# TECHNICAL PROTOCOL FOR EVALUATING NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER

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# TABLE OF CONTENTS

1.0 INTRODUCTION ..... 1-1

2.0 PROTOCOL FOR IMPLEMENTING NATURAL ATTENUATION ..... 2-1
2.1 REVIEW AVAILABLE SITE DATA AND DEVELOP PRELIMINARY CONCEPTUAL MODEL ..... 2-3
2.2 INITIAL SITE SCREENING ..... 2-5
2.2.1 Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation ..... 2-14
2.2.1.1 Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation ..... 2-15
2.2.1.1.1 Electron Acceptor Reactions (Reductive Dehalogenation) ..... 2-15
2.2.1.1.2 Electron Donor Reactions ..... 2-17
2.2.1.1.3 Cometabolism ..... 2-18
2.2.1.2 Behavior of Chlorinated Solvent Plumes ..... 2-18
2.2.1.2.1 Type 1 Behavior ..... 2-18
2.2.1.2.2 Type 2 Behavior ..... 2-19
2.2.1.2.3 Type 3 Behavior ..... 2-19
2.2.1.2.4 Mixed Behavior ..... 2-19
2.2.2 Bioattenuation Screening Process ..... 2-20
2.3 COLLECT ADDITIONAL SITE CHARACTERIZATION DATA IN SUPPORT OF NATURAL ATTENUATION AS REQUIRED ..... 2-28
2.3.1 Soil Characterization ..... 2-29
2.3.2 Groundwater Characterization ..... 2-30
2.3.2.1 Volatile and Semivolatile Organic Compounds ..... 2-31
2.3.2.2 Dissolved Oxygen ..... 2-32
2.3.2.3 Nitrate ..... 2-32
2.3.2.4 Iron (II) ..... 2-32
2.3.2.5 Sulfate ..... 2-33
2.3.2.6 Methane ..... 2-33
2.3.2.7 Alkalinity ..... 2-33
2.3.2.8 Oxidation-Reduction Potential ..... 2-33
2.3.2.9 Dissolved Hydrogen ..... 2-34
2.3.2.10 pH, Temperature, and Conductivity ..... 2-36
2.3.2.11 Chloride ..... 2-36
2.3.3 Aquifer Parameter Estimation ..... 2-37
2.3.3.1 Hydraulic Conductivity ..... 2-37
2.3.3.1.1 Pumping Tests ..... 2-37
2.3.3.1.2 Slug Tests ..... 2-38
2.3.3.1.3 Downhole Flowmeter ..... 2-38
2.3.3.2 Hydraulic Gradient ..... 2-39
2.3.3.3 Processes Causing an Apparent Reduction in Total

## TABLE OF CONTENTS - Continued

Contaminant Mass ..... 2-39
2.3.4 Optional Confirmation of Biological Activity ..... 2-41
2.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF NATURAL ATTENUATION ..... 2-41
2.4.1 Conceptual Model Refinement ..... 2-42
2.4.1.1 Geologic Logs ..... 2-42
2.4.1.2 Cone Penetrometer Logs ..... 2-42
2.4.1.3 Hydrogeologic Sections ..... 2-43
2.4.1.4 Potentiometric Surface or Water Table Map(s) ..... 2-43
2.4.1.5 Contaminant and Daughter Product Contour Maps ..... 2-43
2.4.1.6 Electron Acceptor, Metabolic Byproduct, and Alkalinity Contour Maps ..... 2-44
2.4.2 Pre-Modeling Calculations ..... 2-45
2.4.2.1 Analysis of Contaminant, Daughter Product, Electron Acceptor, Metabolic Byproduct, and Total Alkalinity Data ..... 2-45
2.4.2.2 Sorption and Retardation Calculations ..... 2-46
2.4.2.3 NAPL/Water Partitioning Calculations ..... 2-46
2.4.2.4 Groundwater Flow Velocity Calculations ..... 2-46
2.4.2.5 Biodegradation Rate-Constant Calculations ..... 2-46
2.5 SIMULATE NATURAL ATTENUATION USING SOLUTE FATE AND TRANSPORT MODELS ..... 2-47
2.6 CONDUCT A RECEPTOR EXPOSURE PATHWAYS ANALYSIS ..... 2-47
2.7 EVALUATE SUPPLEMENTAL SOURCE REMOVAL OPTIONS ..... 2-49
2.8 PREPARE LONG-TERM MONITORING PLAN ..... 2-49
2.9 CONDUCT REGULATORY NEGOTIATIONS ..... 2-52

3.0 REFERENCES ..... 3-1

Appendix A: Field Investigation Methodologies
Appendix B: Important Processes Affecting the Fate and Transport of Organic Compounds in the Subsurface
Appendix C: Data Interpretation and Calculations
Appendix D: Modeling the Fate and Transport of Contaminants Dissolved in Groundwater
Appendix E: Natural Attenuation Demonstration at Plattsburgh AFB, New York
Appendix F: Natural Attenuation Demonstration at Cape Canaveral Air Station, Florida

## TABLE OF CONTENTS - Continued

### FIGURES


| No. | Title | Page |
|---|---|---|
| 1.1 | Significant Chemical Fate and Transport Mechanisms in the Subsurface | 1-3 |
| 2.1 | Natural Attenuation of Chlorinated Solvents Flow Chart | 2-2 |
| 2.2 | Reductive Dehalogenation of Chlorinated Ethenes | 2-16 |
| 2.3 | Initial Screening Process Flow Chart | 2-21 |
| 2.4 | Data Collection Points Required for Screening | 2-23 |
| 2.5 | Example Migration Pathways and Exposure Routes for Potential Receptors of Fuel Hydrocarbons and Chlorinated Solvents | 2-48 |
| 2.6 | Hypothetical Long-Term Monitoring Strategy - Non-Discharging Plume | 2-50 |
| 2.7 | Hypothetical Long-Term Monitoring Strategy - Discharging Plume | 2-51 |


### TABLES


| No. | Title | Page |
|---|---|---|
| 2.1 | Soil, Soil Gas, and Groundwater Analytical Protocol | 2-6 |
| 2.2 | Analytical Parameters and Weighting for Preliminary Screening | 2-11 |
| 2.3 | Analytical Parameters and Weighting for Preliminary Screening | 2-22 |
| 2.4 | Interpretation of Points Awarded During Screening Step 1 | 2-25 |
| 2.5 | Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process | 2-35 |

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## List of Acronyms and Abbreviations

| | |
|---|---|
| AAR | American Association of Railroads |
| AFB | Air Force Base |
| AFCEE | Air Force Center for Environmental Excellence |
| ASTM | American Society for Testing and Materials |
| bgs | below ground surface |
| BRA | baseline risk assessment |
| BRAC | Base Realignment and Closure |
| BTEX | benzene, toluene, ethylbenzene, xylenes |
| CAP | corrective action plan |
| CERCLA | Comprehensive Environmental Response, Compensation and Liability Act |
| cfm | cubic feet per minute |
| CFR | Code of Federal Regulations |
| COPC | chemical of potential concern |
| CPT | cone penetrometer testing |
| CSM | conceptual site model |
| DAF | dilution/attenuation factor |
| DERP | Defense Environmental Restoration Program |
| DO | dissolved oxygen |
| DOD | Department of Defense |
| DQO | data quality objective |
| EE/CA | engineering evaluation/cost analysis |
| FS | feasibility study |
| gpd | gallons per day |
| $\Delta G_r^\circ$ | standard (Gibbs) free energy |
| HDPE | high-density polyethylene |
| HSSM | Hydrocarbon Screening Spill Model |
| HSWA | Hazardous and Solid Waste Amendments of 1984 |
| ID | inside-diameter |
| IDW | investigation derived waste |
| IRP | Installation Restoration Program |
| L | liter |
| LEL | lower explosive limit |
| LNAPL | light nonaqueous-phase liquid |

| | |
|---|---|
| LTM | long-term monitoring |
| LTMP | long-term monitoring plan |
| LUFT | leaking underground fuel tank |
| MAP | management action plan |
| MCL | maximum contaminant level |
| MDL | method detection limit |
| µg | microgram |
| µg/kg | microgram per kilogram |
| µg/L | microgram per liter |
| mg | milligram |
| mg/kg | milligrams per kilogram |
| mg/L | milligrams per liter |
| $mg/m^3$ | milligrams per cubic meter |
| mm Hg | millimeters of mercury |
| MOC | method of characteristics |
| MOGAS | motor gasoline |
| NAPL | nonaqueous-phase liquid |
| NCP | National Contingency Plan |
| NFRAP | no further response action plan |
| NOAA | National Oceanographic and Atmospheric Administration |
| NOEL | no-observed-effect level |
| NPL | National Priorities List |
| OD | outside-diameter |
| OSHA | Occupational Safety and Health Administration |
| OSWER | Office of Solid Waste and Emergency Response |
| PAH | polycyclic aromatic hydrocarbon |
| PEL | permissible exposure limit |
| POA | point-of-action |
| POC | point-of-compliance |
| POL | petroleum, oil, and lubricant |
| ppmv | parts per million per volume |
| psi | pounds per square foot |
| PVC | polyvinyl chloride |
| QA | quality assurance |
| QC | quality control |
| RAP | remedial action plan |
| RBCA | risk-based corrective action |
| RBSL | risk-based screening level |
| redox | reduction/oxidation |
| RFI | RCRA facility investigation |

| | |
|---|---|
| RI | remedial investigation |
| RME | reasonable maximum exposure |
| RPM | remedial project manager |
| SAP | sampling and analysis plan |
| SARA | Superfund Amendments and Reauthorization Act |
| scfm | standard cubic feet per minute |
| SPCC | spill prevention, control, and countermeasures |
| SSL | soil screening level |
| SSTL | site-specific target level |
| SVE | soil vapor extraction |
| SVOC | semivolatile organic compound |
| TC | toxicity characteristic |
| TCLP | toxicity-characteristic leaching procedure |
| TI | technical impracticability |
| TMB | trimethylbenzene |
| TOC | total organic carbon |
| TPH | total petroleum hydrocarbons |
| TRPH | total recoverable petroleum hydrocarbons |
| TVH | total volatile hydrocarbons |
| TVPH | total volatile petroleum hydrocarbons |
| TWA | time-weighted-average |
| UCL | upper confidence limit |
| US | United States |
| USGS | US Geological Survey |
| UST | underground storage tank |
| VOCs | volatile organic compounds |

## Definitions

*Aerobe*: bacteria that use oxygen as an electron acceptor.

*Anabolism*: The process whereby energy is used to build organic compounds such as enzymes and nucleic acids that are necessary for life functions. In essence, energy is derived from catabolism, stored in high-energy intermediate compounds such as adenosine triphosphate (ATP), guanosine triphosphate (GTP) and acetyl-coenzyme A, and used in anabolic reactions that allow a cell to grow (Chapelle, 1993).

*Anthropogenic*: Man-made.

*Catabolism*: The process whereby energy is extracted from organic compounds by breaking them down into their component parts.

*Coefficient of Variation*: Sample standard deviation divided by the mean.

*Cometabolism:* The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound.

*Daughter Product*: A compound that results directly from the biodegradation of another. For example *cis*-1,2-dichloroethene (*cis*-1,2-DCE)is commonly a daughter product of trichloroethene (TCE).

*Dehydrohalogenation*: Elimination of HX resulting in formation of an alkene.

*Diffusion*: The process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion.

*Dihaloelimination*: Reductive elimination of two halide substituents resulting in formation of an alkene.

*Dispersivity*: A property that quantifies mechanical dispersion in a medium.

*Effective Porosity*: The percentage of void volume that contributes to percolation; roughly equivalent to the specific yield.

*Electron Acceptor*: A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride.

*Electron Donor*: A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.

*Electrophile*: A reactive species that accepts an electron pair.

*Elimination*: Reaction where two groups such as chlorine and hydrogen are lost from adjacent carbon atoms and a double bond is formed in their place.

*Epoxidation*: A reaction wherein an oxygen molecule is inserted in a carbon-carbon double bond and an epoxide is formed.

*Facultative Anaerobes*: microorganisms that use (and prefer) oxygen when it is available, but can also use alternate electron acceptors such as nitrate under anaerobic conditions when necessary.

*Fermentation*: Microbial metabolism in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidized and reduced daughter products.

*Heterotroph*: Organism that uses organic carbon as an external energy source and as a carbon source.

*Hydraulic Conductivity*: The relative ability of a unit cube of soil, sediment, or rock to transmit water.

*Hydraulic Head*: The height above a datum plane of the surface of a column of water. In the groundwater environment, it is composed dominantly of elevation head and pressure head.

*Hydraulic Gradient*: The maximum change in head per unit distance.

*Hydrogenolysis*: A reductive reaction in which a carbon-halogen bond is broken, and hydrogen replaces the halogen substituent.

*Hydroxylation*: Addition of a hydroxyl group to a chlorinated aliphatic hydrocarbon.

*Lithotroph*: Organism that uses inorganic carbon such as carbon dioxide or bicarbonate as a carbon source and an external source of energy.

*Mechanical Dispersion*: A physical process of mixing along a flow path in an aquifer resulting from differences in path length and flow velocity. This is in contrast to mixing due to diffusion.

*Metabolic Byproduct*: A product of the reaction between an electron donor and an electron acceptor. Metabolic byproducts include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, and chloride.

*Monooxygenase*: A microbial enzyme that catalyzes reactions in which one atom of the oxygen molecule is incorporated into a product and the other atom appears in water.

*Nucleophile*: A chemical reagent that reacts by forming covalent bonds with electronegative atoms and compounds.

*Obligate Aerobe*: Microorganisms that can use only oxygen as an electron acceptor. Thus, the presence of molecular oxygen is a requirement for these microbes.

*Obligate Anaerobes*: Microorganisms that grow only in the absence of oxygen; the presence of molecular oxygen either inhibits growth or kills the organism. For example, methanogens are very sensitive to oxygen and can live only under strictly anaerobic conditions. Sulfate reducers, on the other hand, can tolerate exposure to oxygen, but cannot grow in its presence (Chapelle, 1993).

*Porosity*: The ratio of void volume to total volume of a rock or sediment.

*Respiration*: The process of coupling oxidation of organic compounds with the reduction of inorganic compounds, such as oxygen, nitrate, iron (III), manganese (IV), and sulfate.

*Solvolysis*: A reaction in which the solvent serves as the nucleophile.

*Substitution*: A reaction in which one substituent on a molecule is replaced by another.

## Compounds Considered in This Document

| Abbreviation | Chemical Abstracts Service (CAS) Name | CAS Number | Other Names | Molecular Formula |
|---|---|---|---|---|
| PCE | tetrachloroethene | 127-18-4 | perchloroethylene; tetrachloroethylene | $C_2Cl_4$ |
| TCE | trichloroethene | 79-01-6 | trichloroethylene | $C_2HCl_3$ |
| 1,1-DCE | 1,1-dichloroethene | 75-35-4 | 1,1-dichloroethylene; vinylidine chloride | $C_2H_2Cl_2$ |
| trans-1,2-DCE | (E)-1,2-dichloroethene | 156-60-5 | trans-1,2-dichloroethene; trans-1,2-dichloroethylene | $C_2H_2Cl_2$ |
| cis-1,2-DCE | | 156-59-2 | cis-1,2-dichloroethene; cis-1,2-dichloroethylene | $C_2H_2Cl_2$ |
| VC | chloroethene | 75-01-4 | vinyl chloride; chloroethylene | $C_2H_3Cl$ |
| 1,1,1-TCA | 1,1,1-trichloroethane | 71-55-6 | | $C_2H_3Cl_3$ |
| 1,1,2-TCA | 1,1,2-trichloroethane | 79-00-5 | | $C_2H_3Cl_3$ |
| 1,1-DCA | 1,1-dichloroethane | 75-34-3 | | $C_2H_4Cl_2$ |
| 1,2-DCA | 1,2-dichloroethane | 107-06-02 | | $C_2H_4Cl_2$ |
| CA | chloroethane | 75-00-3 | | $C_2H_5Cl$ |
| CF | trichloromethane | 67-66-3 | chloroform | $CHCl_3$ |
| CT | tetrachloromethane | 56-23-5 | carbon tetrachloride | $CCl_4$ |
| Methylene Chloride | dichloromethane | 75-09-2 | methylene dichloride | $CH_2Cl_2$ |
| CB | chlorobenzene | 108-90-7 | | $C_6H_5Cl$ |
| 1,2-DCB | 1,2-dichlorobenzene | 95-50-1 | o-dichlorobenzene | $C_6H_4Cl_2$ |
| 1,3-DCB | 1,3-dichlorobenzene | 541-73-1 | m-dichlorobenzene | $C_6H_4Cl_2$ |
| 1,4-DCB | 1,4-dichlorobenzene | 106-46-7 | p-dichlorobenzene | $C_6H_4Cl_2$ |
| 1,2,3-TCB | 1,2,3-trichlorobenzene | 87-61-6 | | $C_6H_3Cl_3$ |
| 1,2,4-TCB | 1,2,4-trichlorobenzene | 120-82-1 | | $C_6H_3Cl_3$ |
| 1,3,5-TCB | 1,3,5-trichlorobenzene | 108-70-3 | | $C_6H_3Cl_3$ |
| 1,2,3,4-TECB | 1,2,3,4-tetrachlorobenzene | 634-66-2 | 1,2,3,4-TCB | $C_6H_2Cl_4$ |
| 1,2,3,5-TECB | 1,2,3,5-tetrachlorobenzene | 634-90-2 | 1,2,3,5-TCB | $C_6H_2Cl_4$ |
| 1,2,4,5-TECB | 1,2,4,5-tetrachlorobenzene | 95-94-3 | | $C_6H_2Cl_4$ |
| HCB | hexachlorobenzene | 118-74-1 | | $C_6Cl_6$ |
| EDB | 1,2-dibromoethane | 106-93-4 | ethylene dibromide; dibromoethane | $C_2H_4Br_2$ |

# SECTION 1

# INTRODUCTION

Over the past several years remediation by natural attenuation has become increasingly accepted as a remedial alternative for organic compounds dissolved in groundwater. The United States Environmental Protection Agency (USEPA) defines natural attenuation as (OSWER, 1996):

> *The term "Natural Attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants.*

In practice, natural attenuation also is referred to by several other names, such as intrinsic remediation, intrinsic bioremediation, natural restoration, or passive bioremediation. The goal of any site characterization effort is to understand the fate and transport of the contaminants of concern over time in order to assess any current or potential threat to human health or the environment. Natural attenuation processes, such as biodegradation, can often be dominant factors in the fate and transport of contaminants. Thus, consideration and quantification of natural attenuation is essential to a more thorough understanding of contaminant fate and transport.

The intent of this document is to present a technical protocol for data collection and analysis in support of natural attenuation with long-term monitoring (LTM) for restoration of groundwater contaminated with chlorinated solvents and groundwater contaminated with mixtures of fuels and chlorinated aliphatic hydrocarbons. Specifically, this protocol is designed to evaluate the fate in groundwater of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons that have regulatory standards. Because documentation of natural attenuation requires detailed site characterization, the data collected under this protocol can be used to compare the relative effectiveness of other remedial options and natural attenuation. In some cases, the information collected using this protocol will show that natural degradation processes will reduce the concentrations of these

contaminants below risk-based corrective action criteria or 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.

This protocol is aimed at improving the site characterization process. It contains methods and recommended strategies for completing the remedial investigation process. Emphasis is placed on developing a more complete understanding of the site through the conceptual site model process, early pathways analysis, and evaluation of remedial processes to include natural attenuation.

Natural attenuation in groundwater systems 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, although abiotic destruction of some compounds does occur. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization. Figure 1.1 shows the significant fate and transport mechanisms that influence contaminant migration in the subsurface. The natural attenuation of fuel hydrocarbons is described in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*, recently published by the Air Force Center for Environmental Excellence (AFCEE) (Wiedemeier *et al.*, 1995d). This document differs from the technical protocol for intrinsic remediation of fuel hydrocarbons because it focuses on the individual processes of chlorinated aliphatic hydrocarbon biodegradation which are fundamentally different from the processes involved in the biodegradation of fuel hydrocarbons.

For example, biodegradation of fuel hydrocarbons, especially benzene, toluene, ethylbenzene, and xylenes (BTEX), is mainly limited by electron acceptor availability, and generally will proceed until all of the contaminants biochemically accessible to the microbes are destroyed. In the experience of the authors, there appears to be an inexhaustible supply of electron acceptors in most, if not all, hydrogeologic environments. On the other hand, the more highly chlorinated solvents such as perchloroethene (PCE) and trichloroethene (TCE) typically are biodegraded under natural conditions via reductive dechlorination, a process that requires both electron acceptors (the chlorinated aliphatic hydrocarbons) and an adequate supply of electron donors. Electron donors include fuel hydrocarbons or other types of anthropogenic carbon (e.g., landfill leachate) or natural organic carbon. If the subsurface environment is depleted of electron donors before the chlorinated aliphatic hydrocarbons are removed, reductive dechlorination will cease, and natural attenuation may no longer be protective of human health and the environment. This is the most significant difference between the processes of fuel hydrocarbon and chlorinated aliphatic hydrocarbon biodegradation.

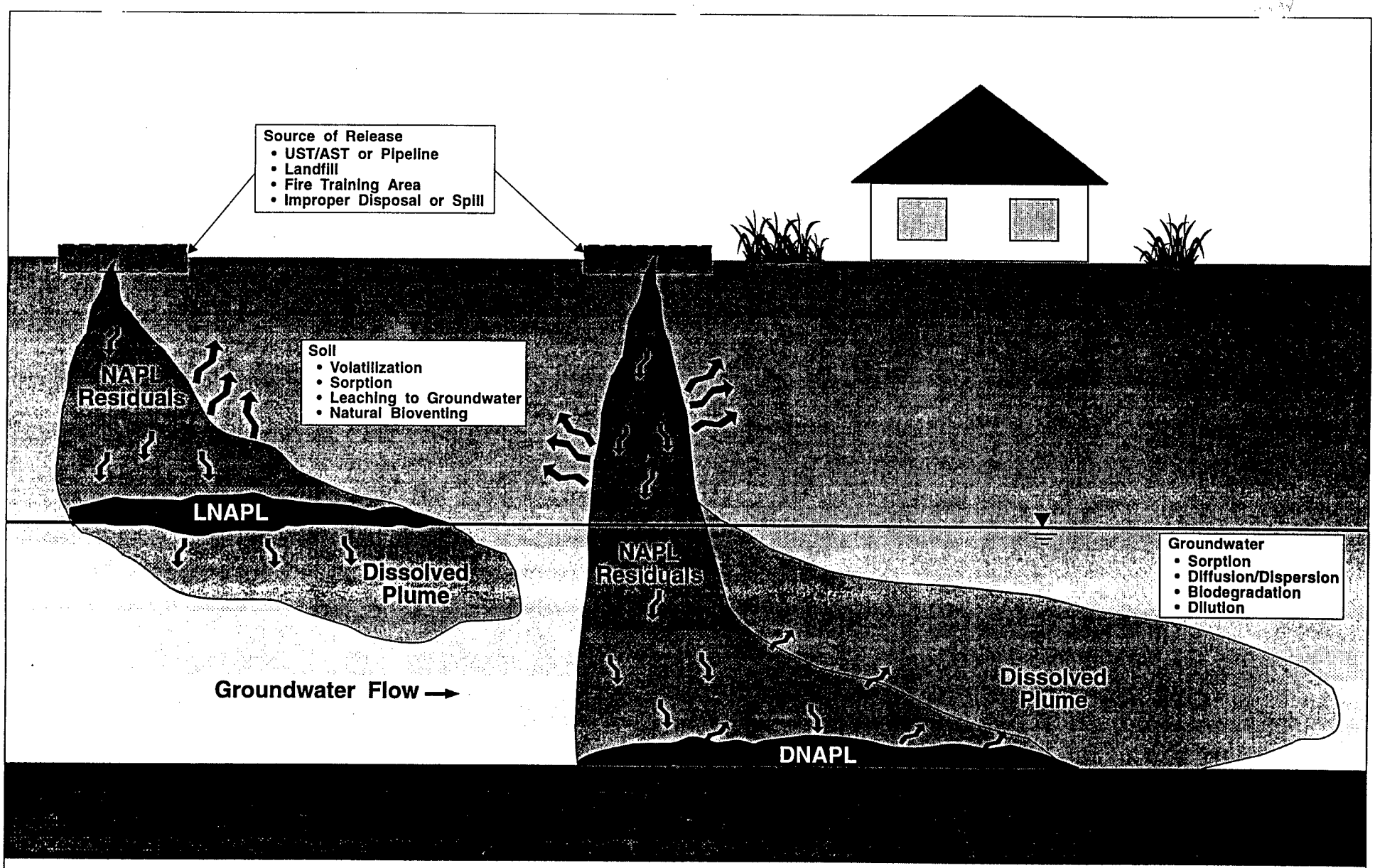



Figure 1.1
Significant Chemical Fate and Transport Mechanisms in the Subsurface

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For this reason, it is more difficult to predict the long-term behavior of chlorinated aliphatic hydrocarbon plumes than fuel hydrocarbon plumes. Thus, it is important to have a good understanding of the important natural attenuation mechanisms. In addition to having a better understanding of the processes of advection, dispersion, dilution from recharge, and sorption, it is necessary to better quantify biodegradation. This requires an understanding of the interactions between chlorinated aliphatic hydrocarbons, anthropogenic or natural carbon, and inorganic electron acceptors at the site. Detailed site characterization is required to adequately document and understand these processes.

