$

Where: $BTEX_{Bio,A}$ = change in BTEX concentration via aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction as reflected by alkalinity
0.13 = mg/L (average) BTEX degraded per mg/L alkalinity produced according to the stoichiometry presented in Section B.5.4
A_B = background alkalinity concentration (as $CaCO_3$, mg/L)
A_P = measured alkalinity (as $CaCO_3$, mg/L) in the plume

By knowing the volume of contaminated groundwater, the background alkalinity, and the alkalinity measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation. As an example, consider a site where the groundwater has a background alkalinity of 430 mg/L. If the highest alkalinity within the BTEX plume is 998 mg/L, the groundwater at this site has accepted carbon dioxide equivalent to an expressed assimilative capacity of 0.13(998 mg/L - 430 mg/L) = 74 mg/L (74,000 µg/L) of total BTEX during aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction.

C.3.3.4 Calculating Rates of Biodegradation

C.3.3.4.1 Instantaneous Reaction

Borden and Bedient (1986) show that the microbially mediated reaction between dissolved oxygen and BTEX can be considered instantaneous relative to normal groundwater flow velocities. Thus, all available dissolved oxygen will be utilized instantaneously, and the change in BTEX concentration resulting from aerobic biodegradation is given by modifying equation C.3.24 to the form:

$$\Delta C_{BTEX} = 0.32(O_B) \qquad \text{eq. C.3.30}$$

Where: ΔC_{BTEX} = change in BTEX concentration [M/L^3]
0.32 = ratio of mass BTEX degraded per unit mass of dissolved oxygen consumed
O_B = background dissolved oxygen concentration

Example C.3.6: Instantaneous Reaction

Aerobic biodegradation is occurring in a sandy aquifer. The measured total BTEX concentration in a unit volume of saturated aquifer material is 10 mg/L. If this same unit volume of aquifer material has a dissolved oxygen concentration of 7 mg/L, what is the resulting total BTEX concentration resulting from aerobic respiration?

Solution:

From equation C.3.30, the mass of total BTEX biodegraded is:

$$\Delta C_{BTEX} = 0.32(7\frac{mg}{L}) = 2.24\frac{mg}{L}$$

Subtracting the change in BTEX concentration caused by the biodegradation reaction gives:

Resulting total BTEX concentration = 10 mg/L - 2.24 mg/L = 7.76 mg/L

C.3.3.4.2 First-Order Decay

As with a large number of processes, the change in solute concentration in the groundwater over time often can be described using a first-order rate constant. In one dimension, first order decay is described by the following ordinary differential equation:

$$\frac{dC}{dt} = kt \qquad \text{eq. C.3.31}$$

Where: C = concentration at time t [M/L^3]
k = overall attenuation rate (first-order rate constant) [1/T]

Solving this differential equation yields:

$$C = C_o e^{-kt} \qquad \text{eq. C.3.32}$$

The overall attenuation rate groups all processes acting to reduce contaminant concentrations and includes advection, dispersion, dilution from recharge, sorption, and biodegradation. To determine the portion of the overall attenuation that can be attributed to biodegradation, these effects must be accounted for, and subtracted from the total attenuation rate. Two methods for determining first-order biodegradation rates at the field scale are presented herein. The first method involves the use of a conservative tracer to compute a decay rate. The second method was derived by Buscheck and Alcantar (1995) and is valid for steady-state plumes. Wiedemeier *et al.* (1995a) compare the use of these two methods. Table C.3.15 lists representative first-order decay rate constants.

Table C.3.15

Representative First-Order Rate Constants

Reference	Anaerobic Decay Rate (week^{-1})
Chapelle (1994)	0.07[a/]
Wilson *et al.* (1994)	1.3[a/]
Wiedemeier *et al.* (1995a)	0.07 to 0.22[a/]
Wiedemeier *et al.* (1995a)	0.20 to 0.30[b/]
Wiedemeier *et al.* (1995a)	0.16 to 0.27[c/]
Wiedemeier *et al.* (1995a)	0.06 to 0.20[d/]
Wiedemeier *et al.* (1995a)	0.04 to 0.20[e/]
Stauffer *et al.* (1994)	0.07[b/] to 0.13[e/]
MacIntyre *et al.* (1994)	0.07 to 0.14[e/]
MacIntyre *et al.* (1994)	0.049 to 0.084[b/]
MacIntyre *et al.* (1994)	0.044 to 0.083[f/]

a/ For total BTEX
b/ For benzene
c/ For toluene
d/ Ethylbenzene
e/ For xylene
f/ For naphthalene

C.3.3.4.2.1 Use of Conservative Tracer

In order to ensure that observed decreases in contaminant concentrations can be attributed to biodegradation, measured concentrations of BTEX must be corrected for the effects of advection, dispersion, dilution from recharge, and sorption, as described in Section C.3.3.2. Substituting the TMB-corrected concentration, $C_{B,corr}$, at a downgradient point (B) for C in equation C.3.32, and the measured concentration, C_A, at an upgradient point (A) for C_o, this relationship becomes:

$$C_{corr} = C_{o,measured} e^{-\lambda t} \qquad \text{eq. C.3.33}$$

Where: C_{corr} = TMB-corrected contaminant concentration at time t at downgradient point
$C_{o,\,measured}$ = measured contaminant concentration at upgradient point
λ = first-order biological decay rate (first-order rate constant) [1/T]

The rate constant in this equation is no longer the total attenuation rate, k, but is the biological decay rate, λ, because the effects of advection, dispersion, dilution from recharge, and sorption have been removed (Section C.3.3.2). This relationship can be used to calculate the first-order biological decay rate constant between two points by solving equation C.3.33 for λ:

$$\lambda = -\frac{\ln\left(\frac{C_{Corr}}{C_{o,measured}}\right)}{t} \qquad \text{eq. C.3.34}$$

The travel time, t, between two points is given by:

$$t = \frac{x}{v_c} \qquad \text{eq. C.3.35}$$

Where: x = distance between two points [L]
v_c = retarded solute velocity [L/T]

Another way to determine the first-order rate constant from a set of TMB-corrected data is to make a log-linear plot of TMB-corrected total BTEX concentration (or the TMB-corrected concentration of a specific compound, such as benzene) versus travel time. If the data plot along a straight line, the relationship is first order and an exponential regression analysis can be performed. The exponential regression analysis gives the equation of the line of best fit for the data being regressed from a log-linear plot and has the general form:

$$y = be^{mx} \qquad \text{eq. C.3.36}$$

Where: y = y axis value
b = y intercept
m = slope of regression line
x = x-axis value

When using TMB as a conservative tracer, y is the contaminant concentration, x is the downgradient travel time from point (A), and m is the biodegradation rate constant, λ. The correlation coefficient, R^2, is a measure of how well the regression relationship approximates the data. Values of R^2 can range from 0 to 1; the closer R^2 is to 1, the more accurate the equation describing the trend in the data. Values of R^2 greater than 0.80 are generally considered good; R^2 values greater than 0.90 are considered excellent. Several commonly available spreadsheets can be used to facilitate the exponential regression analysis. The following example illustrates the use of this technique.

Example C.3.7: First-Order Decay Rate Constant Calculation Using Conservative Tracer

Dissolved BTEX is migrating in a shallow, sandy aquifer that has almost no clay. Seven points along two flow paths parallel to the direction of groundwater flow were chosen for comparison of corrected and observed BTEX concentrations to assess the effects of advection, dispersion, dilution from recharge, and sorption, and to determine biodegradation rate constants (Figure C.3.5). Table C.3.16 contains BTEX and TMB data for these points. One flow path (points A, B, and D) coincides with the highest observed BTEX concentrations, and thus coincides with the observed centerline of the dissolved BTEX plume. The other flow path (points A, B, C, E, F, and G) is located somewhat off the centerline of the plume, closer to the plume periphery. The gradient at the site is 0.046 m/m and the hydraulic conductivity is 0.0084 cm/sec. Assume that the effective porosity is 25 percent. Total organic carbon measured in four soil samples ranges from 0.0069 to 0.0094 percent. Using this information, calculate the first-order decay rate constant for BTEX.

Table C.3.16

BTEX and TMB Data for Examples C.3.7 and C.3.8

Sample Location	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	Xylene (µg/L)	Total BTEX (µg/L)	1,3,5-TMB (µg/L)	1,2,4-TMB (µg/L)	1,2,3-TMB (µg/L)
A	5,600	5,870	955	9,050	21,475	417	1,270	436
B	4,260	3,910	816	7,350	16,336	485	1,310	515
C	458	10	454	765	1,687	125	176	60
D	6	18	103	1,555	1,682	396	433	223
E	7	10	23	47	87	144	143	43
F	0	0	4	36	40	78	159	58
G	0	3	2	15	20	2	5	3

Solution:

An accurate first-order biological decay rate can be calculated only if it can be shown that biodegradation is a first-order process. BTEX concentrations must first be plotted on log-linear paper to ensure that biodegradation is a first order process. Several steps must be completed to make such a plot. The first step is to use TMB and equation C.3.21 to correct measured BTEX concentrations for the effects of dispersion, dilution, and sorption. Table C.3.17 contains TMB-corrected BTEX concentrations. The calculations presented in the table confirm that biodegradation of BTEX is occurring at this site because the TMB-corrected concentrations are greater than the observed concentrations. Section C.3.3.2 and example C.3.5 show how to determine the percentage of BTEX lost to biodegradation. Wiedemeier *et al.* (1995b) discuss the use of TMB-corrected BTEX concentrations to determine the percent-change in BTEX concentrations caused by biodegradation.

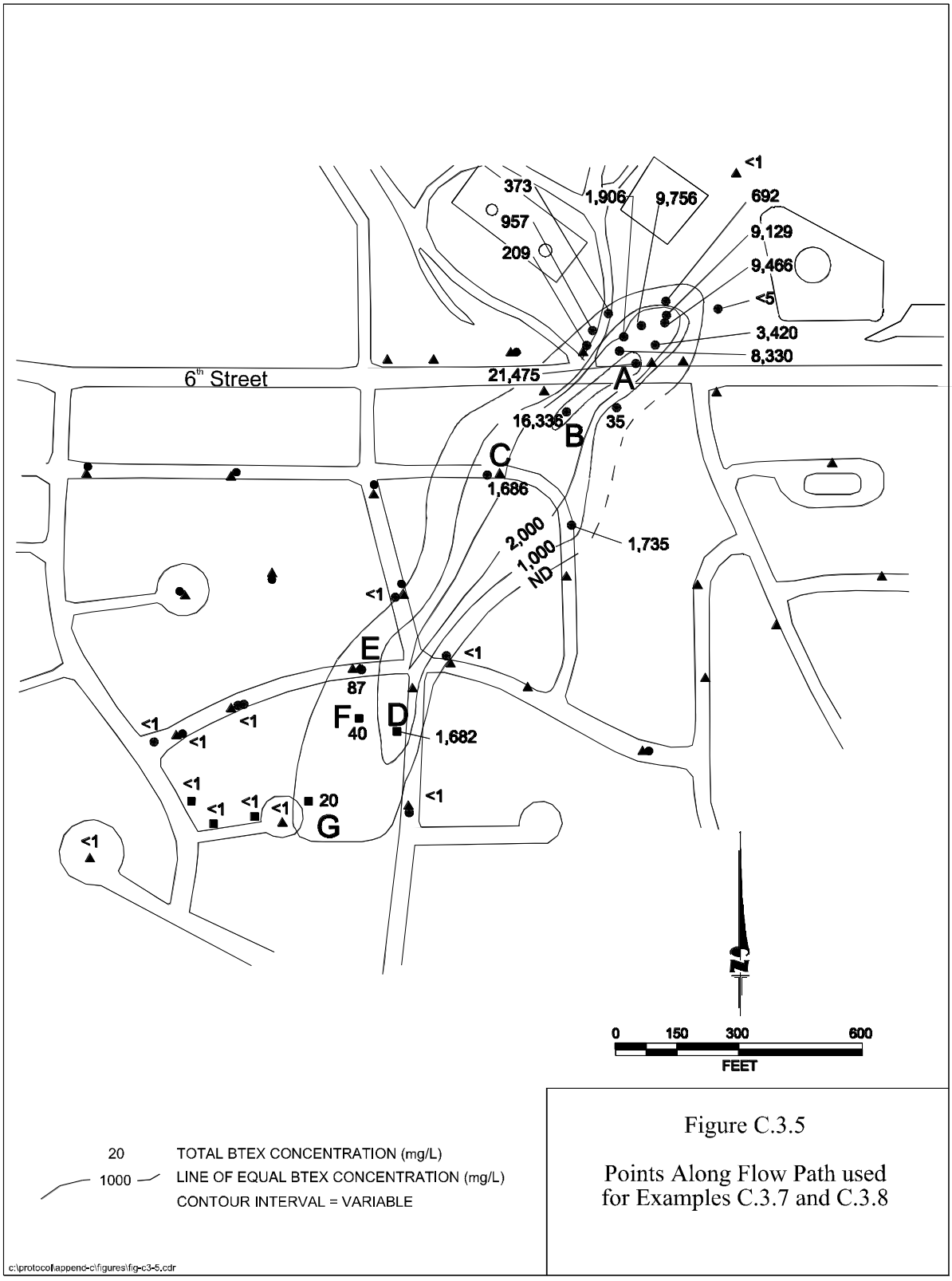


Figure C.3.5

Points Along Flow Path used for Examples C.3.7 and C.3.8

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Table C.3.17

1,3,5-Trimethylbenzene-Corrected Benzene, Toluene, Ethylbenzene, and Xylene Concentrations for Examples C.3.7 and C.3.8

Sample Location	Distance Downgradient (m)	Travel Time from Point A (days)	TMB-Corrected Benzene Concentration (µg/L)	TMB-Corrected Toluene Concentration (µg/L)	TMB-Corrected Ethylbenzene Concentration (µg/L)	TMB-Corrected Xylene Concentration (µg/L)	TMB-Corrected Total BTEX Concentration (µg/L)
A	0	0	5,600	5,870	955	9,050	21,475
B[a/]	67	50	4,260	3,910	816	7,350	16,336
C	137	102	1,777	39	816[b/]	2,967	6,546
D	335	250	7	22	126	1,904	2,060
E[a/]	305	228	7	10	23	47	87
F	335	250	0	0	7	67	74
G	410	306	c/	c/	c/	c/	c/

a/ TMB concentrations increased slightly between points A and B and points C and E. This suggests that 1,3,5-TMB is perfectly recalcitrant to biodegradation between these points, and that observed decreases in BTEX concentrations are due entirely to biodegradation.
b/ Ethylbenzene is more recalcitrant than 1,3,5-TMB between points B and C.
c/ 1,3,5-TMB not recalcitrant between points F and G.

The next step is to determine the retarded solute transport velocity at the site in the area where contaminant and tracer concentration data are available. Because of the low organic carbon concentration (<0.1 percent) and low clay mineral content observed in the shallow saturated zone, retardation of BTEX is not likely to be an important process affecting solute transport at this site, so the retarded solute transport velocity can be assumed to be equal to the groundwater seepage velocity. Using the data presented above, the average groundwater velocity at the site is 1.34 m/day (eq. B.2.1): Using this information it is possible to determine the residence time of the solute between two points using equation C.3.35. Figure C.3.6 is a log-linear plot of TMB-corrected dissolved BTEX concentration *vs.* downgradient travel time along the center-line of the groundwater flow path (path ABD). Figure C.3.7 is a log-linear plot of TMB-corrected total dissolved BTEX concentrations versus downgradient travel time along the flow path ABCEFG. Point G is not included in this figure because TMB was not conservative between points F and G, presumably because dissolved oxygen is present at a concentration of 1.2 mg/L at point G. Dissolved oxygen was not observed in any of the other points used in this example. This suggests that anaerobic processes dominate in the core of the plume. Figures C.3.6 and C.3.7 show that biodegradation along these flow paths is approximated by first-order kinetics.

After the travel time between points has been determined and the total BTEX concentrations have been corrected for the effects of dilution, an exponential regression analysis is performed for each of the BTEX compounds and total BTEX using the plots presented as Figures C.3.6 and C.3.7 using any of the commonly used spreadsheet programs available today. Table C.3.18 shows the results of these regression analyses. These rate constants are within the range indicated in the recent literature (Table C.3.15). Values of R^2 for the regression analyses presented in Table C.3.18 are generally greater than 0.9, indicating a good correlation between the regression analyses and the data.

Figure C.3.6
Plot of Trimethylbenzene-Corrected BTEX Concentration versus Travel Time Along Flow Path ABD

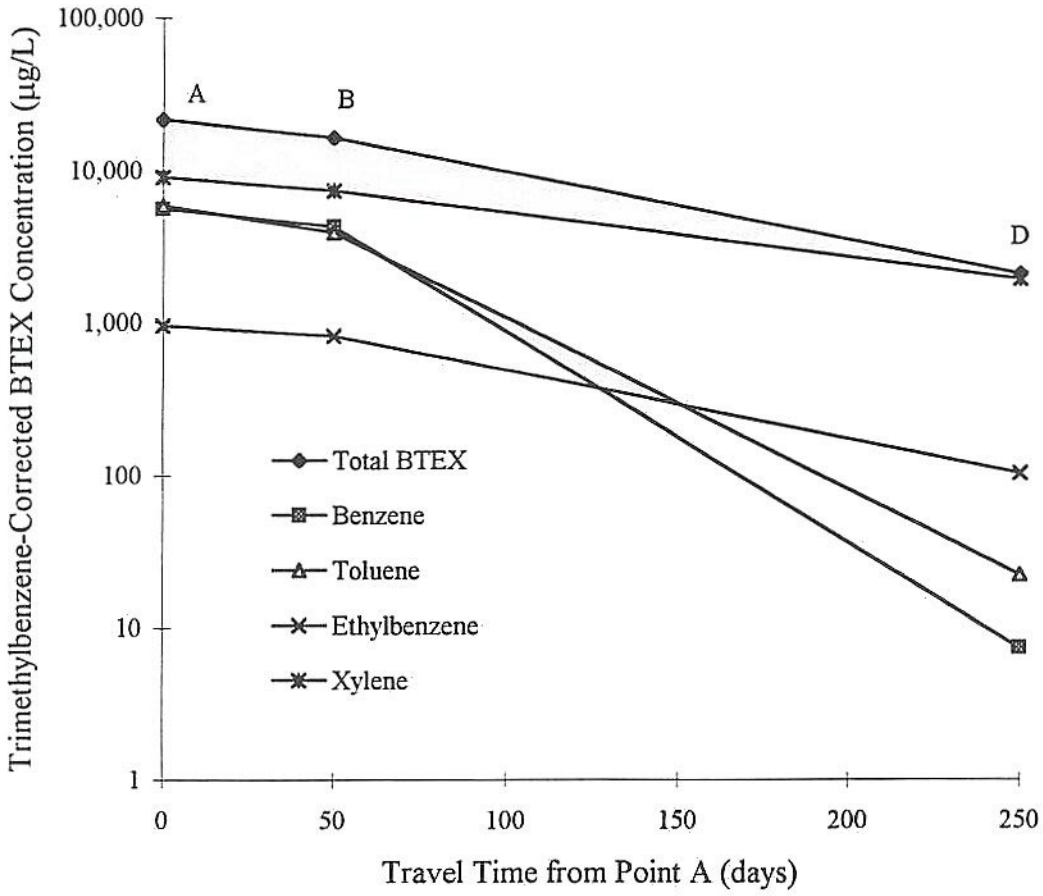

Figure C.3.7
Plot of Trimethylbenzene-Corrected BTEX Concentration versus Travel Time Along Flow Path ABCEFG

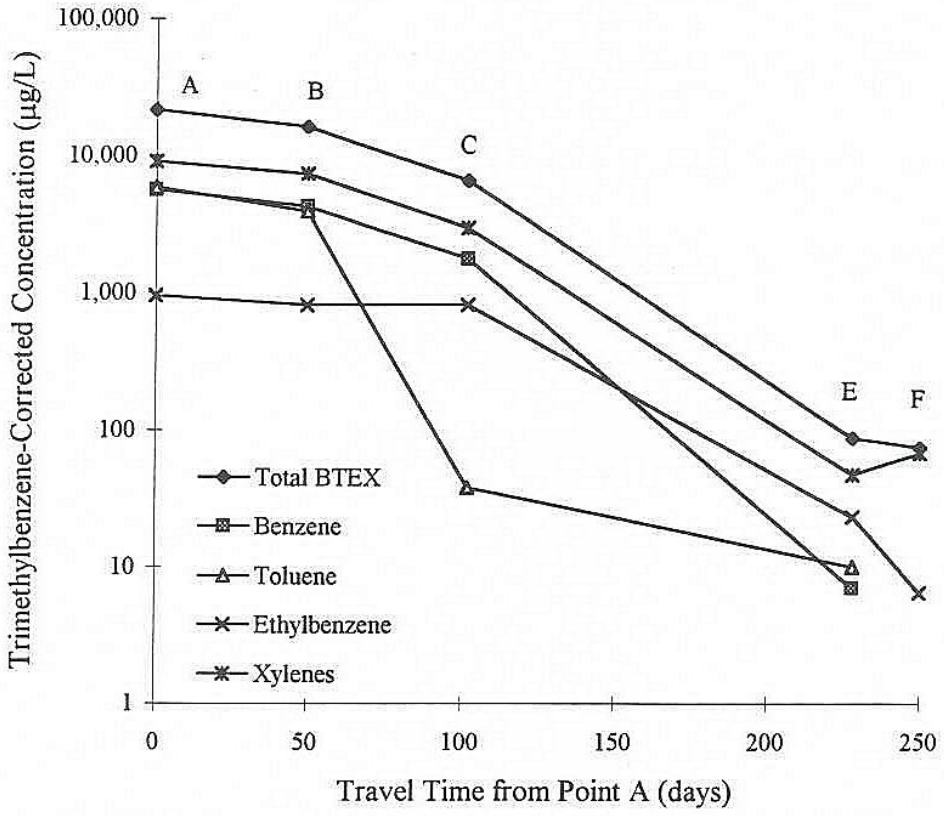

Table C.3.18

Results of Exponential Regression Analyses[a/] using Conservative Tracer

Compound	Calculated y Intercept (b)[a/]	Slope (m)	R^2	Biodegradation Rate Constant[c/] (λ, day^{-1})
Flow Path ABD				
benzene	9,249	-0.028	0.98	0.028
toluene	8,229	-0.023	0.98	0.023
ethylbenzene	1,095	-0.009	0.98	0.009
xylene	9,507	-0.006	0.99	0.006
total BTEX	23,568	-0.010	0.99	0.010
Flow Path ABCEFG[b/]				
benzene	13,948	-0.031	0.92	0.031
toluene	5,465	-0.031	0.84	0.031
ethylbenzene	2,094	-0.021	0.90	0.021
xylene	16,560	-0.023	0.95	0.023
total BTEX	42,091	-0.026	0.96	0.026

a/ General form of the exponential relationship is $y = be^{mx}$ where y = concentration, b = calculated y intercept, m = slope of regression line, and x = travel time.
b/ Point G not used for TMB analysis because TMB not biologically recalcitrant between points F and G.
c/ λ = slope of regression line.