The cost to evaluate natural attenuation at sites contaminated with fuel hydrocarbons at over 50 Air Force sites using the AFCEE protocol (Wiedemeier *et al.*, 1995) ranges from $100,000 to $175,000 for sites ranging in size from a few acres to hundreds of acres, depending on site conditions. The cost to fully implement this protocol for 12 sites contaminated with chlorinated solvents ranges from $100,000 to $200,000, depending on site conditions. These costs are relevant only for typical sites at Air Force bases; other sites may cost more or less. These costs include 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 reach cleanup goals and 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 chlorinated aliphatic hydrocarbons or mixtures of fuel hydrocarbons and chlorinated aliphatic 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 AFCEE - Technology Transfer Division protocols for natural attenuation of fuel hydrocarbons (Wiedemeier *et al.*, 1995d), bioventing (Hinchee *et al.*, 1992) or free product recovery protocol (AFCEE, 1995) that allow practitioners to adequately evaluate these alternatives in subsequent feasibility studies. It is not the intent of this document to replace existing USEPA or state-specific guidance on conducting remedial investigations.

AFCEE provides a 'toolbox' to US Air Force remedial project managers that includes a Remediation Matrix - Hierarchy of Preferred Alternatives. This matrix identifies natural attenuation as the first option to be evaluated for remediation of contaminated groundwater at Air Force sites. This matrix implies only that natural attenuation should be evaluated prior to

proceeding (if necessary) to more costly solutions (e.g., groundwater extraction and treatment or another engineered solution), not that natural attenuation be selected as a presumptive remedy. The USEPA has not identified natural attenuation as a presumptive remedy at the time of this writing.

Chlorinated solvents are released into the subsurface as either aqueous-phase or non-aqueous phase liquids. Typical Air Force releases include 1) rinseates (aqueous and nonaqueous phase); 2) relatively pure solvents that are more dense than water; or 2) release as mixtures of fuel hydrocarbons and chlorinated aliphatic hydrocarbons which, depending on the relative proportion of each, may be more or less dense that water. This protocol is also applicable to other scenarios including releases such as PCE from dry cleaning establishments, releases of solvents from recycling establishments, chemical disposal to landfills, and releases from hazardous waste storage facilities. If the NAPL is more dense than water the material is referred to as a "dense nonaqueous-phase liquid," or DNAPL. If the NAPL is less dense than water the material is referred to as a "light nonaqueous-phase liquid," or LNAPL. Contaminant sources generally consist of 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). In general, the greatest mass of contaminant is associated with these NAPL source areas, not with the aqueous phase. In fact at any given time between one part in 100 and one part in 10,000 is dissolved in groundwater. As groundwater or recharge moves through the NAPL source areas, soluble constituents partition into the water to generate a plume of dissolved contamination. After further releases have been stopped, these NAPL source areas tend to slowly weather away as the soluble components, such as BTEX or TCE, are depleted. In cases where mobile NAPL 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 NAPL removal is not feasible with available technology. In fact, the quantity of mobile NAPL recovered by commonly used recovery techniques is a trivial fraction of the total NAPL available to contaminate groundwater. Frequently less than 10 percent of the total NAPL mass in a spill can be recovered by mobile NAPL recovery.

In comparison to conventional engineered remediation technologies, natural attenuation of chlorinated solvents is advantageous because:

- During natural attenuation, contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide, ethene, and water), not just transferred to another phase or location within the environment;

- Natural attenuation is nonintrusive and allows continuing use of infrastructure during remediation;
- Natural attenuation does not generate remediation wastes;
- Engineered remedial technologies can pose greater risk to potential receptors than natural attenuation when contaminants are transferred into the atmosphere during remediation activities;
- Natural attenuation is often less costly than currently available remediation technologies;
- Natural attenuation can be used in conjunction with, or as a follow-up to, other (active) remedial measures;
- Natural attenuation is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime); and
- Those compounds that are the most mobile and toxic generally are the most susceptible to biodegradation.

Natural attenuation has the following potential limitations:

- Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in groundwater velocity, pH, electron acceptor concentrations, electron donor concentrations, and potential future releases;
- Aquifer heterogeneity may complicate site characterization, as it will with any remedial technology;
- Time frames for complete remediation may be relatively long; and
- Intermediate products of biodegradation (e.g., vinyl chloride) can be more toxic than the original contaminant.

This document describes (1) those processes that bring about natural attenuation, (2) the site characterization activities that may be performed to conduct a full-scale evaluation of natural attenuation, (3) natural attenuation modeling using analytical or numerical solute fate and transport models, and (4) the post-modeling activities that should be completed to ensure successful support and verification of remediation by natural attenuation. The objective of the work described herein is to quantify and provide defensible data in support of natural attenuation at sites where naturally occurring subsurface attenuation processes are capable of reducing dissolved chlorinated aliphatic hydrocarbon and/or fuel hydrocarbon concentrations to acceptable levels. A comment made by a member of the regulatory community summarizes what is required to successfully implement natural attenuation:

> *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 remediation by natural attenuation, the proponent must scientifically demonstrate that attenuation 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 natural attenuation of chlorinated aliphatic hydrocarbons, including:

1) Observed reductions in contaminant concentrations along the flow path downgradient from the source of contamination.

2) Documented loss of contaminant mass at the field scale using

   a) Chemical and geochemical analytical data including;
      - decreasing parent compound concentrations
      - increasing daughter compound concentrations
      - depletion of electron acceptors and donors
      - increasing metabolic byproduct concentrations

   b) A conservative tracer and a rigorous estimate of residence time along the flow path to document contaminant mass reduction and to calculate biological decay rates at the field scale.

3) Microbiological laboratory or field data that support the occurrence of biodegradation and give rates of biodegradation.

At a minimum, the investigator must obtain the first two lines of evidence or the first and third lines of evidence. Either the second and third line of evidence is crucial to the natural attenuation demonstration because they provide biodegradation rate constants. These rate constants are used in conjunction with the other fate and transport parameters to predict contaminant concentrations and to assess risk at downgradient points of compliance.

The first line of evidence is simply an observed reduction in the concentration of released contaminants downgradient from the NAPL source area along the groundwater flow path. This line of evidence does not prove that contaminants are being destroyed because the reduction in contaminant concentration could be the result of advection, dispersion, dilution from recharge, sorption, and volatilization (i.e., the majority of apparent contaminant loss could be due to dilution). However, this line of evidence is critical to determine if any current pathway is

complete. Conversely, an increase in the concentrations of some contaminants, most notably degradation products such as VC, also could be indicative of natural attenuation.

In order to support remediation by natural attenuation at most sites, the investigator will have to show that contaminant mass is being destroyed. This is done using either, or both, of the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed, not just being diluted or sorbed to the aquifer matrix. For most contaminants, biodegradation is the most important process, but for certain contaminants nonbiological reactions are also important. The second line of evidence is divided into two components:

- Using chemical analytical data in mass balance calculations to show that decreases in contaminant and electron acceptor/donor concentrations can be directly correlated to increases in metabolic end products/daughter compounds. This evidence can be used to show that electron acceptor/donor 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 and present information on degradation.
- Using measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The third line of evidence, microbiological laboratory or field data, can be used to show that indigenous biota are capable of degrading site contaminants at a particular rate. Microcosm studies should only be undertaken when they are absolutely necessary to obtain biodegradation rate estimates that could not be obtained using the second line of evidence.

This document presents a technical course of action that allows converging lines of evidence to be used to scientifically document the occurrence and quantify rates of natural attenuation. Such a "weight-of-evidence" approach will greatly increase the likelihood of successfully implementing natural attenuation at sites where natural processes are restoring the environmental quality of groundwater. Ideally, the first two lines of evidence should be used in the natural attenuation demonstration. To further document natural attenuation, or at sites with complex hydrogeology, it may not be possible to obtain a field-scale biodegradation rate; in this case, microbiological laboratory data can be useful.

Development of an adequate database during the iterative site characterization process is an important step in the documentation of natural attenuation. Site characterization should provide

data on the location, nature, and extent of contaminant sources. 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 receptor exposure points. Methodologies for determining these parameters are discussed in Appendix A.

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 concentrations of the dissolved contaminant plume. Several types of model can be used to simulate dissolved contaminant transport and attenuation. Appendix D describes three scenarios regarding modeling efforts, including analytical, numerical, and no model necessary. The natural attenuation modeling effort has three primary objectives:

- To predict the future extent and concentration of a dissolved contaminant plume by simulating the combined effects of contaminant loading, advection, dispersion, sorption, and biodegradation;
- To assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory or risk-based levels intended to be protective of human health and the environment; and
- To provide technical support for the natural attenuation remedial 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 analysis of receptor exposure pathways. If natural attenuation is sufficient to mitigate risks to potential receptors, the proponent of natural attenuation has a reasonable basis for negotiating this option with regulators.

Natural attenuation is achieved when naturally occurring attenuation mechanisms, such as biodegradation, bring about a reduction in the total mass of a contaminant dissolved in groundwater. In many cases, natural attenuation will reduce dissolved contaminant concentrations to below regulatory standards such as maximum contaminant levels (MCLs) before the contaminant plume reaches potential receptors. To date, this protocol has been fully or partially implemented at 10 Air Force sites including Plattsburgh Air Force Base (AFB), NY; Hill AFB, Utah; Offutt AFB, NE; Rickenbacker AFB, OH; Columbus AFB; Westover Air Force

Reserve Base (AFRB), MA; and Cape Canaveral AFB, FL. At the 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 (NRMRL) in Ada, Oklahoma, Subsurface Protection and Remediation Division; and Parsons Engineering Science, Inc. (Parsons ES). It is designed to facilitate implementation of natural attenuation at chlorinated aliphatic hydrocarbon-contaminated sites owned by the United States Air Force and other United States Department of Defense (DOD) 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 natural attenuation option. Section 3 presents the references used in preparing this document. Appendix A describes the collection of site characterization data necessary to support natural attenuation, and provides soil and groundwater sampling procedures and analytical protocols. Appendix B provides an in-depth discussion of the destructive and nondestructive mechanisms of natural attenuation. Appendix C covers data interpretation and pre-modeling calculations. Appendix D describes solute fate and transport modeling in support of natural attenuation. Appendix D also describes the post-modeling monitoring and verification process. Appendices E and F present case studies of site investigations and modeling efforts conducted in support of natural attenuation of solvents, using the methods described in this document.

# SECTION 2

# PROTOCOL FOR IMPLEMENTING NATURAL ATTENUATION

The primary objective of the natural attenuation investigation is to determine whether natural processes of contaminant degradation will reduce contaminant concentrations in groundwater to below regulatory standards before potential receptor exposure pathways are completed. Further, natural attenuation should be evaluated to determine if it can meet all appropriate federal and state remediation objectives for a given site. This requires that projections of the potential extent and concentrations of the contaminant plume in time and space be made. These projections should be based on historic variations in, and the current extent and concentrations of, the contaminant plume, in conjunction with measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent of natural attenuation to provide sufficient evidence to demonstrate that the mechanisms of natural attenuation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of solute fate and transport models with 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 confirms the natural reduction and removal of the dissolved contaminant plume.

Figure 2.1 outlines the steps involved in a natural attenuation demonstration and shows the important regulatory decision points for implementing natural attenuation. The key steps outlined in this figure include:

1) Review available site data and develop preliminary conceptual model. Determine if receptor pathways have already been completed. Respond as appropriate;
2) Apply the screening process described in Section 2.2 to assess the potential for natural attenuation;
3) If natural attenuation is selected as potentially appropriate, perform site characterization to support natural attenuation;
4) Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of natural attenuation;

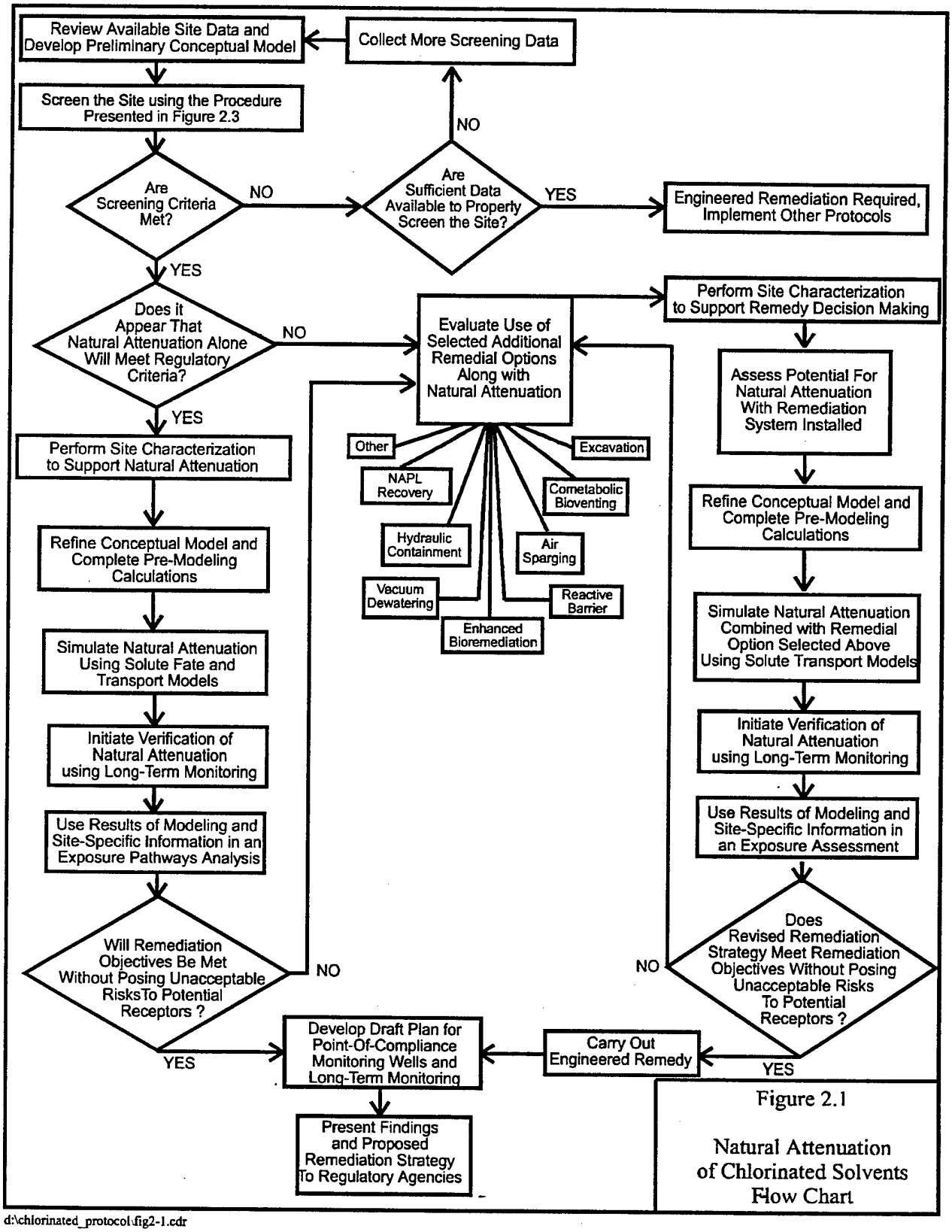



Figure 2.1

Natural Attenuation of Chlorinated Solvents Flow Chart

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5) Simulate natural attenuation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term, as necessary;

6) Identify potential receptors and exposure points and conduct an exposure pathways analysis;

7) Critically and realistically evaluate practicability and potential efficiency of supplemental source control. Compare the benefits of source removal to the practicability and potential efficiency of source removal;

8) Prepare long-term monitoring and verification plan for the selected alternative - natural attenuation alone or in concert with supplemental remediation systems; and

9) Present findings to regulatory agencies and negotiate for the selected alternative.

The following sections describe each of these steps in more detail.

## 2.1 REVIEW AVAILABLE SITE DATA AND DEVELOP PRELIMINARY CONCEPTUAL MODEL

The first step in the natural attenuation investigation is to review available site-specific data. Once this is done it is possible to use the initial site screening processes presented in Section 2.2 to determine if natural attenuation 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 facilitate 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 NAPL ?
    --More than one source area possible or present ?
    --Divergent or coalescing plumes ?
  - Three-dimensional distribution of mobile and residual NAPL and dissolved contaminants. The distribution of mobile and residual NAPL will be used to define the dissolved plume source area.
  - Groundwater and soil chemical data.
  - Historical water quality data showing variations in contaminant concentrations.
  - 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 receptor exposure points:
  - Groundwater wells.
  - Downgradient and crossgradient groundwater discharge points.

In some cases, few or no site-specific data are available. If this is the case, all future site characterization activities should include collecting the data necessary to screen the site for potential natural attenuation. The additional costs incurred by such data collection are greatly outweighed by the cost savings that will be realized if natural attenuation is selected. Moreover, much of the data collected in support of natural attenuation can be used to design and support other remedial measures.

Available site characterization data should be used to develop a conceptual model for the site. The conceptual model is a three-dimensional representation of the NAPL source area, 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 conceptual model of the groundwater system 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 natural attenuation 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 nature, magnitude, 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,
  - A sampling and analysis plan (SAP), and
  - Any data requirements listed in Section 2.1 that have not been adequately addressed.

Table 2.1 contains the recommended soil and groundwater analytical protocol for natural attenuation of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons. Any plan to collect additional groundwater and soil quality data should include the analytes listed in this table. Table 2.2 lists the availability of these analyses and the recommended data quality requirements.

## 2.2 INITIAL SITE SCREENING

After reviewing available site data and developing a preliminary conceptual model, an assessment of the potential for natural attenuation must be made. As stated previously, existing data can be useful to determine if natural attenuation might be sufficient to prevent a dissolved contaminant plume from completing receptor exposure pathways, or from reaching a predetermined point of compliance (POC), in concentrations above applicable federal, state, or risk-based standards. Determining the likelihood of exposure pathway completion is an important component of the natural attenuation investigation. This is achieved by estimating the migration and future extent of the plume based on (1) contaminant properties, including volatility, sorptive properties, and biodegradability; (2) aquifer properties, including hydraulic gradient, hydraulic conductivity, porosity and total organic carbon (TOC) concentrations, and (3) the location of the plume and contaminant source relative to potential receptor exposure points (i.e., the distance between the leading edge of the plume and the potential receptor exposure points). These parameters (estimated or actual) are used in this section to make a preliminary assessment of the effectiveness of natural attenuation in reducing contaminant concentrations.

## Table 2.1 Soil, Soil Gas, 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 | Aromatic and chlorinated hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX]; chlorinated compounds) | SW8260A | Handbook method | Data are used to determine the extent of soil contamination, the contaminant mass present, and the potential need for source removal | Each soil sampling round | Sample volume approximately 100 ml; subsample and extract in the field using methanol or appropriate solvent; cool to 4°C | Fixed-base |
| Soil | Total organic carbon (TOC) | SW9060 modified for soil samples | Procedure must be accurate over the range of 0.1–5 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 Gas | Methane, $O_2$, $CO_2$ | Field Soil Gas Analyzer | | Useful for determining bioactvity in vadose zone. | At initial sampling and respiration testing | Reusable 3-liter Tedlar bags. | Field |
| Soil Gas | Fuel and Chlorinated VOCs | EPA Method TO-14 | | Useful for determining chlorinated and BTEX compounds in soil | At initial sampling | 1-liter Summa Canister | Fixed-base |
| Water | Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds) | SW8260A | Handbook method; analysis may be extended to higher molecular weight alkyl benzenes | Method of analysis for BTEX and chlorinated solvents/byproducts, which are the primary target analytes for monitoring natural attenuation; 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 sulfuric acid to pH 2 | 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. | Concentrations less than 1 mg/L generally indicate an anaerobic pathway | Each sampling round | Measure dissolved oxygen onsite 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 at least 40 mL of water in a glass or plastic container; add $H_2SO_4$ to pH less than 2, keep cool | 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 headspace-free container to eliminate introduction of oxygen and analyze as soon as possible | Field |
| Water | Sulfate ($SO_4^{2-}$) | IC method E300 | Method E300 is a Handbook method, do not use the field method if this method is used. | Substrate for anaerobic microbial respiration | Each sampling round | Collect at least 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, do not use the fixed-base laboratory method if this method is used. | Same as above | Each sampling round | Collect at least 40 mL of water in a glass or plastic container; cool to 4°C | Field |
| Water | Methane, ethane, and ethene | Kampbell *et al.*, 1989 or SW3810 Modified | Method published by researchers at the US Environmental Protection Agency. Limited to few commercial labs. | 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, keep cool | Fixed-base |

## Table 2.1 (Continued)

| Matrix | Analysis | Method/Reference | Comments | Data Use | Recommended Frequency of Analysis | Sample Volume, Sample Container, Sample Preservation | Field or Fixed-Base Laboratory |
|---|---|---|---|---|---|---|---|
| Water | Alkalinity | Hach alkalinity test kit model AL AP MG-L | Phenolphthalein method | General water quality parameter used (1) to measure the buffering capacity of groundwater, and (2) as a marker to verify that all site samples are obtained from the same groundwater system; | Each sampling round | Collect 100 mL of water in glass container | Field |
| Water | Oxidation-reduction potential (ORP) | 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 ORP of groundwater influences and is influenced by the nature of the biologically mediated degradation of contaminants; the ORP 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 |
| Water | Major Cations | SW6010 | Protocols/Handbook methods | Can be used to evaluate other remedial actions. | 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 | IC method E300 | 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. Final product of chlorinated solvent reduction. | 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 100 mL of water in a glass container | Field |
| Water | Total Organic Carbon | SW9060 | Laboratory | Used to classify plume and to determine if cometabolism is possible in the absence of anthropogenic carbon | Each sampling round | Collect 100 mL of water in a glass container, cool | Laboratory |
| Soil | Biologically Available Iron (III) | Under development | HCl extraction followed by quantification of released iron (III) | Optional method that should be used when fuel hydrocarbons or vinyl chloride are present in the groundwater to predict the possible extent of removal of fuel hydrocarbons and vinyl chloride via iron reduction. | One round of sampling in five borings, five cores from each boring | Minimum 1inch diameter core samples collected into plastic liner. Cap and prevent aeration | Laboratory |
| Water | Hydrogen ($H_2$)[a/] | Equilibration with gas in the field. Determined with a reducing gas detector. | Specialized analysis | Determine terminal electron accepting process. Predicts the possibility for reductive dechlorination. | One round of sampling | Sampled at well head requires the production of 100mL per minute of water for 30 minutes | Field |

**NOTES:**

* Analyses other than those listed in this table may be required for regulatory compliance.

a/ Optional

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.

## Table 2.2

## Data Quality Objectives to Implement the Natural Attenuation Protocol *

| Matrix | Analysis | Method/Reference | Minimum Limit of Quantification | Precision | Availability | Potential Data Quality Problems |
|---|---|---|---|---|---|---|
| Soil | Aromatic and chlorinated hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX]; chlorinated compounds) | SW8260A | 1 mg/Kg | Coefficient of Variation of 20 percent | Common Laboratory Analysis | Volatiles lost during shipment to laboratory; prefer extraction in the field. |
| Soil | Total organic carbon (TOC) | SW9060 modified for soil samples | 0.1 percent | Coefficient of Variation of 20 percent | Common laboratory analysis | Samples must be collected from contaminant-transporting (i.e., transmissive) intervals. |
| Soil Gas | Methane, $O_2$, $CO_2$ | Field Soil Gas Analyzer | 1 percent (volume/volume) | Coefficient of Variation of 20 percent. | Readily available field instrument | Instrument must be properly calibrated. |
| Soil Gas | Fuel and Chlorinated VOCs | EPA Method TO-14 | 1 ppm (volume/volume) | Coefficient of Variation of 20 percent | Common laboratory analysis | Potential for atmospheric dilution during sampling. |
| Water | Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds) | SW8260A | MCLs | Coefficient of Variation of 10 percent. | Common laboratory analysis | Volatilization during shipment and biodegradation due to improper preservation |

## Table 2.2 (Continued)

| Matrix | Analysis | Method/Reference | Minimum Limit of Quantification | Precision | Availability | Potential Data Quality Problems |
|---|---|---|---|---|---|---|
| Water | Oxygen | Dissolved oxygen meter | 0.2 mg/L | Standard deviation of 0.2 mg/L | Common field instrument | Improperly calibrated electrodes or bubbles behind the membrane or a fouled membrane or introduction of atmospheric oxygen during sampling |
| Water | Nitrate | IC method E300 | 0.1 mg/L | Standard deviation of 0.1 mg/L | Common laboratory analysis | Must be preserved |
| Water | Iron (II) ($Fe^{2+}$) | Colorimetric Hach Method # 8146 | 0.5 mg/L | Coefficient of Variation of 20 percent. | Common field analysis | Possible interference from turbidity (must filter if turbid). Keep out of sunlight and analyze within minutes of collection. |
| Water | Sulfate ($SO_4^{2-}$) | IC method E300 | 5 mg/L | Coefficient of Variation of 20 percent. | Common laboratory | Fixed-base |
| Water | Sulfate ($SO_4^{2-}$) | Hach method # 8051 | 5 mg/L | Coefficient of Variation of 20 percent. | Common field analysis | Possible interference from turbidity (must filter if turbid). Keep sample cool |
| Water | Methane, ethane, and ethene | Kampbell *et al.*, 1989 or SW3810 Modified | 1 µg/L. | Coefficient of Variation of 20 percent. | Specialized laboratory analysis. | SOP must be thoroughly understood by the laboratory before sample submittal. Sample must be preserved against biodegradation and collected without headspace (to minimize volatilization) |

## Table 2.2 (Continued)

| Matrix | Analysis | Method/Reference | Minimum Limit of Quantification | Precision | Availability | Potential Data Quality Problems |
|---|---|---|---|---|---|---|
| Water | Alkalinity | Hach alkalinity test kit model AL AP MG-L | 50 mg/L | Standard deviation of 20 mg/L | Common field analysis | Analyze sample within 1 hour of collection |
| Water | Oxidation-reduction potential (ORP) | A2580B | plus or minus 300 mV | plus or minus 50 mV | Common field probe | Improperly calibrated electrodes or introduction of atmospheric oxygen during sampling. |
| Water | pH | Field probe with direct reading meter. | 0.1 standard units | 0.1 standard units | Common field meter | Improperly calibrated instrument; time sensitive |
| Water | Temperature | Field probe with direct reading meter. | 0 degrees Celsius | Standard deviation of 1 degrees Celsius | Common field probe | Improperly calibrated instrument; time sensitive |
| Water | Conductivity | E120.1/SW9050, direct reading meter | 50 $\mu S/cm^2$ | Standard deviation of 50 $\mu S/cm^2$ | Common field probe | Improperly calibrated instrument |
| Water | Major Cations | SW6010 | 1 mg/L | Coefficient of Variation of 20 percent. | Common laboratory analysis | Possible colloidal interferences |
| Water | Chloride | IC method E300 | 1 mg/L | Coefficient of Variation of 20 percent. | Common laboratory analysis | ---- |
| Water | Chloride (optional, see data use) | Hach Chloride test kit model 8-P | 1 mg/L | Coefficient of Variation of 20 percent. | Common field analysis | Possible interference from turbidity |
| Water | Total Organic Carbon | SW9060 | 0.1 mg/L | Coefficient of Variation of 20 percent. | Common laboratory analysis | |
| Soil | Biologically Available Iron (III) | Under development | 50 mg/Kg | Coefficient of Variation of 40 percent. | Specialized laboratory analysis | Sample must not be allowed to oxidize |
| Water | Hydrogen ($H_2$)[a/] | See Appendix A | 0.1 nM | Standard deviation of 0.1 nM. | Specialized field analysis | Numerous, see Appendix A |

If, after completing the steps outlined in this section, it appears that natural attenuation will be a significant factor in contaminant removal, detailed 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, possibly in conjunction with natural attenuation. Even so, the collection of data in support of the natural attenuation option can be integrated into a comprehensive remedial strategy and may help reduce the cost and duration of engineered remedial measures such as intensive source removal operations or pump-and-treat technologies.

### 2.2.1 Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation

Because biodegradation is the most important destructive process acting to reduce contaminant concentrations in groundwater, an accurate estimate of the potential for natural biodegradation is important to consider when determining whether groundwater contamination presents a substantial threat to human health and the environment. This information also will be useful when selecting the remedial alternative that will be most cost effective at eliminating or abating these threats should natural attenuation alone not prove to be sufficient.

Over the past two decades, numerous laboratory and field studies have demonstrated that subsurface microorganisms can degrade a variety of chlorinated solvents (e.g., Bouwer *et al.*, 1981; Miller and Guengerich, 1982; Wilson and Wilson, 1985; Nelson *et al.*, 1986; Bouwer and Wright, 1988; Lee, 1988; Little *et al.*, 1988; Mayer *et al.*, 1988; Arciero *et al.*, 1989; Cline and Delfino, 1989; Freedman and Gossett, 1989; Folsom *et al.*, 1990; Harker and Kim, 1990; Alvarez-Cohen and McCarty, 1991a, 1991b; DeStefano *et al.*, 1991; Henry, 1991; McCarty *et al.*, 1992; Hartmans and de Bont, 1992; McCarty and Semprini, 1994; Vogel, 1994). Whereas fuel hydrocarbons are biodegraded through use as a primary substrate (electron donor), chlorinated aliphatic hydrocarbons may undergo biodegradation through three different pathways: use as an electron acceptor; use as an electron donor; or through cometabolism, where degradation of the chlorinated organic is fortuitous, and there is no benefit to the microorganism. At a given site, one or all of these processes may be operating, although at many sites the use of chlorinated aliphatic hydrocarbons as electron acceptors appears to be most important under natural conditions. In this case biodegradation of chlorinated aliphatic hydrocarbons will be an electron-donor-limited process. Conversely, biodegradation of fuel hydrocarbons is an electron-acceptor-limited process.

In a pristine aquifer, native organic carbon is used as an electron donor, and dissolved oxygen (DO) is used first as the prime electron acceptor. Where anthropogenic carbon (e.g., as fuel hydrocarbons) is present, it also will be used as an electron donor. After the DO is consumed,

anaerobic microorganisms typically use additional electron acceptors (as available) in the following order of preference: nitrate, ferric iron oxyhydroxide, sulfate, and finally carbon dioxide. Evaluation of the distribution of these electron acceptors can provide evidence of where and how chlorinated aliphatic hydrocarbon biodegradation is occurring. In addition, because chlorinated aliphatic hydrocarbons may be used as electron acceptors or electron donors (in competition with other acceptors or donors), isopleth maps showing the distribution of these compounds and their daughter products can provide evidence of the mechanisms of biodegradation working at a site. As with BTEX, the driving force behind oxidation-reduction reactions resulting in chlorinated aliphatic hydrocarbon degradation is electron transfer. Although thermodynamically favorable, most of the reactions involved in chlorinated aliphatic hydrocarbon reduction and oxidation do not proceed abiotically. Microorganisms are capable of carrying out the reactions, but they will facilitate only those oxidation-reduction reactions that have a net yield of energy.

#### 2.2.1.1 Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation

The following sections describe the biodegradation of those compounds that are most prevalent and whose behavior is best understood.

##### *2.2.1.1.1 Electron Acceptor Reactions (Reductive Dehalogenation)*

The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination. During this process, the chlorinated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. Figure 2.2 illustrates the transformation of chlorinated ethenes via reductive dechlorination. In general, reductive dechlorination occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. During reductive dechlorination, all three isomers of DCE can theoretically be produced; however, Bouwer (1994) reports that under the influence of biodegradation, *cis*-1,2-DCE is a more common intermediate than *trans*-1,2-DCE, and that 1,1-DCE is the least prevalent of the three DCE isomers when they are present as daughter products. Reductive dechlorination of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in the concentration of chloride ions.

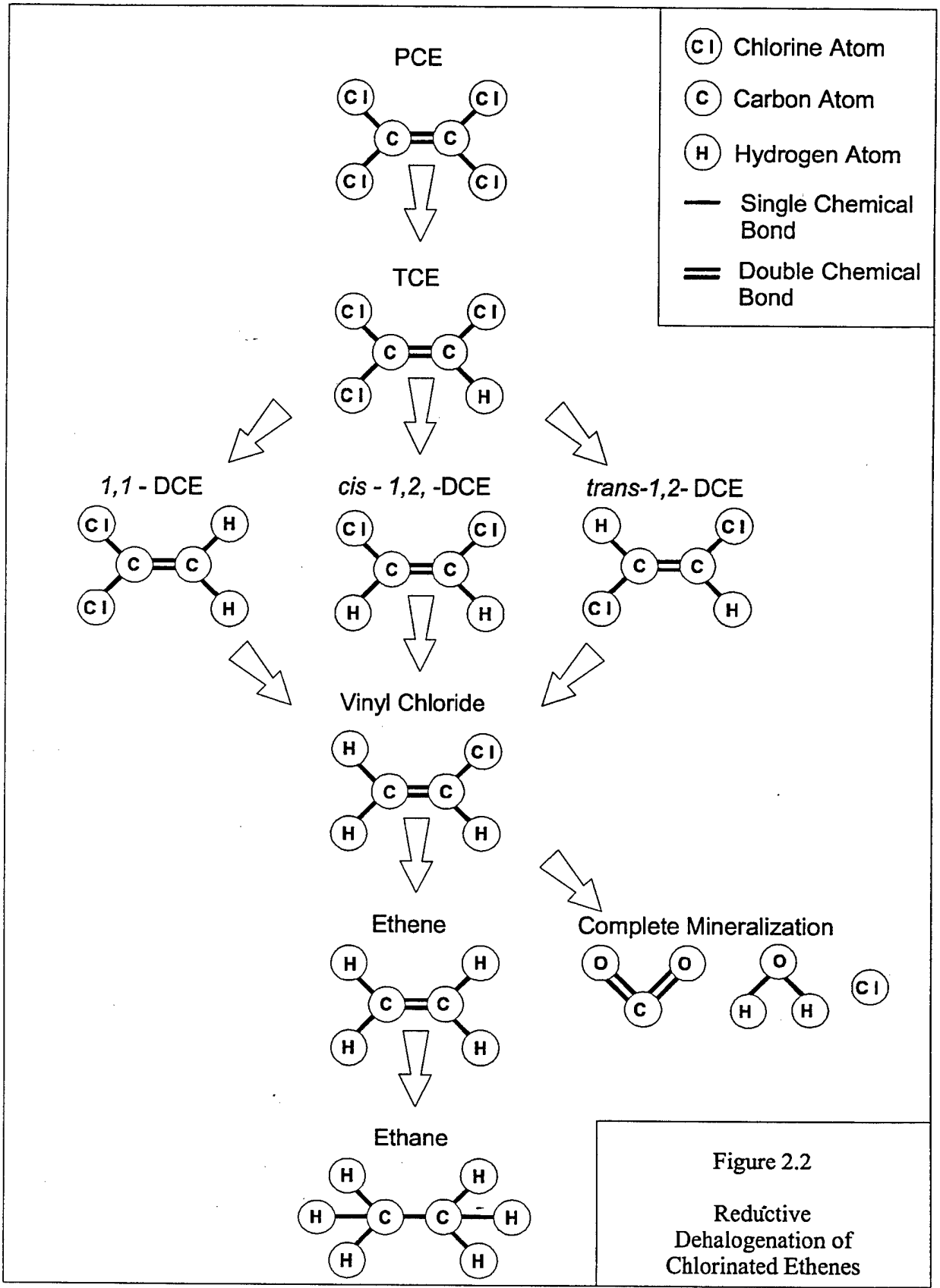



Figure 2.2

Reductive Dehalogenation of Chlorinated Ethenes

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Reductive dechlorination affects each of the chlorinated ethenes differently. Of these compounds, PCE is the most susceptible to reductive dechlorination because it is the most oxidized. Conversely, VC is the least susceptible to reductive dechlorination because it is the least oxidized of these compounds. As a result, the rate of reductive dechlorination decreases as the degree of chlorination decreases (Vogel and McCarty, 1985; Bouwer, 1994). Murray and Richardson (1993) have postulated that this rate decrease may explain the accumulation of VC in PCE and TCE plumes that are undergoing reductive dechlorination. Reductive dechlorination has been demonstrated under nitrate- and iron-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under sulfate-reducing and methanogenic conditions (Bouwer, 1994). Because chlorinated aliphatic hydrocarbon compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth in order for this process to occur (Bouwer, 1994). Potential carbon sources include natural organic matter, fuel hydrocarbons, or other anthropogenic organic compounds such as those found in landfill leachate.

*2.2.1.1.2 Electron Donor Reactions*

Murray and Richardson (1993) write that microorganisms are generally believed to be incapable of growth using PCE and TCE as a primary substrate (i.e., electron donor). However, under aerobic and some anaerobic conditions, the less oxidized chlorinated aliphatic hydrocarbons (e.g., VC) can be used as the primary substrate in biologically mediated oxidation-reduction reactions (McCarty and Semprini, 1994). In this type of reaction, the facilitating microorganism obtains energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. In contrast to reactions in which the chlorinated aliphatic hydrocarbon is used as an electron acceptor, only the least oxidized chlorinated aliphatic hydrocarbons can be used as electron donors in biologically mediated oxidation-reduction reactions. McCarty and Semprini (1994) describe investigations in which VC and 1,2-dichloroethane (DCA) were shown to serve as primary substrates under aerobic conditions. These authors also document that dichloromethane has the potential to function as a primary substrate under either aerobic or anaerobic environments. In addition, Bradley and Chapelle (1996) show evidence of mineralization of VC under iron-reducing conditions so long as there is sufficient bioavailable iron (III). Aerobic metabolism of VC may be characterized by a loss of VC mass and a decreasing molar ratio of VC to other chlorinated aliphatic hydrocarbon compounds.

*2.2.1.1.3 Cometabolism*

When a chlorinated aliphatic hydrocarbon is biodegraded via cometabolism, the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the organisms for other purposes. The organism receives no known benefit from the degradation of the chlorinated aliphatic hydrocarbon. Rather, the cometabolic degradation of the chlorinated aliphatic hydrocarbon may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). Cometabolism is best documented in aerobic environments, although it potentially could occur under anaerobic conditions. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994). Vogel (1994) further elaborates that the rate of cometabolism increases as the degree of dechlorination decreases. During cometabolism, the chlorinated alkene is indirectly transformed by bacteria as they use BTEX or another substrate to meet their energy requirements. Therefore, the chlorinated alkene does not enhance the degradation of BTEX or other carbon sources, nor will its cometabolism interfere with the use of electron acceptors involved in the oxidation of those carbon sources.

2.2.1.2 Behavior of Chlorinated Solvent Plumes

Chlorinated solvent plumes can exhibit three types of behavior depending on the amount of solvent, the amount of biologically available organic carbon in the aquifer, the distribution and concentration of natural electron acceptors, and the types of electron acceptors being used. Individual plumes may exhibit all three types of behavior in different portions of the plume. The different types of plume behavior are summarized below.

*2.2.1.2.1 Type 1 Behavior*

Type 1 behavior occurs where the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate), and microbial degradation of this anthropogenic carbon drives reductive dechlorination. When evaluating natural attenuation of a plume exhibiting type 1 behavior the following questions must be answered:

1) Is the electron donor supply adequate to allow microbial reduction of the chlorinated organic compounds? In other words, will the microorganisms "strangle" before they "starve" [i.e., will they run out of chlorinated aliphatic hydrocarbons used as electron acceptors before they run out of anthropogenic carbon used as the primary substrate?

2) What is the role of competing electron acceptors (e.g., dissolved oxygen, nitrate, iron (III) and sulfate)?

3) Is VC oxidized, or is it reduced?

Appendices B and C discuss what these questions mean and how they are answered. Type 1 behavior results in the rapid and extensive degradation of the more highly-chlorinated solvents such as PCE, TCE, and DCE.

*2.2.1.2.2 Type 2 Behavior*

Type 2 behavior dominates in areas that are characterized by relatively high concentrations of biologically available native organic carbon. Microbial utilization of this natural carbon source drives reductive dechlorination (i.e., it is the primary substrate for microorganism growth). When evaluating natural attenuation of a type 2 chlorinated solvent plume, the same questions as those posed in the description of type 1 behavior must be answered. Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents than Type 1 behavior, but under the right conditions (e.g., areas with high natural organic carbon contents), this type of behavior also can result in rapid degradation of these compounds.

*2.2.1.2.3 Type 3 Behavior*

Type 3 behavior dominates in areas that are characterized by inadequate concentrations of native and/or anthropogenic carbon, and concentrations of dissolved oxygen that are greater than 1.0 mg/L. Under these aerobic conditions reductive dechlorination will not occur. The most significant natural attenuation mechanisms for PCE, TCE, and DCE will be advection, dispersion, and sorption. However, VC can be rapidly oxidized under these conditions.

*2.2.1.2.4 Mixed Behavior*

As mentioned above, a single chlorinated solvent plume can exhibit all three types of behavior in different portions of the plume. This can be beneficial for natural biodegradation of chlorinated aliphatic hydrocarbon plumes. For example, Wiedemeier *et al.* (1996a) describe a plume at Plattsburgh AFB, New York that exhibits Type 1 behavior in the source area and Type 3 behavior downgradient from the source. The most fortuitous scenario involves a plume in which PCE, TCE, and DCE are reductively dechlorinated with accumulation of VC near the source area (Type 1 or Type 2 behavior), then VC is oxidized (Type 3 behavior), either aerobically or via iron reduction further downgradient. Vinyl chloride is oxidized to carbon dioxide in this type of plume

and does not accumulate. The following sequence of reactions occurs in a plume that exhibits this type of mixed behavior.

$$PCE \rightarrow TCE \rightarrow DCE \rightarrow VC \rightarrow \text{Carbon Dioxide}$$

In general, TCE, DCE, and VC may attenuate at approximately the same rate, and thus these reactions may be confused with simple dilution. Note that no ethene is produced during this reaction. Vinyl chloride is removed from the system much faster under these conditions than it is under VC-reducing conditions.

A less desirable scenario, but one in which all contaminants may be entirely biodegraded, involves a plume in which all chlorinated aliphatic hydrocarbons are reductively dechlorinated via Type 1 or Type 2 behavior. Vinyl chloride is reduced to ethene, which may be further reduced to ethane or methane. The following sequence of reactions occur in this type of plume.

$$PCE \rightarrow TCE \rightarrow DCE \rightarrow VC \rightarrow \text{Ethene} \rightarrow \text{Ethane}$$

This sequence has been investigated by Freedman and Gossett (1989). In this type of plume, VC degrades more slowly than TCE, and thus tends to accumulate.

### 2.2.2 Bioattenuation Screening Process

Based on the experience of the authors, it is estimated that for 80 percent of fuel-hydrocarbon spills at federal facilities, natural attenuation can bring concentrations to below MCLs prior to discharge. For spills of chlorinated aliphatic hydrocarbons at federal facilities however, natural attenuation alone can bring concentrations to below MCLs prior to discharge for approximately 20 percent of spills. However, NA in conjunction with other remedial options should allow us to meet environmental cleanup goals at lower costs at most sites. With this in mind, it is easy to understand why an accurate assessment of the potential for natural biodegradation of chlorinated compounds should be made before investing in a detailed study of natural attenuation. The screening process presented in this section is outlined in Figure 2.3. This approach should allow the investigator to determine if natural bioattenuation of PCE, TCE, DCE, TCA, and chlorobenzenes is likely to be a viable remedial alternative before additional time and money are expended. The data required to make the preliminary assessment of natural attenuation also can be used to aid the design of an engineered remedial solution should the screening process suggest that natural attenuation is not feasible. Table 2.3 presents the analytical screening criteria.

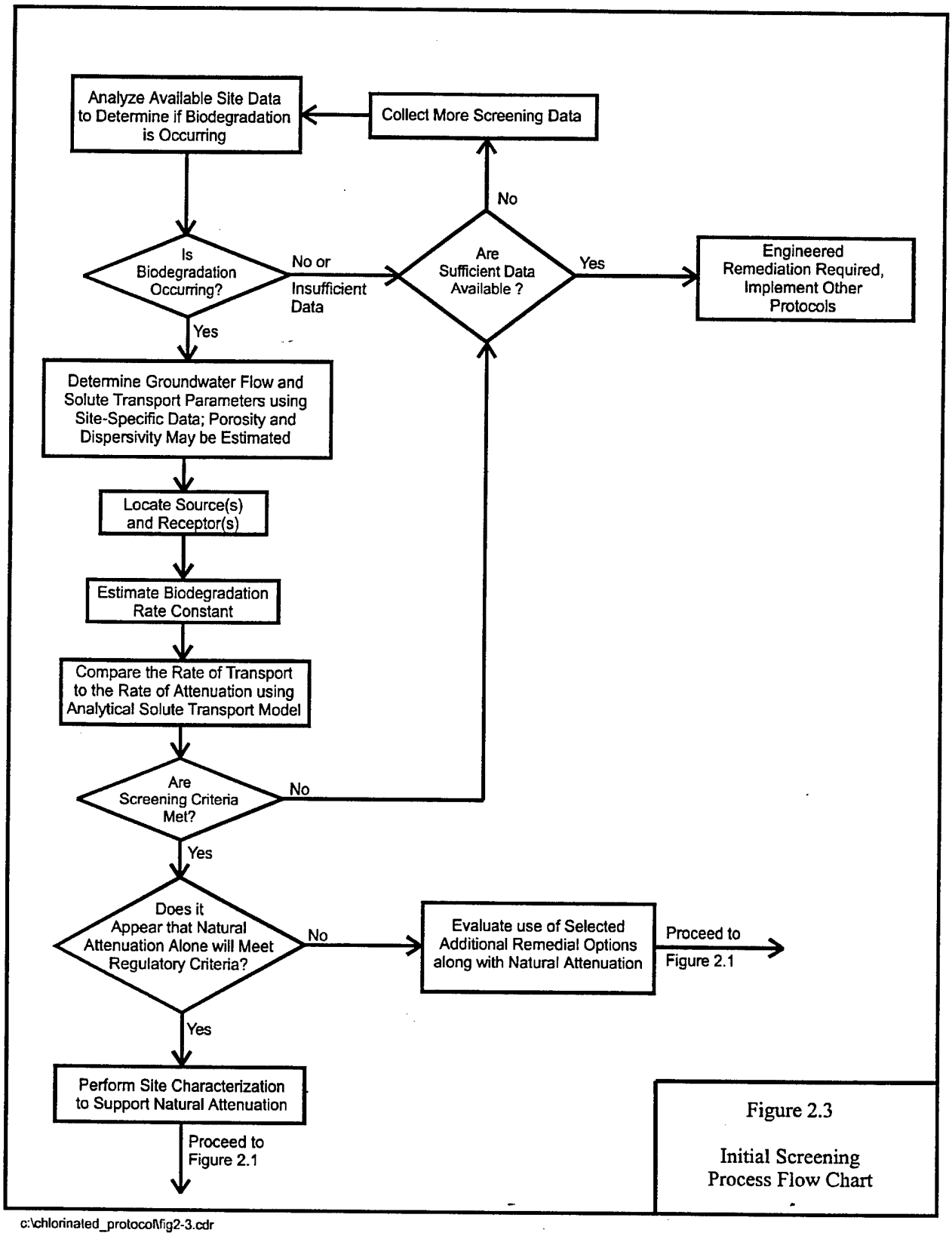



Figure 2.3

Initial Screening Process Flow Chart

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## Table 2.3

## Analytical Parameters and Weighting for Preliminary Screening[a/]

| Analysis | Concentration in Most Contaminated Zone | Interpretation | Value |
|---|---|---|---|
| Oxygen* | <0.5 mg/L | Tolerated, suppresses the reductive pathway at higher concentrations | 3 |
| Oxygen* | >1 mg/L | VC may be oxidized aerobically | -3 |
| Nitrate* | <1 mg/L | At higher concentrations may compete with reductive pathway | 2 |
| Iron II* | >1 mg/L | Reductive pathway possible | 3 |
| Sulfate* | <20 mg/L | At higher concentrations may compete with reductive pathway | 2 |
| Sulfide* | >1 mg/L | Reductive pathway possible | 3 |
| Methane* | <0.5 mg/L<br>>0.5 mg/L | VC oxidizes<br>Ultimate reductive daughter product, VC Accumulates | 0<br>3 |
| Oxidation Reduction Potential* (ORP) | <50 millivolts (mV)<br><-100mV | Reductive pathway possible<br>Reductive pathway likely | 1<br>2 |
| pH* | 5 < pH < 9<br>5 > pH >9 | Optimal range for reductive pathway<br>Outside optimal range for reductive pathway | 0<br>-2 |
| TOC | > 20 mg/L | Carbon and energy source; drives dechlorination; can be natural or anthropogenic | 2 |
| Temperature* | > 20°C | At T >20°C biochemical process is accelerated | 1 |
| Carbon Dioxide | >2x background | Ultimate oxidative daughter product | 1 |
| Alkalinity | >2x background | Results from interaction of carbon dioxide with aquifer minerals | 1 |
| Chloride* | >2x background | Daughter product of organic chlorine | 2 |
| Hydrogen | >1 nM | Reductive pathway possible, VC may accumulate | 3 |
| Hydrogen | <1 nM | VC oxidized | 0 |
| Volatile Fatty Acids | > 0.1 mg/L | Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source | 2 |
| BTEX* | > 0.1 mg/L | Carbon and energy source; drives dechlorination | 2 |
| PCE* | | Material released | 0 |
| TCE* | | Material released<br>Daughter product of PCE | 0<br>2[a/] |
| DCE* | | Material released<br>Daughter product of TCE.<br>If cis is greater than 80% of total DCE it is likely a daughter product of TCE | 0<br>2[a/] |
| VC* | | Material released<br>Daughter product of DCE | 0<br>2[a/] |
| Ethene/Ethane | >0.01mg/L<br>>0.1 mg/L | Daughter product of VC/ethene | 2<br>3 |
| Chloroethane* | | Daughter product of VC under reducing conditions | 2 |
| 1,1,1-Trichloroethane* | | Material released | 0 |
| 1,2-dichlorobenzene* | | Material released | 0 |
| 1,3- dichlorobenzene* | | material released | 0 |
| 1,4- dichlorobenzene* | | material released | 0 |
| chlorobenzene* | | Material released or daughter product of dichlorobenzene | 2[a/] |
| 1,1-DCE* | | Daughter product of TCE or chemical reaction of 1,1,1-TCA | 2[a/] |

* Required analysis.

a/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

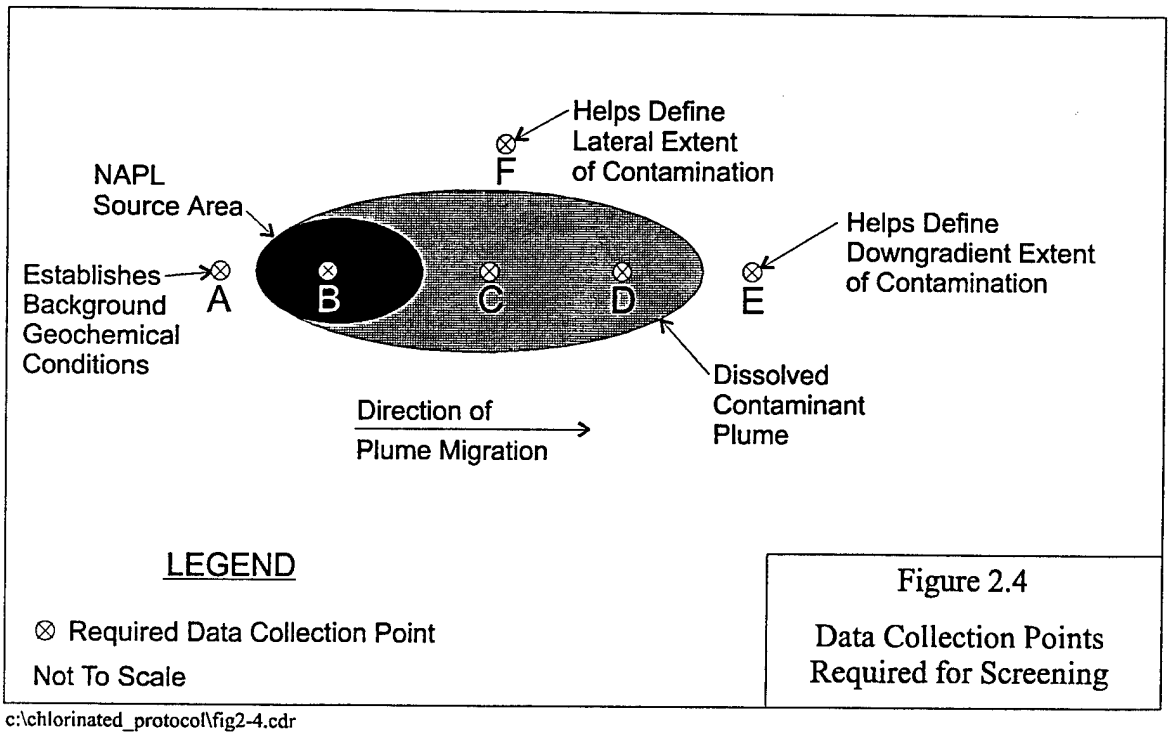



Figure 2.4

Data Collection Points
Required for Screening

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The following information is required for the screening process:

- The chemical and geochemical data presented in Table 2.3 for a minimum of six (6) samples. Figure 2.4 shows the schematic locations of these data collection points Note: if other contaminants are suspected, then data on the concentrations and distribution of these compounds also should be obtained
- Locations of source(s) and receptor exposure points.
- An estimate of the transport velocity and direction of groundwater flow

Once these data have been collected, the screening process can be undertaken. The following steps summarize the screening processes:

1) Determine if biodegradation is occurring using geochemical data

   If biodegradation is occurring, proceed to step 2. If it is not, assess the amount and types of data available. If data are insufficient to determine if biodegradation is occurring, collect supplemental data.