C.3.3.4.2.2 Method of Buscheck and Alcantar (1995)

Buscheck and Alcantar (1995) derive a relationship that allows calculation of first-order decay rate constants for steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation. For a steady-state plume, the first-order decay rate is given by (Buscheck and Alcantar, 1995):

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)\right]^2 - 1\right) \qquad \text{eq. C.3.37}$$

Where: λ = first-order biological decay rate
v_c = retarded contaminant velocity in the x-direction
α_x = dispersivity
k/v_x = slope of line formed by making a log-linear plot of contaminant concentration versus distance downgradient along flow path

Example C.3.8: First-Order Rate Constant Calculation Using Method of Buscheck and Alcantar (1995)

From the data given in Table C.3.16 calculate the first order-decay rate constant due to biodegradation. The locations of the data points are shown in Figure C.3.4. Because of extremely low total organic carbon in the aquifer matrix, and lack of clay minerals, the retarded contaminant velocity, v_c, is assumed to be the same as the advective groundwater velocity (1.34 m/day). A longitudinal dispersivity of 15 m was estimated by using one-tenth of the distance between the spill source and the longitudinal centroid of the plume.

Solution:

The first step is to confirm that the contaminant plume has reached a steady-state configuration. This is done by analyzing historical data to make sure the plume is no longer migrating downgradient and contaminant concentrations are not changing significantly through time. This is generally the case for older spills where the source has not been removed. The next step is to make a log-linear plot of contaminant concentration versus distance downgradient. Figures C.3.8 and C.3.9 present log-linear plots of measured BTEX concentrations versus distance downgradient along flow paths ABD and ABCEFG, respectively using the data presented in Table C.3.16. Using linear regression, the ratio k/v is determined and entered into equation C.3.37. Exponential regressions were completed for each of the BTEX compounds and total BTEX along each flow path using the relationship shown in equation C.3.37. When using the method of Buscheck and Alcantar (1995), y in the regression analysis is the contaminant concentration, x is the distance downgradient from point (A), and m is the ratio k/v. The value of k/v determined from the regression analysis is entered into equation C.3.37 and the biodegradation rate constant, λ, is calculated. Table C.3.19 presents the results of the regression analyses.

Values of R^2 for the regression analyses presented in Table C.3.19 are generally greater than 0.9, and in some cases approach 1.0. Only one regression has an R^2 value less that 0.80. First-order biodegradation rate constants calculated using the method of Buscheck and Alcantar (1995) range from 0.008 day^{-1} (xylene) to 0.038 day^{-1} (benzene) along flow path ABD and range from 0.028 day^{-1} (xylene and ethylbenzene) to 0.042 day^{-1} (benzene) along flow path ABCEFG. This method also shows (like example C.3.7) that benzene is the most readily degraded compound at this site, as indicated by the biodegradation rate. Use of two methods to determine first-order decay rate constants at the field scale is a good check on the accuracy of the calculations.

C.3.3.4.2.3 Comparison of Conservative Tracer Method and Method of Buscheck and Alcantar (1995)

The use of a conservative tracer and the method of Buscheck and Alcantar (1995) provide comparable results in examples C.3.7 and C.3.8. For all of the BTEX compounds, the rate constants calculated using TMB as a tracer are less than those calculated using the method of Buscheck and Alcantar. This suggests that TMB-corrected data can be used to conservatively estimate biodegradation rates, particularly for plumes that have not reached steady-state.

Figure C.3.8
Plot of BTEX Concentration versus Distance Downgradient Along Flow Path ABD

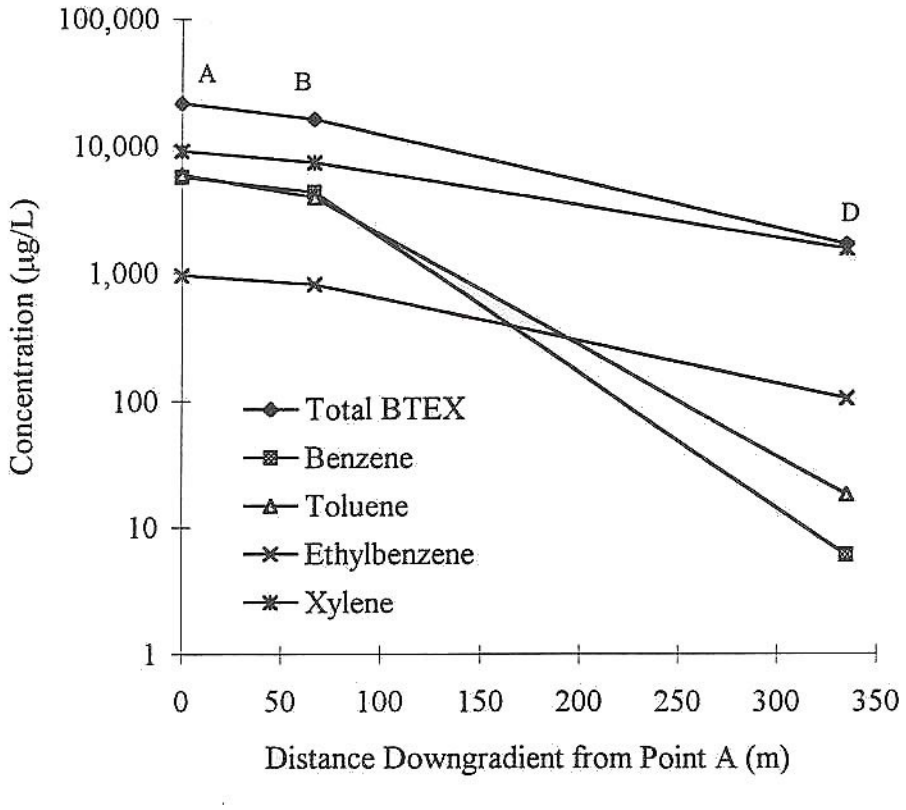

Figure C.3.9
Plot of BTEX Concentration versus Distance Downgradient
Along Flow Path ABCEFG

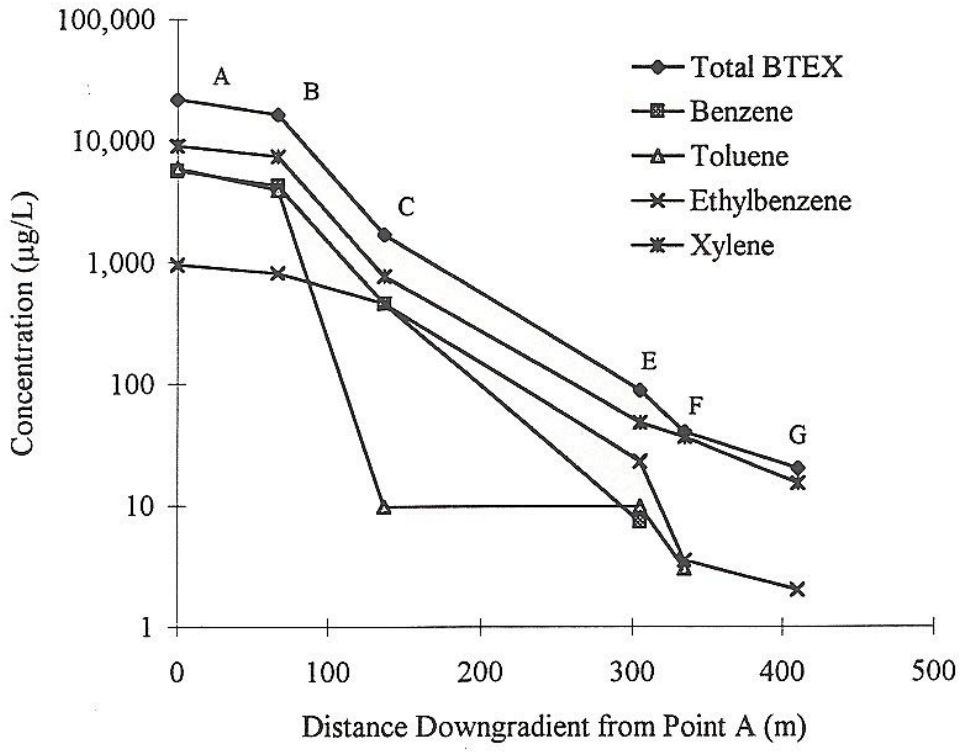

Table C.3.19

Results of Exponential Regression Analyses[a/] using Method of Buscheck and Alcantar (1995)

Compound	Calculated y Intercept (b)[a/]	Slope (m = k/v)	R^2	Biodegradation Rate Constant[b/] (λ, day^{-1})
Flow Path ABD				
benzene	9,430	-0.022	0.98	0.039
toluene	8,390	-0.018	0.98	0.031
ethylbenzene	1,095	-0.007	0.98	0.010
xylene	9,693	-0.005	0.99	0.007
total BTEX	24,028	-0.008	0.99	0.012
Flow Path ABCEFG				
benzene	10,021	-0.023	0.97	0.042
toluene	3,716	-0.022	0.78	0.039
ethylbenzene	1,978	-0.017	0.94	0.029
xylene	11,414	-0.017	0.98	0.029
total BTEX	28,651	-0.019	0.98	0.033

a/ General form of the exponential relationship is $y = be^{mx}$, where y = concentration, b = calculated intercept, m = slope of regression line, and x = distance downgradient.
b/ From equation C.3.37.

C.3.4 DESIGN, IMPLEMENTATION, AND INTERPRETATION OF MICROCOSM STUDIES

C.3.4.1 Overview

If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of intrinsic bioremediation. They are the only "line of evidence" that allows an unequivocal mass balance on the biodegradation of environmental contaminants. If the microcosm study is properly designed, it will be easy for decision makers with non-technical backgrounds to interpret. The results of a microcosm study are strongly influenced by the nature of the geological material submitted to study, by the physical properties of the microcosm, by the sampling strategy, and the duration of the study. In addition, microcosm studies are time consuming and expensive. A microcosm study should only be undertaken at sites where there is considerable uncertainty concerning the biodegradation of fuel hydrocarbons based on soil and groundwater samples alone.

Material for a microcosm study should not be selected until the geochemical behavior of the site is well understood. Contaminant plumes may consume oxygen, nitrate, sulfate, and produce iron II, manganese II, or methane. These processes usually operate concurrently in different parts of the plume. Regions where each process prevails may be separated in directions parallel to groundwater flow by hundreds of meters, in directions perpendicular to groundwater flow by tens

of meters, and vertically by only a few meters. Rate constants and constraints for petroleum hydrocarbon biodegradation will be influenced by the prevailing geochemistry. Material from microcosms must be acquired for depth intervals and locations that have been predetermined to be representative of the prevailing geochemical milieu in the plume.

Hydrocarbon biodegradation supported by oxygen and nitrate can not be adequately represented in microcosm. In the field, organisms that use oxygen or nitrate proliferate until they become limited by the supply of electron acceptor. After that time, the rate of hydrocarbon degradation is controlled by the supply of electron acceptor through diffusion or hydrodynamic dispersion. Microcosms have been used successfully to simulate sulfate-reducing, iron-reducing, and methanogenic regions of plumes. Oxygen is toxic to sulfate-reducing and methanogenic microorganisms. Material should be collected and secured in a manner that precludes oxygenation of the sample.

Batch microcosms that are sacrificed for each analysis usually give more interpretable results than column microcosms or batch microcosms that are sampled repetitively. For statistical reasons, at least three microcosms should be sampled at each time interval. If one assumes a first order rate law, and no lag, a geometrical time interval for sampling should be the most efficient. An example would be sampling after 0 weeks, 2 weeks, 1 month, 2 months, 4 months, and 8 months. As a practical matter, long lags frequently occur, and the rate of bioremediation after the lag is rapid. A simple linear time scale is most likely to give interpretable results.

The batch microcosms should have approximately the same ratio of solids to water as the original material. Most of the microbes are attached to solids. If a microcosm has an excess of water, and the contaminant is mostly in the aqueous phase, the microbes must process a great deal more contaminant to produce the same relative change in the contaminant concentration. The kinetics at field scale would be underestimated.

Microcosms are inherently time consuming. At field scale, the residence time of a plume may be several years to decades. Slow rates of transformation may have a considerable environmental significance. A microcosm study that lasts only a few weeks or months may not have the resolution to detect slow changes that are still of environmental significance. Further, microcosms often show a pattern of sequential utilization, with toluene and the xylenes degrading first, and benzene and ethylbenzene degrading at a later time. Degradation of benzene or ethylbenzene may be delayed by as much as a year.

As a practical matter, batch microcosms with an optimal solids to water ratio, sampled every 2 months in triplicate for up to 18 months, can resolve biodegradation from abiotic losses with a rate detection limit of 0.001 to 0.0005 per day. Many plumes show significant attenuation of contamination at field-calibrated rates that are slower than the detection limit of today's microcosm technology. The most appropriate use of microcosms is to document that contaminant attenuation is largely a biological process. Rate constants for modeling purposes are more appropriately acquired from field-scale studies.

C.3.4.2 Case Study on a Gasoline Spill at Arvida, North Carolina

One of the best case studies comparing field scale processes and microcosms is still underway. Prepublication material on the study was generously supplied on February 14, 1995 by Melody J. Hunt, Morton A. Barlaz, and Robert C. Borden at North Carolina State University. Their study will be used to illustrate the most recent practices for using microcosms to simulate BTEX plumes.

C.3.4.2.1 Material and Methods

C.3.4.2.1.1 Sediment and Groundwater Collection

Three separate cores of aquifer sediment were obtained at a site in Rocky Point, NC: one near the source area (RP0), one approximately halfway between the source area and the end of the plume boundaries (RP150), and one near the end of the detected plume boundaries (RP300) (Figure C.3.10). All sediment was obtained under strictly anaerobic conditions by drilling below the water table with a hollow-stem auger, and advancing a sterile coring tube. The tube was brought to the surface, immediately capped with sterile butyl rubber stoppers and transported to the laboratory on ice, where it was extruded in an anaerobic glovebox under nitrogen atmosphere within 12 hours. The first and last 1.00 centimeter of soil were removed, and the outer portions of the soil pared away. The remaining sediment was anaerobically transferred into sterile mason jars and stored at $4^{o}C$. Prior to use, soil from each core was mixed and passed through a No. 8 sieve in an anaerobic chamber.

Anaerobic groundwater was collected at the time of sediment removal from adjacent wells screened at the same depth interval as the borehole from which the sediment was recovered. The dissolved oxygen, pH, Eh, and temperature of the groundwater were measured at the time of collection. The water was pumped from the well using a Waterra pump through a closed

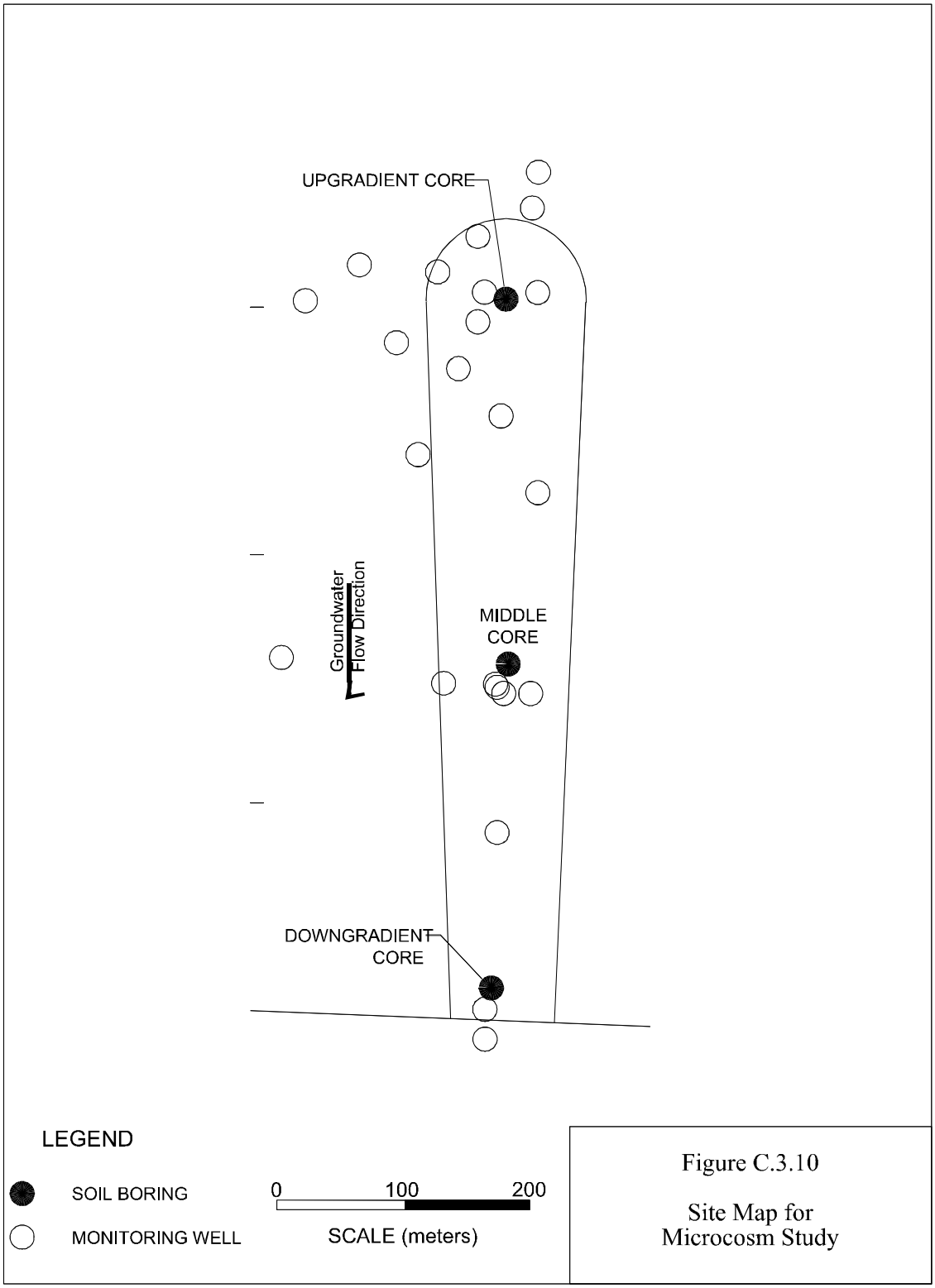

Figure C.3.10

Site Map for Microcosm Study

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system of polyethylene tubing equipped with a 0.45-micron filter, and collected in a nitrogen-sparged, 2.3-L (80-ounce) bottle. The collection bottle was sealed with a two-holed rubber stopper connected to a second nitrogen-sparged bottle, which released pressure as water entered the collection bottle and prevented air from entering the system on the backstroke of the pump. Well headspace was continually sparged with argon during collection. The water was transported on ice to the laboratory where it was stored at 4°C prior to use. All equipment and containers coming into contact with the water and sediment were pre-sterilized.