2) Determine groundwater flow and solute transport parameters.

   Dispersivity and porosity may be estimated from literature but the hydraulic conductivity and the groundwater gradient and flow direction must be determined from field data. The investigator should use the highest hydraulic conductivity measured at the site during the preliminary screening because solute plumes tend to follow the path of least resistance (i.e., highest hydraulic conductivity). This will give the "worst-case" estimate of the solute migration distance over a given period of time.

3) Locate source(s) and receptor exposure points.

4) Estimate the biodegradation rate constant.

   Biodegradation rate constants can be estimated using a conservative tracer found commingled with the contaminant plume, as described in Appendix C and by Wiedemeier *et al.* (1996b). When dealing with a plume that contains only chlorinated solvents, this procedure can be modified to use chloride as a tracer. Rate constants derived from microcosm studies can also be used. If it is not possible to estimate the biodegradation rate using these procedures, then use a range of accepted literature values for biodegradation of the contaminants of concern. Appendix C presents a range of biodegradation rate constants for various compounds.

5) Compare the rate of transport to the rate of attenuation.

   Use analytical solutions or a screening model such as BIOSCREEN.

6) Determine if screening criteria are met.

**Step 1: Determine if Biodegradation is Occurring**

The first step in the screening process is to sample at least six (6) wells that are representative of the contaminant flow system (Figure 2.4) and analyze them for the parameters listed in Table 2.3 (see also Section 2.3.2). These samples should include (1) a sample from the most contaminated portion of the aquifer (generally in the area where NAPL currently is present or was present in the past); (2) samples collected downgradient from the NAPL source area but still in the dissolved contaminant plume; (3) samples collected downgradient from the dissolved contaminant plume; and (4) samples collected from upgradient and lateral locations that are not impacted by the plume.

The sample collected in the NAPL source area allows determination of the dominant terminal electron-accepting processes operating at the site. In conjunction with the sample collected in the NAPL source zone, samples collected in the dissolved plume downgradient from the NAPL source zone allow the investigator to determine if the plume is degrading with distance along the flow path and to determine the distribution of electron acceptors and donors and metabolic byproducts along the flow path. The sample collected downgradient from the dissolved plume aids in plume delineation and allows the investigator to determine if metabolic byproducts are present in an area of groundwater that has been remediated. The upgradient and lateral samples allow delineation of the plume and determination of background concentrations of the electron acceptors and donors.

After these samples have been analyzed for the parameters listed in Table 2.3, the investigator should analyze the data to determine if biodegradation is occurring. The right-hand column of Table 2.3 contains scoring values that can be used as a test to assess the likelihood that biodegradation is occurring. This method relies on the fact that biodegradation will cause

predictable changes in groundwater chemistry. For example, if the dissolved oxygen concentration in the area of the plume with the highest contaminant concentration is less than 0.5 milligrams per liter (mg/L), 3 points are awarded. Table 2.4 summarizes the range of possible scores and gives an interpretation for each score. If the score totals 15 or more points, it is likely that biodegradation is occurring, and the investigator should proceed to Step 2.

**Table 2.4**
**Interpretation of Points Awarded During Screening Step 1**

| Score | Interpretation |
|---|---|
| 0 to 5 | Inadequate evidence for biodegradation of chlorinated organics |
| 6 to 14 | Limited evidence for biodegradation of chlorinated organics |
| 15 to 20 | Adequate evidence for biodegradation of chlorinated organics |
| > 20 | Strong evidence for biodegradation of chlorinated organics |

The following two examples illustrate how step 1 of the screening process is implemented. The site used in the first example is a former fire training area contaminated with chlorinated solvents mixed with fuel hydrocarbons. The presence of the fuel hydrocarbons appears to reduce the ORP of the groundwater to the extent that reductive dechlorination is favorable. The second example contains data from a dry cleaning site contaminated only with chlorinated solvents. This site was contaminated with spent cleaning solvents that were dumped into a shallow dry well situated just above a well-oxygenated, unconfined aquifer with low organic carbon concentrations.

Example 1: Strong Evidence for Biodegradation of Chlorinated Organics

| Analyte | Concentration in Most Contaminated Zone | Points Awarded |
|---|---|---|
| Dissolved Oxygen | 0.1 mg/L | 3 |
| Nitrate | 0.3 mg/L | 2 |
| Iron (II) | 10 mg/L | 3 |
| Sulfate | 2 mg/L | 2 |
| Methane | 5 mg/L | 3 |
| ORP | -190 mV | 2 |
| Chloride | 3 times background | 2 |
| PCE (released) | 1,000 µg/L | 0 |
| TCE (none released) | 1,200 µg/L | 2 |
| cis-DCE (none released) | 500 µg/L | 2 |
| VC (none released) | 50 µg/L | 2 |
| | Total Points Awarded | 23 Points |

In this example the investigator can infer that biodegradation is likely occurring and may proceed to Step 2.

Example 2: Biodegradation Unlikely

| Analyte | Concentration in Most Contaminated Zone | Points Awarded |
|---|---|---|
| Dissolved Oxygen | 3 mg/L | -3 |
| Nitrate | 0.3 mg/L | 2 |
| Iron (II) | Not Detected (ND) | 0 |
| Sulfate | 10 mg/L | 2 |
| Methane | ND | 0 |
| ORP | 100 mV | 0 |
| Chloride | background | 0 |
| TCE (released) | 1,200 µg/L | 0 |
| cis-DCE (none released) | ND | 0 |
| VC (none released) | ND | 0 |
| | Total Points Awarded | 1 Point |

In this example the investigator can infer that biodegradation is probably not occurring or is occurring too slowly to contribute to natural attenuation. In this case, the investigator should critically evaluate other natural attenuation mechanisms or implement engineered remediation systems.

**Step 2: Determine Groundwater Flow and Solute Transport Parameters**

After it has been shown that biodegradation is occurring, it is important to quantify groundwater flow and solute transport parameters. This will make it possible to use a solute transport model to quantitatively estimate the concentration of the plume and its direction and rate of travel. To use an analytical model it is necessary to know the hydraulic gradient and hydraulic conductivity for the site and to have estimates of porosity and dispersivity. It also is helpful to know the coefficient of retardation. Quantification of these parameters is discussed in detail in Appendix B.

In order to make the modeling as accurate as possible, the investigator must have site-specific hydraulic gradient and hydraulic conductivity data. To determine the groundwater flow and solute transport direction, it is necessary to have at least three accurately surveyed wells at the site. The porosity and dispersivity are generally estimated using accepted literature values for the types of sediments found at the site. If the investigator has total organic carbon data for soil, it is possible to estimate the coefficient of retardation; otherwise it is conservative to assume that the solute transport and groundwater velocities are the same.

**Step 3: Locate Sources and Receptor Exposure Points**

To determine the length of flow for the predictive modeling to be conducted in Step 5, it is important to know the distance between the source of contamination, the toe of the dissolved plume, and any potential downgradient or cross-gradient receptor exposure points.

**Step 4: Estimate the Biodegradation Rate**

Biodegradation is the most important process that degrades contaminants in the subsurface; therefore, the biodegradation rate is one of the most important model input parameters. Biodegradation of chlorinated aliphatic hydrocarbons can commonly be represented as a first-order rate constant. It is generally best to use site-specific biodegradation rates. Calculation of site-specific biodegradation rates is discussed in Appendix C. If it is not possible to determine site-specific biodegradation rates, then it will be necessary to use literature values for the biodegradation rate of the contaminant of interest. A useful approach is to start with average values, and then to vary the model input to predict "best-case" and "worst-case" scenarios. Estimated biodegradation rates can be used only after it has been shown that biodegradation is occurring (see Step 1).

**Step 5: Compare the Rate of Transport to the Rate of Attenuation**

At this early stage in the natural attenuation demonstration, comparison of the rate of solute transport to the rate of attenuation is best accomplished using an analytical model. Several analytical models are available, but the BIOSCREEN model (developed by the Technology Transfer Division of AFCEE) is probably the simplest to use. This model is non-proprietary and is available from the Robert S. Kerr Research Center's home page on the Internet (www.epa.gov/ada/bioscreen.html). The BIOSCREEN model is based on Domenico's (1987) solution to the advection-dispersion equation, and allows use of either a first-order biodegradation rate or an instantaneous reaction between contaminants and electron acceptors to simulate the effects of biodegradation. To model transport of chlorinated aliphatic hydrocarbons using BIOSCREEN, only the first-order decay rate option should be used. BIOCHLOR, a similar model, is under development by the Technology Transfer Division of AFCEE. This model will likely use the same analytical solution as BIOSCREEN, but will be geared toward evaluating transport of chlorinated compounds under the influence of biodegradation.

The primary purpose of comparing the rate of transport to the rate of attenuation is to determine if the residence time along the flow path is adequate to be protective of human health and the environment (i.e., to qualitatively estimate if the contaminant is attenuating at a rate fast enough to allow degradation of the contaminant to acceptable concentrations before receptors are exposed). It is important to perform a sensitivity analysis to help evaluate the confidence in the

preliminary screening modeling effort. If modeling shows that receptors will not be exposed to contaminants at concentrations above risk-based corrective action criteria, then the screening criteria are met, and the investigator can proceed with the natural attenuation evaluation.

**Step 6: Determine if Screening Criteria are Met**

Before proceeding with the full-scale natural attenuation evaluation, the investigator should ensure that the answers to both of the following questions are yes:

- Has the plume moved a shorter distance than expected based on the known (or estimated) time since the contaminant release and the contaminant velocity, as calculated from site-specific measurements of hydraulic conductivity and hydraulic gradient, and estimates of effective porosity and contaminant retardation?
- Is it likely that the contaminant is attenuating at rates sufficient to be protective of human health and the environment at potential exposure points (e.g., at a point of discharge to a sensitive environmental resource)?

If the answer to these questions is yes, then the investigator is encouraged to proceed with the full-scale natural attenuation demonstration.

## 2.3 COLLECT ADDITIONAL SITE CHARACTERIZATION DATA IN SUPPORT OF NATURAL ATTENUATION AS REQUIRED

Detailed site characterization is necessary to document the potential for natural attenuation to meet cleanup objectives. 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 a natural attenuation investigation. The first is to collect the data needed to 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 concentrations of a contaminant plume through solute fate and transport modeling. It is the responsibility of the proponent to "make the case" for natural attenuation. Thus, detailed site characterization is required to achieve these goals and to support this remedial option. Adequate site characterization in support of natural attenuation requires that the following site-specific parameters be determined:

- Extent and types 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, or other site activity.
- 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, and
  - Areas of local groundwater recharge and discharge.
- Identification of current and future potential exposure pathways, receptors, and exposure points.

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

### 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. As appropriate, soil gas data may be collected and analyzed to better characterize soil contamination. Depending on the status of the site, this work may 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 natural attenuation investigation.

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), and through collection of soil gas samples. 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 or to accommodate site-specific conditions.

The analytical protocol to be used for soil and soil gas sample analyses is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to document natural attenuation, including the effects of sorption and biodegradation. Each analyte is discussed separately below.

- **Volatile Organic Compounds**: Knowledge of the location, distribution, concentration, and total mass of contaminants of regulatory concern sorbed to soils or present as mobile or immobile NAPL is required to calculate contaminant partitioning from NAPL into groundwater.
- **Total Organic Carbon**: Knowledge of the TOC content of the aquifer matrix is important for sorption and solute-retardation calculations. TOC samples should be collected from a background location in the stratigraphic horizon(s) where most contaminant transport is expected to occur.
- **Oxygen and Carbon Dioxide**: Oxygen and carbon dioxide soil gas measurements can be used to identify areas in the unsaturated zone where biodegradation is occurring. This can be a useful and relatively inexpensive way to identify NAPL source areas (AFCEE, 1994).
- **Fuel and Chlorinated Volatile Organic Compounds**: Knowledge of the distribution of contaminants in soil gas can be used as a cost-effective way to estimate the extent of soil contamination.

### 2.3.2 Groundwater Characterization

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of natural attenuation, groundwater samples must be collected and analyzed. Biodegradation of organic compounds, whether natural or

anthropogenic, brings about measurable changes in the chemistry of groundwater in the affected area. By measuring these changes, it is possible to document and quantitatively evaluate the importance of natural attenuation at a site.

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

The analytical protocol for groundwater sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to delineate dissolved contamination and to document natural attenuation, including the effects of sorption and biodegradation. Data obtained from the analysis of groundwater for these analytes is used to scientifically document natural attenuation 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 natural attenuation demonstration.

#### 2.3.2.1 Volatile and Semivolatile Organic Compounds

These analytes are used to determine the type, concentration, and distribution of contaminants and daughter products in the aquifer. At a minimum, the volatile organic compound (VOC) analysis (Method SW8260a) should be used, with the addition of the trimethylbenzene isomers if fuel hydrocarbons are present or suspected. The combined dissolved concentrations of BTEX and trimethylbenzenes should not be greater than about 30 mg/L for a JP-4 spill (Smith *et al.*, 1981) or about 135 mg/L for a gasoline spill (Cline *et al.*, 1991; American Petroleum Institute, 1985). If these compounds are found in higher concentrations, sampling errors such as emulsification of LNAPL in the groundwater sample likely have occurred and should be investigated.

Maximum concentrations of chlorinated solvents dissolved in groundwater from neat solvents should not exceed their solubilities in water. Appendix B contains solubilities for common contaminants. If contaminants are found in concentrations greater than their solubilities, then sampling errors such as emulsification of NAPL in the groundwater sample have likely occurred and should be investigated.

#### 2.3.2.2 Dissolved Oxygen

Dissolved oxygen is the most thermodynamically favored electron acceptor used by microbes for the biodegradation of organic carbon, whether natural or anthropogenic. Anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L and hence reductive dechlorination will not occur. This is why it is important to have a source of carbon in the aquifer that can be used by aerobic microorganisms as a primary substrate. During aerobic respiration, dissolved oxygen concentrations decrease. After depletion of dissolved oxygen, anaerobic microbes will use nitrate as an electron acceptor, followed by iron (III), then sulfate, and finally carbon dioxide (methanogenesis). Each sequential reaction drives the ORP of the groundwater downward into the range within which reductive dechlorination can occur. Reductive dechlorination is most effective in the ORP range corresponding to sulfate reduction and methanogenesis, but dechlorination of PCE and TCE also may occur in the ORP range associated with denitrification or iron (III) reduction. Because reductive dechlorination is most effective in the sulfate-reduction and methanogenesis ORP range, competitive exclusion between sulfate reducers, methanogens, and reductive dechlorinators can occur.

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 the potential for aeration as described in Appendix A.

#### 2.3.2.3 Nitrate

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation of organic carbon via denitrification. In order for reductive dechlorination to occur, nitrate concentrations in the contaminated portion of the aquifer must be less than 1.0 mg/L.

#### 2.3.2.4 Iron (II)

In some cases iron (III) is used as an electron acceptor during anaerobic biodegradation of organic carbon. 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 and VC (see Section 2.2.1.1.2).

2.3.2.5 Sulfate

After dissolved oxygen and nitrate 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. Concentrations of sulfate greater than 20 mg/L may cause competitive exclusion of dechlorination.

2.3.2.6 Methane

During methanogenesis acetate is split to form carbon dioxide and methane, or carbon dioxide is used as an electron acceptor, and is reduced to methane. Methanogenesis generally occurs after oxygen, nitrate, 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 above background concentrations in groundwater in contact with fuels is indicative of microbial degradation of fuel hydrocarbons. Methane also is associated with spills of pure chlorinated solvents. It is not known if the methane comes from chlorinated solvent carbon or from native dissolved organic carbon.

2.3.2.7 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 carbon dioxide-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 carbon dioxide 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 the experience of the authors, biodegradation of organic compounds rarely, if ever, generates enough acid to impact the alkalinity of groundwater.

2.3.2.8 Oxidation-Reduction Potential

The ORP 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. Oxidation-reduction reactions in groundwater containing organic compounds (natural or anthropogenic) are usually biologically mediated, and therefore, the ORP of a groundwater system depends upon and influences rates of

biodegradation. Knowledge of the ORP of groundwater also is important because some biological processes operate only within a prescribed range of ORP conditions. The ORP of groundwater generally ranges from -400 millivolts (mV) to 800 mV.

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

#### 2.3.2.9 Dissolved Hydrogen

Concentrations of dissolved hydrogen can also be used to evaluate redox processes in groundwater systems (Lovley and Goodwin, 1988; Lovley et al., 1994; Chapelle et al., 1995). $H_2$ is continuously produced in anoxic groundwater systems by fermentative microorganisms that decompose natural and anthropogenic organic matter. This $H_2$ is then consumed by respiratory microorganisms that use nitrate, Fe(III), sulfate, or $CO_2$ as terminal electron acceptors. This continuous cycling of $H_2$ is called *interspecies hydrogen transfer*. Significantly, nitrate-, Fe(III)-, sulfate- and $CO_2$-reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing the $H_2$ that is being continually produced. Nitrate reducers are highly efficient $H_2$ utilizers and maintain very low steady-state $H_2$ concentrations. Fe(III) reducers are slightly less efficient and thus maintain somewhat higher $H_2$ concentrations. Sulfate reducers and methanogenic bacteria are progressively less efficient and maintain even higher $H_2$ concentrations. Because each terminal electron accepting process has a characteristic $H_2$ concentration associated with it, $H_2$ concentrations can be an indicator of predominant redox processes. These characteristic ranges are given in Table 2.5. An analytical protocol for quantifying $H_2$ concentrations in groundwater is given in Appendix A.

**Table 2.5**

**Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process**

| Terminal Electron Accepting Process | Hydrogen ($H_2$) Concentration (nanomoles per liter) |
|---|---|
| Denitrification | < 0.1 |
| Iron (III) Reduction | 0.2 to 0.8 |
| Sulfate Reduction | 1 to 4 |
| Methanogenesis | 5-20 |

Oxidation-reduction potential (ORP) measurements are based on the concept of thermodynamic equilibrium and, within the constraints of that assumption, can be used to evaluate redox processes in groundwater systems. The $H_2$ method is based on the ecological concept of interspecies hydrogen transfer by microorganisms and, within the constraints of that assumption, can also be used to evaluate redox processes. These methods, therefore, are fundamentally different. A direct comparison of these methods (Chapelle et al., 1996) has shown that ORP measurements were effective in delineating oxic from anoxic ground water, but that ORP measurements could not distinguish between nitrate-reducing, Fe(III)-reducing, sulfate-reducing, or methanogenic zones in an aquifer. In contrast, the $H_2$ method could readily distinguish between different anaerobic zones. For those sites where distinguishing between different anaerobic processes is important information $H_2$ measurements are an available technology for making such distinctions.

In practice, it is preferable to interpret $H_2$ concentrations in the context of electron acceptor (oxygen, nitrate, Fe(III), sulfate) availability and the presence of the final products (Fe(II), hydrogen sulfide, methane) of microbial metabolism (Chapelle *et al.*, 1995). For example, if sulfate concentrations in groundwater are less than 0.5 mg/L, methane concentrations are greater than 0.5 mg/L, and $H_2$ concentrations are in the 5-20 nM range, it can be concluded with a high degree of certainty that methanogenesis is the predominant redox process in the aquifer. Similar logic can be applied to identifying denitrification (presence of nitrate, $H_2$<0.1 nM), Fe(III) reduction (production of Fe(II), $H_2$ 0.2 to 0.8 nM), and sulfate reduction (presence of sulfate, production of sulfide, $H_2$ 1-4 nM).

2.3.2.10 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 ORP 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 chlorinated aliphatic hydrocarbons and 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, with oxygen 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°C increase in temperature ("Q"$_{10}$ rule) over the temperature range between 5 and 25°C.

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

2.3.2.11 Chloride

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

During biodegradation of chlorinated hydrocarbons dissolved in groundwater, chloride is released into the groundwater. This results in chloride concentrations in groundwater in the contaminant plume that are elevated relative to background concentrations. Because of the neutral chemical behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates, as discussed in Appendix C.

### 2.3.3 Aquifer Parameter Estimation

Estimates of aquifer parameters are necessary to accurately evaluate contaminant fate and transport.

#### 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 test wells should be selected after consideration is given to subsurface stratigraphy. Information about subsurface stratigraphy should come from geologic logs for continuous cores or from cone penetrometer tests. The rate of filling of a Hydropunch can be used to determine local hydraulic conductivity at the same time the water sample is collected. An alternate method to delineate zones with high hydraulic conductivity is to use pressure dissipation data from cone penetrometer tests.

##### *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. If pumping tests are conducted in wells with more than fifteen feet of screen, a down-hole flowmeter test can be used to determine the interval actually contributing to flow.

*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 ideally should be conducted in wells that are narrowly screened in the most transmissive zones in the aquifer.

*2.3.3.1.3 Downhole Flowmeter*

Borehole flowmeter tests are conducted to investigate the relative vertical distribution of horizontal hydraulic conductivity in the screened interval of a well or the uncased portion of a borehole. These tests can be done to identify any preferential flow pathways within the portion of an aquifer intersecting the test well screen or the open borehole. The work of Molz and Young (1993), Molz *et al.* (1994) , Young and Pearson (1995), and Young (1995) describes the means by which these tests may be conducted and interpreted.

In general , measurements of ambient groundwater flow rates are collected at several regularly spaced locations along the screened interval of a well. Next, the well is pumped at a steady rate, and the measurements are repeated. The test data may be analyzed using the methods described by Molz and Young (1993) and Molz *et al.* (1994) to define the relative distribution of horizontal hydraulic conductivity within the screened interval of the test well. Estimates of bulk hydraulic conductivity from previous aquifer tests can be used to estimate the absolute hydraulic conductivity distribution at the test well.

Using flowmeter test data, one may be able to more thoroughly quantify the three-dimensional hydraulic conductivity distribution at a site. This is important for defining contaminant migration pathways and understanding solute transport at sites with heterogeneous aquifers. Even at sites where the hydrogeology appears relatively homogeneous, such data may point out previously undetected zones or layers of higher hydraulic conductivity that control contaminant migration. In addition, groundwater velocities calculated from hydraulic conductivity data may be used to evaluate site data or for simple transport calculations. In these cases, it is also important to have the best estimate possible of hydraulic conductivity for those units in which the contaminants are migrating.

#### 2.3.3.2 Hydraulic Gradient

The horizontal hydraulic gradient is the change in hydraulic head (feet of water) divided by the distance of groundwater flow between head measurement points. 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 low-elevation 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, natural attenuation 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 reductions in contaminant concentrations and apparent reductions in the total mass of contaminant in a system. Processes causing apparent reductions 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.

Dilution results in a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system due to the introduction of additional water to the system. The two most common causes of dilution (real or apparent) are infiltration and sampling from monitoring wells screened over large vertical intervals. Infiltration can cause an apparent reduction in contaminant mass by mixing unaffected waters 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. To avoid potential dilution during sampling, 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. Appendix C contains example calculations showing of how to correct for the effects of dilution.

The retardation of organic solutes caused by sorption is an important consideration when simulating the effects of natural attenuation over time. 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. The processes of contaminant sorption and retardation are discussed in Appendix B.

The dispersion of organic solutes in an aquifer is another important consideration when simulating natural attenuation. 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 vertically as well as parallel and perpendicular to the direction of groundwater flow.

To accurately determine the mass of contaminant transformed to innocuous byproducts, it is important to correct measured contaminant concentrations for those processes that cause an apparent reduction in contaminant mass. This is accomplished by normalizing the measured concentration of each of the contaminants to the concentration of a tracer that is biologically recalcitrant. Because chloride is produced during the biodegradation of chlorinated solvents, this analyte can be used as a tracer.. For chlorinated solvents undergoing reductive dechlorination, it is also possible to use the organic carbon in the original chlorinated solvent and daughter products as a tracer. Trimethylbenzene and tetramethylbenzene are two chemicals found in fuel hydrocarbon plumes that also may be useful as tracers. 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 may be used.

### 2.3.4 Optional Confirmation of Biological Activity

Extensive evidence can be found in the literature showing that biodegradation of chlorinated solvents and fuel hydrocarbons frequently occurs under natural conditions. Many references from the large body of literature in support of natural attenuation are listed in Section 3 and discussed in Appendix B. The most common technique used to show explicitly that microorganisms capable of degrading contaminants present at a site is the microcosm study.

If additional evidence (beyond contaminant and geochemical data and supporting calculations) supporting natural attenuation is required, a microcosm study using site-specific aquifer materials and contaminants can be undertaken.

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. The results of a well-designed microcosm study will be easy for decision makers with nontechnical backgrounds to interpret. Results of such studies 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 uncertainty concerning the biodegradation of contaminants.

Biodegradation rate constants determined by microcosm studies often are higher than rates achieved in the field. 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.

## 2.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF NATURAL ATTENUATION

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 natural attenuation and to help simulate natural attenuation over time. It is the responsibility of the proponent to "make the case" for natural attenuation. This being the case, all available data must be integrated in such a way that the evidence is sufficient to support the conclusion that natural attenuation 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 on the basis of previously collected 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 refined 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 and daughter product 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 contaminants or contaminant odor. It is also important to correlate the results of VOC 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, along with geologic boring 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 and/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 higher hydraulic head to areas of lower 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 LNAPL, a correction must be made for the water table deflection caused by the LNAPL. This correction and potentiometric surface map preparation are discussed in Appendix C.

### 2.4.1.5 Contaminant and Daughter Product Contour Maps

Contaminant and daughter product contour maps should be prepared for all contaminants present at the site 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. Detection of daughter products not present in the released NAPL (e.g., *cis*-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination.

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 NAPL 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, if confident that chlorinated solvents present as NAPL are commingled with fuels, to use cone penetrometer 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), chloride, and methane] during biodegradation. In addition, a contour map should be prepared for alkalinity and ORP. The electron acceptor, metabolic byproduct, alkalinity, and ORP contour maps provide evidence of the occurrence of biodegradation at a site.

Contour maps should be prepared for 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.

Contour maps should be prepared for the metabolic byproducts iron (II), chloride, 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.

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, NAPL/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, Daughter Product, Electron Acceptor, Metabolic Byproduct, and Total Alkalinity Data

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

Comparison of contaminant, electron acceptor, electron donor, and metabolic byproduct distributions can help identify significant trends in site biodegradation. Dissolved oxygen concentrations below background in an area with organic contamination are indicative of aerobic biodegradation of organic carbon. Similarly, nitrate and sulfate concentrations below background in an area with contamination are indicative of anaerobic biodegradation of organic carbon. Likewise, elevated concentrations of the metabolic byproducts iron (II), chloride, and methane in areas with contamination are indicative of biodegradation of organic carbon. In addition, elevated concentrations of total alkalinity (as $CaCO_3$) in areas with contamination are indicative of biodegradation of organic compounds via aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction. 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 graphical evidence of these relationships.

Detection of daughter products not present in the released NAPL (e.g., *cis*-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination. The contour maps described in Section 2.4.1 in conjunction with NAPL analyses can be used to show that reductive dechlorination is occurring.

#### 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. Sorption and retardation calculations should be completed for all contaminants and any tracers. Sorption and retardation calculations are described in Appendix C.

#### 2.4.2.3 NAPL/Water Partitioning Calculations

If NAPL remains at the site, partitioning calculations should be made to account for the partitioning from this phase into groundwater. Several models for NAPL/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 NAPL 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 contaminants dissolved in groundwater. In many cases, biodegradation of contaminants 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, sorption, 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 contaminant 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).

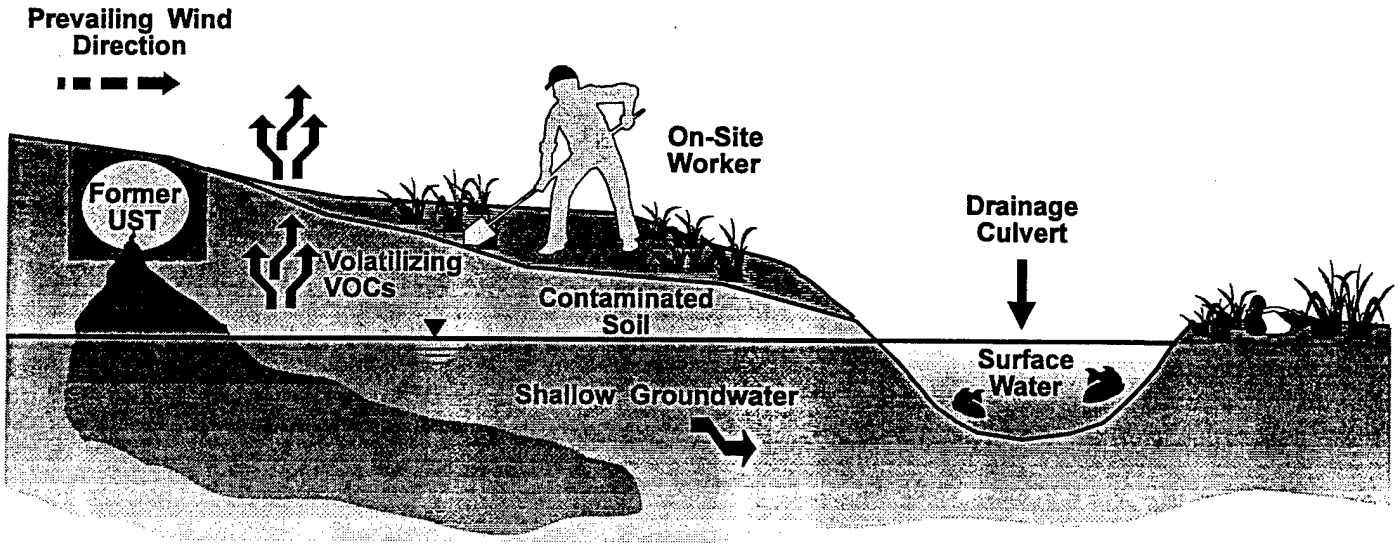
## 2.5 SIMULATE NATURAL ATTENUATION USING SOLUTE FATE AND TRANSPORT MODELS

Simulating natural attenuation allows prediction of the migration and attenuation of the contaminant plume through time. Natural attenuation 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 natural attenuation 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 solute transport are adequate to simulate natural attenuation.

Several well-documented and widely accepted solute fate and transport models are available for simulating the fate and transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation. Solute fate and transport modeling is described in Appendix D.

## 2.6 CONDUCT A RECEPTOR 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 natural attenuation should combine all available data and information to negotiate for implementation of this remedial option. Supporting the natural attenuation option generally will involve performing a receptor exposure pathways analysis. This analysis includes identifying potential human and ecological receptors and points of exposure under current and future land and groundwater use scenarios. Figure 2.5 presents some of the potential migration pathways, exposure routes, and potential receptors for contaminants associated with fuels and chlorinated solvents. 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 assessed.




| Possible Site Sources | Affected Media | Release Mechanisms/ Migration Pathways | Exposure Routes | | Potential Receptors | |
|---|---|---|---|---|---|---|
| • Leaks from transfer, supply and return pipelines.<br>• Leaks from USTs.<br>• Surface spills/ overfills.<br>• Landfills<br>• FireTraining Areas | Soil | • Direct releases of contaminants into soils.<br>• Leaching of surface spills into subsurface soils.<br>• Surface erosion/deposition of contaminated soil by either water or wind.<br>• Contaminants volatilizing into the atmosphere.<br>• Disturbance of contaminated soils by excavation.<br>• Leaching of contaminants into groundwater. | Human | • Incidental ingestion.<br>• Dermal contact.<br>• Inhalation of volatilizing contaminants.<br>• Inhalation of fugitive dust. | Current | • Onsite workers. |
| | | | | | Future | • Onsite workers. |
| | | | Ecological | | | • No exposed population due to industrial land use. |
| | Groundwater | • Direct releases of contaminants into groundwater.<br>• Leaching of surface spills into groundwater.<br>• Downgradient migration of site contaminants with groundwater flow.<br>• Contaminants volatilizing into vadose zone soil.<br>• Migration and discharge of contaminated groundwater into off-site surface water. | Human | • Ingestion.<br>• Dermal contact. | Current | • Onsite construction workers. |
| | | | | | Future | • Onsite construction workers. |
| | | | Ecological | | | • No exposed population due to industrial land use. |
| | Surface Water | • Surface runoff of precipitation.<br>• Discharge of contaminated groundwater into surface water.<br>• Discharge of leachate into surface water. | Human | • Incidental ingestion.<br>• Dermal contact. | Current | • Onsite workers. |
| | | | | | Future | • Onsite workers. |
| | | | Ecological | | | • No measured concentrations >Plan A surface water criteria. |

Figure 2.5
Example Migration Pathways and Exposure Routes for Potential Receptors of Fuel Hydrocarbons and Chlorinated Solvents

## 2.7 EVALUATE SUPPLEMENTAL SOURCE REMOVAL OPTIONS

Source removal or reduction may be necessary to reduce plume expansion if the exposure pathways analysis suggests that one or more exposure pathways may be completed before natural attenuation can reduce chemical concentrations below federal, state, or risk-based levels of concern. Several technologies suitable for source reduction or removal are listed on Figure 2.1. Other technologies also may be used as dictated by site conditions and local regulatory requirements. If a solute fate and transport model has been prepared for a site, the impact of source removal can readily be evaluated by modifying the contaminant source term; this will allow for a reevaluation of the exposure pathways analysis.

## 2.8 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 Air Force installation boundary. Thus, there frequently is sufficient time and space for natural attenuation alone to reduce contaminant concentrations in groundwater to acceptable levels. Experience at 40 Air Force sites contaminated with fuel hydrocarbons evaluated using the protocol presented by Wiedemeier *et al.* (1995d) suggests that many fuel hydrocarbon plumes are relatively stable, or are moving slowly with respect to groundwater flow. This information is complemented by data collected by Lawrence Livermore National Laboratories in a study of over 1,100 leaking underground fuel tank sites performed for the California State Water Resources Control Board (Rice *et al.*, 1995). These examples demonstrate the efficacy of using long-term monitoring to track plume migration and to validate or refine modeling results. There is not a large enough database available at this time to assess the stability of chlorinated solvent plumes, but it is the experience of the authors that chlorinated solvent plumes are likely to migrate further downgradient than fuel hydrocarbon plumes before reaching steady-state equilibrium or before receding.

The long-term monitoring 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 natural attenuation is occurring at rates sufficient to protect potential downgradient receptors. The long-term monitoring plan should be developed based on site characterization data, the results of solute fate and transport modeling, and the results of the receptor exposure pathways analysis.

For plumes that do not discharge to surface water bodies, the long-term monitoring 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 (or point-of-action) wells are intended to detect movements of the plume outside the negotiated perimeter of containment, and to trigger an action to manage potential expansion. Figure 2.6 depicts 1) an upgradient well in unimpacted groundwater; 2) a well in the NAPL source area; 3) a well downgradient of the NAPL 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 contaminant concentrations are below regulatory acceptance levels and soluble electron acceptors are depleted with respect to unimpacted groundwater; and 6) three point-of-compliance wells.

Although the final number and placement of long-term monitoring and point-of-compliance/action wells should be determined through regulatory negotiation, the locations of long-term monitoring wells should be based on the behavior of the plume as revealed during the initial site characterization and on regulatory considerations. Point-of-compliance wells should be placed 5 years travel time upgradient from potential receptors. To be conservative, this distance should be based on the advective velocity of the groundwater, not the solute transport velocity. If the property line is less than 5 years travel time, the point-of-compliance wells often are placed near and upgradient from the property line. The final number and location of point-of-compliance monitoring wells also will depend on regulatory considerations. Local practice may be more stringent than this recommendation.

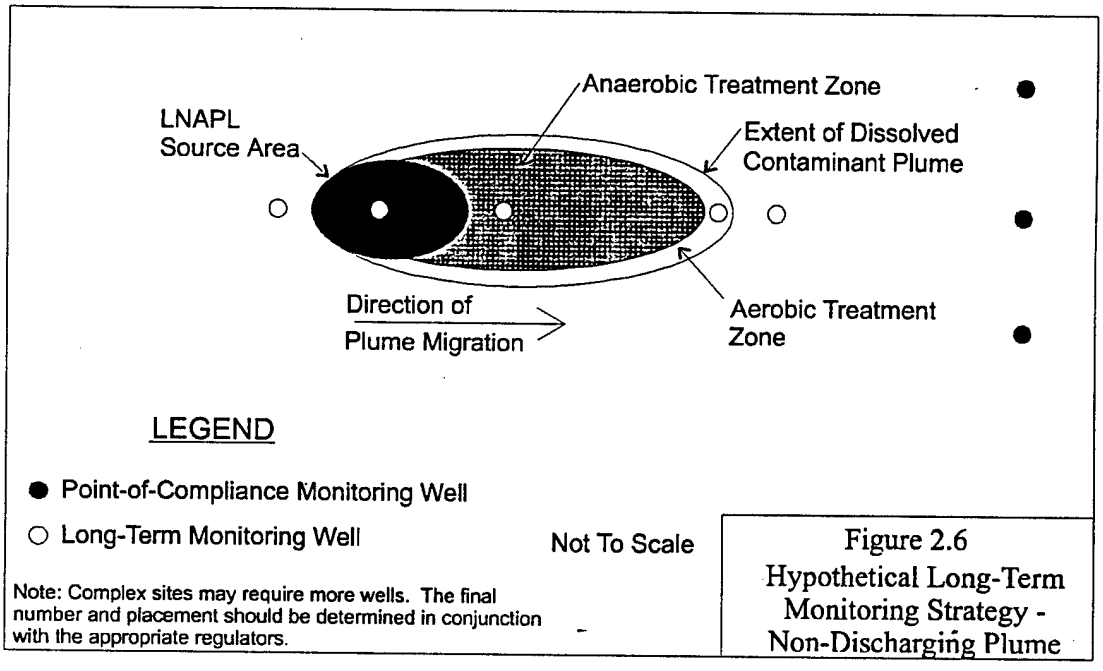



Figure 2.6
Hypothetical Long-Term Monitoring Strategy - Non-Discharging Plume

For sites where contaminated groundwater discharges to surface water, the philosophy of monitoring is not well developed. However, at a minimum information is needed on the impact of the groundwater plume on the surface water body. Figure 2.7 depicts 1) an upgradient well in unimpacted groundwater; 2) a well in the NAPL source area; 3) a well downgradient of the NAPL source area in a zone of anaerobic treatment; and 4) surface water collection points.

The results of a solute fate and transport model can be used to help site the long-term monitoring and point-of-compliance 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 or cone penetrometer testing should be prepared prior to monitoring well installation.

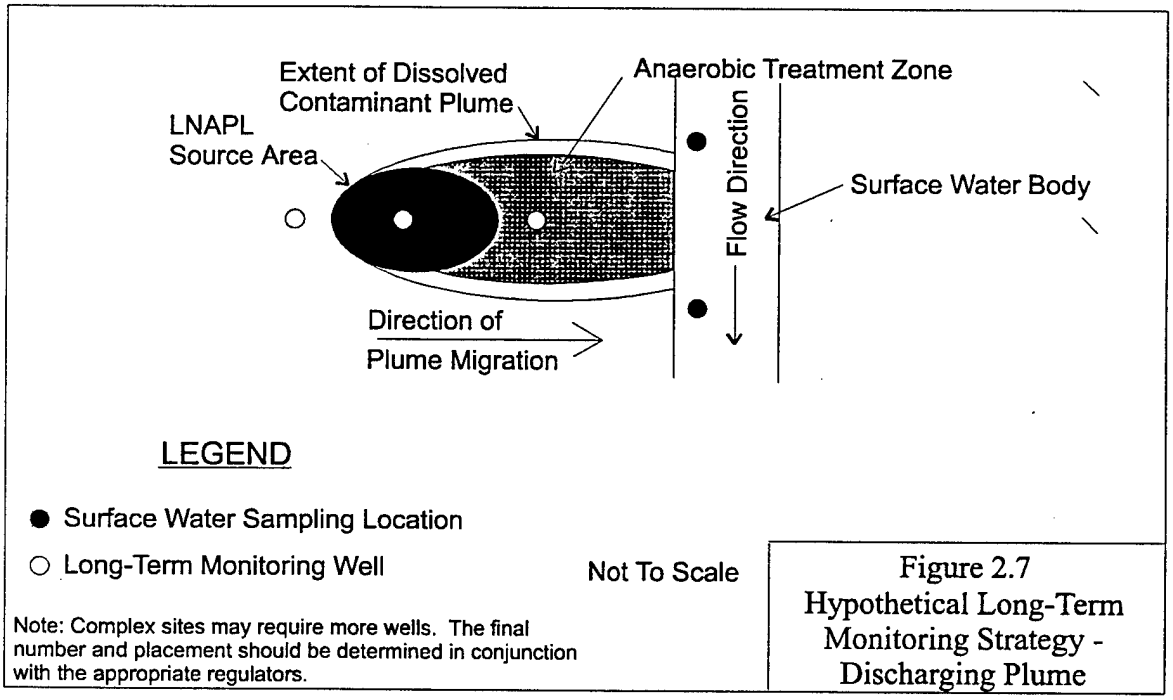



Figure 2.7
Hypothetical Long-Term Monitoring Strategy - Discharging Plume

A groundwater sampling and analysis plan should be prepared in conjunction with point-of-compliance and long-term monitoring well placement. For long-term monitoring wells, groundwater analyses should include VOC constituents of concern, dissolved oxygen, nitrate, iron (II), sulfate, and methane. For point-of-compliance wells, groundwater analyses should be limited to VOC constituents of concern.. 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 LNAPL thickness measurements must be made during each sampling event. Except at sites with very low hydraulic conductivity and gradients, quarterly

sampling of long-term monitoring 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 point-of-compliance monitoring wells and groundwater flow velocity. The final sampling frequency should be determined after consideration is given to well spacing and solute transport velocity. Along with potentiometric surface measurements, groundwater samples should be collected quarterly for at least one year. If it is shown during this period that groundwater flow is consistent, then the sampling frequency should be based on well spacing and solute transport velocities. One method that can be used to assign sampling frequency is to divide the distance between monitoring wells by the advective groundwater velocity.

## 2.9 CONDUCT REGULATORY NEGOTIATIONS

The purpose of regulatory negotiations is to provide scientific documentation that supports natural attenuation 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 natural attenuation investigation should be presented in a consistent and complementary manner at the regulatory negotiations. Of particular interest to the regulators will be proof that natural attenuation 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 model assumptions should be conservative, and all available evidence in support of natural attenuation 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 natural attenuation 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.

# SECTION 3

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# APPENDIX A

# FIELD INVESTIGATION METHODOLOGIES

# TABLE OF CONTENTS - APPENDIX A

A1 INTRODUCTION ..... A1-1

A2 SUBSURFACE INVESTIGATION METHODOLOGIES ..... A2-1
A.2.1 TRADITIONAL DRILLING TECHNIQUES ..... A2-2
A.2.2 CONE PENETROMETER ..... A2-3
A.2.3 HYDRAULIC PERCUSSION ..... A2-4
A.2.4 HAND AUGER ..... A2-5
A.2.5 HAND DRIVEN ..... A2-5

A3 SOIL CHARACTERIZATION METHODOLOGIES ..... A3-1
A.3.1 SAMPLE ACQUISITION ..... A3-1
A.3.2 PHYSICAL DESCRIPTION ..... A3-2
A.3.3 FIXED-BASE LABORATORY ANALYSES ..... A3-3

A4 GROUNDWATER CHARACTERIZATION METHODOLOGIES ..... A4-1
A.4.1 GROUNDWATER MONITORING LOCATIONS, DEPTHS, AND SCREENED INTERVALS ..... A4-1
A.4.2 TYPES OF GROUNDWATER SAMPLING LOCATIONS ..... A4-2
A.4.2.1 Monitoring Wells ..... A4-2
A.4.2.2 Monitoring Points ..... A4-4
A.4.2.3 Grab Sampling ..... A4-5
A.4.3 MEASUREMENT OF STATIC FLUID LEVELS ..... A4-5
A.4.3.1 Water Level and Total Depth Measurements ..... A4-5
A.4.3.2 Mobile LNAPL Thickness Measurements ..... A4-6
A.4.3 GROUNDWATER EXTRACTION ..... A4-7
A.4.3.1 Methods ..... A4-7
A.4.3.2 Development ..... A4-9
A.4.3.3 Purging ..... A4-9
A.4.3.4 Sampling ..... A4-11
A.4.4 GROUNDWATER ANALYTICAL PROCEDURES ..... A4-12
A.4.4.1 Standard Well Head Analyses ..... A4-13
A.4.4.2 Dissolved Hydrogen Analysis ..... A4-13
A.4.4.2.1 Sampling Method ..... A4-14
A.4.4.2.2 Analytical Method ..... A4-15
A.4.4.3 Field Analytical Laboratory Analyses ..... A4-17
A.4.4.4 Fixed-Base Laboratory Analyses ..... A4-18

A5 SURFACE WATER AND SEDIMENT CHARACTERIZATION METHODOLOGIES ..... A5-1
A.5.1 Surface Water Sample Collection ..... A5-1
A.5.2 Sediment Sample Collection ..... A5-2

A6 SAMPLE HANDLING ..... A6-1
A.6.1 SAMPLE PRESERVATION, CONTAINERS, AND LABELS ..... A6-1
A.6.2 SAMPLE SHIPMENT ..... A6-1
A.6.3 CHAIN-OF-CUSTODY CONTROL ..... A6-2
A.6.4 SAMPLING RECORDS ..... A6-3

A7 AQUIFER CHARACTERIZATION METHODOLOGIES ..... A7-1
A.7.1 HYDRAULIC CONDUCTIVITY ..... A7-1
A.7.1.1 Slug Tests ..... A7-1
A.7.1.2 Pump Tests ..... A7-3
A.7.1.2.1 Pumping Test Design ..... A7-3
A.7.1.2.2 Preparation for Testing ..... A7-5
A.7.1.2.2 Conducting the Pumping Test ..... A7-6
A.7.1.3 Downhole Flow Meter Measurements ..... A7-8
A.7.2 HYDRAULIC GRADIENT ..... A7-9
A.7.3 DIRECT MEASUREMENT OF GROUNDWATER VELOCITY ..... A7-9

## FIGURES

**No.** **Title** **Page**

A.4.1 Diagram Showing the Suggested Procedure for Dissolved Oxygen and ORP Sampling ..... A4-12
A.4.2 Schematic Showing the "Bubble Strip" Method for Measuring Dissolved Hydrogen Concentrations in Groundwater ..... A4-15

# SECTION A-1

# INTRODUCTION

Detailed site characterization is an important aspect of the remediation by natural attenuation demonstration. Typically, it is necessary to collect additional site-specific data in order to successfully complete the demonstration. This appendix presents an overview of field techniques that can be used to collect the data used to support natural attenuation. Selection of locations for field investigation activities and analytical protocols used for soil and water samples are discussed in Section 2 of the protocol document.

During all field investigation activities, special care should be taken to prevent contamination of the sampled matrices. The primary way that sample contamination can occur is through contact with improperly cleaned equipment. To prevent such contamination, proper equipment decontamination procedures must be developed and followed. Procedures will vary according to site contaminants, equipment type, field activity, sample matrix, rinseate handling requirements, and regulatory requirements. All equipment requires decontamination prior to initiation of site activities and between sampling locations. New, disposable equipment does not require decontamination if factory-sealed and found acceptable by the investigating field scientist. In addition to the use of properly cleaned equipment, new, clean, disposable gloves (of a material appropriate to the activity and contaminant type/concentration) should be worn at each new sampling location.

Basic health and safety precautions are required for every piece of equipment and every methodology discussed in this section. It is the responsibility of the investigator to be aware of and to communicate all health and safety issues to the field team; therefore, a site specific health and safety plan must be developed prior to initiating investigation activities. At a minimum this plan must contain:

- A safety and health risk analysis for chemical, physical, and biological hazards associated with the site conditions, anticipated contaminants, equipment, field activities, and climate;

- An emergency response plan with applicable emergency response numbers; and
- Precautionary measures to be implemented to insure the safety of site workers.

This appendix consists of six sections, including this introduction. Section A-2 discusses subsurface investigation methodologies. Section A-3 discusses soil characterization methodologies. Section A-4 discusses groundwater characterization methodologies. Section A-5 discusses surface water and sediment characterization methodologies. Section A-6 discusses sample handling procedures. Section A-7 discusses aquifer characterization methodologies.

# SECTION A-2

# SUBSURFACE INVESTIGATION METHODOLOGIES

The ideal technologies for a natural attenuation investigation are those which can rapidly provide a large amount of information in a very short period of time while producing low quantities of waste. The following subsections briefly introduce several alternatives that are available for performing subsurface investigations in support of remediation by natural attenuation. Although some of these alternatives more closely achieve the objectives of an remediation by natural attenuation investigation than others, considerations such as site geology, site hydrogeology, future well use, or regulatory concerns may dictate the selection of the subsurface investigation method for any given site. It is crucial for the proponent for the remediation by natural attenuation investigation to consider all of these issues prior to selecting a technology appropriate for their site. If during the investigation it becomes necessary to change methodologies, the same concerns must be readdressed.