C.3.4.2.1.2 Microcosm Construction

The study objective was to simulate ambient conditions to the maximum extent possible. Multiple replicate microcosms were prepared within 2 weeks of sample collection for each of the three locations. Microcosms were constructed in a Coy anaerobic chamber. The microcosms contained 35 gm wet sediment and 16 mL groundwater (dry soil:water=1.8 g/mL). All of the microcosms were spiked with a stock solution containing sterile anaerobic deionized water, resazurin (0.0002 percent final concentration), benzene, toluene, ethylbenzene, o-xylene, and m-xylene (BTEX) to yield final concentrations representative of field conditions. BTEX concentration ranged from 10 to 20 micromoles (µM). Anaerobic water was prepared by boiling deionized water under a nitrogen headspace. The water was then autoclaved for 20 minutes at 121°C. After addition of the spike solution(s), the microcosms were filled with groundwater to eliminate all headspace, and sealed with a teflon lined, grey butyl rubber stopper (West Co., Lititz, PA) and an aluminum crimp.

Abiotic controls were amended with 1 to 2 millimoles (mM) mercuric chloride and autoclaved at 250°C for 30 minutes on two consecutive days prior to addition of the BTEX spike solution. A second set of abiotic controls contained autoclaved groundwater, mercuric chloride, resazurin, and BTEX, but no aquifer material. These latter microcosms enabled differentiation between sorption to aquifer material and sorption-diffusion into the stopper. All manipulations were performed in an anaerobic chamber. All bottles, caps, and instruments coming in contact with the sediment or water were autoclaved prior to use. All microcosms were incubated in the dark at 16°C in anaerobic incubation jars with oxygen scavenging catalyst envelopes (BBL Gas Pak Jar System, Fisher Scientific, Raleigh, NC) and dry redox indicator strips. The incubation jars were evacuated and refilled with nitrogen three times after removing microcosms for sampling. Triplicate live and abiotic microcosms were destructively sampled at monthly intervals for approximately 1 year. Results are presented as the average of three destructively sampled microcosms measured at each time point.

C.3.4.2.1.3 Aqueous Sampling and Analyses

The microcosms were sampled in the anaerobic chamber by simultaneously removing approximately 2.0 mL of free liquid in a gas-tight syringe while puncturing the stopper with a needle so that a vacuum did not develop. The first 1.0 mL was injected into a 10 mL vial sealed with a black butyl rubber stopper (Geomicrobial Technologies, Inc., Ochelata, OK). The vials were then inverted to minimize losses and stored at 4^{o}C for methane analysis (performed within 48 hours). To prepare a sample for methane analysis, 3.0 mL of high purity deionized water was injected to pressurize the vial slightly. Next, a 1.0 mL headspace sample was removed from the vial using a gas-tight syringe and immediately injected into a Shimadzu 9A GC equipped with a 1.5 m by 3.2 mm stainless steel column packed with Hayesep T 100/120 mesh (Altech, Deerfield , IL) and an FID. The dissolved concentration of methane in a microcosm was calculated using Henry's Law constants and assuming that all dissolved methane in the 1.0 mL aliquot volatilized in the sampling vial. Between 0.25 and 1.0 mL of the remaining 1.0 mL of sample from the microcosm was placed in a closed test tube and diluted to 5 mL for BTEX analysis. BTEX analysis was performed in accordance with USEPA Method 602 using a Tekmar® Purge-and-Trap Model LSC 2000 and a Perkin Elmer® Model 900 auto system or Perkin Elmer® 8500 Gas Chromatograph equipped with a 75m DB-624 Megabore capillary column (J & W Scientific, Folsom, CA) and a flame ionization detector. Measurements of dissolved iron, total sulfur, sulfate, thiosulfate, and sulfite were obtained by passing 3 mL of remaining liquid in the microcosm through a 0.2-micron filter (Gelman Sciences, Ann Arbor, MI) into separate vials containing 0.5N HCL. Samples were stored at 4^{o}C and analyzed within 2 weeks of BTEX sampling. Iron and total sulfur were analyzed using Perkin Elmer® II plasma coupled argon emission spectrometer (AES ICP). Sulfate, thiosulfate, and sulfite were analyzed by ion chromatography. The aqueous concentrations of BTEX and the inorganics were determined by comparing peak areas in samples with those of external standards. The pH of the microcosms was measured in the anaerobic chamber after liquid was removed for all other dissolved analysis.

C.3.4.2.1.4 Results

Comparison of the attenuation of benzene and toluene in microcosms constructed from material from the midpoint of a plume of BTEX undergoing iron reduction shows that toluene has been largely depleted at the midpoint of the plume, but is present in material immediately upgradient. Toluene attenuated rapidly and without a lag. Toluene also attenuated in the abiotic control. This represents loss from solution due to diffusion through the septum of the microcosm, and sorption to the microcosm solids. The attenuation of benzene was not different from the controls for at least 180 days, then benzene attenuated to trivial concentrations over the next 220

days. The rate of attenuation of benzene and toluene in the abiotic controls were very similar, indicating that removal was truly due to an abiotic process (Figure C.3.11).

Figure C.3.12 presents data on microcosms constructed from the end-point of the plume. The residence time between the mid-point and end-point samples is approximately 6 years. Toluene is entirely depleted in groundwater at this location. Notice that the degradation of toluene is much slower than in microcosms constructed from the mid-point samples. Toluene attenuation is not different from the control until after day 70. This material was not preacclimated to toluene, because there was no significant exposure to toluene in the field. Benzene attenuation was not different from its control until toluene was depleted, then its concentration was reduced to low levels. The attenuation in the controls at the end point of the plume was very similar to attenuation in the controls at the mid-point, suggesting that the mechanisms that attenuate the organics in the controls act very uniformly.

Microcosms constructed from material collected from the source area showed no evidence of biological attenuation (Figure C.3.13). It is possible that microorganisms at this location have failed to acclimate to anaerobic biodegradation. It is also possible that soluble electron acceptors, such as oxygen, nitrate, and sulfate have been depleted, and long term exposure to the BTEX has exhausted the supply of iron minerals available for iron reduction.

Figure C.3.14 illustrates frequently seen responses in microcosm studies. Notice that the concentration of benzene in the microcosms containing sediment actually appears to increase in the initial sampling intervals. This effect is not well understood, but is very commonly seen. Also notice that the rate of attenuation in the microcosms containing only water is slower than the living but inactive microcosms, which in turn are slower than the abiotic control with sediment. This indicates that the sediment is actively sorbing benzene from water, and that sorption is stronger in the autoclaved control. This effect reduces the sensitivity of the microcosm assay, but is a conservative error.

BTEX Removal Rates: Effective first-order removal rates for BTEX were estimated using the equation $C=C_0e^{-kt}$, where k is the apparent first-order decay rate (T^{-1}), t is time, and C_0 is the initial concentration. Decay rates were calculated over the time period in which biological losses were observed. The rate of biological loss is represented as the difference between the decay rates in the live and abiotic microcosms taken over the time period of measured loss.

Figure C.3.11
Benzene and Toluene Attenuation at Midpoint of the Plume

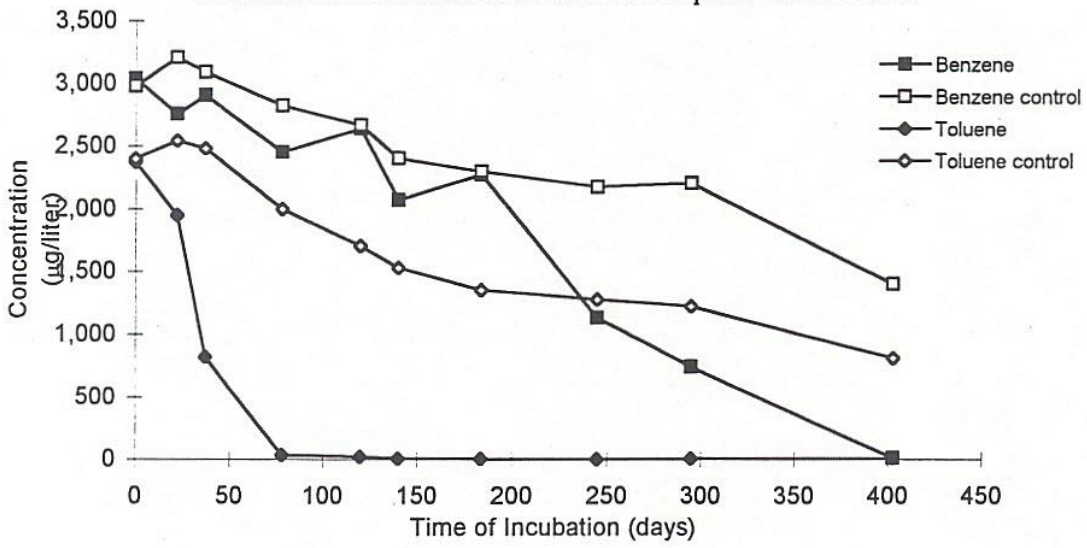


Figure C.3.12
Benzene and Toluene Attenuation at Downgradient End of Plume

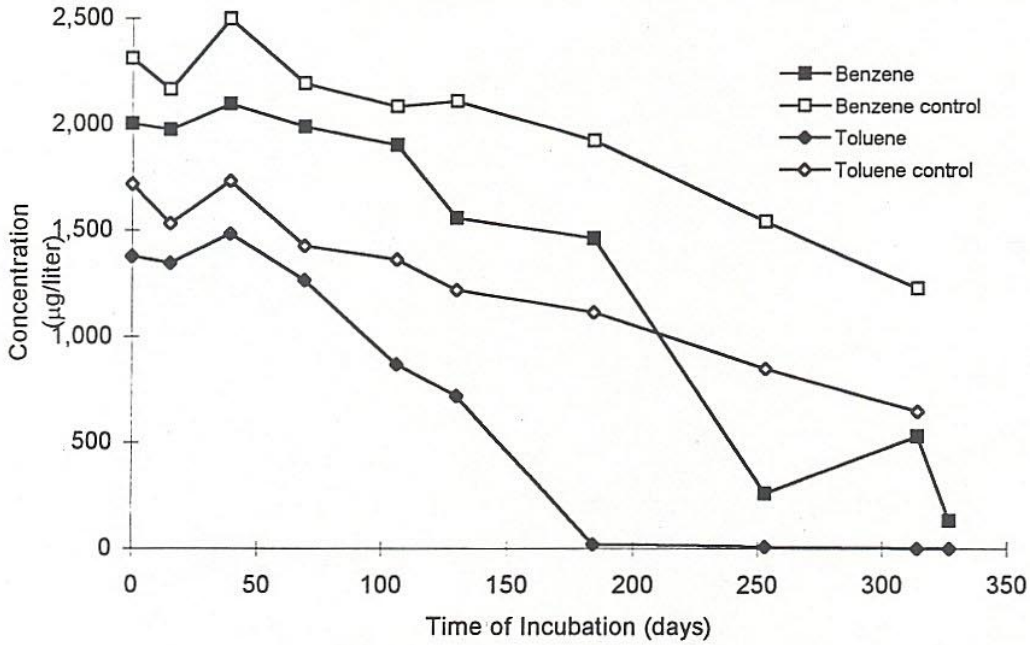


Figure C.3.13
Attenuation of Benzene and Toluene in the Source Area

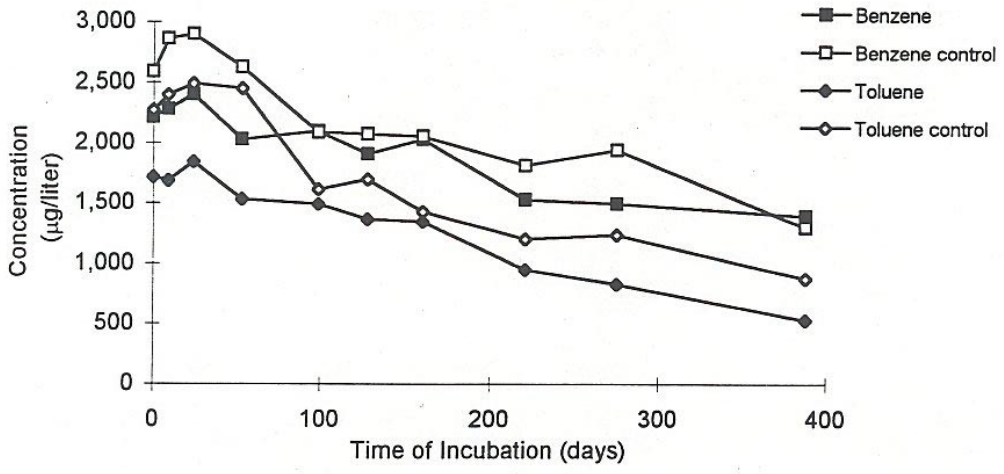
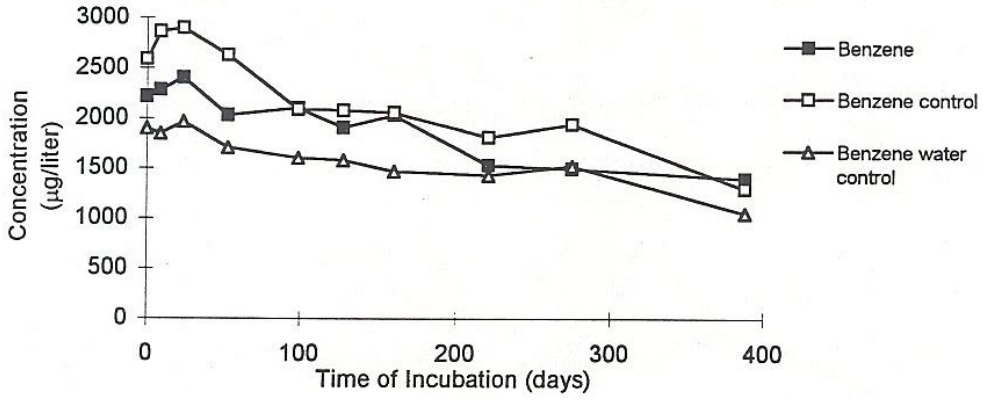


Figure C.3.14
Benzene Depletion in Live Microcosm and Two Controls



The microcosm decay rates are compared to field-measured intrinsic remediation rates in Table C.3.20. The rate constants in the microcosms were much greater than rates actually 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.

Table C.3.20

Microcosm *vs.* Field BTEX Intrinsic Remediation Rates

Compound	**Microcosms**[a/]			**Field**[b/]
	Live Microcosms	Control Microcosms	Biological Loss	
	First-Order Rate Constant (per day)			
Benzene	0.0258	0.0021	0.0237	0.0002
Toluene	0.0489	0.0043	0.0446	0.0021
Ethylbenzene	0.0056	0.0037	0.0019	0.0015
o-Xylene	0.0611	0.0052	0.0559	0.0011
m+p-Xylene				0.0013
m-Xylene	0.0234	0.0030	0.0204	

a/ From Hunt *et al.* (1995)

b/ From Borden *et al.* (1994)

SECTION D-1

INTRODUCTION

Prediction of the migration and degradation of a dissolved contaminant plume using a solute transport model is an important component of the intrinsic remediation demonstration. In order for a model to adequately predict the fate and transport of a dissolved hydrocarbon plume, it must be capable of modeling solute transport under the influence of advection, dispersion, sorption, and biodegradation. Models used to simulate groundwater flow and solute transport can be classified according to the mathematical technique used to solve the governing partial differential equation. Analytical solutions and numerical solutions are the two mathematical techniques most commonly used to solve the advective-dispersive equation. The following sections describe the mathematical relationships that describe one-, two-, and three-dimensional solute transport and the numerical techniques used to solve these relationships. Also included is a discussion of analytical and numerical models and model selection. Finally, consideration is given to whether or not a model is necessary to successfully implement intrinsic remediation at a given site.

D.1.1 MATHEMATICAL EXPRESSIONS USED TO DESCRIBE SOLUTE TRANSPORT AND INTRINSIC REMEDIATION

The mathematical relationships that describe groundwater flow and solute transport are based on the equation of continuity and Darcy's Law. Combination of these relationships for transient conditions yields a parabolic partial differential equation. Combination of these relationships for steady-state conditions yields an elliptical partial differential equation. The following sections present the one-, two-, and three-dimensional partial differential equations that describe solute transport by the processes of advection, dispersion, sorption, and biodegradation. Several texts derive these equations (Bear, 1972; Freeze and Cherry, 1979; Bedient *et al.*, 1994; Segol, 1994).

D.1.1.1 One-Dimensional Reactive Solute Transport

The one-dimensional partial differential equation describing transient solute transport with first-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.1}$$

Where: C = solute concentration
t = time
D_x = hydrodynamic dispersion along flow path
x = distance along flow path
v_x = groundwater seepage velocity in x direction
R = coefficient of retardation
λ = first-order biological decay rate constant

This is a parabolic partial differential equation. Under steady-state conditions, the change in contaminant concentration with respect to time becomes zero, leaving the elliptical partial differential equation:

$$0 = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.2}$$

D.1.1.2 Two-Dimensional Reactive Solute Transport

The two-dimensional partial differential equation describing transient solute transport with first-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.3}$$

Where: C = solute concentration
t = time
D_x = hydrodynamic dispersion along flow path
D_y = hydrodynamic dispersion transverse to flow path
x = distance along flow path
y = distance transverse to flow path
v_x = groundwater seepage velocity in x direction
R = coefficient of retardation
λ = first-order biological decay rate constant

This is a parabolic partial differential equation. Under steady-state conditions, the change in contaminant concentration with respect to time becomes zero, leaving the elliptical partial differential equation:

$$0 = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.4}$$

D.1.1.3 Three-Dimensional Reactive Solute Transport

The three-dimensional partial differential equation describing transient solute transport with first-order biodegradation in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R}\frac{\partial^2 C}{\partial z^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.5}$$

Where: C = solute concentration
t = time
D_x = hydrodynamic dispersion along flow path
D_y = hydrodynamic dispersion transverse to flow path
D_z = vertical hydrodynamic dispersion
x = distance along flow path
y = distance transverse to flow path
z = vertical distance transverse to flow path
v_x = groundwater seepage velocity in x direction
R = coefficient of retardation
λ = first-order decay rate constant

This is a parabolic partial differential equation. Under steady-state conditions, the change in contaminant concentration with respect to time becomes zero, leaving the elliptical partial differential equation:

$$0 = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R}\frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R}\frac{\partial^2 C}{\partial z^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. D.1.6}$$

D.1.2 ANALYTICAL VERSUS NUMERICAL MODELS AND MODEL SELECTION

Partial differential equations that describe solute transport can be solved analytically or numerically. Analytical methods (models) provide exact, closed-form solutions, and numerical methods (models) provide approximate solutions. The type of model selected to simulate site conditions will depend on the results of data review and conceptual model development. Solute transport modeling is both an art and a science. The "art" involves the ability to select the most reasonable set of assumptions that will yield a model that is not too complex to be solved by available mathematical techniques, yet is sufficiently detailed to accurately represent the system being modeled. A balance between simplifying assumptions and actual subsurface conditions must be reached to allow successful simulation of contaminant fate and transport.