Prior to initiating any intrusive subsurface activities, proposed drilling locations must be cleared. It is particularly useful if all utility lines in the investigation area are marked should changes to the investigation become necessary. In addition, in order to expedite the investigation, all necessary digging, coring, drilling, and groundwater monitoring point installation permits should be obtained prior to mobilizing to the field.

At the conclusion of subsurface investigations, each sampling location that is not used to install a groundwater monitoring point or well should be restored as closely to its original condition as possible. Where possible, holes should be sealed with bentonite chips, pellets, or grout to eliminate any creation or enhancement of contaminant migration pathways to the groundwater.

## A.2.1 TRADITIONAL DRILLING TECHNIQUES

Traditional drilling techniques include those methods that traditionally have been used to install drinking water supply wells. Examples of traditional drilling techniques include hollow stem auger, rotary, air percussion, and chain tool. They have in common the advantage of being capable of installing wells of varying diameters to drinking water well specifications. Each of these techniques also allow for visual description of the materials and can allow for easy stratigraphic correlation. In general, the equipment required by each of these techniques is readily available. Disadvantages of traditional drilling techniques include their expense, time requirements, and waste generation. Not only do these techniques produce soil/fluids from the drilling process, frequently, in order to properly develop wells by these techniques, a large volume of groundwater must be extracted during a lengthy development. Although the advantages and disadvantages listed above are common to most traditional drilling techniques, they are applicable to varying degrees. Furthermore, drilling depth and subsurface stratigraphy are important considerations when evaluating the efficacy of each of these techniques.

Hollow stem auger has been the most widely used traditional drilling technique in environmental investigations, because it is very effective in the most commonly investigated geologic setting encountered during environmental investigations: unconsolidated deposits at shallow depths. Although less common, a chain tool can also be effective under similar geologic conditions. When installing wells, a chain tool may require a little more time, but may prove to be less disruptive to the formation in the vicinity of the well screen. Both techniques are well suited to collecting continuous soil samples using a CME® split-barrel continuous sampling device, or similar. This capability is extremely important because detailed knowledge of the subsurface can be critical to the successful demonstration of remediation by natural attenuation.

At greater depths and in more competent formations, rotary and air hammer techniques are frequently used. Rotary techniques are also suited to penetration of cobbly units that may prove difficult or impenetrable to a hollow stem auger or chain tool. With rotary rigs, the fastest drilling rates are usually achieved by using drilling fluids such as mud or water; however, these fluids may require handling as IDW and may clog the pore space in the vicinity of the well screen. As long as air circulation can be maintained in the borehole, an air hammer can be particularly useful in competent bedrock formations without introducing drilling fluids.

## A.2.2 CONE PENETROMETER

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. Penetration force is typically supplied by a pair of large hydraulic cylinders bolted to the truck frame. In tight soils, push capacity is more often limited by the structural bending capacity of the push rods than by the weight of the truck. Cone penetrometers operate well in most unconsolidated deposits; however, they may not be able to penetrate and may be damaged by cobbles, gravel layers, very stiff clays, and cemented units.

The penetrometer probe generally consists of a 60-degree conical tip attached to a 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.

The cone penetrometer can be a very effective tool for collecting large quantities of subsurface information in a short period of time with virtually no waste generation. A cone penetrometer also can be used for installation of groundwater monitoring points, and specially equipped penetrometers can be used to screen for mobile and residual fuel hydrocarbon contamination using laser induced fluorescence (LIF). Although the equipment is fairly expensive, the overall efficiency can make this option relatively inexpensive.

Most of the disadvantages of CPT are linked to the advantages. For instance, the speed and minimal waste associated with CPT are directly related to the process of determining lithology in situ; however, this does not allow for visual description of subsurface materials. Isolated soil samples can be retrieved for visual description to calibrate the cone penetrometry log, but the procedure cannot be performed frequently (nor continuously) without impairing the efficiency of the penetrometer. And while CPT can be very effective at precisely determining changes in lithology on the basis of grain

size, the lack of a visual description prevents stratigraphic correlation on the basis of other parameters, such as color.

Monitoring points installed using a cone penetrometer illustrate another advantage that comes with disadvantages. CPT allows for rapid placement of discreet groundwater sampling points at a precise depth selected on the basis of real-time, detailed, stratigraphic logs. The most effective emplacement technique allows for installation of monitoring points of not greater than approximately 0.5 inch ID. While these points may not require much development or purging, groundwater extraction for development, purging, and sampling becomes extremely inefficient if the depth to groundwater is greater than approximately 25 feet. In addition, the monitoring point emplacement technique typically does not allow for installation of a sand pack, bentonite seal, and grout slurry as may be required by regulations.

### A.2.3 HYDRAULIC PERCUSSION

A variety of sampling tools can be advanced through unconsolidated soils using relatively inexpensive hydraulically powered percussion/probing machines (e.g., Geoprobe®). These sorts of systems are frequently mounted on pickup trucks or all-terrain vehicles, and as a result of their small size and versatility, can access many locations that larger equipment cannot.

Hydraulic percussion systems provide for the rapid collection of soil, soil gas, and groundwater samples at shallow depths while minimizing the generation of investigation-derived waste materials. Specifically undisturbed, continuous soils samples can rapidly be collected for visual observation, field analysis, and/or laboratory analysis. In addition groundwater samples can be collected through the probe rods, or groundwater monitoring points can be installed for later sample collection. Although monitoring points installed by hydraulic percussion systems can vary considerably in design and can include sandpacks and seals, monitoring points are typically narrow in diameter. As a result, it can be difficult to sample points where the groundwater elevation is greater than 25 feet bgs. Furthermore, the narrow diameter may not comply with regulatory standards or future use needs.

### A.2.4 HAND AUGER

In the proper environmental setting, a hand auger can be used to perform rapid, low-cost shallow subsurface investigations. Hand augers have the added advantage of mobility; they can be used in access-restricted locations (forests, wetlands, steep terrain, narrow passages between buildings, etc.) with little difficulty. The greatest problem with hand augers is their overall lack of versatility. For instance, gravel as well as certain stiff clays can be virtually impossible to penetrate, and the groundwater table can not typically be penetrated by more than a few feet. Even so groundwater sample collection and monitoring point installation are possible only where the augered borehole has relatively stable sidewalls. Hand augers are also limited with respect to soil sampling because the augering process tends to disturb the soil prior to removal from the borehole.

### A.2.5 HAND DRIVEN

Like hand augers, driving devices, such as slide hammers or sledges, can be used to perform rapid, low-cost subsurface investigations in locations that can be difficult or impossible to access by vehicle-mounted equipment. This technique can be used to collect undisturbed soil samples and to place temporary groundwater monitoring points. The technique is also limited to shallow depths but is less sensitive to the depth to groundwater than the hand auger. Hand driven monitoring points typically do not include installation of a sand pack, bentonite seal, and grout slurry as may be required by regulations. Often the process of driving devices into the ground by hand can be extremely labor intensive for the amount of progress made; therefore, an effective combination can consist of hand augering to the desired soil sampling depth or the groundwater table, followed by sample collection or monitoring point installation using a driven device.

# SECTION A-3

# SOIL CHARACTERIZATION METHODOLOGIES

As part of an RNA evaluation for contaminants in groundwater, soil characterization factors into development of a site conceptual model, estimation of continuing source strength, and modeling of fate and transport. The following sections describe soil sample acquisition, description, field screening, and laboratory analysis procedures. Samples should be collected in accordance with local, state, and federal requirements.

## A.3.1 SAMPLE ACQUISITION

Soil samples can be collected using a variety of methods, depending upon the method used to advance boreholes. In all cases, the goal is to collect relatively undisturbed samples to allow lithologic logging and to provide useable samples for field screening and for submission to an analytical laboratory.

When using hollow-stem auger or chain tool methods, relatively undisturbed continuous soil samples can be collected with split-barrel samplers that are either advanced using a hydraulic hammer or are driven along with the advancing auger. These are well-tested methods that are useful in most types of soils except for saturated sands, in which samples tend to liquefact and slide out of the barrel. Collection of continuous samples allows a more thorough description of site geology, with only a slight increase in the time required for drilling. These methods also can be used to collect samples in various types of liners, such as acetate or brass sleeves. These sleeves can be cut, capped, and shipped with a minimum of effort. When using sleeves, the samples are disturbed less, but description of the soils may be hindered if the liners are not clear. Other traditional drilling methods (i.e., rotary) do not produce samples that can be used for chemical analysis, and will also make geologic interpretation more difficult due to the disturbed nature of the material.

If CPT or hydraulic percussion methods are used, soil sampled can be collected using a hydraulically driven sampler. When soil samples are collected using a probe-drive sampler, the probe-drive sampler serves as both the driving point and the sample collection device and is attached to the leading end of the driving rods. To collect a soil sample, the sampler is pushed or driven to the desired sampling depth, the drive point is retracted to open the sampling barrel, and the sampler is subsequently pushed into the undisturbed soils. The soil cores are retained within brass, stainless steel, or clear acetate liners inside the sampling barrel. The probe rods are then retracted, bringing the sampling device to the surface. The soil sample can then be extruded from the liners for lithologic logging, or the liners can be capped and undisturbed samples submitted to the analytical laboratory for testing.

If a hand auger is used, samples will be slightly disturbed, but still useful. In this case, the soil is merely removed from the auger bucket and logged or put into sample containers. Removing soil from the auger bucket may prove difficult where soils are clayey. Below the water table, it may be impossible to retain sandy soils in the bucket. Hand driven samplers are similar to probe-drive samplers, except that all pushing power is provided manually,

Following sample acquisition, the coordinates and elevation of all soil sampling locations should be surveyed. Horizontal coordinates should be measured to the nearest 0.1 foot relative to an established coordinate system, such as state planar. The elevation of the ground surface also should be measured to the nearest 0.1 foot relative to USGS mean sea level (msl) data.

## A.3.2 PHYSICAL DESCRIPTION

Physical characterization of soils should be performed at all sampling locations and a descriptive log prepared for the materials encountered. If using CPT, the descriptive logs should consist of continuous computer-generated interpretations supplemented by periodic sensory confirmation and description. Otherwise, continuous sampling with interpretation and description is recommended in order to precisely identify and isolate changes in lithology. The descriptive log should contain:

- Sample interval (top and bottom depth);
- Sample recovery;

- Presence or absence of contamination;
- Lithologic 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; and
- Depths of lithologic contacts and/or significant textural changes measured and recorded to the nearest 0.1 foot.

In addition representative samples should be photographed, labeled, and stored.

### A.3.3 FIXED-BASE LABORATORY ANALYSES

Portions of selected samples should be sent to the fixed-base laboratory for analysis. It is desirable to sample and submit a relatively undisturbed sample, if possible. Undisturbed samples are typically collected in brass, stainless steel, or clear acetate liners inside of a sampling barrel. Upon removal from the barrel, liners are cut to length (if desired) and capped. If the selected drilling technique, site conditions, or project requirements do not permit collection of undisturbed soils, samples for analysis of volatile constituents should be transferred immediately to an appropriate container in such a way as to minimize volatilization during the transfer and headspace in the sample container. The analytical protocol to be used for soil sample analysis is presented in Table 2.1. This analytical protocol includes the parameters necessary to document the effects of sorption and to estimate the magnitude of the continuing source. The protocol document describes each soil analytical parameter and the use of each analyte in the remediation by natural attenuation demonstration.

Each laboratory soil sample will be placed in an analyte-appropriate sample container and delivered as soon as possible to the analytical laboratory for analysis of total hydrocarbons, aromatic hydrocarbons, VOCs, and moisture content using the procedures presented in Table 3.1. In addition, at least two samples from locations upgradient, crossgradient, or far downgradient of the contaminant source will be analyzed for TOC.

# SECTION A-4

# GROUNDWATER CHARACTERIZATION METHODOLOGIES

This section describes the scope of work required to collect groundwater quality samples and to perform field analyses in support of the remediation by natural attenuation demonstration. 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. Samples should be collected in accordance with local, state, and federal requirements.

## A.4.1 GROUNDWATER MONITORING LOCATIONS, DEPTHS, AND SCREENED INTERVALS

Groundwater monitoring locations should be selected on the basis of the preliminary conceptual site model and information on the distribution of contaminants in the target plume. At a minimum, one monitoring location should be placed upgradient from the contaminant plume, one location should be placed in the suspected source area, two locations should be placed within the plume, and three locations should be placed various distances downgradient and crossgradient from the plume. The actual number of monitoring locations could be considerably higher and should be related to site conditions and the size of the source.

It is very often desirable to collect vertical extent samples at several or all of the groundwater monitoring locations. This decision is based on the presence of confining units, the thickness of the aquifer, the type and source of contamination, and suspected variations in subsurface transmissivity. 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.

Typically the shallowest groundwater monitoring depth is chosen to intersect the water table. This allows for the monitoring of LNAPL and seasonal water level fluctuations, as well as dissolved contaminant concentrations in the portion of the aquifer closest to the typical source. Deeper locations are selected on the basis of contaminant distribution, typically above or below suspected confining units or in zones believed to possess higher transmissivity. To ensure well integrity, clustered monitoring wells/monitoring points generally should be completed in separate boreholes.

Screen lengths of not more than 5 feet are recommended to help mitigate the dilution of water samples from potential vertical mixing of contaminated and uncontaminated groundwater. Screening a larger area of the saturated zone will result in averaging of contaminant concentrations and hydraulic properties. 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 TYPES OF GROUNDWATER SAMPLING LOCATIONS

Groundwater samples for the remediation by natural attenuation demonstration can be collected from monitoring wells, monitoring points, or grab sampling locations. Monitoring points and grab locations provide rapid and inexpensive access to shallow groundwater, and yield groundwater samples that are appropriate for site characterization and plume definition. Conventional monitoring wells are required for sites with groundwater elevations more than approximately 25 feet below ground surface. They also are recommended for long-term monitoring (LTM) and point-of-compliance (POC) groundwater sampling, and may be required for regulatory compliance.

Following installation, the location and elevation of all groundwater monitoring locations should be surveyed. Horizontal coordinates should be measured to the nearest 0.1 foot relative to an established coordinate system, such as state planar. The elevation of the ground surface also should be measured to the nearest 0.1 foot relative to USGS mean sea level (msl) data.. Other elevations, including the measuring point, should be measured to the nearest 0.01 foot.

### A.4.2.1 Monitoring Wells

Monitoring wells are commonly installed in support of an remediation by natural attenuation demonstration. As used in this document, monitoring wells are assumed to

have, at a minimum, a sand pack, a bentonite seal, an annular seal, a surface seal, and an inside diameter of at least 2 inches. Monitoring wells are extremely versatile and can be used for groundwater sampling, aquifer testing, product recovery systems, long-term monitoring, and point-of-compliance monitoring. Although versatile, monitoring wells are relatively expensive to install and create relatively large quantities of waste during installation, development, and sampling. Detailed well installation procedures are described in the following paragraphs. Of course, local protocols, regulations, type of drill rig, and site conditions should dictate actual well completion details.

Upon completion to the desired depth of a borehole with a diameter at least 4 inches larger than the outside diameter of the proposed well, the monitoring well can be installed. At a minimum, blank well casing and screen should be constructed of Schedule 40 polyvinyl chloride (PVC) with an inside diameter (ID) of 2 inches. Frequently, this diameter must be increased if the well may be used for a pumping test or certain types of product or groundwater recovery. The screens should be factory slotted with appropriately sized openings (typically 0.010-inch). All well 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.

Once the well is in place, sand, bentonite, and grout are used to fill the remaining borehole annulus. Appropriately-sized sand must be packed along the entire length of the screen; however, it is desirable to limit the amount that the sand pack extends to either side of the screen (i.e., at least 6 inches but less than 2 feet) because the added sand pack can increase the portion of the aquifer that is effectively screened. A bentonite seal is placed on top of the sand pack. If conditions permit, this seal should have a minimum thickness of 2 feet. A cement-bentonite grout is used to fill the remainder of the annular space between the bentonite seal and the surface completion. Depending on site conditions and facility preferences, either flush-mount or stick-up surface completions can be used. Site conditions and local, state, and federal requirements should ultimately dictate materials selection and construction details.

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.

### A.4.2.2 Monitoring Points

Where site conditions and the regulatory environment permit, monitoring points are ideal tools for rapidly and cost-effectively obtaining site data in support of an remediation by natural attenuation demonstration. Monitoring points can be installed and sampled rapidly while generating a minimal volume of waste. Furthermore, some monitoring points cannot be used for groundwater or free product level measurements. For these reasons, it is always useful when a site has a handful of monitoring wells. Detailed monitoring point installation procedures are described in the following paragraphs. Of course, local protocols, regulations, available equipment, and site conditions should dictate actual well completion details.

In this document, monitoring points are considered temporary or permanent groundwater sampling locations that do not meet the specifications of monitoring wells. Typically monitoring points are installed in small diameter boreholes using CPT, hydraulic percussion, or manually-powered equipment. As a result monitoring points usually have an ID of less than 2 inches. In addition, because of the extremely small to nonexistent annular space between the borehole wall and the monitoring point materials, they seldom have a sand pack, bentonite seal, and grout seal, particularly with an annulus of 2 inches. 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.

Like monitoring wells, monitoring points are typically constructed of Schedule 40 PVC casing and screen; however, monitoring points also can be constructed from Teflon®-lined tubing attached to a stainless steel, wire mesh screen. Because the screens are often installed without a sand pack, a slot size of 0.010 inch or smaller should be used. All monitoring point casing and screen 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. Site conditions and local, state, and federal requirements should ultimately dictate materials selection and construction details.

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

### A.4.2.3 Grab Sampling

Groundwater grab samples are temporally and spatially discrete samples collected from boreholes that are abandoned upon completion of sampling. In highly transmissive aquifers, the collection of grab samples can provide a rapid cost-effective alternative to the use of monitoring points. Like monitoring points, collection of grab samples generates minimal waste; however, they are not appropriate for aquifer testing, remediation systems, or long-term monitoring. Furthermore, because the locations are abandoned upon completion of sampling, analytical results cannot be confirmed, and groundwater levels at all locations cannot be collected over the space of a few hours for use in the development of groundwater flow maps. In addition, if the aquifer is not particularly transmissive, sample collection can require hours resulting in inefficient equipment utilization. For these reasons, installation and sampling of monitoring points typically is recommended where feasible. Several of the more common instruments used to collect groundwater grab samples include the HydroPunch®, Geoprobe®, cone penetrometer, or hand-driven points.

## A.4.3 MEASUREMENT OF STATIC FLUID LEVELS

### A.4.3.1 Water Level and Total Depth Measurements

Prior to purging or developing any water from a groundwater sampling location, the static water level should be measured. At all locations of sufficient diameter, an electric water level probe should be used to measure the depth to groundwater below the datum to the nearest 0.01 foot. Small diameter probes are commercially available for measurement of water levels in monitoring points and through Geoprobe®, HydroPunch®, and CPT pushrods. 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. If measuring from the ground surface, an accuracy better than 0.1 foot is probably not practical. Based on these measurements the volume of water to be developed or purged from the location 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 as well as the LNAPL.

If a sufficiently narrow water level probe is unavailable, hollow, high-density polyethylene (HDPE) tubing connected to a manometer can be used to determining depth to groundwater. The manometer will indicate when groundwater is reached as the HDPE tubing is inserted into the monitoring location. 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, if possible.

### A.4.3.2 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.4.3 GROUNDWATER EXTRACTION

Varied equipment and methods are available for the extraction of groundwater. The approach is determined on the basis of application (development, purging, or sampling), hydrogeologic conditions, monitoring location dimensions, and regulatory requirements.

Groundwater produced during extraction activities must be handled in a manner consistent with the investigation-derived waste (IDW) plan for the site. The method of handling and disposal will depend on location and type of source, site contaminants, degree of contamination (e.g., free product, odor, air monitoring measurements), and applicable base, local, state, and federal regulations.

### A.4.3.1 Methods

Portable groundwater extraction devices from three generic classifications are commonly used for RNA investigations: grab, suction lift, and positive displacement. The selection of the type of device(s) for the investigation is based on type of activity, well/point dimensions, and hydrogeologic conditions.

A bailer is the most common grab sampling device. Bailers can be used at any depth in wells with a minimum diameter of 0.5 inch; however, groundwater extraction becomes less efficient as the well (and hence the bailer diameter) decreases. Disposable bailers can be used to avoid decontamination expenses and potential cross-contamination problems. Drawbacks for bailers include agitation/aeration of the groundwater and the inability to maintain a steady, non-turbulent flow required to establish a true flow-through cell. Agitation/aeration can be minimized, but not eliminated, through careful immersion into and extraction from the standing column of water in the well/point. Aeration also can be an issue during transfer of the sample from the bailer to the sample container. Once again, this aeration can be minimized, but not eliminated. As a result of aeration, and because a true flow-through cell cannot be established, accurate dissolved oxygen and ORP measurements can be difficult to obtain. Although adverse for purging and sampling, the turbulence created by the use of a bailer can be beneficial for development.

The suction lift technology is best represented in environmental investigations by the peristaltic pump. A peristaltic pump extracts water using a vacuum created by cyclically advancing a sealed compression along flexible tubing. This pumping technique means that extracted water contacts nothing other than tubing that can be easily replaced between sampling locations. This reduces the possibility of cross contamination. Furthermore, peristaltic pumps can be used to extract minimally-disturbed groundwater from any size monitoring location at variable low-flow rates. Because of these features, representative samples are simple to collect, and reliable flow-through cells are simple to establish. The biggest drawback with a peristaltic pump is the maximum achievable pumping depth which is equivalent to the height of water column that can be supported by a perfect vacuum. This effectively limits the use of a peristaltic pump to monitoring locations with groundwater depths of less than approximately 25 feet. Also, off-gasing can occur in the tubing as a result of the reduced pressures and high-rate of cyclical loading. If bubbles are observed in the tubing during purging or sampling, the flow rate of the peristaltic pump must be slowed. If bubbles are still apparent, the tubing should be checked for holes and replaced. The final potential disadvantage with a peristaltic pump is the low flow rate. Although advantageous for sampling, this can be inappropriate during purging or development at locations with large extraction volumes. ?? (199? PUT REFERENCE) show that the use of peristaltic pumps does not compromise sample integrity as long as no bubbles form during sampling.

Positive displacement pumps, also called submersible pumps, include for example bladder, Keck®, Grundfos Redi-Flo II®, Bennett® and Enviro-Tech Purger ES® pumps. Each of these pumps operates downhole at depths of up to a few hundred feet and rates of up to several gallons per minute. Therefore, submersible pumps are particularly useful for applications requiring the extraction of large volumes of water or for the extraction of groundwater from depths in excess of 25 feet. Because the pumps operate downhole, they require appropriately-sized wells. At a minimum, an inside well diameter of at least 1.5 inches typically is required; however, much larger well diameters can be required depending on the selected pump type, extraction depth, and extraction rate. Because typical submersible pump design results in contact between the groundwater and internal as well as external surfaces of the pump, rigorous decontamination and quality assurance procedures must be implemented to avoid cross contamination if a pump that is not dedicated to the well is used for sampling.

### A.4.3.2 Development

Monitoring wells and points should be developed prior to sampling to remove fine sediments from the portion of the formation adjacent to the screen. Development is not required for grab sampling locations. Because development is intended to enhance groundwater production and quality through the removal of fine sediments in the immediate vicinity of the screen, high flow rates and downhole turbulence are beneficial. This is particularly true for monitoring wells because of the formation disturbance usually associated with installation. Development can be accomplished using any of the methods discussed in Section A.4.3.1 with selection dependent on well/point dimensions, well/point installation procedures, and hydrogeologic conditions.

Development is accomplished through the removal of water from the well/point in combination with screen/sand pack cleansing through agitation of the downhole groundwater. The "agitation" is typically provided by pumping at a high flow rate; surging with the pump, a surge block, or a bailer; and/or pumping along the entire length of the screen. As a rule, the more "agitation" that can be provided, the "better" the development. Typically during development, groundwater is extracted until dissolved oxygen, pH, temperature, specific conductivity, and water clarity (turbidity) stabilize. Monitoring well/point development should occur a minimum of 24 hours prior to sampling. Development water must be handled in accordance with the site IDW plan.

It is important to maintain a record of development for each location. The development record should include the following information, at a minimum:

- Monitoring point/well number;
- Date and time of development;
- Development method;
- Monitoring point/well depth;
- Volume of water produced;
- Description of water produced;
- Post-development water level and monitoring point/well depth; and
- Field analytical measurements, including pH, temperature, and specific conductivity.

### A.4.3.3 Purging

Purging consists of the evacuation of water from the monitoring location prior to sampling, so that "fresh" formation water will enter the monitoring location and be available for sampling. Because sampling can occur immediately upon completion of purging, it is best to limit groundwater agitation, and consequently, aeration of the

groundwater and volatilization of contaminants. Two sources for agitation include the purging device and the cascading of water down the screen as the water level in the well drops. To avoid agitation, a low-disturbance device such as a peristaltic pump or bladder pump is recommended for purging, while equipment such as bailers should be avoided. To avoid aeration, wells/points screened below the water table should be pumped at a rate which prevents lowering of the water table to below the top of the screen, and if practical, wells/points screened across the water table should be pumped at a rate that lowers the total height of the water column no more than 10 percent.

Typically the volume of water contained within the monitoring well/point casing is used to estimate the amount of groundwater that should be removed during the purge. As a general rule, three times the calculated volume should be removed from the well/monitoring point; however, this can be reduced to between 1 and 3 volumes for low-producing wells and wells with a very large water column, but a very short screened interval. Purging should continue until parameters such as pH, temperature, specific conductance, dissolved oxygen, and ORP stabilize. Sampling should occur as soon after purging as practical, and definitely within 24 hours. Purge waters must be handled in accordance with the site IDW plan.

If a monitoring well/monitoring point is evacuated to a dry state during purging, the monitoring well/monitoring point should be allowed to recharge, and the sample should be collected as soon as sufficient water is present in the monitoring well or monitoring point to obtain the necessary sample quantity. Sample compositing or sampling over a lengthy period by accumulating small volumes of water at different times to obtain a sample of sufficient volume should be avoided.

It is important to record purge information as a part of the sampling record for each location. At a minimum, the following information pertaining to the purge should be recorded:

- Monitoring point/well number;
- Date and time of purge;
- Purge method;
- Monitoring point/well depth;
- Volume of water produced;
- Description of water produced;
- Post-purge water level; and
- Field analytical measurements, including pH, temperature, specific conductivity, dissolved oxygen concentration, and ORP.

### A.4.3.4 Sampling

Sampling should occur as soon as practical and within 24 hours following the purge. The object of sampling is the collection of representative groundwater samples. This means that impact to the sample as a result of turbulence, contact with equipment, or a change in conditions must be minimized. The use of a peristaltic pump with dedicated HDPE tubing is recommended for monitoring locations where the depth to water is less than 25 feet because the peristaltic pump is capable of providing a steady, low-flow, stream of groundwater which has contacted only dedicated tubing. In addition, conditions are relatively unchanged, so long as care is taken to ensure that the pumping suction does not cause the groundwater to boil as a result of the reduced pressure. Where the depth to groundwater is greater than 25 feet, a dedicated positive displacement pump, when available, is best. A carefully-lowered, disposable bailer is considered the next best alternative. Because of the decontamination difficulties and the resulting potential for cross-contamination associated with most positive displacement pumps, sampling through these pumps is not recommended unless the pumps are dedicated.

A flow-through cell, such as the one pictured on Figure A.4.1, should be used for the measurement of well-head parameters, including pH, temperature, specific conductance, dissolved oxygen, and ORP. When using a pump to purge or sample, the pump discharge tubing should be positioned near the bottom of the cell. If using a bailer, the water should be drained from the bottom of the bailer through tubing into the cell. In either case, the tubing should be immersed alongside the dissolved oxygen probe beneath the water level in the cell. This will minimize aeration and keep water flowing past the dissolved oxygen probe's sampling membrane. The probes for the other parameters are less sensitive to positioning within the flow through cell.

Samples should be collected directly from the pump discharge tube or bailer into a sample container of appropriate size, style, and preservation for the desired analysis. Water should be directed down the inner walls of the sample bottle to minimize aeration of the sample. All samples to be analyzed for volatile constituents (e.g., SW8010, SW8020, SW8240, SW8260, and TPH-g) or dissolved gases (e.g., methane, ethane, and ethene) must be filled and sealed so that no air space remains in the container. Sample handling procedures are further described in Section A.6.

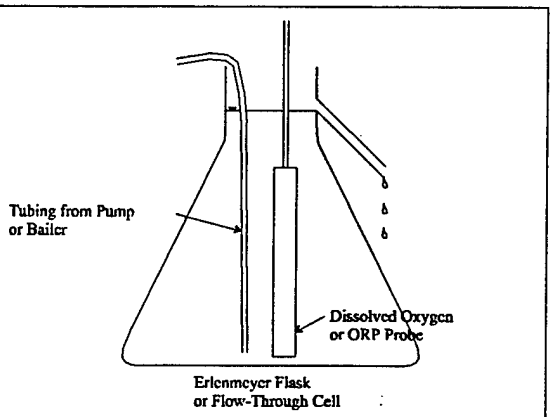



Figure A.4.1

Diagram Showing the Suggested Procedure for Dissolved Oxygen and ORP Sampling

## A.4.4 GROUNDWATER ANALYTICAL PROCEDURES

In order to demonstrate the efficacy of RNA, field and laboratory analyses should be performed on all groundwater samples using the analytical procedures listed in Table 2.1. As a result of analyte properties and available detection equipment, analyses can be performed at the sampling location, a portable field laboratory, or a fixed-base laboratory. The dissolved hydrogen analysis is unique in that it requires a combination of well-head and field laboratory procedures that are somewhat different from other field method; therefore, it is presented in a separate subsection. Several of the analytes or parameters can be measured in more than one manner; consequently, the methods provided in this section should not be considered absolute. Rather, these methods have been proven to provide reliable information.

In order to obtain accurate and defensible data, it is critical that quality assurance procedures are followed for all analyses. These procedures generally fall into the following categories:

- Collection and handling of samples;
- Calibration of direct read meters, chromatographs, colorimeters, and field instruments per manufacturer's instructions;
- Decontamination of equipment and containers; and
- Confirmation of results through analysis of blanks, duplicates, and other quality control samples.

Actual procedures are equipment and analysis specific, and must be developed accordingly.

### A.4.4.1 Standard Well Head Analyses

Standard well head analyses include pH, conductivity, temperature, dissolved oxygen, and ORP because these parameters can be measured with a direct-reading meter. This allows all of these parameters to be used as indicators for groundwater stability during development and purging activities. In addition, dissolved oxygen and ORP can be used to provide real time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Temperature, dissolved oxygen, and ORP also are measured at the well head in unfiltered, unpreserved, "fresh" water because these parameters can change significantly within a short time following sample acquisition. Section 2.3.2 of the protocol document describes each analysis and its use in the demonstration of RNA.

It is critical that samples collected for well head analyses are disturbed and aerated as little as possible; therefore, the use of a flow through cell, as described in Section A.4.3 and illustrated on Figure A.4.1, is recommended. Where this is not possible, measurements can be made in a clean glass container separate from those intended for laboratory analysis. Where groundwater extraction disturbs the sample, downhole 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, and inadequate decontamination can create potential cross contamination problems if performed prior to sample collection for the other analytes. After sample acquisition, the downhole groundwater may be too disturbed to collect an accurate downhole DO measurement.

### A.4.4.2 Dissolved Hydrogen Analysis

As described in Section 2.3.2.9, dissolved hydrogen ($H_2$) concentrations can be an indicator of microbially mediated redox processes in groundwater systems. Determination of $H_2$ concentrations is a two-step process in the field: sampling at the well head and analysis with a reducing gas detector.

Hydrogen is highly volatile, and this chemical property can be used to measure $H_2$ concentrations in groundwater. The principle is to continuously pump groundwater

through a gas-sampling bulb containing a nitrogen or air "bubble" so that the $H_2$ can partition between the gas and liquid phases until the concentration of $H_2$ in the bubble comes into equilibrium with concentration of $H_2$ in the groundwater. The bubble is then analyzed for $H_2$ and the concentration of $H_2$ in the groundwater is calculated using the Ideal Gas Law and Henry's Law. This method is referred to as the "bubble strip" method (Chapelle et al., ;1995), because the bubble "strips" $H_2$ out of the water.

*A.4.4.2.1 Sampling Method*

The following procedures are recommended for the collection of a sample for analysis by the "bubble strip" method:

1. Place the intake hose of a peristaltic pump, a Bennett positive displacement pump, or a bladder pump into the PVC or other non-metal sampling well at the depth of the screened interval.
   - Do not sample for $H_2$ with electrical submersible pumps because they may produce hydrogen.
   - Do not sample for $H_2$ from wells with metal screens or casings because they may produce hydrogen and interfere with measurements.
   - Do not sample for $H_2$ from wells that have not been in place at least 2 months.
2. Attach a glass, 250-ml gas-sampling bulb (Figure A.4.2) to the outflow end of the hose.
3. Turn on the pump and adjust the flow rate to between 400 and 700 mL/min.
4. Briefly hold the outlet end of the sampling bulb in the upright position to remove any gas bubbles from the bulb.
5. Place the bulb in a horizontal position and inject 20 mL of hydrogen-free $N_2$ gas through the septum (Figure A.4.2).
6. Allow the $N_2$ bubble to come into equilibrium with the flowing groundwater. This equilibration process takes approximately 20 minutes.
7. Remove 3-5 mL of the gas bubble using a 10 mL glass syringe with attached mini-inert valve.
8. Close the valve to seal the sample.
9. Wait an additional 5 minutes and repeat steps 7 and 8.
10. Analyze both samples on the hydrogen detector, as described in Section A.4.4.2.2.
11. Resample the well if the $H_2$ concentrations of the duplicate samples do not agree within 10 percent.

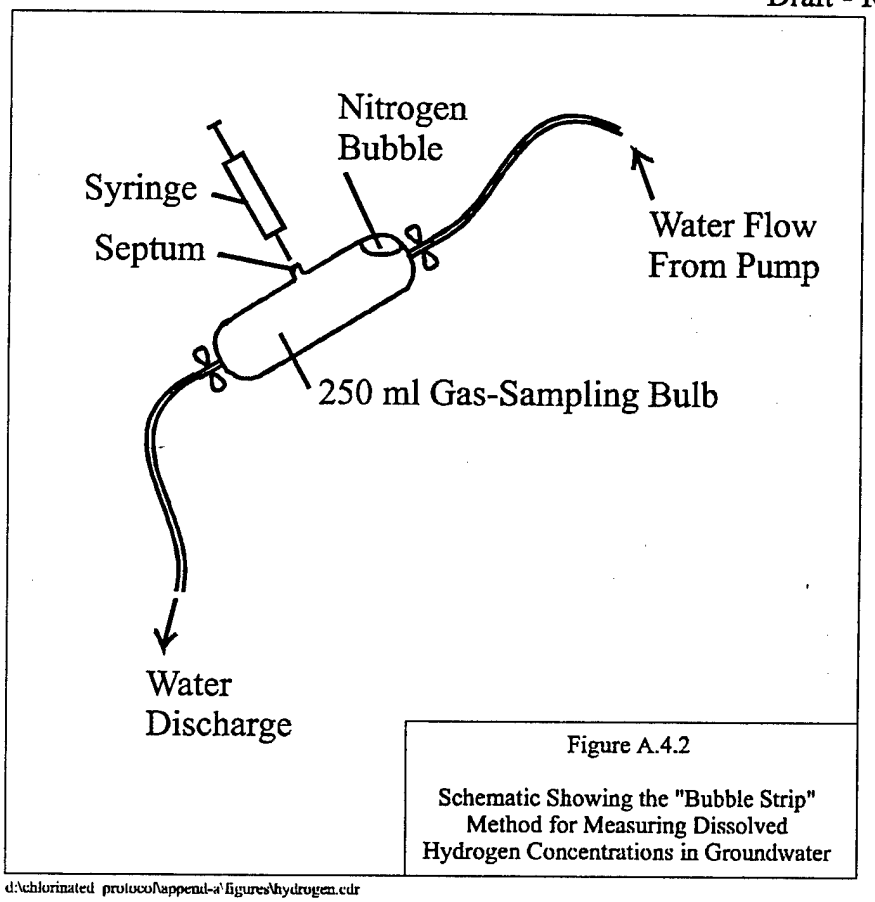



Figure A.4.2

Schematic Showing the "Bubble Strip" Method for Measuring Dissolved Hydrogen Concentrations in Groundwater

d:\chlorinated protocol\append-a\figures\hydrogen.cdr

*A.4.4.2.2 Analytical Method*

Concentrations of $H_2$ in the nitrogen bubble are determined by gas chromatography (GC) with reduction gas detection (Trace Analytical, Menlo Park, CA). To perform this analysis, a gaseous sample is injected into the stream of a carrier gas such as $N_2$. The sample is transported by the carrier through a separation column where the components of the sample are separated on the basis of variations in their transport efficiency through the column matrix. The column is packed with CarboSieve II which separates chemical species primarily on the basis of molecular size. The separated components elute from the column and pass through a heated bed of HgO where the reduced gases (primarily $H_2$ and CO) are oxidized and Hg vapor is released. The concentration of Hg vapor released is directly proportional to the concentration of reduced gases present in the sample and is detected by means of an ultraviolet photometer. Because chlorinated solvents can destroy the HgO bed, the column is backflushed immediately after the $H_2$ peak is quantified.

The concentration of $H_2$ dissolved in the groundwater can be calculated from the equilibrated concentration in the nitrogen gas bubble as follows:

1) Prepare a calibration curve for $H_2$ using a 100 ppm Scotty II standard gas mixture. The calibration curve should range from 0.1 to 10.0 µL/L (ppm).
2) Analyze the gas sample taken from the gas-sampling bulb, obtaining results ($C_B$) in units of µL/L (ppm) in the gas phase.
3) Calculate the aqueous concentration of $H_2$ ($C_w$ in nanomoles per liter (nM)) in equilibrium with the equilibrated bubble gas ($C_B$, µL/L (ppm)) sample using the conversion factor:

$$C_W = 0.81 C_B \qquad \text{eq. A.4.1}$$

This conversion factor is derived from the Ideal Gas Law and Henry's Law as follows:

$$PV = nRT \quad \text{(Ideal Gas Law)} \qquad \text{eq. A.4.2}$$

Rearrange to give:

$$\frac{n}{V} = \frac{P}{RT} \qquad \text{eq. A.4.3}$$

Where n = the quantity of gas in moles
V = the volume the gas occupies in Liters
P = the partial pressure of the gas in atm
T = the temperature in °K
R = the gas constant (R = 0.08205 atm L $mole^{-1}$ $°K^{-1}$)

Thus the concentration of a pure gas at atmospheric pressure and room temperature is 40.9 mmoles/L. For a 100 ppm calibration standard (ie. 100 µL/L), the $H_2$ concentration in molar units is:

$$(40.9 mmoles / L_{H_2})(10^4 L_{H_2} / L_{gas})(10^6 nmoles / mmole) = 4090 nmoles / L_{gas} \qquad \text{eq. A.4.4}$$

The dissolved $H_2$ concentration in the aqueous phase is given by Henry's Law:

$$C_w = \frac{C_h}{H_{H_2}} \qquad \text{eq. A.4.5}$$

$$Conversion factor = \frac{40.9 nmoles\, L^{-1}\, ppm^{-1})}{50.4} = 0.81 \qquad \text{eq. A.4.6}$$

Where $C_w$ = the dissolved $H_2$ concentration in nmoles/L
$C_h$ = the equilibrated bubble $H_2$ concentration in nmoles/L

$H_{H2}$ = the dimensionless Henry's Law coefficient for the distribution of $H_2$ between the gaseous and dissolved phases ($H_{H2}$ = 50.4).

4) Identify the predominant terminal electron accepting process for the water sample using the characteristic ranges presented in Table 2.4

### A.4.4.3 Field Analytical Laboratory Analyses

The field analytical laboratory analyses to be used for groundwater samples are presented in Table 2.1. These analyses include parameters that are time sensitive or can be performed accurately, easily, and inexpensively on site. In addition, results obtained from field laboratory analyses provide real time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. This real-time data can be used to guide the RNA investigation at sites with limited or ambiguous hydrogeologic and plume information. Section 2.3.2 of the protocol document describes each analysis and its use in the demonstration of RNA.

In preparation for field laboratory analysis, all glassware or plasticware used in the analyses must be cleaned thoroughly by washing with a solution of laboratory-grade, phosphate-free detergent (such as Alconox®) and water, and rinsing with deionized water and ethanol to prevent interference or cross contamination between measurements. If concentrations of an analyte are above the range detectable by the titrimetric method, the analysis should be repeated by diluting the groundwater sample with double-distilled water until the analyte concentration falls to a level within the range of the method. All rinseate and sample reagents accumulated during groundwater analysis must be handled appropriately, including collection, labeling, storage, and disposal.

Carbon dioxide ($CO_2$) is a byproduct of naturally occurring aerobic and anaerobic biodegradation processes that occur in groundwater. $CO_2$ concentrations in groundwater can be measured in the field by titrimetric analysis using CHEMetrics® Method 4500 (0 to 250 mg/L as $CO_2$), or similar.

Alkalinity in groundwater helps buffer the groundwater system against acids generated through both aerobic and anaerobic biodegradation processes. Alkalinity of the groundwater sample will be measured in the field by titrimetric analysis using USEPA-approved Hach® Method 8221 (0 to 5,000 mg/L as calcium carbonate), or similar.

Nitrate-nitrogen concentrations are of interest because nitrate can act as an electron acceptor during hydrocarbon biodegradation under anaerobic soil or groundwater

conditions. Nitrate-nitrogen is also a potential nitrogen source for hydrocarbon-degrading bacteria biomass formation. Nitrite-nitrogen is an intermediate byproduct in both ammonia nitrification and in nitrate reduction in anaerobic environments. Nitrate- and nitrite-nitrogen concentrations in groundwater can be measured in the field by colorimetric analysis using a portable colorimeter (such as the Hach® DR/700). Nitrate concentrations in groundwater samples can be analyzed after preparation with Hach® Method 8039 (0 to 30.0 mg/L nitrate), or similar. Nitrite concentrations in groundwater samples can be analyzed after preparation with USEPA-approved Hach® Method 8507 (0 to 0.35 mg/L nitrite), or similar.

Sulfate in groundwater is a potential electron acceptor for fuel-hydrocarbon biodegradation in anaerobic environments, and sulfide is resultant after sulfate reduction. Sulfate and sulfide concentrations can be measured by colorimetric analysis with a portable colorimeter (such as the Hach® DR/700) after appropriate sample preparation. USEPA-approved Hach® Methods 8051 (0 to 70.0 mg/L sulfate) and 8131 (0.60 mg/L sulfide) (or similar) can be used to prepare samples and analyze sulfate and sulfide concentrations, respectively.

Iron is an important trace nutrient for bacterial growth, and different states of iron can affect the oxidation/reduction potential of the groundwater and act as an electron acceptor for biological metabolism under anaerobic conditions. Iron concentrations can be measured in the field by colorimetric analysis with portable colorimeter (such as a Hach® DR/700) after appropriate sample preparation. Hach® Method 8008 for total soluble iron (0 to 3.0 mg/L ferric + ferrous iron) and Hach® Method 8146 for ferrous iron (0 to 3.0 mg/L) (or similar) can be used to prepare and quantitate the samples. Ferric iron is quantitated by subtracting ferrous iron levels from total iron levels.

Manganese is a potential electron acceptor under anaerobic environments. Manganese concentrations can be quantitated in the field using colorimetric analysis with a portable colorimeter (such as a Hach® DR/700). USEPA-approved Hach® Method 8034 (0 to 20.0 mg/L), or similar, can be used to prepare the samples for quantitation of manganese concentrations.

#### A.4.4.4 Fixed-Base Laboratory Analyses

The fixed-base laboratory analyses to be used for groundwater samples are presented in Table 2.1. These analyses include the parameters that cannot be easily or accurately

performed in the field, but are necessary to document natural attenuation of fuel hydrocarbons and chlorinated solvents in groundwater. Section 2.3.2 of the protocol document describes each analysis and its use in the demonstration of RNA.

Prior to sampling, arrangements should be made with the analytical laboratory (or other supplier) to provide a sufficient number of appropriate sample containers for the samples (including quality control samples) to be collected. All containers, preservatives, and shipping requirements should be consistent with the analytical protocol. For samples requiring chemical preservation, preservatives are best added to containers by the laboratory (or other supplier) prior to shipping. Sample handling is discussed in Section A.6.

# SECTION A-5

# SURFACE WATER AND SEDIMENT CHARACTERIZATION METHODOLOGIES

At sites where surface water bodies are affected (or potentially affected) by contamination, surface water and sediment sample collection and analysis may be required as a component of the remediation by natural attenuation demonstration.

## A.5.1 Surface Water Sample Collection

Surface water can be collected with a peristaltic pump using exactly the same equipment and procedures to collect water from a well. The sampling tubing can be introduced into the water from a barge or boat, or from a dock. The depth to the sediment should be sounded, then the tubing introduced to a level a very few inches above the sediment layer. A weight can be used to keep tire tubing straight. Alternately, ½ inch PVC pipe can be inserted to the correct depth, then sample with tubing just as if it were a well.

Many plumes discharge at some distance away the shoreline of lakes or large rivers. Samples should be taken at locations where the elevation of the sediment-to-water interface corresponds to the elevation of the contaminate plume: in the aquifer. Many plumes are driven down into aquifers by recharge. Conversely, the flow path bends sharply up underneath a gaining stream at the point of discharge. Water just above the sediment in the center of a stream or small river should be sampled. If possible, the stage of a stream or river at a gauging station near the point of sampling should determined to estimate the discharge of the stream or river at the time of sampling. Losing streams or rivers should not be sampled at high stage when they are losing water because groundwater plumes would be pushed away from the sediment interface. To ensure that the stream is not losing, the elevation of standing water in monitoring wells near the river should be higher than the stage of the river or stream at the time of sampling. The same considerations apply to tidal environments or areas with wind seiches on large bodies of

water. Surface water should be sampled when the tide is out, or the wind is blowing off-shore.

### A.5.2 Sediment Sample Collection

Sediment samples below the water surface can be collected using stainless steel core barrel tubing with a drop-out end point. The sample tubing can be hand driven to the desired depth from a boat, then pulled up after sampling is finished using a mechanical jack. An alternative technique is to place open-end two-inch diameter PVC tubing to a desired depth, then insert flexible tubing and collect the sediment as a slurry into a suction flask connected to a peristaltic pump.

# SECTION A-6

# 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.6.1 SAMPLE PRESERVATION, CONTAINERS, AND LABELS

Sample containers and appropriate container lids must be purchased or provided by the analytical laboratory. Any required chemical preservatives should be added to the sample containers by the analytical laboratory prior to shipping the containers to the site or alternatively, at the time of sampling. The sample containers should be filled and tightly sealed in accordance with accepted procedures for the sample matrix and the type of analysis to be conducted. 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.6.2 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;

- Place samples in a cooler containing ice to maintain a shipping temperature of approximately 4 degrees centigrade (°C), if required by the requested analyses;
- Include a properly completed chain-of-custody form, as described in the following subsection; and
- 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.6.3 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 include 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.6.4 SAMPLING RECORDS

In order to provide complete documentation of the sampling event, detailed records must be maintained by the field scientist. 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 such as pH, temperature, specific conductivity, dissolved oxygen concentration, and redox potential (groundwater samples); and
- Any other relevant information.

# SECTION A-7

# AQUIFER CHARACTERIZATION METHODOLOGIES

Adequate characterization of the groundwater flow and contaminant transport system is an important component of the natural attenuation demonstration. The following sections describe methodologies that are recommended to characterize the hydrogeologic system.

## A.7.1 HYDRAULIC CONDUCTIVITY

Hydraulic conductivity is a measure of an aquifer's capacity to transmit water and governs groundwater flow and contaminant transport in the subsurface. Methods for determining hydraulic conductivity in the field can include slug tests, pumping tests, and downhole flowmeter measurements. The method selected for a given site will depend on the dimensions, locations, and screened intervals of site wells and monitoring points; site stratigraphy; equipment availability; budget; and waste handling requirements.

### A.7.1.1 Slug 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. Because hydraulic conductivity varies spatially within and between aquifers and because slug test results reflect aquifer conditions only in the immediate vicinity of the tested well, slug tests should be conducted in as many wells as possible at a site. Slug tests can be used for both confined and unconfined aquifers that have transmissivities of less than approximately 7,000 square feet per day ($ft^2$/day). Slug tests are accomplished by removing a solid slug (rising head) or introducing a solid slug (falling head), and then allowing the water level to stabilize while taking water level measurements at closely spaced time intervals. The method presented herein discusses the use of falling head and rising head slug tests in sequence. The analysis of slug test data is discussed in Appendix C.

Slug testing should not proceed until water level measurements show that static water level equilibrium has been achieved. Unvented wells should be uncapped at least 24 hours prior to initiating the test in order to allow the static water level to come to equilibrium. The protective casing should remain locked during this time to prevent vandalism. During the slug test, the water level change should be influenced only by the introduction or removal of the slug volume. Other factors, such as inadequate well development or extended pumping, may lead to inaccurate results. It is the field scientist's responsibility to decide when static equilibrium has been reached in the well.

The following equipment is needed to conduct a slug test:

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

The falling head test is the first step in the two-step slug-testing procedure. The following steps describe the recommended falling head slug test procedure:

1. Decontaminate all downhole equipment.
2. Record pre-test information including: well number, personnel, climatic data, ground surface elevation, measuring point elevation, equipment identifications, and date.
3. Measure and record the static water level in the well to the nearest 0.01 foot.
4. Lower the decontaminated pressure transducer into the well and allow the displaced water to return to within 0.01 foot of the original static level.
5. Lower the decontaminated slug into the well to just above the water surface in the well.
6. Start 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.
7. Terminate data recording when the water level has recovered at least 80 percent from the initial slug displacement.

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 has recovered at least 80 percent from the initial slug displacement.

It is advisable to produce hard copies or backup electronic copies of the data logger output (drawdown vs. time) daily and before transporting the logger from the field site.

### A.7.1.2 Pump Tests

A pumping test involves pumping one well at a constant rate for a specified length of time and collecting periodic water level measurements in both the pumped well and nearby observation wells in order to determine aquifer hydraulic characteristics representative of a large area. As a rule, pumping tests provide more representative measurements of hydraulic parameters; however, they require a greater commitment of resources (time, money, and equipment) that cannot be afforded by all projects. In addition, for pumping test results to be representative, site hydrogeologic conditions should not change appreciably over short distances. This section outlines methods that can be used for conducting pump tests in both confined and unconfined aquifers. For a more detailed discussion of how to conduct a pumping test, the reader is referred to the work of Dawson and Istok (1991), Kruseman and de Ridder (1991), and Driscoll (1986).

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.

#### *A.7.1.2.1 Pumping Test Design*

Prior to performing an aquifer pumping test, all available site and regional hydrogeologic information should be assembled and evaluated. Such data should include groundwater flow direction, hydraulic gradients, other geohydraulic properties, site stratigraphy, well construction details, regional water level trends, and the performance of other pumping wells in the vicinity of the test area. This information is used to select test duration, proposed pumping rates, and pumping well and equipment dimensions.