Analytical solutions provide exact, closed-form solutions to the governing advection-dispersion equation by making significant simplifying assumptions. The more closely the actual system

approximates these assumptions, the more accurate the analytical model will be in predicting solute fate and transport. Analytical solutions are continuous in time and space and provide information on the temporal and spatial distribution of hydraulic head or solute concentrations for the governing initial and boundary conditions. The main advantage of analytical solutions is that they are simple to use and they provide a good first approximation of solute transport in relatively simple hydrogeologic settings. Analytical solutions are generally limited to steady, uniform flow or radial flow, and should not be used for groundwater flow or solute transport problems in strongly anisotropic or heterogeneous media. In some cases, such as where potential receptors are a great distance away, or where the aquifer is extremely homogeneous and isotropic, the analytical solution may adequately describe contaminant fate and transport. At a minimum, analytical models are useful for conceptual model development and can aid in siting additional data collection points. The analytical solutions of the advective-dispersive equation presented herein give solute concentration as a function of time and distance from the source of contamination. Analytical solutions are sometimes used to verify the accuracy of numerical solutions. This is done by applying both the exact analytical solution and the numerical solution to the same groundwater flow system and comparing the results. Several well-documented and widely accepted analytical models are available for modeling the fate and transport of fuel hydrocarbons under the influences of advection, dispersion, sorption, and biodegradation. The use of analytical solute transport models is described in Section D-3.

Analytical models are used to estimate the impacts of contamination on a site given the qualifying assumptions used to develop the model. Analytical models are best utilized for order-of-magnitude results because a number of potentially important processes are treated in the model in an approximate manner, or are ignored completely. For example, analytical models may include terms describing a variety of chemical and hydrological processes, but usually are not capable of incorporating subsurface heterogeneity. Because of the nature of the simplifying assumptions, analytical models may overestimate the spread of contamination. This makes the model predictions conservative. The more conservative a model is, the more confidence there should be that potential receptors will not be impacted by site contamination. This will aid in implementation of intrinsic remediation.

Numerical solutions provide approximate solutions to the advection-dispersion equation. Numerical solutions are particularly useful for complex groundwater flow and contaminant transport systems having irregular geometry and significant aquifer heterogeneity. Many of the assumptions required for the analytical solutions are not necessary when numerical techniques are used to solve the governing solute transport equation. Several well-documented and widely

accepted numerical models are available for modeling the fate and transport of fuel hydrocarbons dissolved in groundwater under the influences of advection, dispersion, sorption, and biodegradation. Numerical fate and transport models are described in Section D-4.

Figure D.1.1 shows a decision process that can be used to determine if an analytical or a numerical model is most appropriate to simulate site conditions. The specific modeling objectives of the project, the available data, and the conceptual model should be the primary factors governing model selection. Much of the success of solute fate and transport modeling lies in the ability to properly conceptualize the processes governing contaminant transport, to select a model that simulates the most important processes at a site, and to achieve reasonable model predictions. Any model used for an intrinsic remediation demonstration should be properly validated through sufficient previous application at a variety of field sites.

Subsurface contaminant transport models incorporate a number of theoretical assumptions about the natural processes governing the transport and fate of contaminants. All modeling involves simplifying assumptions concerning parameters of the physical and chemical system that is being simulated. These parameters will influence the type and complexity of the equations that are used in the model to represent the system mathematically. Relatively simple analytical models may be useful to define the possible magnitude of a contaminant problem. Analytical models provide exact solutions, but employ simplifying assumptions to provide tractable solutions. If limited data are available, or the hydrogeologic conditions are simple, an analytical model can be selected to simulate contaminant fate and transport. If an analytical model is selected to perform the modeling, basic source, aquifer hydraulic, and chemical parameters are entered into the model. The basic parameters typically include groundwater seepage velocity, hydraulic conductivity, saturated thickness of the aquifer, porosity, source area configuration and contaminant concentrations, leakage rates, dispersion coefficients, retardation values, and decay rates.

Numerical models are less burdened by simplifying assumptions and are capable of addressing more complicated problems. However, they require significantly more data, and their solutions are inexact numerical approximations. Numerical models require input parameters similar to those used for analytical models, but their spatial distribution must be known to make the use of a numerical model warranted. Unlike analytical models, numerical models allow subsurface heterogenieties and varying aquifer parameters to be simulated if the requisite data are available.

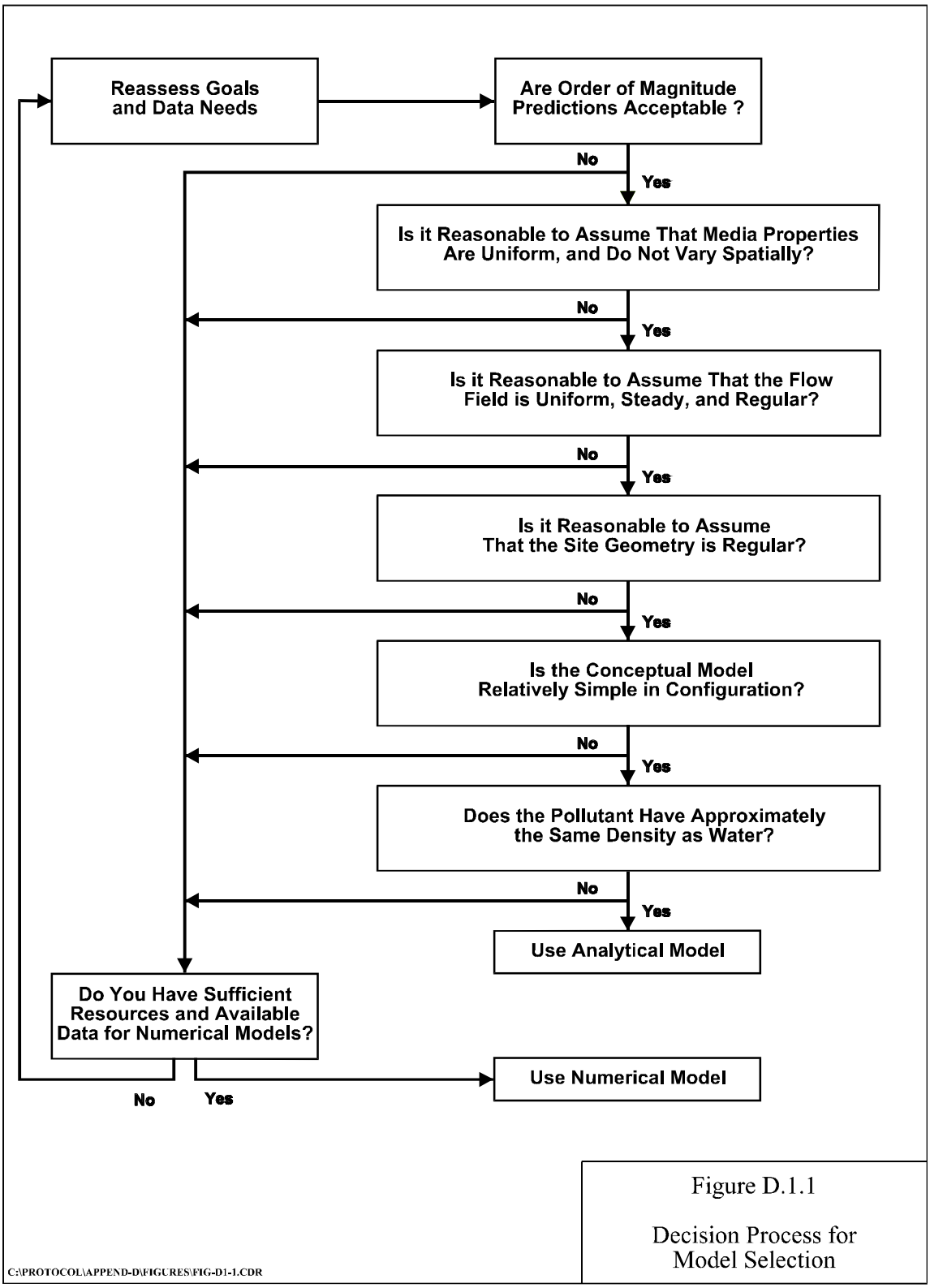


Figure D.1.1

Decision Process for Model Selection

D1-6

Numerical models require a reasonably good understanding of the three-dimensional distribution of both aquifer hydraulic properties and the contaminants. Implementation of a numerical model is much more complex than implementation of an analytical model, and generally requires an experienced hydrogeologist who is familiar with the model code. The groundwater flow and transport equations in numerical models typically are solved using either finite difference or finite element mathematical solution techniques. These solution methods are iterative numerical approximations to the governing partial differential equation describing solute fate and transport.

The final decision to use an analytical or numerical solute transport model should be based on the complexity of the problem, the amount of available data, and the importance of the decisions that will be based upon the model. As an example, consider a site located 5 miles from the nearest potential receptor. The database for this site consists of five sampling points with one round of sampling data from each point. The aquifer system at the site consists of 50 feet of unconsolidated, well-sorted, medium-grained sand overlying a horizontal shale unit. The shallow water table is 5 feet below the surface. Such a site is an excellent candidate for an analytical model. Consider on the other hand, a site located approximately 1,000 feet from the nearest potential receptor. The database for this site consists of 40 data points for which there are 5 years of quarterly groundwater quality sample analyses. The aquifer at this site consists of 10 feet of poorly sorted, silty sand, underlain by 5 feet of well-sorted, medium-grained sand, underlain by 20 feet of silt. The quarterly groundwater quality data indicate that a dissolved benzene, toluene. Ethylbenzene, and xylene (BTEX) plume is migrating downgradient from the source area. In this situation, a numerical model would be the most appropriate tool to predict the fate and transport of the dissolved BTEX plume.

D.1.3 IS A MODEL REALLY NECESSARY?

One of the first questions to ask before proceeding with implementation of a solute transport model is: "Is a model really necessary?" The answer to this question will depend on several factors, including the rate of plume migration and expansion and the locations of potential receptors. For example, if there are abundant historical data available for the site, and these data show that the dissolved BTEX plume has reached a steady-state configuration or is receding, then a solute transport model probably is not necessary to determine if potential receptors will be impacted. However, a model of this site would allow an investigator to estimate how long it will take for the plume to entirely degrade. If on the other hand, the plume is close to a potential receptor and there are no historical data available, then a solute transport model in conjunction

with the appropriate data can be useful in predicting solute fate and transport, including clean up times and potential migration distance.

Two questions will invariably arise during an intrinsic remediation demonstration. These questions are: 1) will potential receptors be impacted by the contaminant plume?, and 2) how long will the contaminant plume persist? If the proponent of intrinsic remediation is unable to provide plausible and defensible answers to these questions, it is unlikely that intrinsic remediation will be accepted by regulators. When properly used with an adequate database of appropriate data, solute transport models can help provide answers to these questions.

SECTION D-2

MODEL DEVELOPMENT AND IMPLEMENTATION

An overview of the steps that must be taken to successfully implement a groundwater flow and solute transport model is presented in this section. The majority of the material presented herein is applicable to both analytical and numerical solute transport models. A distinction is made when the material is relevant to one type of model.

D.2.1 CONCEPTUAL MODEL

The first step in the modeling process is development of the conceptual model. Preliminary versions of the conceptual model can be as simple as plotting the location of the contaminant source on a topographic map. The conceptual model is a three-dimensional representation of the groundwater flow and solute transport system based on available geological, hydrological, climatological, and geochemical data for the site. The purpose of the conceptual model is the integration of available data into a coherent representation of the system to be modeled. After development, the conceptual model is used to aid in model selection and to develop the appropriate analytical or numerical solute transport model. When possible, the preliminary conceptual model should be developed before arriving in the field to collect additional data so that data collection points can be optimized. After collection of site-specific data during the iterative site-characterization phase of the intrinsic remediation demonstration, the preliminary conceptual model should be refined.

Successful conceptual model development involves:

- Definition of the problem to be solved;
- Designing the conceptual model;
- Model selection;
- Determination of additional data requirements; and
- Integration of available data including:
    - Local geologic and topographic maps
    - Hydraulic data

- Site stratigraphy
- Contaminant concentration and distribution data (isopleth maps).

Most of the conceptual model development process will be completed when all of the maps, sections, and calculations discussed in section C-2 have been completed. The only requirement will then be to integrate these data into a coherent representation of the site.

D.2.2 INITIAL AND BOUNDARY CONDITIONS

The solution of any time-dependent (transient) differential equation requires specification of the conditions at the periphery of the flow system (boundary conditions) and the conditions at the beginning of the model simulation (initial conditions). For steady-state models, only boundary conditions must be specified. The purpose of any model is to transform a given set of input parameters (e.g., hydraulic conductivity, dispersivity, sorption, and biodegradation) into a set of predictions (e.g., water levels, contaminant concentrations and fluxes, etc.). The results of a model are made applicable to the area of interest by choosing input parameters and boundary conditions that are representative of the site. Accurate definition of boundary and initial conditions is a very important part of the groundwater flow and solute transport modeling process. The following sections describe the initial and boundary conditions commonly used for groundwater flow and solute transport models.

D.2.2.1 Initial Conditions

Initial conditions are used to describe conditions at the instant the simulation begins. Initial conditions must be specified for transient groundwater flow and solute transport problems. It is not necessary to define initial conditions for steady-state models. This is because steady-state conditions are used to represent a system that is not changing with time.

D.2.2.1.1 Groundwater Flow

For groundwater flow models, initial conditions are used to specify the values of the variable under consideration (usually hydraulic head) at the instant the model simulation begins (i.e., at t = 0) and generally have the form:

$$h(x,y,z,0) = f(x,y,z) \qquad \text{eq. D.2.1}$$

Where f(x,y,z) is a function that describes the variation in hydraulic head, h, in the x, y, and z directions at time t = 0.

D.2.2.1.2 Solute Transport

Initial conditions for solute transport models are used to specify the solute concentration, C, in the system at the instant the model simulation begins (i.e., at t = 0) and have the form:

$$C(x,y,z,0) = f(x,y,z) \qquad \text{eq. D.2.2}$$

Where f(x,y,z) is a function that describes the variation in contaminant concentration in the x, y, and z directions at time t=0. Initial conditions for solute transport generally have the form:

$$C(x,y,z,0) = 0 \qquad \text{eq. D.2.3}$$

or

$$C(x,y,z,0) = C_i \qquad \text{eq. D.2.4}$$

Where: C = contaminant concentration
C_i = initial contaminant concentration
x = distance downgradient of the source
y = distance transverse to the source in the horizontal direction
z = distance transverse to the source in the vertical direction

Equation D.2.3 is used as the initial condition for systems devoid of contamination prior to the introduction of the contaminant or prior to the model simulation. Equation D.2.4 is used as the initial condition for systems that have dissolved contamination prior to the introduction of additional contamination or prior to the model simulation.

D.2.2.2 Boundary Conditions

Model boundaries are mathematical statements that specify the dependent variable (head or contaminant concentration) or the flux (derivative of the head or contaminant concentration with respect to time) at the model grid boundaries. Boundary conditions describe the interaction between the system being modeled and its surroundings. The solution of any differential equation requires specification of the conditions at the periphery of the flow system. Boundary conditions are used to include the effects of the hydrogeologic system outside the area being modeled with the system being modeled, while at the same time allowing the isolation of the desired model domain from the larger hydrogeologic system. In effect, the boundaries of the model tell the area immediately inside the boundaries what to expect from the outside world. Three types of boundary conditions generally are utilized to describe groundwater flow and solute transport. Boundary conditions are referred to as the first type (Dirichlet), the second type (Neumann), and

the third type (Cauchy). Table D.2.1 summarizes boundary conditions for groundwater flow and solute transport.

Table D.2.1

Common Designations for Several Important Boundary Conditions
(Modified From Franke *et al.*, 1987)

Boundary Condition	Boundary Type	Formal Name	General Mathematical Description	
			Groundwater Flow	Contaminant Transport
Specified-Head or Specified-Concentration	Type One	Dirichlet	$H = f(x,y,z,t)$	$C = f(x,y,z,t)$
Specified-Flux	Type Two	Neumann	$\frac{\partial H}{\partial n} = f(x,y,z,t)$	$\frac{\partial C}{\partial n} = f(x,y,z,t)$
Head-Dependent or Concentration-Dependent Flux	Type Three (mixed-boundary condition)	Cauchy	$\frac{\partial H}{\partial n} + cH = f(x,y,z,t)$	$\frac{\partial C}{\partial n} + cC = f(x,y,z,t)$

Proper design of model boundary conditions is of paramount importance in numerical model implementation. When using a numerical model, hydrologic boundaries such as constant-head features (e.g., lakes, etc.) or constant-flux features should, when possible, coincide with the perimeter of the model. In areas that lack obvious hydrologic boundaries, constant-head or constant-flux boundaries can be specified at the numerical model perimeter as long as the perimeter is far enough removed from the contaminant plume that transport calculations will not be affected. It is generally a good idea to make the modeled area large enough so that model boundaries can be placed far enough away from the plume to have minimal impact. This may not be possible in all cases, such as where the plume is near a surface water body. In such cases, it may be necessary to calibrate the model using different boundary conditions until a good match to observed conditions is achieved. In this case, sensitivity analyses should be performed to analyze the effects of various combinations of boundary conditions.

D.2.2.2.1 First-Type Boundary Condition (Dirichlet, Specified-Head or -Concentration)

This type of boundary condition is referred to as the first-type boundary condition or the Dirichlet boundary condition. With this type of boundary condition, values of head (groundwater flow) or concentration (solute transport) are specified along the boundary. Type one boundary conditions are used to describe the boundary if the hydraulic head or solute concentration at the boundary is independent of flow conditions in the model domain. The constant-head or constant-

concentration boundary is a special type of specified-head boundary wherein the head or solute concentration is fixed at the boundary.

D.2.2.2.1.1 Groundwater Flow (Specified-Head Boundary)

Specified-head boundaries (Dirichlet condition) are boundaries for which the hydraulic head is specified as a function of location and time. Specified-head boundaries are expressed mathematically as:

$$H = f(x,y,z,t) \qquad \text{eq. D.2.5}$$

Where: H = total hydraulic head
x = distance downgradient of the source
y = distance transverse to the source in the horizontal direction
z = distance transverse to the source in the vertical direction
t = time

Hydraulic head in surface water bodies is commonly a function of location and time. The type one boundary condition is often used to model the interaction between surface water bodies and groundwater. As an example, consider an aquifer that is bounded by a large stream whose stage is independent of groundwater seepage. Moving upstream or downstream along the boundary, the hydraulic head changes in relation to the slope of the stream channel and decreases downstream. If the surface elevation of the stream is fairly constant in time, the head can be specified as a function of position alone, $H = f(x,y,z)$ at all points along the streambed. If the stream stage varies with time, the head is specified as a function of position and time, and $H = f(x,y,z,t)$ at all points along the streambed. In both examples, heads along the stream are determined by circumstances external to the groundwater flow system and maintain these specified values throughout the problem solution, regardless of the stresses to which the groundwater system is subjected (Franke *et al.*, 1987). Figure D.2.1 shows an example of a specified-head boundary.

A constant-head boundary is a special type of specified-head boundary that occurs where a part of the boundary of the aquifer system coincides with a surface that has a total hydraulic head that is constant in both time and space. An example of a constant-head boundary would be a large lake where water levels do not fluctuate significantly through time. The hydraulic head is fixed (constant) for all points of this boundary, i.e.,

$$H = constant \qquad \text{eq. D.2.6}$$

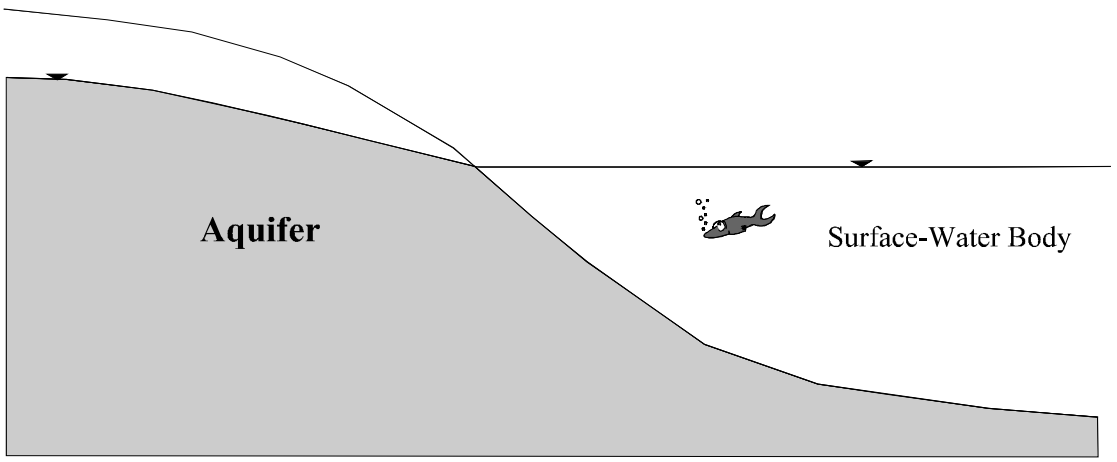


Figure D.2.1

Specified Head (Type One)
Boundary Condition

C:\PROTOCOL\APPEND-D\FIGURES\FIG-D2-1.CDR

D2-6

Both specified-head and constant-head boundaries have an important "physical" characteristic in models of groundwater systems because in order to maintain the prescribed head, they provide an inexhaustible source of water. No matter how much water is removed from the system, the specified-head boundaries will continue to supply the amount of water necessary to maintain the head specified at the boundary, even if that amount is not reasonable in the real system (Franke *et al.*, 1987). Careful consideration should be given to this fact when a specified-head boundary is selected. It is generally considered acceptable to use this type of boundary as long as the boundary is located far enough from a pumping well that it will be unaffected or only minimally affected by pumping.

D.2.2.2.1.2 Solute Transport (Specified-Concentration)

Specified-concentration boundaries (Dirichlet condition) are boundaries for which the contaminant concentration is specified as a function of location and time. Specified-concentration boundaries are expressed mathematically as:

$$C = C_o(x,y,z,t) \qquad \text{eq. D.2.7}$$

Where: C = contaminant concentration
C_o = initial contaminant concentration
x = x coordinate of boundary
y = y coordinate of boundary
z = z coordinate of boundary
t = time

A constant-concentration boundary is a special type of specified-concentration boundary that occurs where a part of the boundary surface of the aquifer system coincides with a surface that has a contaminant concentration that is constant in both time and space. At the upgradient end of the system, the first-type boundary condition states that at x = 0, and for all time, t, the concentration is C_o (i.e., a continuous source of constant concentration). This is described mathematically as:

$$C(0,t) = C_o \qquad \text{eq. D.2.8}$$

This boundary condition is used to calculate concentrations in a system where there is a continuous source of dissolved contamination at the upgradient flow boundary. An example would be a light nonaqueous-phase liquid (LNAPL) spill that receives fresh product at a rate that is balanced by LNAPL mass loss through weathering. The maximum BTEX concentration in groundwater beneath the LNAPL plume is dictated by the partitioning relationships described in

Section C.3.2.2. In reality, such a system is rare. Once a source of LNAPL contamination has been identified it is generally removed and the LNAPL is subjected to weathering though the processes of volatilization, dissolution, and biodegradation. Because of their physiochemical characteristics, the BTEX compounds are some of the first compounds to be removed from the LNAPL in the subsurface. As a result, their mass fractions will be reduced, and through time, the concentrations of BTEX being released into the underlying groundwater will be reduced. Because of this, most contaminant source areas should be modeled as decaying sources.

D.2.2.2.2 Second-Type Boundary Condition (Neumann, Specified-Flux)

This type of boundary condition is referred to as the second-type boundary condition or the Neumann boundary condition. This boundary condition specifies the flux of groundwater or contaminant mass perpendicular to the boundary, and is equated to the normal derivative of head or concentration with respect to the direction perpendicular to the flow boundary.

D.2.2.2.2.1 Groundwater Flow (Specified-Flux)

Specified-flux boundaries are boundaries for which the flux of water across the boundary can be specified as a function of position and time. Flux, *q*, is defined as the volume of water crossing a unit cross-sectional area per unit time and, following Darcy's Law, is given by the hydraulic conductivity times the first derivative of head with respect to the direction perpendicular to the flow boundary. The units of flux are $L^3/L^2/T$. If the direction perpendicular to the boundary corresponds with an axis of hydraulic conductivity, then the flux is given by (Franke *et al.*, 1987):

$$q = -K\frac{\partial H}{\partial n} \qquad \text{eq. D.2.9}$$

Where: q = volumetric flux
K = hydraulic conductivity
H = total hydraulic head
n = distance perpendicular to the boundary

In the most general case, the flux across the boundary is specified as a function of position and time, i.e.:

$$q = f(x,y,z,t) \qquad \text{eq. D.2.10}$$

or, if K is constant:

$$\frac{\partial H}{\partial n} = f(x, y, z, t) \qquad \text{eq. D.2.11}$$

In some cases, the flux might be constant with time, but specified as a function of position, i.e.:

$$q = f(x,y,z) \qquad \text{eq. D.2.12}$$

or, if K is constant:

$$\frac{\partial H}{\partial n} = f(x, y, z) \qquad \text{eq. D.2.13}$$

In the simplest case, the flux across the boundary is specified in space and in time, i.e.:

$$q = constant \qquad \text{eq. D.2.14}$$

or, if K is constant:

$$\frac{\partial H}{\partial n} = constant \qquad \text{eq. D.2.15}$$

An example where the flux across the boundary is often assumed to be specified in space and in time is areal recharge to a water-table aquifer by infiltration.

No-flow boundaries (impervious boundaries) are a special type of specified-flux boundary where the flux is constant in space and time and is zero, i.e.:

$$q = constant = 0 \qquad \text{eq. D.2.16}$$

or, if K is a constant:

$$\frac{\partial H}{\partial n} = constant = 0 \qquad \text{eq. D.2.17}$$

Examples of no-flow boundaries include groundwater divides and impermeable hydrostratigraphic units.

It is important to note that in all three of the cases listed above, the flux across the boundary is specified prior to the modeling simulation, is not affected by stresses to the groundwater system, and therefore is not allowed to deviate from the value specified prior to modeling. For systems where the flux varies as a function of hydraulic head along the boundary, the third-type boundary condition should be used.

D.2.2.2.2.2 Solute Transport (Specified-Concentration Gradient)

The second-type boundary condition specifies the concentration gradient across a section of the boundary surface and is described mathematically by the first derivative of concentration with respect to the direction perpendicular to the flow boundary.

In the most general case the concentration gradient is a function of location and time:

$$\frac{dC}{dn} = f(x, y, z, t) \qquad \text{eq. D.2.18}$$

Where: C = solute concentration
n = distance perpendicular to the boundary
x = distance downgradient of the source
y = distance transverse to the source in the horizontal direction
z = distance transverse to the source in the vertical direction
t = time

In some cases, the flux might be constant with time, but specified as a function of position:

$$\frac{dC}{dn} = f(x, y, z) \qquad \text{eq. D.2.19}$$

In the simplest case, the flux across the boundary is specified in space and in time:

$$\frac{dC}{dn} = constant \qquad \text{eq. D.2.20}$$

In some cases there may be no concentration gradient across the boundary. This is a special type of specified-concentration-gradient boundary where the concentration gradient is constant in space and time and is zero:

$$\frac{dC}{dn} = constant = 0 \qquad \text{eq. D.2.21}$$

D.2.2.2.3 Third-Type Boundary Condition (Cauchy, Variable-Flux)

The third-type boundary condition specifies the flux of groundwater (volumetric flow rate) or contaminant along the boundary as a function of hydraulic head or contaminant concentration, and is equated to the normal derivative of head or concentration with respect to the direction normal to the flow boundary and the hydraulic head or contaminant concentration. This type of boundary condition is referred to as the third-type boundary condition or the Cauchy boundary condition.

D.2.2.2.3.1 Groundwater Flow (Head-Dependent Flux Boundary)

This type of boundary condition is used to describe situations where the flux across a part of the boundary surface changes in response to changes in hydraulic head within the aquifer system adjacent to the boundary. In these situations the flux is a specified function of that head, and varies during the model simulation as the head varies (Franke *et al.*, 1987). Head-dependent flux boundaries (Cauchy or mixed-boundary conditions) occur where the flux across the boundary is calculated from a given boundary head value. This type of flow boundary is sometimes referred to as a mixed-boundary condition because it is a combination of a specified-head boundary and a specified-flow boundary. The general mathematical description of the variable-flux boundary is given by (Franke *et al.*, 1987):

$$q = -K\frac{\partial H}{\partial n} + cH \qquad \text{eq. D.2.22}$$

Where: q = volumetric flux
K = hydraulic conductivity
c = constant
H = total hydraulic head
n = distance perpendicular to the boundary

Head-dependent flow boundaries are used to model leakage across semipermeable boundaries. An example is the upper surface of an aquifer overlain by a semiconfining unit that is in turn overlain by a surface water body. Aquifers in contact with lakes typically exhibit this type of boundary condition because clay and silt tends to accumulate at the bottom of lakes. Figure D.2.2 illustrates this scenario. The flux across the semiconfining bed in this figure is expressed mathematically as (Bear, 1979):

$$q = -K'\frac{(H_0 - H)}{B'} \qquad \text{eq. D.2.23}$$

Where: q = volumetric flux
H = head in the aquifer
H_0 = head in external zone (separated from the aquifer by semipermeable layer)
K' = hydraulic conductivity of semipermeable layer
B' = thickness of semipermeable layer

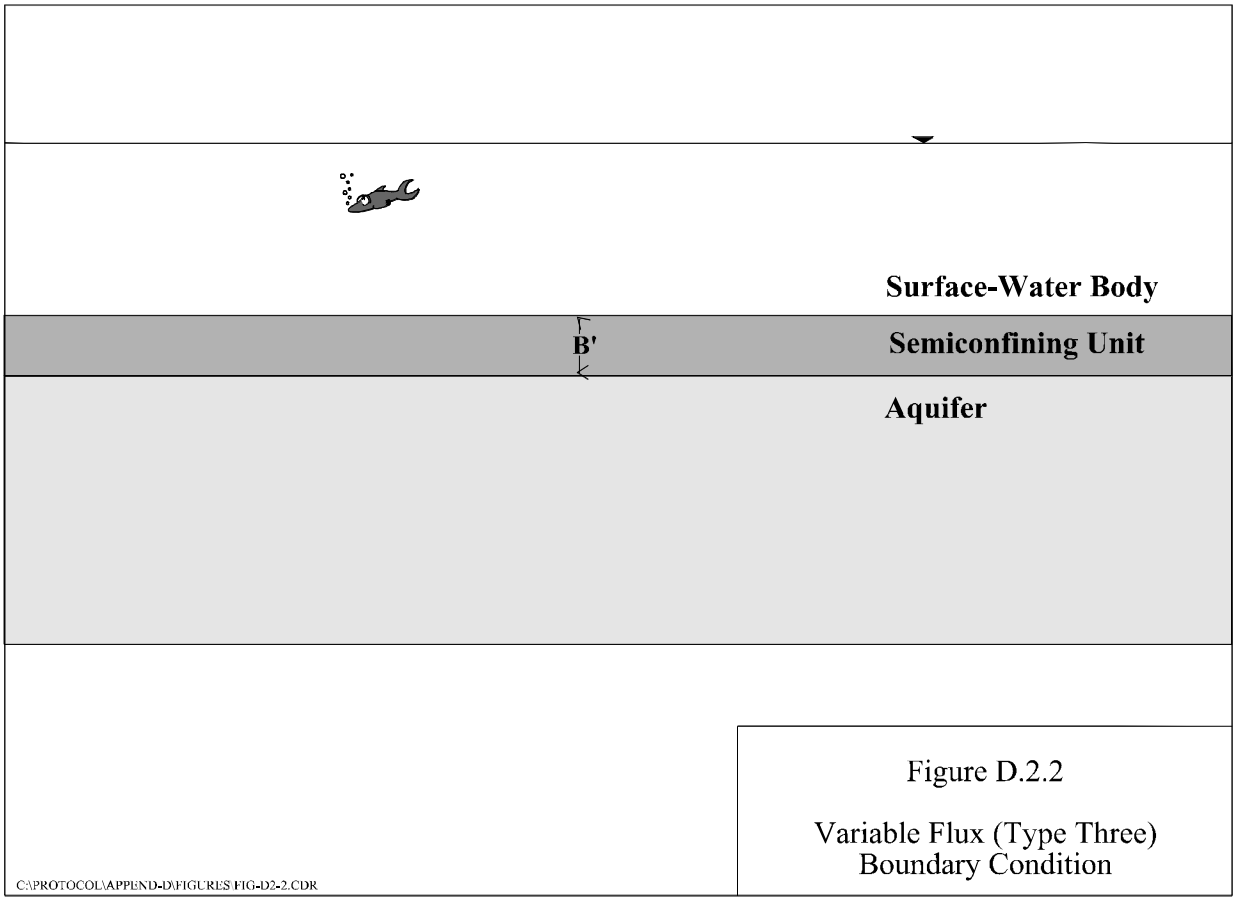


Figure D.2.2

Variable Flux (Type Three)
Boundary Condition

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D.2.2.2.3.2 Solute Transport (Concentration-Dependent Concentration Gradient)

This type of boundary condition is used where the concentration gradient across the boundary is dependent on the difference between a specified concentration on one side of the boundary and the solute concentration on the opposite side of the boundary (Wexler, 1992). For a one-dimensional system, this type of boundary condition is described mathematically as (Wexler, 1992; Bear, 1979):

$$v_x C - D_x \frac{\partial C}{\partial x} = v_x C_o, \qquad x = 0 \qquad \text{eq. D.2.24}$$

This boundary condition best describes solute concentrations at the upgradient boundary of a homogeneous flow system where a well-mixed solute enters the system by advection across the boundary and is transported downgradient from the boundary by advection and dispersion (Wexler, 1992).

D.2.3 MODEL INPUT

Data required to complete a groundwater model, analytical or numerical, include:

- Hydraulic conductivity;
- Initial hydraulic head distribution;
- Flow direction and gradient;
- Effective porosity;
- Coefficient of hydrodynamic dispersion;
- Coefficient of retardation;
- Initial solute concentrations;
- Contaminant source concentration configuration, and rate of source decay (or removal);
- Distribution and continuity of aquifer and aquitards (thickness, continuity, areal extent, interconnections, etc.);
- Groundwater recharge and discharge (infiltration, evapotransporation, pumpage from wells, discharges to surface water, etc.);
- Definition of physical and chemical boundary conditions; and
- Rates of chemical reactions, particularly biodegradation.

Collection of data is discussed in Appendix A. Premodeling calculations are discussed in Appendix C.

D.2.3.1 Analytical Model Input

Analytical modeling can be performed using commonly available spreadsheets or mathematical analysis programs such as MathCAD®. Because analytical solutions are algebraic expressions, input into these models is very straightforward and usually consists of entering the parameter values in appropriate locations.

D.2.3.2 Numerical Model Input

Numerical models are developed by replacing the continuous hydrogeologic domain with a discretized domain consisting of an array of nodes and associated blocks or elements (a model grid). Aquifer hydraulic and chemical parameters are assigned to each grid cell. Design of an appropriate model grid at the outset of modeling is important for successful model implementation. The most important aspects of grid design are selecting an appropriate size for the model grid, proper orientation of the grid, and choosing appropriate boundary conditions.

Numerous factors must be considered when selecting the size of grid cells to be used. There is a trade-off between grid spacing, model accuracy, and being able to model the entire area potentially affected by the contaminant plume. As in differential calculus, the smaller the grid spacing, the more accurate the numerical model will be, and the numerical solution will approach the exact solution as the grid spacing approaches zero. Additionally, more grid nodes increases the demands placed on the computer and longer calculation times will result. Because large numerical errors may arise if the solute being modeled comes in contact with a model boundary, the model grid must be designed so that it is large enough that the solute plume will not intersect a model boundary.

D.2.4 MODEL CALIBRATION

To ensure that a groundwater flow and solute transport model is capable of accurately predicting the future extent and concentration of a contaminant plume, it must be calibrated to observed hydraulic and contaminant data. Calibration involves trial-and-error adjustment of key model input parameters such as hydraulic conductivity, dispersivity, soil sorption coefficient, recharge, effective porosity, boundary conditions, and biodegradation rate until an adequate match between observed and simulated hydraulics and contaminant distribution is achieved. In general, the parameters that have the most impact on the results of contaminant fate and transport modeling are hydraulic conductivity, head distribution (gradient), boundary conditions, and biodegradation rates. Historical groundwater data are required to properly calibrate a groundwater flow and solute transport model.

Numerical solute transport model calibration differs from analytical solute transport model calibration. Calibration of a numerical solute transport model is a two-step process; first the groundwater flow system is calibrated, and then the solute transport system is calibrated. Calibration of the numerical flow model demonstrates that the model is capable of matching hydraulic conditions observed at the site; calibration of a contaminant transport model superimposed upon the calibrated flow model helps verify that contaminant loading and transport conditions are being appropriately simulated. Groundwater flow is calibrated by altering transmissivity in a trial-and-error fashion until simulated heads approximate observed field values within a prescribed accuracy. After calibration of the flow model, the numerical solute transport model should be calibrated by altering hydraulic parameters and transport parameters in a trial-and-error fashion until the simulated BTEX plume approximates observed field values. Because analytical models do not calculate head as a function of time (gradients and hydraulic head considerations are addressed by the groundwater velocity that is entered into the model), only solute transport can be calibrated. The analytical solute transport model is calibrated by altering hydraulic parameters and transport parameters in a trial-and-error fashion until the simulated BTEX plume approximates observed field values.

D.2.4.1 Groundwater Flow Calibration

Calibrating the model to groundwater flow involves comparing measured water levels against simulated water levels over the same period of time. If the flow simulation is steady-state, then the simulated water levels need only be compared with one set of data. Hydraulic conductivity is an important aquifer characteristic that determines the ability of the water-bearing strata to transmit groundwater. Transmissivity is the product of the hydraulic conductivity and the thickness of the aquifer. In conjunction with boundary conditions, hydraulic conductivity or transmissivity values will govern the calculated head solution. An accurate estimate of hydraulic conductivity is also important to help quantify advective groundwater flow velocities and to define the flushing potential of the aquifer and the quantity of electron-acceptor-charged groundwater that is entering the site from upgradient locations.

Saturated thickness data from previous reports, geologic logs, and water level measurements are used in conjunction with hydraulic conductivity to estimate an initial transmissivity for the model domain. To better match heads in the model to observed values, transmissivities are progressively varied in blocks and rows until the simulated water levels for cells corresponding to the selected well locations match the observed water levels as closely as possible. This is often

done manually, although codes that can determine the most appropriate parameter values are available.

The root mean squared (RMS) error is commonly used to express the average difference between simulated and measured heads. RMS error is the average of the squared differences between measured and simulated heads, and can be expressed as:

$$\mathrm{RMS} = \left[\frac{1}{n} \sum_{i=1}^{n} \left(h_m - h_s \right)_i^2 \right]^{0.5} \qquad \text{eq. D.2.25}$$

Where: n = the number of points where heads are being compared
h_m = measured head value
h_s = simulated head value.

The RMS error between observed and calibrated values should be such that the calculated calibration error is less than 10 percent of the average head drop over the model domain. If sufficient data are available, it may be possible to produce a model with a calibration error of less than 5 percent. Calibration error may be described by:

$$CE = \frac{RMS}{\Delta H_T} \bullet 100$$

Where: CE = Calibration error (as a percentage)
RMS = Root mean square error [L]
ΔH_T = Total head change over model domain [L]

Another qualitative method of checking the calibrated model head distribution involves a comparison of calculated heads and observed heads. When calculated heads are plotted versus observed heads, the points should scatter randomly about a straight line. Such a plot also can be used to check if there are any variations in the modeled head distribution that indicate a need to reevaluate parameters in a specific portion of the model domain (e.g., heads are consistently low in the vicinity of a boundary). Figure D.2.3 is an example of such a plot.

Other parameters that may be adjusted during model calibration include effective porosity, recharge, and hydraulic boundary conditions.

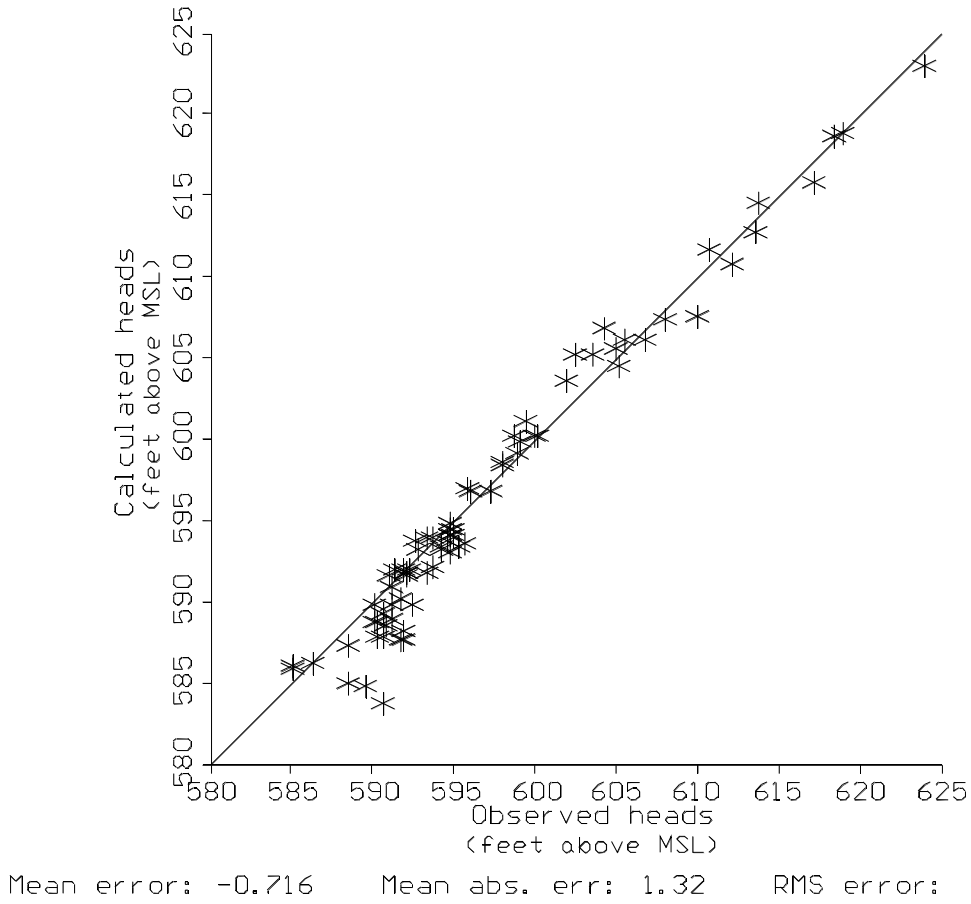

Figure D.2.3

Example
Plot of Calibrated Heads
vs. Observed Heads

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D.2.4.2 Calibrating the Model to Contaminant Distribution

Calibrating a model to contaminant fate and transport involves comparing the observed changes in plume extent and concentration to the predicted changes in extent and concentration over the same period of time. This requires historical contaminant data that may not be available when the model is first developed. Because of this, there will be uncertainty in the model predictions and the model should be reevaluated as more groundwater analytical data become available.

Model input parameters affecting the distribution and concentration of the simulated BTEX plume should be modified so that model predictions match dissolved BTEX concentrations. To do this, model runs are made using the calibrated hydraulic parameters with available BTEX plume data. If the contaminant distribution is known at two different times, the plume can be calibrated over time. Plume calibration is achieved by varying the source terms, the anaerobic decay coefficient, the coefficient of retardation, the effective porosity, and dispersivity until the BTEX plume is calibrated reasonably well to the existing plume in terms of migration distance, configuration, BTEX concentrations, and BTEX concentration changes in the plume area.

D.2.5 SENSITIVITY AND UNCERTAINTY ANALYSES

Any groundwater model is influenced by uncertainty owing to the inability to define the exact spatial and temporal distribution of aquifer and chemical parameter values at the field site. A sensitivity analysis is performed by varying model input parameters over reasonable ranges to establish the effect of uncertainty on the model. Sensitivity analyses should be performed on all models to evaluate the reasonableness of model predictions.

The iterative model calibration process involves modifying several input parameters until a reasonable match of the hydraulic regime and contaminant fate and transport observations is reached. Thus, numerous variations of model input could produce the same results. To determine those model input parameters that have the greatest impact on modeling results, sensitivity analyses should be performed. Sensitivity analysis involves varying model input parameters to determine the impact of different parameter values on the model output. All solute transport models are sensitive to hydraulic conductivity (which has a great effect on transport velocity), dispersivity, retardation coefficients, and biodegradation rates. Based on the work of Rifai *et al.* (1988), the Bioplume II model is most sensitive to changes in the coefficient of reaeration, the coefficient of anaerobic decay, and the hydraulic conductivity of the media, and is less sensitive to changes in the retardation factor, porosity, and dispersivity. At a minimum, the

sensitivity analyses must involve varying these model input parameters over the range of plausible values.

The results of sensitivity analyses can be shown graphically by displaying the modeled BTEX concentrations versus distance along the centerline of the plume. This manner of displaying data is useful because the figures allow easy visualization of the changes in BTEX concentration caused by varying model input parameters. The results of the sensitivity analysis will tell the modeler which parameters have the greatest influence on the site model. This allows the prediction of worst-case scenarios.

In conjunction with (or as part of) the sensitivity analysis, the modeler may also provide an uncertainty analysis. This is done to determine the sensitivity of the model results to uncertainty in site-specific parameters. For example, a range of values for a specific parameter may be measured at a site, and the calibrated model may use an intermediate value. To check the sensitivity of the model to the uncertainty in this parameter, model runs would be made using the upper and lower values of the measured range of that parameter. By comparing the results of these model runs to the calibrated model results, the effects of uncertainty associated with that parameter and the effect of the uncertainty on model predictions can then be assessed. In effect, the uncertainty analysis is a focused sensitivity analysis in which the parameters are varied within a range indicated by a statistical evaluation of site data. Where limited data are available, such an analysis may not be feasible.

D.2.6 PREDICTION

After the solute transport model has been calibrated and the sensitivity analyses have been performed, the model can be used to predict the fate and transport of contaminants. To do this, the model should be run with the input parameters determined to be most accurate based on model calibration and sensitivity analyses. Additional scenarios also can be simulated, such as source removal or reduction.

D.2.7 MODEL DOCUMENTATION AND REPORTING

Model documentation is a very important component of the modeling effort. If the reader cannot determine how the model was set up and implemented, the model is of little use. At a minimum, model documentation must include a discussion of how the model code was selected, a listing of all simplifying assumptions, boundary and initial conditions used, how model input parameters were determined (whether measured, estimated, or assumed), the process used to

interpolate the data spatially, how the model was calibrated and what types of sensitivity/uncertainty analyses were performed. Figure D.2.4 gives an example table of contents from a report that was used to successfully implement intrinsic remediation at a site contaminated with fuel hydrocarbons. Appendices E and F present examples of such reports.

D.2.8 POST-MODEL MONITORING, VERIFICATION, AND ADJUSTMENT

An important component of the intrinsic remediation demonstration is development of a long-term monitoring (LTM) plan that will allow the contaminant plume to be tracked through time. Long-term monitoring of the contaminant plume will allow the solute transport model to be verified. A model is considered verified if data collected after model implementation supports the predictions made by the model. If these data do not agree with what the model predicted, then the model should be recalibrated using the new data.

To demonstrate attainment with site-specific remediation goals and to verify the predictions made by the solute transport model developed for the site, the LTM plan consists of identifying the locations of two separate groundwater monitoring networks and developing a groundwater sampling and analysis strategy. The strategy described in this section is designed to monitor BTEX plume migration over time and to verify that intrinsic remediation is occurring at rates sufficient to protect potential receptors. In the event that data collected under the LTM program indicate that naturally occurring processes are insufficient to protect human health and the environment, contingency controls to augment the beneficial effects of intrinsic remediation can be implemented.

D.2.8.1 Monitoring Networks

Two separate sets of wells should be installed at the site as part of the intrinsic remediation with LTM remedial alternative. The first set should consist of at least four LTM wells located in, upgradient, and downgradient of the observed BTEX plume to verify the results of the solute transport model and to ensure that natural attenuation is occurring at rates sufficient to minimize

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Figure D.2.4

Example Table of Contents

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plume expansion. This network of wells can consist of existing or newly installed wells screened within the shallow aquifer to provide short-term confirmation and verification of the quantitative groundwater modeling results. The second set of groundwater monitoring wells, point-of-compliance (POC) wells, should be located downgradient from the plume along a line perpendicular to the groundwater flow direction. The purpose of the POC wells is to verify that no BTEX compounds exceeding state or federal health-protective groundwater standards migrate beyond the area under institutional control. This network should consist of at least three groundwater monitoring wells. The LTM wells should be sampled for analysis of the parameters listed in Table 2.1. The POC wells should be sampled for dissolved oxygen and BTEX, plus any other parameters required for regulatory compliance.

D.2.8.1.1 Long-Term Monitoring Wells

In at least four locations, groundwater wells within, upgradient, and downgradient of the existing BTEX contaminant plume should be used to monitor the effectiveness of intrinsic remediation in reducing total contaminant mass and minimizing contaminant migration at the site. At least one of these wells should be placed in the anaerobic treatment zone, one should be placed in the aerobic treatment zone, and another well is typically placed downgradient from the aerobic treatment zone. An upgradient well provides background data. This network will supplement the POC wells to provide early confirmation of model predictions and to allow additional response time if necessary.

D.2.8.1.2 Point-of-Compliance Wells

Three POC monitoring wells should be installed downgradient from the leading edge of the BTEX plume. The purpose of the POC wells is to verify that no contaminated groundwater exceeding state or federal regulatory standards migrates beyond the area under institutional control. Although these wells should be placed beyond the point where model results suggest that the contaminant plume will migrate (at concentrations exceeding chemical-specific groundwater standards), these POC wells are the technical mechanisms used to demonstrate protection of human health and the environment and compliance with site-specific numerical remediation goals. As with the LTM wells, the POC wells must be screened in the same hydrogeologic unit(s) as the contaminant plume.

SECTION D-3

ANALYTICAL SOLUTE TRANSPORT MODELS

Analytical models provide exact, closed-form solutions to the governing advection-dispersion equations presented in Section D-1. The use of analytical models requires the user to make several simplifying assumptions about the solute transport system. For this reason, analytical models are most valuable for relatively simple hydrogeologic systems that are relatively homogeneous and isotropic and have uniform geometry (straight boundaries and constant thickness, width, and length). Heterogeneous and anisotropic hydrogeologic systems can be modeled using analytical models only if the system is simplified and average hydraulic characteristics are used. As an example, consider a hydrogeologic system composed of several layers with differing thicknesses and hydraulic conductivities. This system could be simulated using an analytical model by averaging the hydraulic conductivity over the entire thickness being modeled by dividing the sum of the products of each layer's thickness and hydraulic conductivity by the total aquifer thickness (Walton, 1991).

Table D.3.1 lists the analytical models presented in this section. Each model presented is capable of simulating advection, dispersion, sorption, and biodegradation (or any first-order decay process). The assumptions required for each modeling scenario are listed in the relevant section. One-, two-, and three-dimensional analytical solutions to the advection-dispersion equation that are capable of simulating systems that have a continuing source of contamination or a source that is decaying over time are presented in this section (with the exception of a two-dimensional solution for a decaying source). Models that simulate a continuous source of contamination are good for determining the worst-case distribution of the dissolved contaminant plume. This is unrealistic, however, if for no other reason, because source concentrations decrease over time via natural weathering processes. As discussed in Appendix C, natural weathering processes can be slow, so it often will be necessary to implement an engineered solution for source removal. The models used to simulate a decaying source are especially applicable where an engineered solution is implemented for source removal. An important model input parameter for such models is the source decay rate. Appendix C discusses methods that can be used to quantify source-removal rates.

Table D.3.1

Analytical Models Commonly used to Simulate Solute Transport

Processes Simulated	Description	Authors	Section
One-Dimensional Models			
Advection, dispersion, linear sorption, and biodegradation - Constant Source Term	Solute transport in a semi-infinite system with a continuous source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of time and distance	Bear, 1972; van Genuchten and Alves, 1982; and Wexler, 1992	D.3.2.1
Advection, dispersion, linear sorption, and biodegradation - Decaying Source Term	Solute transport in a semi-infinite system with a decaying source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of time and distance	van Genuchten and Alves, 1982	D.3.2.2
Two-Dimensional Models			
Advection, dispersion, linear sorption, and biodegradation - Constant Source Term	Solute transport in a semi-infinite system with a continuous source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of time and distance	Wilson and Miller, 1978	D.3.3.1
Three-Dimensional Models			
Advection, dispersion, linear sorption, and biodegradation - Constant Source Term	Solute transport in a semi-infinite system with a continuous source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of distance from the source and time	Domenico, 1987	D.3.4.1
Advection, dispersion, linear sorption, and biodegradation - Decaying Source Term	Solute transport in a semi-infinite system with a decaying source of contamination. Biodegradation is simulated using a first-order decay rate constant. Solute concentration is given as a function of distance from the source and time	Domenico, 1987 modified for decaying source concentration	D.3.4.2

D.3.1 INITIAL AND BOUNDARY CONDITIONS FOR ANALYTICAL SOLUTE TRANSPORT MODELS

D.3.1.1 Upgradient (Inflow) Boundary Conditions

The first-type and third-type boundary conditions discussed in Section D-1 are used to describe solute concentrations at the upgradient (inflow) boundary of an analytical model. The third-type boundary condition is more accurate than the first-type boundary condition. This is because the first-type boundary condition assumes that the concentration gradient across the upgradient boundary is zero the instant flow begins (Wexler, 1992). This tends to overestimate the mass of solute in the system for early time (Wexler, 1992). Table D.3.2 lists typical boundary conditions used to describe the upgradient boundary of a solute transport system for analytical models.

Table D.3.2

Overview of Upgradient Boundary Conditions used to Simulate the Addition of Contaminants to a Hydrogeologic System

Type of Source Being Simulated	Type of Boundary	One-Dimensional Form
Constant Concentration	Type One	$C(0,t) = C_o$
Pulse-Type Loading with Constant Concentration	Type One	$C(0,t) = C_o$, $0<t\leq t_o$ $C(0,t) = 0$, $t>t_o$
Decaying Source, Exponential Decay with Source Concentration approaching 0	Type One	$C(0,t) = C_o e^{-\lambda t}$
Exponential Decay with Source Concentration approaching C_a	Type One	$C(0,t) = C_a + C_b e^{-\lambda t}$
Constant Flux with Constant Input Concentration	Type Three	$v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = v_x C_o$
Pulse-Type Loading with Constant Input Fluxes	Type Three	$v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = v_x C_o$, $0<t\leq t_o$ $v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = 0$, $t>t_o$

t_o = time at which concentration changes during pulse loading.
Source: Domenico and Schwartz (1990).

D.3.1.2 Downgradient (Outflow) Boundary Conditions

Solute transport systems can be simulated as systems of finite length, semi-infinite length, and infinite length. For systems where the outflow boundary is sufficiently far from the source of contamination that the downgradient boundary will not influence solute concentrations within the area of interest, the system can be treated as semi-infinite (Wexler, 1992). Semi-infinite systems are modeled using a first-type or second-type boundary condition at the downgradient boundary.

D.3.1.3 Lateral and Vertical Boundary Conditions

Lateral and vertical boundary conditions apply to two- and three-dimensional models only. One-dimensional models require only inflow and outflow boundaries. In two- and three-dimensional systems, impermeable or no-flux (no-flow) boundaries may be present at the base, top, or sides of the aquifer (Wexler, 1992). Because there is no flux across the boundary, and molecular diffusion across the boundary is assumed negligible, the general third-type boundary condition simplifies to a second-type boundary condition, and the boundary conditions are expressed as (Wexler, 1992):

$$\frac{dC}{dy} = 0, \quad y = 0 \text{ and } y = W \qquad \text{eq. D.3.1}$$

and

$$\frac{dC}{dz} = 0, \quad z = 0 \text{ and } z = H \qquad \text{eq D.3.2}$$

Where: C = contaminant concentration
y = distance in the y direction
W = width of the aquifer
H = height of the aquifer

In many cases, the lateral and vertical boundaries of the system may be far enough away from the area of interest that the system can be treated as being infinite along the y- and z- axes. If this is the case, then the boundary conditions are specified as (Wexler, 1992):

$$C=0, \frac{dC}{dy} = 0, \qquad y = \pm\infty \qquad \text{eq. D.3.3}$$

and

$$C=0, \frac{dC}{dz} = 0, \qquad z = \pm\infty \qquad \text{eq. D.3.4}$$

D.3.2 ONE-DIMENSIONAL ANALYTICAL MODELS

Models presented in this section include a solution for a semi-infinite system with a constant contaminant source of constant concentration and first-order decay of solute (modified from Bear, 1972, by van Genuchten and Alves, 1982, and by Wexler, 1992,) and a solution for a semi-infinite system with a point source of diminishing concentration and first-order decay of solute (van Genuchten and Alves, 1982).

Equation D.1.1 is the one-dimensional partial differential equation describing transient solute transport with advection, dispersion, sorption, and first-order biodegradation in the saturated zone. For large values of time when the system has reached steady-state equilibrium, solute transport with advection, dispersion, sorption, and biodegradation is described by equation D.1.2. The biodegradation of BTEX compounds can commonly be approximated using first-order kinetics.

D.3.2.1 Semi-infinite System with Constant Source

One analytical solution for equation D.1.1 under the initial and boundary conditions listed below is given by (From Wexler, 1992, equation 60, p. 18, modified from Bear, 1972, p. 630 and van Genuchten and Alves, 1982, p. 60):

$$C(x,t) = \frac{C_o}{2}\left\{\exp\left[\frac{x}{2\frac{D_x}{R}}\left(\frac{v_x}{R} - \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right)\right] \bullet erfc\left[\frac{x - t\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}}{2\sqrt{\frac{D_x}{R}t}}\right]\right.$$

$$\left. + \exp\left[\frac{x}{2\frac{D_x}{R}}\left(\frac{v_x}{R} + \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right)\right] \bullet erfc\left[\frac{x + t\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}}{2\sqrt{\frac{D_x}{R}t}}\right]\right\} \qquad \text{eq. D.3.5}$$

Where $C(x,t)$ = contaminant concentration at a distance, x, downgradient from source at time t
C_o = initial contaminant concentration at source
x = distance downgradient of upgradient boundary
t = time
D_x = longitudinal hydrodynamic dispersion coefficient
v_x = unretarded linear groundwater flow velocity
R = coefficient of retardation
λ = first-order decay rate constant for dissolved contaminant
erfc = complimentary error function (Table D.3.3)

Boundary Conditions:

$$C = C_o, \quad x = 0$$

$$C, \frac{\partial C}{\partial x} = 0, \quad x = \infty$$

Initial Condition:

$$C = 0, \quad 0 < x < \infty \quad \text{at } t = 0$$

Assumptions:

- Fluid is of constant density and viscosity
- Biodegradation of solute is approximated by first-order decay
- Flow is in the x-direction only, and velocity is constant
- The longitudinal hydrodynamic dispersion, D_x, is constant
- Sorption is approximated by the linear sorption model

Table D.3.3

Table of Error Functions

x	erf (x)	erfc(x)		x	erf(x)	erfc(x)
0	0	1		1.1	0.880205	0.119795
0.05	0.056372	0.943628		1.2	0.910314	0.089686
0.1	0.112463	0.887537		1.3	0.934008	0.065992
0.15	0.167996	0.832004		1.4	0.952285	0.047715
0.2	0.222703	0.777297		1.5	0.966105	0.033895
0.25	0.276326	0.723674		1.6	0.976348	0.023652
0.3	0.328627	0.671373		1.7	0.983790	0.016210
0.35	0.379382	0.620618		1.8	0.989091	0.010909
0.4	0.428392	0.571608		1.9	0.992790	0.007210
0.45	0.475482	0.524518		2.0	0.995322	0.004678
0.5	0.520500	0.479500		2.1	0.997021	0.002979
0.55	0.563323	0.436677		2.2	0.998137	0.001863
0.6	0.603856	0.396144		2.3	0.998857	0.001143
0.65	0.642029	0.357971		2.4	0.999311	0.000689
0.7	0.677801	0.322199		2.5	0.999593	0.000407
0.75	0.711156	0.288844		2.6	0.999764	0.000236
0.8	0.742101	0.257899		2.7	0.999866	0.000134
0.85	0.770668	0.229332		2.8	0.999925	0.000075
0.9	0.796908	0.203092		2.9	0.999959	0.000041
0.95	0.820891	0.179109		3.0	0.999978	0.000022
1	0.842701	0.157299				

erfc(x)=1-erf(x)

erfc(-x)=1+erf(x)

erf(-x)=-erf(x)

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\, du$$

For steady-state conditions, solute transport is described by equation D.1.2 and the solution reduces to (Wexler, 1992, equation 62, p. 20):

$$C(x) = C_o \exp\left[\frac{x}{2\frac{D_x}{R}}\left(\frac{v_x}{R} - \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\lambda\frac{D_x}{R}}\right)\right] \qquad \text{eq. D.3.6}$$

Example D.3.1:

Given the hydraulic and contaminant transport parameters below plot the change in concentration through time at a location 30 m downgradient of the source using equation D.3.5. At what time does the concentration at this point reach steady-state equilibrium?

Solution:

Hydrogeologic Data

Hydraulic conductivtiy $K := (3.15)\cdot\frac{m}{day}$

Hydraulic gradient $I := 0.02\frac{m}{m}$

Effective porosity $n_e := 0.25$

Total porosity $n := 0.35$

Longitudinal dispersivity $\alpha_x := 30\cdot m$

Initial Contaminant Concentration $C_o := 12\cdot\frac{mg}{liter}$

Retardation Coefficient Calculation

Contaminant Decay Rate $\lambda := 0.01\cdot\frac{1}{day}$

Soil sorption coefficient $K_{oc} := 79\frac{mL}{gm}$

Particle mass density (for quartz) $\rho_s := 2.65\frac{gm}{cm^3}$

Bulk density $\rho_b := \rho_s\cdot(1-n)$ $\rho_b = 1.722\cdot\frac{gm}{cm^3}$

Organic carbon content $f_{oc} := 0.8\%$

Retardation coefficient $R := 1 + \frac{\rho_b\cdot K_{oc}\cdot f_{oc}}{n_e}$ $R = 5.354$

Groundwater Hydraulics Calculations

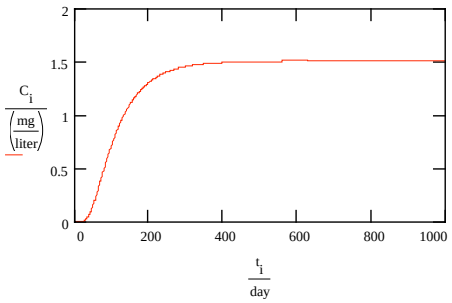
Groundwater velocity (pore-water) $v_x := \frac{K\cdot I}{n_e}$ $v_x = 0.252\cdot\frac{m}{day}$

Retarded Contaminant velocity $v_c := \frac{v_x}{R}$ $v_c = 0.047\cdot\frac{m}{day}$

Longitudinal dispersion coefficient $D_x := \alpha_x\cdot v_x$ $D_x = 7.56\cdot\frac{m^2}{day}$

Change in Concentration with Time Calculation $i := 1..1000$ $\Delta t := 1\cdot day$ $t_i := \Delta t\cdot i$ $x := 30\cdot m$

$$C_i := \frac{C_o}{2}\cdot\left[\exp\left[\frac{x}{2\cdot\frac{D_x}{R}}\cdot\left[\frac{v_x}{R} - \sqrt{\left[\left(\frac{v_x}{R}\right)^2 + 4\cdot\lambda\cdot\frac{D_x}{R}\right]}\right]\right]\cdot\left[1 - \operatorname{erf}\left[\frac{x - t_i\cdot\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\cdot\lambda\cdot\frac{D_x}{R}}}{2\cdot\sqrt{\frac{D_x}{R}\cdot t_i}}\right]\right] + \exp\left[\frac{x}{2\cdot\frac{D_x}{R}}\cdot\left[\frac{v_x}{R} + \sqrt{\left(\frac{v_x}{R}\right)^2 + 4\cdot\lambda\cdot\frac{D_x}{R}}\right]\right]\cdot\left[1 - \operatorname{erf}\left[\frac{x + t_i\cdot\sqrt{\left(\frac{v_x}{R}\right)^2 + 4\cdot\lambda\cdot\frac{D_x}{R}}}{2\cdot\sqrt{\frac{D_x}{R}\cdot t_i}}\right]\right]\right]$$



$C_1 = 0\cdot\frac{mg}{liter}$ $C_{400} = 1.494\cdot\frac{mg}{liter}$

$C_{100} = 0.714\cdot\frac{mg}{liter}$ $C_{500} = 1.504\cdot\frac{mg}{liter}$

$C_{200} = 1.303\cdot\frac{mg}{liter}$ $C_{1000} = 1.508\cdot\frac{mg}{liter}$

$C_{300} = 1.455\cdot\frac{mg}{liter}$

Plume reaches steady-state equilibrium after approximately 400 days

D.3.2.2 Semi-infinite System with Decaying Source

The analytical relationships presented in the preceding section are useful for simulating solute transport at sites with a constant source of contamination. In reality, contaminant source concentrations generally decrease over time via weathering of mobile and residual LNAPL. Temporal variations in source concentrations are simulated using the third-type boundary condition. van Genuchten and Alves (1982) give a solution to equation D.1.1 for a decaying contaminant source and a solute subject to first-order decay. For cases where the decay rate for the dissolved contaminant, λ, is not equal to the decay rate for the source, γ:

$$C(x,t) = C_o A(x,t) + C_s E(x,t) \qquad \text{eq. D.3.7}$$

Where:

$$A(x,t) = \exp(-\lambda t)\left\{1 - \frac{1}{2} erfc\left[\frac{Rx - v_x t}{2\sqrt{D_x R t}}\right] - \left[\frac{v_x^2 t}{\pi D_x R}\right]^{1/2} \exp\left[-\frac{(Rx - v_x t)^2}{4 D_x R t}\right] + \frac{1}{2}\left[1 + \frac{v_x x}{D_x} + \frac{v_x^2 t}{D_x R}\right] \exp\left[\frac{v_x x}{D_x}\right] erfc\left[\frac{Rx + v_x t}{2\sqrt{D_x R t}}\right]\right\} \qquad \text{eq. D.3.8}$$

and

$$E(x,t) = \exp(-\gamma t)\left\{\left(\frac{v_x}{v_x + v_x\sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}}\right) \exp\left[\frac{\left(v_x - v_x\sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}\right)x}{2 D_x}\right] erfc\left[\frac{Rx - t v_x\sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}}{2\sqrt{D_x R t}}\right] + \left(\frac{v_x}{v_x - v_x\sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}}\right) \exp\left[\frac{\left(v_x + v_x\sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}\right)x}{2 D_x}\right] erfc\left[\frac{Rx + t v_x\sqrt{1 + \frac{4 D_x R}{v_x^2}(\lambda - \gamma)}}{2\sqrt{D_x R t}}\right] + \frac{v_x^2}{2 D_x R(\lambda - \gamma)} \exp\left[\frac{v_x x}{D_x} - (\lambda - \gamma)t\right] erfc\left[\frac{Rx + v_x t}{2\sqrt{D_x R t}}\right]\right\} \qquad \text{eq. D.3.9}$$

Where $C(x,t)$ = contaminant concentration at a distance, x, downgradient from the source at time t

C_o = initial dissolved contaminant concentration at boundary

C_s = concentration of injected contaminant (source term)

x = distance downgradient of upgradient boundary

t = time

D_x = longitudinal hydrodynamic dispersion coefficient

v_x = unretarded linear groundwater flow velocity

R = coefficient of retardation

λ = first-order decay rate constant for dissolved contaminant

γ = first-order decay rate constant for source term

Assumptions:

- Homogeneous, isotropic aquifer
- Fluid is of constant density and viscosity
- Biodegradation is approximately first-order
- Flow is in the x-direction only, and velocity is constant, uniform flow field
- The longitudinal hydrodynamic dispersion, D_x, is constant
- There is no advection or dispersion into or out of the aquifer
- Sorption is approximated by the linear sorption model.
- The source fully penetrates the aquifer

Boundary Conditions:

$$\left(-D_x \frac{\partial C}{\partial x} + v_x C\right)\Bigg|_{x=0} = v_x C_s \exp(-\alpha t)$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0$$

Initial Condition:

$$C(x,0) = C_o$$

Because the source is decaying, the solute transport system will never reach truly steady-state conditions, and therefore, no steady-state solution is available.

Example D.3.2:

Consider a system where a fresh spill of mobile LNAPL consisting of fresh JP-4 jet fuel is floating on the water table in a medium- to coarse-grained sandy aquifer. Immediately after the spill, a mobile LNAPL recovery system was installed to remediate this continuing source of groundwater contamination, and a bioventing system was installed to remove fuel residuals from the unsaturated zone. It is estimated that it will take 8 years to reduce BTEX concentrations in the residual and mobile LNAPL to levels that will no longer cause dissolved groundwater contamination above regulatory guidelines. Based on the results of calculations completed using a conservative tracer, the first-order biodegradation rate constant is 0.026 per day. The hydraulic conductivity is 0.084 cm/sec and the hydraulic gradient is 0.046 m/m. The total organic carbon (TOC) content of the aquifer is 0.001 percent. The dispersivity is estimated to be 15 m. Will the plume reach the regulatory POC well located 450 m downgradient from the source along the property boundary in concentrations above regulatory guidelines? The applicable groundwater

standard for benzene is 5 μg/L. How long will it take for the dissolved plume to disappear at points located 10 and 100 m downgradient from the source? What will the contaminant distributions be at t = 1 year and t = 5 years.

Solution:

The first step is to determine the groundwater seepage velocity. From Appendix C, Table C.3.2, the effective porosity for medium- to coarse-grained sands ranges from 15 to 35 percent. Using the median effective porosity of 25 percent, the groundwater seepage velocity is (from equation C.3.6):

$$v_x = -\frac{0.0084\frac{cm}{sec} \bullet 0.046\frac{m}{m}}{0.25} = 1.34\frac{m}{day}$$

Because the organic carbon content of the aquifer is less than 0.1 percent, sorption is not expected to play an important role in slowing the contaminant plume, so the coefficient of retardation is assumed to be 1.0.

Next determine the first-order rate constant for the contaminant source, γ. Dissolved total BTEX concentrations in groundwater immediately beneath the mobile LNAPL plume were 35 mg/L before implementation of remedial actions. After 8 years, the dissolved total BTEX concentration in groundwater immediately beneath the mobile LNAPL plume will be 0.001 mg/L. Using the first-order relationship presented in equation C.3.31 (Appendix C) and substituting γ for λ, and solving for γ yields:

$$\gamma = -\frac{\ln\frac{C}{C_o}}{t} = -\frac{\ln\frac{0.001 mg/L}{35 mg/L}}{8 years} = 1.31/year = 0.0036/day$$

The use of a spreadsheet program or one of the mathematical software programs, such as Mathcad® simplifies solution of analytical models. The following pages illustrate the use of Mathcad® to solve this problem.

Contaminant Concentration at Point of Compliance Well

Hydraulic conductivity	$K := 0.0084\frac{cm}{sec}$	Solute Decay Rate	$\lambda := 0.032\frac{1}{day}$
Hydraulic gradient	$I := 0.046\frac{ft}{ft}$	Source Decay Rate	$\gamma := 0.0036\frac{1}{day}$
Effective porosity	$n_e := 0.25$	Groundwater velocity (seepage)	$v_x := \frac{K \cdot I}{n_e}$ $v_x = 1.335 \cdot \frac{m}{day}$
Longitudinal dispersivity	$\alpha_x := 15 \cdot m$	Retardation coefficient	$R := 1$
Concentration of Injected Contaminant	$C_s := 35 \cdot \frac{mg}{liter}$	Coefficient of Hydrodynamic Dispersion (Longitudinal)	$D_x := \alpha_x \cdot v_x$ $D_x = 20.031 \cdot \frac{m^2}{day}$
Initial Dissolved Contaminant Concentration	$C_o := 0 \cdot \frac{mg}{liter}$		

$i := 1 .. 1500$ $\Delta t := 1 \cdot day$ $t_i := \Delta t \cdot i$ $x := 450 \cdot m$ $ug := \frac{mg}{1000}$

For Retarded Flow with Biodegradation and a Decaying Source (van Genuchten and Alves, 1982)

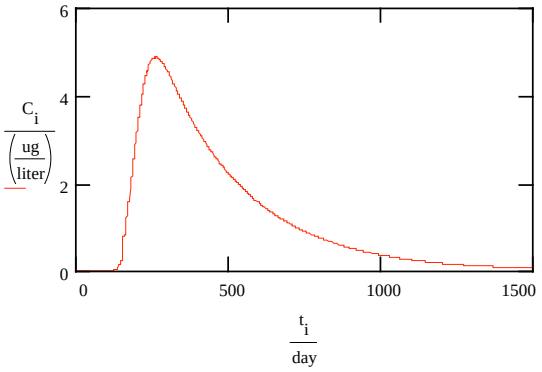
$$C_i := C_o \cdot \exp\left(-\lambda \cdot t_i\right) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x - v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right) - \left(\frac{v_x^2 \cdot t_i}{\pi \cdot D_x \cdot R}\right) \cdot \exp\left[-\frac{\left(R \cdot x - v_x \cdot t_i\right)^2}{4 D_x \cdot R \cdot t_i}\right] + \frac{1}{2} \cdot \left(1 + \frac{v_x \cdot x}{D_x} + \frac{v_x^2 \cdot t_i}{D_x \cdot R}\right) \cdot \exp\left(\frac{v_x \cdot x}{D_x}\right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right] \ldots$$

$$+ C_s \cdot \exp\left(-\gamma \cdot t_i\right) \cdot \left[\left[\frac{v_x}{v_x + v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x - v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot x}{2 D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x - t_i \cdot \left[v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right]}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right]\right] \ldots\right.$$

$$+ \left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x + v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot x}{2 D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x + t_i \cdot v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right]\right] \ldots$$

$$\left.+ \left[\frac{v_x^2}{2 D_x \cdot R \cdot (\lambda - \gamma)}\right] \cdot \exp\left[\frac{v_x \cdot x}{D_x} - \left[(\lambda - \gamma) \cdot t_i\right]\right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right]$$

Total BTEX concentration versus time at the point of compliance well



Based on the model of van Genuchten and Alves (1982), the concentration of benzene at the POC well will not exceed the MCL

Contaminant Concentration versus Time at a Well Located 10 meters Downgradient of the Source Area

$K := 0.0084\frac{cm}{sec}$ $I := 0.046\frac{ft}{ft}$ $n_e := 0.25$ $v_x := \frac{K \cdot I}{n_e}$ $v_x = 1.335 \cdot \frac{m}{day}$ $\alpha_x := 15 \cdot m$ $D_x := \alpha_x \cdot v_x$ $D_x = 20.031 \cdot \frac{m^2}{day}$

$\lambda := 0.032\frac{1}{day}$ $\gamma := 0.0036\frac{1}{day}$ $C_s := 35\frac{mg}{liter}$ $C_o := 0\frac{mg}{liter}$ $R := 1$

$i := 1..1700$ $\Delta t := 1 \cdot day$ $t_i := \Delta t \cdot i$ $x := 10 \cdot m$ $ug := \frac{mg}{1000}$

For Retarded Flow with Biodegradation and a Decaying Source (van Genuchten and Alves, 1982)

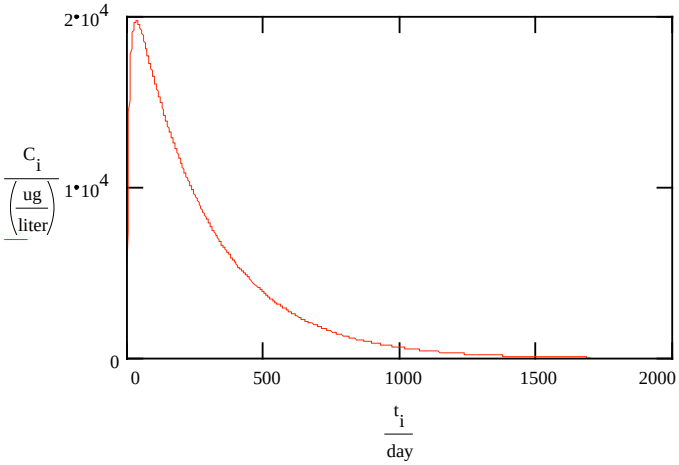
$$C_i := C_o \cdot \exp\left(-\lambda \cdot t_i\right) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x - v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right) - \left(\frac{v_x^2 \cdot t_i}{\pi \cdot D_x \cdot R}\right) \cdot \exp\left[-\frac{\left(R \cdot x - v_x \cdot t_i\right)^2}{4 \cdot D_x \cdot R \cdot t_i}\right] + \frac{1}{2} \cdot \left(1 + \frac{v_x \cdot x}{D_x} + \frac{v_x^2 \cdot t_i}{D_x \cdot R}\right) \cdot \exp\left(\frac{v_x \cdot x}{D_x}\right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right] \ldots$$

$$+ C_s \cdot \exp\left(-\gamma \cdot t_i\right) \cdot \left[\left[\frac{v_x}{v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot x}{2 \cdot D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x - t_i \cdot \left[v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right]}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right]\right] \ldots\right.$$

$$+ \left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot x}{2 \cdot D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x + t_i \cdot v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right]\right] \ldots$$

$$\left.+ \left[\frac{v_x^2}{2 \cdot D_x \cdot R \cdot (\lambda - \gamma)}\right] \cdot \exp\left[\frac{v_x \cdot x}{D_x} - \left[(\lambda - \gamma) \cdot t_i\right]\right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right]$$

Concentration versus time at a point 10 m downgradient of the source



BTEX will not be detected in the well located 10 m from the mobile LNAPL source after approximately 1650 days (4.5 years)

Contaminant Concentration versus Time at a Well Located 100 meters Downgradient of the Source Area

$K := 0.0084\frac{cm}{sec}$ $I := 0.046\frac{ft}{ft}$ $n_e := 0.25$ $v_x := \frac{K \cdot I}{n_e}$ $v_x = 1.335 \cdot \frac{m}{day}$ $\alpha_x := 15 m$ $D_x := \alpha_x \cdot v_x$ $D_x = 20.031 \cdot \frac{m^2}{day}$

$\lambda := 0.032\frac{1}{day}$ $\gamma := 0.0036\frac{1}{day}$ $C_s := 35\frac{mg}{liter}$ $C_o := 0\frac{mg}{liter}$ $R := 1$

$i := 1 .. 1700$ $\Delta t := 1 \cdot day$ $t_i := \Delta t \cdot i$ $x := 100 m$ $ug := \frac{mg}{1000}$

For Retarded Flow with Biodegradation and a Decaying Source (van Genuchten and Alves, 1982)

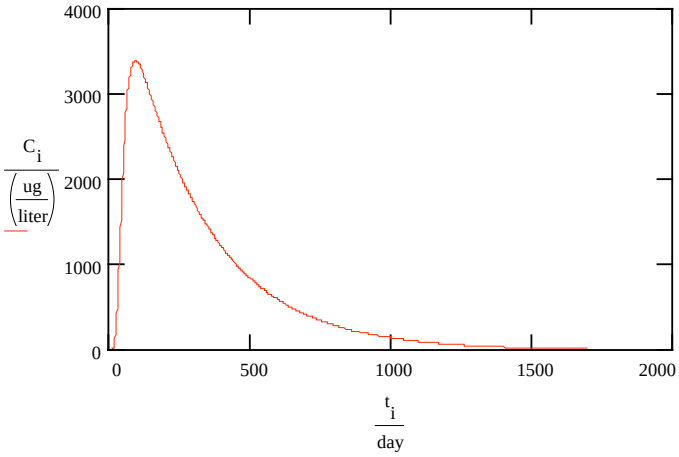
$$C_i := C_o \cdot \exp\left(-\lambda \cdot t_i\right) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x - v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right) - \left(\frac{v_x^2 \cdot t_i}{\pi \cdot D_x \cdot R}\right) \cdot \exp\left[-\frac{\left(R \cdot x - v_x \cdot t_i\right)^2}{4 \cdot D_x \cdot R \cdot t_i}\right] + \frac{1}{2} \cdot \left(1 + \frac{v_x \cdot x}{D_x} + \frac{v_x^2 \cdot t_i}{D_x \cdot R}\right) \cdot \exp\left(\frac{v_x \cdot x}{D_x}\right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right] \ldots$$

$$+ C_s \cdot \exp\left(-\gamma \cdot t_i\right) \cdot \left[\left[\frac{v_x}{v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot x}{2 \cdot D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x - t_i \cdot \left[v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right]}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right]\right] \ldots\right.$$

$$+ \left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\frac{\left[v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot x}{2 \cdot D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x + t_i \cdot v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right]\right] \ldots$$

$$\left.+ \left[\frac{v_x^2}{2 \cdot D_x \cdot R \cdot (\lambda - \gamma)}\right] \cdot \exp\left[\frac{v_x \cdot x}{D_x} - \left[(\lambda - \gamma) \cdot t_i\right]\right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x + v_x \cdot t_i}{2 \cdot \sqrt{D_x \cdot R \cdot t_i}}\right)\right)\right]$$

Concentration versus time at a point 100 m downgradient of the source



BTEX will not be detected in the well located 100 m downgradient from the mobile LNA source after approximately 1650 days (4.5 years)

Contaminant Distribution after One Year

Hydraulic conductivtiy	$K := 0.0084\frac{cm}{sec}$	Solute Decay Rate	$\lambda := 0.032\frac{1}{day}$
Hydraulic gradient	$I := 0.046\frac{ft}{ft}$	Source Decay Rate	$\gamma := 0.0036\frac{1}{day}$
Effective porosity	$n_e := 0.25$	Initial Concentration of Injected Contaminant	$C_s := 35\frac{mg}{liter}$
Longitudinal dispersivity	$\alpha_x := 15 m$	Initial Dissolved Contaminant Concentration	$C_o := 0\frac{mg}{liter}$
Groundwater velocity (pore-water)	$v_x := \frac{K \cdot I}{n_e}$ $v_x = 1.335\frac{m}{day}$	Retardation coefficient	$R := 1$
Longitudinal dispersion coefficient	$D_x := \alpha_x \cdot v_x$ $D_x = 20.031\frac{m^2}{day}$		

$j := 0..400$ $t := 365 day$ $\Delta x := 1 m$ $x_j := \Delta x \cdot j$ $ug := \frac{mg}{1000}$

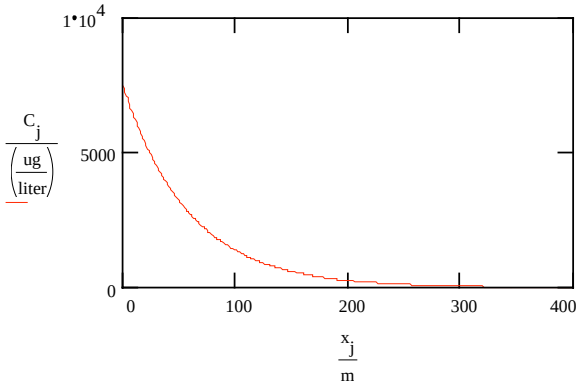
$$C_j := C_o \cdot \exp(-\lambda \cdot t) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j - v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}}\right)\right) - \left(\frac{v_x^2 \cdot t}{\pi \cdot D_x \cdot R}\right) \cdot \exp\left[-\frac{(R \cdot x_j - v_x \cdot t)^2}{4 D_x \cdot R \cdot t}\right] + \frac{1}{2} \cdot \left(1 + \frac{v_x \cdot x_j}{D_x} + \frac{v_x^2 \cdot t}{D_x \cdot R}\right) \cdot \exp\left(\frac{v_x \cdot x_j}{D_x}\right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}}\right)\right)\right] \ldots$$

$$+ C_s \cdot \exp(-\gamma \cdot t) \cdot \left[\left[\frac{v_x}{v_x + v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\left[v_x - v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot \frac{x_j}{2 D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j - t \cdot \left[v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right]}{2 \cdot \sqrt{D_x \cdot R \cdot t}}\right]\right] \ldots\right.$$

$$+ \left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}\right] \cdot \exp\left[\left[v_x + v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}\right] \cdot \frac{x_j}{2 D_x}\right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j + t \cdot v_x \cdot \sqrt{1 + \frac{4 D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t}}\right]\right] \ldots$$

$$\left.+ \left[\frac{v_x^2}{2 D_x \cdot R \cdot (\lambda - \gamma)}\right] \cdot \exp\left[\frac{v_x \cdot x_j}{D_x} - (\lambda - \gamma) \cdot t\right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}}\right)\right)\right]$$

Contaminant distribution along plume centerline at t = 1 year



Contaminant Distribution after Five Years

Hydraulic conductivtiy	$K := 0.0084 \frac{cm}{sec}$	Solute Decay Rate	$\lambda := 0.032 \frac{1}{day}$
Hydraulic gradient	$I := 0.046 \frac{ft}{ft}$	Source Decay Rate	$\gamma := 0.0036 \frac{1}{day}$
Effective porosity	$n_e := 0.25$	Initial Concentration of Injected Contaminant	$C_s := 35 \cdot \frac{mg}{liter}$
Longitudinal dispersivity	$\alpha_x := 15 \cdot m$	Initial Dissolved Contaminant Concentration	$C_o := 0 \cdot \frac{mg}{liter}$
Groundwater velocity (pore-water)	$v_x := \frac{K \cdot I}{n_e}$ $v_x = 1.335 \cdot \frac{m}{day}$	Retardation coefficient	$R := 1$
Longitudinal dispersion coefficient	$D_x := \alpha_x \cdot v_x$ $D_x = 20.031 \cdot \frac{m^2}{day}$		

$j := 0 .. 400$ $t := 1825 day$ $\Delta x := 1 \cdot m$ $x_j := \Delta x \cdot j$ $ug := \frac{mg}{1000}$

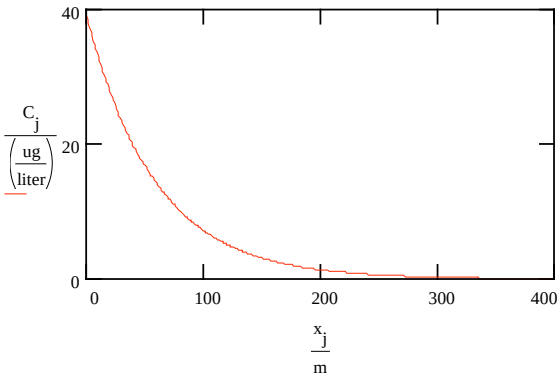
$$C_j := C_o \cdot \exp(-\lambda \cdot t) \cdot \left[1 - \frac{1}{2} \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j - v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right) \right) - \left(\frac{v_x^2 \cdot t}{\pi \cdot D_x \cdot R} \right) \cdot \exp\left[- \frac{(R \cdot x_j - v_x \cdot t)^2}{4 \cdot D_x \cdot R \cdot t} \right] + \frac{1}{2} \cdot \left(1 + \frac{v_x \cdot x_j}{D_x} + \frac{v_x^2 \cdot t}{D_x \cdot R} \right) \cdot \exp\left(\frac{v_x \cdot x_j}{D_x} \right) \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right) \right) \right] \ldots$$

$$+ C_s \cdot \exp(-\gamma \cdot t) \cdot \left[\left[\frac{v_x}{v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}} \right] \cdot \exp\left[\frac{\left[v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right] \cdot x_j}{2 \cdot D_x} \right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j - t \cdot \left[v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right]}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right] \right] \ldots \right.$$

$$+ \left[\frac{v_x}{v_x - v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}} \right] \cdot \exp\left[\frac{\left[v_x + v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)} \right] \cdot x_j}{2 \cdot D_x} \right] \cdot \left[1 - \operatorname{erf}\left[\frac{R \cdot x_j + t \cdot v_x \cdot \sqrt{1 + \frac{4 \cdot D_x \cdot R}{v_x^2} \cdot (\lambda - \gamma)}}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right] \right] \ldots$$

$$\left. + \left[\frac{v_x^2}{2 \cdot D_x \cdot R \cdot (\lambda - \gamma)} \right] \cdot \exp\left[\frac{v_x \cdot x_j}{D_x} - (\lambda - \gamma) \cdot t \right] \cdot \left(1 - \operatorname{erf}\left(\frac{R \cdot x_j + v_x \cdot t}{2 \cdot \sqrt{D_x \cdot R \cdot t}} \right) \right) \right]$$

Contaminant distribution along plume centerline at t = 5 years



D.3.3 TWO-DIMENSIONAL ANALYTICAL MODELS

The model presented in this section is for a semi-infinite system with a constant source of constant concentration and first-order decay of solute (Wilson and Miller, 1978).

Equation D.1.3 is the two-dimensional partial differential equation describing transient solute transport with advection, dispersion, sorption, and first-order biodegradation in the saturated zone. For large values of time when the system has reached steady-state equilibrium, solute transport with advection, dispersion, sorption, and biodegradation is described by equation D.1.4 The biodegradation of BTEX compounds can commonly be approximated using first-order kinetics.

D.3.3.1 Continuous Source

Wilson and Miller (1978) give the following solution to equation D.1.3 (Bedient *et al.*, 1994, p. 136, eq. 6.27)

$$C(x,y,t) = \frac{f_m^{'} \exp\left(\frac{v_x x}{2D_x}\right)}{4\pi n_e \sqrt{D_x D_y}} W\left(u, \frac{r}{B}\right) \qquad \text{eq. D.3.10}$$

Where: f'_m = continuous rate of contaminant injection per vertical unit aquifer [M/LT]

$$\gamma = 1 + 2\frac{B\lambda}{v_x}$$

$W\left(u, \frac{r}{B}\right)$ = Hantush Well Function

$$u = \frac{r^2}{4\gamma D_x t}$$

$$r = \sqrt{\left(x^2 + \frac{D_x y^2}{D_y}\right)\gamma}$$

$$B = 2\frac{D_x}{v_x}$$

Wilson and Miller (1978) give an approximate solution to the Hantush well function. This relationship is:

$$W\left(u,\frac{r}{B}\right)\approx\sqrt{\frac{\pi B}{2r}\exp\left(-\frac{r}{B}\right)erfc\left(-\frac{\frac{r}{B}-2u}{2\sqrt{u}}\right)}$$ eq. D.3.11

This approximation is reasonably accurate (within 10 percent) for r/B>1, and more accurate (within 1 percent) for r/B>10 (Wilson and Miller, 1978).

D.3.4 THREE-DIMENSIONAL ANALYTICAL MODELS

Models presented in this section include a semi-infinite system with constant source of constant concentration and first-order decay of solute (Domenico, 1987) and a semi-infinite system with a decaying source and first-order decay of solute.

Equation D.1.5 is the three-dimensional partial differential equation describing transient solute transport with advection, dispersion, sorption, and first-order biodegradation in the saturated zone. For large values of time (when the system has reached steady state equilibrium), solute transport with advection, dispersion, sorption, and biodegradation is described by equation D.1.6. The biodegradation of BTEX compounds can commonly be approximated using first-order kinetics.

D.3.4.1 Continuous Source

Domenico (1987) developed an analytical solution for a finite (patch) source that incorporates one-dimensional groundwater velocity, longitudinal and transverse dispersion, and first-order decay. For transient conditions (equation D.1.5), the Domenico (1987) solution is given as:

$$C(x,y,z,t)=\frac{C_o}{8}\bullet\exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\}\bullet erfc\left[\frac{x-t\frac{v_x}{R}\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}}{2\sqrt{\alpha_x\frac{v_x}{R}t}}\right]$$ eq. D.3.12

$$\bullet\left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]-erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\}\bullet\left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]-erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\}$$

Where $C(x,y,z,t)$ = contaminant concentration as a function of x,y,z, and t
C_o = initial dissolved contaminant concentration at boundary
x = distance downgradient of upgradient boundary
y = distance lateral to flow direction

z = vertical distance perpendicular to flow direction
Y = source dimension in y direction
Z = source dimension in z direction
t = time
D_x = longitudinal hydrodynamic dispersion
D_y = transverse hydrodynamic dispersion
D_z = vertical hydrodynamic dispersion
v_x = unretarded linear groundwater flow velocity
R = coefficient of retardation
λ = first-order decay rate constant for dissolved contaminant

For steady-state conditions this expression becomes (Domenico, 1987):

$$C(x,y,z,t) = \frac{C_o}{4} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\} \quad \text{eq. D.3.13}$$

Assumptions:

- Fluid is of constant density and viscosity
- Solute may be subject to first-order decay via biodegradation
- Flow is in the x-direction only, and velocity is constant
- The longitudinal dispersion, D_x, is constant
- Sorption is approximated by the linear sorption model.

D.3.4.2 Decaying Source

The change in concentration of a contaminant through time due to first-order decay is given by:

$$C(t) = C_o e^{-\gamma t} \quad \text{eq. D.3.14}$$

Where: $C(t)$ = Source concentration as a function of time
C_o = Initial source concentration
γ = First-order source decay rate constant

This relationship can be used to simulate a contaminant source that is undergoing remediation, either by engineered solutions or natural weathering. Substituting the relationship for changing source concentration as a function of time C(t) for the constant initial concentration C_o in equation D.1.8 gives:

$$C(x,y,z,t) = \frac{C_o e^{-\gamma t}}{8} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet erfc\left[\frac{x - t\frac{v_x}{R}\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}}{2\sqrt{\alpha_x \frac{v_x}{R} t}}\right] \qquad \text{eq. D.3.15}$$

$$\bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\}$$

Where $C(x,y,z,t)$ = contaminant concentration as a function of x, y, z, and t
C_o = initial dissolved contaminant concentration at boundary
x = distance downgradient of upgradient boundary
y = distance lateral to flow direction
z = vertical distance perpendicular to flow direction
Y = source dimension in y direction
Z = source dimension in z direction
t = time
D_x = longitudinal hydrodynamic dispersion
D_y = transverse hydrodynamic dispersion
D_z = vertical hydrodynamic dispersion
v_x = unretarded linear groundwater flow velocity
R = coefficient of retardation
γ = first-order decay rate constant for contaminant source
λ = first-order decay rate constant for dissolved contaminant

Assumptions:

- Fluid is of constant density and viscosity
- Solute may be subject to first-order decay via biodegradation
- Source may be subject to first-order decay via weathering or engineered remediation
- Flow is in the x-direction only, and velocity is constant
- The longitudinal dispersion, D_x, is constant
- Sorption is approximated by the linear sorption model.

SECTION D-4

NUMERICAL MODELS

D.4.1 OVERVIEW OF NUMERICAL MODELS

Numerical models provide inexact and, in some cases, nonunique solutions to the governing advection-dispersion equations presented in Section D-1. As with analytical models, the use of numerical models requires the user to make some simplifying assumptions about the solute transport system. However, fewer simplifying assumptions must be made, so numerical models can simulate more complex systems. For this reason, numerical model codes can be used to simulate complex hydrogeologic systems or contaminant transport affected by complex sets of reactions. Heterogeneous and anisotropic hydrologic systems can be modeled using numerical models, as can transient systems (i.e., systems in which stresses, parameters, or boundary conditions change over time). Another advantage of numerical models is that most codes are capable of simulating contaminant sources that vary over time, allowing simulation of scenarios including source reduction through weathering or through engineered solutions. Appendix C discusses methods that can be used to quantify source removal rates.

D.4.2 APPLICABLE MODEL CODES

Numerical model codes used for the evaluation of natural attenuation processes in groundwater should be capable of simulating advection, dispersion, sorption, and biodegradation (or any first-order decay process). Several codes are available that can be applied to the evaluation of contaminant fate and transport under the influence of these processes. At least four codes are designed specifically for the simulation of reactant-limited solute transport influenced by biodegradation. These include: Bioplume II, Bioplume III, BioTrans©, and Bio1D©. Other codes that are available can be used to evaluate contaminant transport with biodegradation, but biodegradation reaction rates are controlled by a first-order rate constant, rather than by the availability of the reactants. This is not a thorough review of available codes; rather, this overview is to illustrate the variety of available codes that may be useful in evaluating the natural attenuation of contaminants dissolved in groundwater. The selection of a code will ultimately

depend upon the user's needs, the available data, the sophistication of the desired predictions and the limitations of the available model codes.

D.4.2.1 Bioplume II

The Bioplume II model is based upon the US Geological Survey (USGS) two-dimensional (2-D) groundwater flow and solute transport model [method of characteristics (MOC) model] modified to include an oxygen-limited biodegradation component that is controlled by a superimposed plume of dissolved oxygen (Konikow and Bredehoeft, 1978; Rifai *et al.*, 1988). This code also computes concentration changes (for a single species) over time due to advection, dispersion, and sorption. Bioplume II 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 incorporates modified Monod kinetics to simulate the degradation of hydrocarbon compounds and assumes that the hydrocarbons are directly mineralized to carbon dioxide and water through an instantaneous reaction. Anaerobic decay can be simulated using a first-order rate constant, and sources of contaminants or oxygen can be simulated using injection wells or specified-concentration cells. If properly used, the Bioplume II model can present a very conservative estimate of the amount of biodegradation occurring in the subsurface.

D.4.2.2 Bioplume III

Bioplume II is being modified and extended to allow simulation of biodegradation dependent on multiple electron acceptors. The resulting code will be called Bioplume III. This model is being developed by researchers from Rice University and, like the Bioplume II model, will be based upon the USGS two-dimensional (2-D) groundwater flow and solute transport model [method of characteristics (MOC) model]. Bioplume III will allow simulation of first-order biodegradation, instantaneous reactions between electron acceptors [dissolved oxygen, nitrate, iron (III), sulfate, and carbon dioxide) and the dissolved contaminant plume, and Monod kinetics. This model is currently undergoing Beta testing and verification, and should be available by the end of 1995.

D.4.2.3 BioTrans©

BioTrans© is a proprietary solute transport code developed and distributed by Environmental Systems and Technologies, Inc. This code can simulate 2-D dissolved transport and oxygen-

limited decay of up to five separate chemical species in fractured or porous aquifers. Fate and transport calculations can incorporate the effects of advection, dispersion, sorption, and volatilization. Anaerobic biodegradation can be simulated using a first-order rate constant. Contaminant source loading rates can be defined as in Bioplume II, or BioTrans© can compute a time-dependent source rate due to dissolution of LNAPL. This code does not include a routine for simulation of a groundwater flow system. Instead, groundwater velocity data can be imported from other models using a preprocessor.

D.4.2.4 Bio1D©

Bio1D©, a proprietary code developed by GeoTrans, Inc., is a one-dimensional, finite-difference code for simulation of reactive solute transport. This code is capable of simulating aerobic and anaerobic biodegradation and sorption. Compared to other numerical modeling codes, Bio1D© is relatively simple and only offers a few advantages relative to the analytical codes presented in Section D-3. Bio1D© is relatively sophisticated in its ability to simulate substrate-limited biodegradation using different kinetic relations and to simulate sorption under different equilibrium conditions. However, like the analytical models in Section D-3, the code can only simulate conditions in homogeneous steady-state systems, and has the same limitations with respect to source terms. Bio1D© would be most useful for modeling simple systems in which a more rigorous evaluation of the effects of biodegradation and/or sorption is desired. This code also would be useful for estimation of parameters to be used in a more sophisticate solute transport model.

D.4.2.5 Other Codes

Several other codes can simulate solute transport under the influence of advection dispersion, and biodegradation. In these codes, biodegradation can be represented only by a first-order decay constant. However, these codes may be useful in many different situations, depending on the user's needs and the available data, or if a groundwater flow model of the site already has been completed.

MT3D© is a three-dimensional (3D) transport model that can be linked to any block-centered finite-difference flow model (e.g., a model created using the USGS MODFLOW code). This code can simulate advection, dispersion, sorption, and biodegradation (using a first-order decay constant), with source terms specified by the user. This code could be used where a 3D simulation is needed, or where a flow model has previously been constructed and calibrated. MT3D© is a proprietary code developed by S.S Papadopulos and Associates.

FLOTRANS© is another proprietary code, developed by Waterloo Hydrogeologic Software. FLOTRANS© is a 2D code that can simulate steady-state groundwater flow in complex and heterogeneous systems and can simulate transient solute transport in that steady-state flow field. This code can simulate advection, dispersion, sorption, and biodegradation (using a first-order decay coefficient). FLOTRANS© utilizes an interactive graphical interface format, simplifying data input and model output display. FTWORK©, another code developed by GeoTrans, Inc., is a finite-difference code for simulation of complex groundwater flow systems, as well as single-species transport under the influence of advection, dispersion , sorption, and first-order decay. This code also contains a parameter estimation option to assist in calibration of the flow model.

A public-domain code that may be useful is RANDOM WALK. RANDOM WALK is a 2D groundwater flow and solute transport code developed by workers at the Illinois State Water Survey. Groundwater flow solutions may be analytical or numerical (finite difference). Solute transport simulation is achieved through the use of a particle-tracking routine. With respect to solute transport options, this code offers options similar to most of the other codes discussed above, except that wider variety of source-term options are available.