The precise location of an aquifer test is chosen to be representative of the area under study. In addition, the location is selected on the basis of numerous other criteria, including:

- Size of the investigation area;
- Uniformity and homogeneity of the aquifer;
- Distribution of contaminant sources and dissolved contaminant plumes;
- Location of known or suspected recharge or barrier boundary conditions;
- Availability of pumping and/or observation wells of appropriate dimension and screened at the desired depth; and
- Requirements for handling discharge.

The dimensions and screened interval of the pumping well must be appropriate for the tested aquifer. For example, the diameter of the well must be sufficient to accommodate pumping equipment capable of sustaining the desired flow rate at the given water depth. In addition, if testing a confined aquifer that is relatively thin, the pumping well should be screened for the entire thickness of the aquifer. For an unconfined aquifer, the wells should be screened in the bottom one-third or two-thirds of the saturated zone.

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, with one well 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, proposed pumping test duration, and proposed pumping rate. Preliminary pumping results should also be used (if available). Not all projects can afford the luxury of preliminary testing.

The equipment needed to perform aquifer pumping tests includes:

- Pumps
- Gate valve
- Electrical generator
- Conductivity meter, pH meter, and thermometer
- Barometer
- Semi-log and log-log graph paper

- 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
- 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

Pumping equipment should conform to the size of the well and be capable of delivering the estimated range of pumping rates. The selection of flow meter, gate valve, and water transfer lines should be based on anticipated rates of water discharge. Both the discharge rate and test duration should be considered when selecting a tank for storing discharge water if the water cannot be released directly released to the ground, sanitary sewer, storm sewer, or nearby water treatment facility.

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.7.1.2.2 Preparation for Testing*

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. Therefore, for at least 24 hours prior to performing a pumping test, barometric pressure and water levels in the test well, observation wells, and a well beyond the influence of the pumping well should be measured hourly to establish trends in groundwater level fluctuation. If a trend is apparent, the barometric pressure should be used to develop curves depicting the change in water level versus time. These curves should be used to correct the water levels observed during the pumping test. Groundwater levels in the background well as well as barometric pressures should continue to be recorded throughout the duration of 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).

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.

*A.7.1.2.2 Conducting the Pumping Test*

Immediately prior to starting the pump, the water levels should be measured and recorded for all wells to determine the static water levels upon which all drawdowns will be based. 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 away from the well and associated observation wells. Recharge could adversely affect the results. 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 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. 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.

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 120 minutes to 1,440 minutes (one day) and every 2 hours after 1 complete day.

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 may be needed when treatment of the pumped water is required prior to discharge. It is advisable for at least one field member to have experience in the performance of pump tests, and for all field personnel to have a basic familiarity with conducting the test and gathering data.

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 an ever-decreasing

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.7.1.3 Downhole Flow Meter Measurements

Downhole flow meter measurements are used to investigate the relative vertical distribution of horizontal hydraulic conductivity in an open borehole or the screened portion of a well. These measurements are useful for identifying zones of elevated hydraulic conductivity that may contribute to preferential flow pathways and affect contaminant migration. Methodologies for interpreting data from borehole surveys are described by Molz *et al.* (1994).

Flowmeter measurements should be performed at 1- to 3-foot intervals in test wells during both ambient conditions and induced flow conditions. Test data may be analyzed using the methods described by Molz *et al.* (1994) to define the relative distribution of horizontal hydraulic conductivity within the screened interval of each well. Final results should be presented in tabular and graphical forms and accompanied by appropriate interpretation and discussion. Estimates of bulk hydraulic conductivity from previous aquifer tests or results of single-well tests conducted in conjunction with the flow meter survey can be used to estimate the absolute hydraulic conductivity distribution at each well.

Borehole flowmeters should be calibrated prior to testing. Generally, 0.5-inch-ID and 1.0-inch-ID probes will be calibrated using a range of volumetric flowrates potentially applicable to most sites [e.g., approximately 0.04 liters per minute (L/min) to 10 L/min]. The following nine steps outline general procedures that can be used to conduct a downhole flow meter survey at a given location.

1. Measure the water level, organic liquid (NAPL) interfaces (if present), and total depth (TD) prior to initiating the test.

2. Calibrate the flow meter for the range of anticipated flow velocities before introducing the flow meter into the well or borehole.

3. Lower the flow meter to the bottom of the well/borehole.

4. Slowly withdraw the flow meter, pausing to obtain measurements at intervals of approximately 1 to 3 feet, depending on site conditions. This will provide a baseline under static (ambient) conditions.

5. Conduct a short-term, single-well pumping test in the test well to stress the aquifer.

6. Record drawdown using an electronic data logger with a pressure transducer.

7. Monitor and adjust the groundwater extraction rate, as necessary, to maintain constant flow.

8. Obtain the profile of the vertical flow at the same elevations occupied during the ambient profile upon stabilization of the flow rate.

9. Analyze the data collected during the tests to estimate relative distribution of flow into the tested wells and the relative hydraulic conductivity distribution at each location (Molz *et al.*, 1994).

## A.7.2 HYDRAULIC GRADIENT

Hydraulic gradient, defined as the change in groundwater elevation with distance, is a key parameter governing the direction and rate of groundwater flow and contaminant migration. Because groundwater can flow in both the horizontal and vertical planes, both horizontal and vertical gradients are required for a successful RNA demonstration. Hydraulic gradients are generally calculated on the basis of groundwater elevations measured in site monitoring wells or monitoring points using an electric water level indicator. Therefore, for the most complete representation of site hydrogeology, it is important to measure groundwater elevations from as many depths and locations as available. Interpretation of groundwater elevations and the subsequent calculations for hydraulic gradient are discussed in Appendix C.

## A.7.3 DIRECT MEASUREMENT OF GROUNDWATER VELOCITY

Groundwater velocity is directly related to contaminant velocity; therefore, a determination of groundwater velocity is critical to the fate and transport portion of a

RNA demonstration. Typically groundwater velocity is estimated from the hydraulic conductivity, hydraulic gradient, and effective porosity as described in Appendix C; however, direct measurement of groundwater velocity can be obtained from dye trace studies.

# APPENDIX B

# IMPORTANT PROCESSES AFFECTING THE FATE AND TRANSPORT OF ORGANIC COMPOUNDS IN THE SUBSURFACE

# TABLE OF CONTENTS - APPENDIX B


INTRODUCTION ..... B1-1
B.1.1 FATE AND TRANSPORT MECHANISMS ..... B1-1
B.1.2 MATHEMATICAL DESCRIPTION OF SOLUTE FATE AND TRANSPORT ..... B1-3

NONDESTRUCTIVE ATTENUATION MECHANISMS ..... B2-1
B.2.1 ADVECTION ..... B2-1
B.2.2 HYDRODYNAMIC DISPERSION ..... B2-3
B.2.2.1 Mechanical Dispersion ..... B2-3
B.2.2.2 Molecular Diffusion ..... B2-6
B.2.2.3 Equation of Hydrodynamic Dispersion ..... B2-7
B.2.2.4 One-Dimensional Advection-Dispersion Equation ..... B2-10
B.2.3 SORPTION ..... B2-10
B.2.3.1 Mechanisms of Sorption ..... B2-12
B.2.3.2 Sorption Models and Isotherms ..... B2-12
B.2.3.2.1 Langmuir Sorption Model ..... B2-13
B.2.3.2.2 Freundlich Sorption Model ..... B2-14
B.2.3.3 Distribution Coefficient ..... B2-15
B.2.3.4 Coefficient of Retardation ..... B2-17
B.2.3.4.1 Determining the Coefficient of Retardation using $K_{oc}$ ..... B2-18
B.2.3.4.2 Determining the Coefficient of Retardation using Laboratory Tests ..... B2-21
B.2.3.5 One-Dimensional Advection-Dispersion Equation with Retardation ..... B2-23
B.2.4 VOLATILIZATION ..... B2-23
B.2.5 RECHARGE ..... B2-25

DESTRUCTIVE ATTENUATION MECHANISMS - BIOLOGICAL ..... B3-1
B.3.1 OVERVIEW OF BIODEGRADATION ..... B3-3
B.3.2 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS A PRIMARY GROWTH SUBSTRATE ..... B3-7
B.3.2.1 Aerobic Biodegradation of Primary Substrates ..... B3-8
B.3.2.1.1 Aerobic Oxidation of Petroleum Hydrocarbons ..... B3-9
B.3.2.1.2 Aerobic Oxidation of Chlorinated Ethenes ..... B3-9
B.3.2.1.3 Aerobic Oxidation of Chlorinated Ethanes ..... B3-10
B.3.2.1.4 Aerobic Oxidation of Chlorobenzenes ..... B3-10
B.3.2.2 Anaerobic Biodegradation of Primary Substrates ..... B3-10

B.3.2.2.1 Anaerobic Oxidation of Petroleum Hydrocarbons ..... B3-11
B.3.2.2.2 Anaerobic Oxidation of Chlorinated Ethenes ..... B3-11
B.3.2.2.3 Anaerobic Oxidation of Chlorinated Ethanes ..... B3-11
B.3.2.2.4 Anaerobic Oxidation of Chlorobenzenes ..... B3-11
B.3.3 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS AN ELECTRON ACCEPTOR (REDUCTIVE DECHLORINATION) ..... B3-12
B.3.3.1 Reductive Dechlorination of Chlorinated Ethenes ..... B3-14
B.3.3.2 Reductive Dechlorination of Chlorinated Ethanes ..... B3-15
B.3.3.3 Reductive Dechlorination of Chlorobenzenes ..... B3-16
B.3.4 BIODEGRADATION OF ORGANIC COMPOUNDS VIA COMETABOLISM ..... B3-16
B.3.5 THERMODYNAMIC CONSIDERATIONS ..... B3-18
B.3.6 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION WITH RETARDATION AND BIODEGRADATION ..... B3-33

DESTRUCTIVE ATTENUATION MECHANISMS - ABIOTIC ..... B4-1
B.4.1 HYDROLYSIS AND DEHYDROHALOGENATION ..... B4-2
B.4.1.2 Hydrolysis ..... B4-2
B.4.1.2 Dehydrohalogenation ..... B4-3
B.4.2 REDUCTION REACTIONS ..... B4-5

## FIGURES


| No. | Title | Page |
|---|---|---|
| B.2.1 | Breakthrough Curve in One Dimension Showing Plug Flow with Continuous Source Resulting from Advection Only | B2-2 |
| B.2.2 | Breakthrough Curve in One Dimension Showing Plug Flow with Instantaneous Source Resulting from Advection Only | B2-2 |
| B.2.3 | Plume Migration in Two Dimensions (Plan View) Showing Plume Migration Resulting from Advective Flow Only with Continuous and Instantaneous Source | B2-2 |
| B.2.4 | Physical Causing Mechanical Dispersion at the Microscopic Scale | B2-4 |
| B.2.5 | Breakthrough Curve in One Dimension Showing Plug Flow with Instantaneous Source Resulting from Advection Only and the Combined Processes of Advection and Hydrodynamic Dispersion | B2-5 |
| B.2.6 | Breakthrough Curve in One Dimension Showing Plug Flow with Instantaneous Source Resulting from Advection Only and the Combined Processes of Advection and Hydrodynamic Dispersion | B2-6 |
| B.2.7 | Relationship Between Dispersivity and Scale | B2-8 |
| B.2.8 | 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 | B2-11 |
| B.2.9 | 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 | B2-11 |
| B.2.10 | Characteristic Adsorption Isotherm Shapes | B2-14 |
| B.2.11 | Plot of Sorbed Concentration versus Equilibrium Concentration | B2-22 |
| B.3.1 | 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 | B3-2 |
| B.3.2 | 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 | B3-2 |
| B.3.3 | Oxidation-Reduction Potentials for Various Oxidation-Reduction Reactions | B3-8 |
| B.3.4 | Expected Sequence of Microbially-Mediated Redox Reactions and Gibb's Free Energy of the Reaction | B3-32 |

## TABLES


| No. | Title | Page |
|---|---|---|
| B.1.1 | Summary of Important Processes Affecting Solute Fate and Transport | B1-2 |
| B.2.1 | Values of Aqueous Solubility and $K_{oc}$ for Selected Chlorinated Compounds | B2-19 |
| B.2.2 | Values of Aqueous Solubility and $K_{oc}$ for BTEX and Trimethylbenzene Isomers | B2-20 |
| B.2.3 | Data from Hypothetical Batch Test Experiment | B2-22 |
| B.2.4 | Henry's Law Constants and Vapor Pressures for Common Fuel Hydrocarbons and Chlorinated Solvents | B2-25 |
| B.3.1 | Biologic and Abiotic Degradation Mechanisms for Various Anthropogenic Organic Compounds | B3-1 |
| B.3.2 | Some Microorganisms Capable of Degrading Organic Compounds | B3-4 |
| B.3.3 | Trends in Contaminant, Electron Acceptor, Metabolic Byproduct, and Total Alkalinity Concentrations During Biodegradation | B3-7 |
| B.3.4 | Sources, Donors, Acceptors, and Products of Reported Reductive Dechlorinating Laboratory Systems | B3-15 |
| B.3.5 | Electron Donor and Electron Acceptor Half Cell Reactions | B3-19 |
| B.3.6 | Gibbs Free Energy of Formation for Species used in Half Cell Reactions and Coupled Oxidation-Reduction Reactions | B3-21 |
| B.3.7 | Coupled Oxidation-Reduction Reactions | B3-23 |
| B.4.1 | Approximate Half-Lives of Abiotic Hydrolysis and Dehydrohalogenation Reactions Involving Chlorinated Solvents | B4-4 |

# 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 chlorinated solvents and fuel hydrocarbons dissolved in groundwater. 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. 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. Those processes that result degradation of contaminants are referred to as destructive. Nondestructive processes include advection, hydrodynamic dispersion (mechanical dispersion and diffusion), sorption, dilution, and volatilization. Destructive processes include biodegradation and abiotic degradation mechanisms. Biodegradation may be the dominant destructive attenuation mechanism acting on a contaminant, depending upon the type of contaminant and the availability of electron donors or carbon sources. Abiotic degradation processes are also known to degrade chlorinated solvents; where biodegradation is not occurring, these may be the only destructive processes operating. However, the rates of abiotic processes are generally slow relative to biodegradation rates.

Remediation by natural attenuation results from the integration of all the subsurface attenuation mechanisms (both nondestructive and destructive) operating at a given site. Table B.1.1 summarizes the processes that affect fate and transport of chlorinated solvents and fuel hydrocarbons dissolved in groundwater. Important factors to consider include:

- The compound's soil/water distribution coefficient ($K_d$);
- The compound's organic carbon/water partition coefficient ($K_{oc}$);

## Table B.1.1
Summary of Important Processes Affecting Solute Fate and Transport

| 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 properties. | 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 relative to dispersion at most groundwater flow velocities. |
| Sorption | Reaction between aquifer matrix and solute whereby relatively hydrophobic organic 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 apparent solute transport velocity and remove solutes from the groundwater via sorption to the aquifer matrix. |
| Recharge (Simple Dilution) | Movement of water across the water table into the saturated zone. | Dependent on aquifer matrix properties, depth to groundwater, surface water interactions, and climate. | Causes dilution of the contaminant plume and may replenish electron acceptor concentrations, especially dissolved oxygen. |
| Volatilization | Volatilization of contaminants dissolved in groundwater into the vapor phase (soil gas). | Dependent on the chemical's vapor pressure and Henry's Law constant. | Removes contaminants from groundwater and transfers them to soil gas. |
| Biodegradation | Microbially mediated oxidation-reduction reactions that degrade contaminants. | Dependent on groundwater geochemistry, microbial population and contaminant properties. Biodegradation can occur under aerobic and/or anaerobic conditions. | May ultimately result in complete degradation of contaminants. Typically the most important process acting to truly reduce contaminant mass. |
| Abiotic Degradation | Chemical transformations that degrade contaminants without microbial facilitation; only halogenated compounds are subject to these mechanisms in the groundwater environment. | Dependent on contaminant properties and groundwater geochemistry. | Can result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation. |
| Partitioning from NAPL | Partitioning from NAPL into groundwater. NAPL plumes, whether mobile or residual, tend to act as a continuing source of groundwater contamination. | Dependent on aquifer matrix and contaminant properties. as well as groundwater mass flux through or past NAPL plume. | Dissolution of contaminants from NAPL represents the primary source of dissolved contamination in groundwater. |

- The compound's octanol/water partition coefficient ($K_{ow}$);
- The compound's water solubility;
- The compound's vapor pressure;
- The compound's Henry's Law constant (air/water partition coefficient, H);
- Indigenous bacterial population;
- Hydraulic conductivity of aquifer materials;
- Porosity of aquifer materials;
- Total organic carbon content of aquifer materials;
- Bulk density of aquifer materials;
- Aquifer heterogeneity; and
- Ambient groundwater geochemistry.

Nondestructive attenuation mechanisms are discussed in Section B-2. Biodegradation is discussed in Section B-3. Abiotic degradation mechanisms are discussed in Section B-4. It is important to separate nondestructive from destructive attenuation mechanisms during the natural attenuation 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 contaminant migration and attenuation in the saturated zone includes terms for advection, dispersion, sorption, and degradation. 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 degradation of organic contaminants commonly can be approximated using first-order kinetics. In one dimension, the partial differential equation describing solute transport with first-order decay 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]
$\lambda$ = first-order decay rate [T$^{-1}$]

These equations serve to illustrate how the processes of advection, dispersion, sorption, and biotic and abiotic degradation 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, dilution, sorption, and chemical reactions (most notably biodegradation). The change in solute concentration may therefore be stated mathematically as:

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

The following sections describe the most significant reactions affecting this mass balance (and therefore the fate and transport) of organic contaminants in the subsurface. Methods for evaluating the flux through the system will be discussed in Appendix C.

# SECTION B-2

# NONDESTRUCTIVE ATTENUATION MECHANISMS

## B.2.1 ADVECTION

Advective transport is the transport of solutes by the bulk movement of groundwater. Advection is the most important process driving dissolved 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). At and 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]

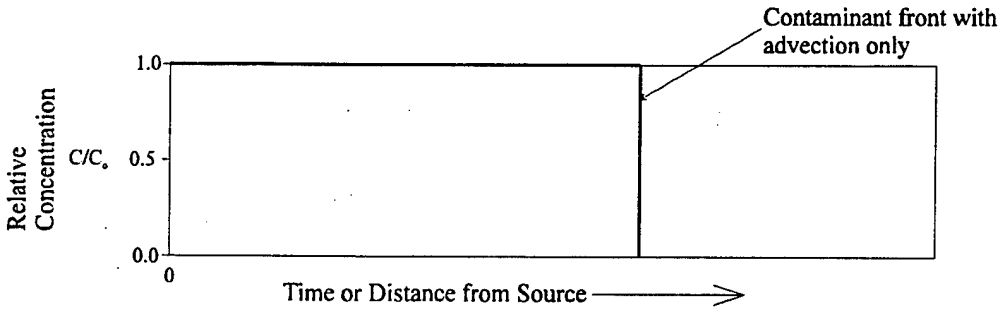



**Figure B.2.1** Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only.

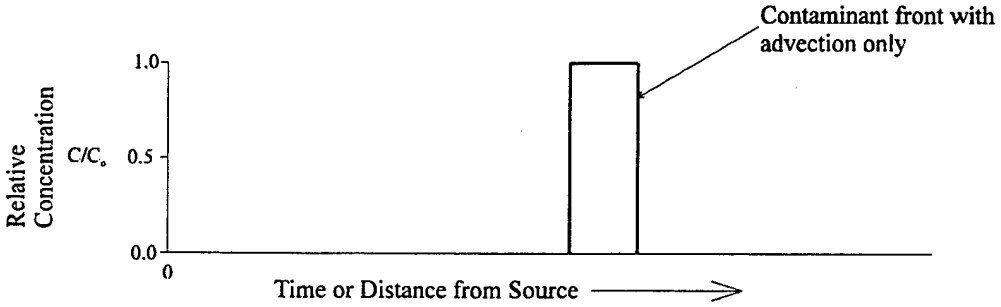



**Figure B.2.2** Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only.

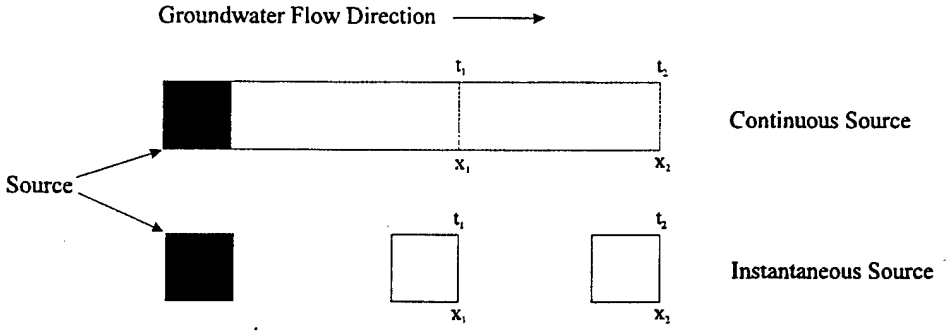



**Figure B.2.3** Plume migration in two dimensions (plan view) showing plume migration resulting from advective flow only with continuous and instantaneous sources.

Equation B.2.2 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.

## B.2.2 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. Dispersion of organic solutes in an aquifer is an important consideration when modeling remediation by natural attenuation. Dispersion of a contaminant dilutes the concentrations of the contaminant, and introduces the contaminant into relatively pristine portions of the aquifer where it may admix with more electron acceptors crossgradient to the direction of groundwater flow. Two very different processes cause hydrodynamic dispersion; mechanical dispersion and molecular diffusion. The variable describing 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. The following sections describe these processes and how they are incorporated into the modified advection-dispersion equation (Equation B.1.1).

### B.2.2.1 Mechanical Dispersion

As defined by Domenico and Schwartz (1990), mechanical dispersion is mixing that occurs as a result of local variations in velocity around some mean velocity of flow. With time, a given volume of solute will gradually become more dispersed as different portions of the mass are transported at the differing velocities. In general, the main cause of variations of both rate and direction of transport velocities is the heterogeneity of the porous aquifer medium. These heterogeneities are present at scales ranging from microscopic (e.g., pore to pore) to macroscopic (e.g., well to well) to megascopic (e.g., a regional aquifer system).

Three processes are responsible for mechanical dispersion on the microscopic scale (Figure B.2.4). 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.

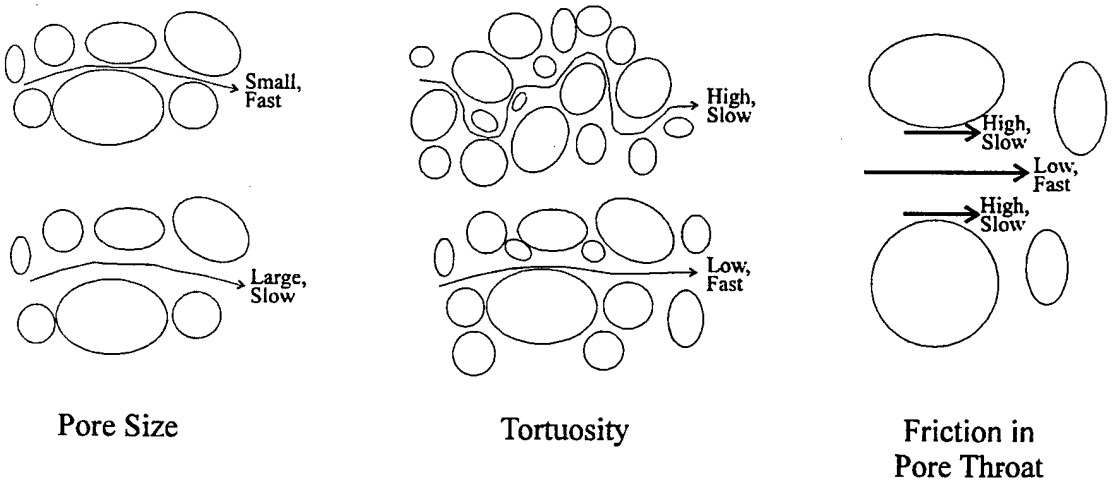



**Figure B.2.4** Physical processes causing mechanical dispersion at the microscopic scale.

Heterogeneity at the macroscopic and megascopic scales also creates variability in groundwater and solute velocities, therefore producing dispersion on a larger scale. Geologic features that contribute to dispersion at the macroscopic scale include stratification characteristics such as changing unit geometry, discontinuous units, and contrasting lithologies, and permeability characteristics such as nonuniform permeability, directional permeability, and trending permeability (Domenico and Schwartz, 1990). Even in aquifer material that appears to be homogeneous, relatively small changes in the fraction of fine sediment can change hydraulic conductivity characteristics enough to produce significant variations in fluid and solute velocities and thus introduce dispersion. Larger geological features will introduce dispersion at the megascopic scale. At this scale, structural features such as faults, dipping strata, folds, or

contacts will create inhomogeneity, as will stratigraphic features such as bedding or other depositional structures.

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.2.5 and B.2.6 illustrate the effects of hydrodynamic dispersion on an advancing solute front. The component of hydrodynamic dispersion contributed by mechanical dispersion is given by the relationship:

$$\text{Mechanical Dispersion} = \alpha_x v_x \qquad \text{eq. B.2.3}$$

Where: $v_x$ = average linear groundwater velocity [L/T]
$\alpha_x$ = 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. On the microscopic scale, longitudinal dispersion occurs because of velocity changes due 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 on the microscopic scale is caused by the tortuosity of the porous medium, which causes flow paths to branch out from the centerline of the contaminant plume.

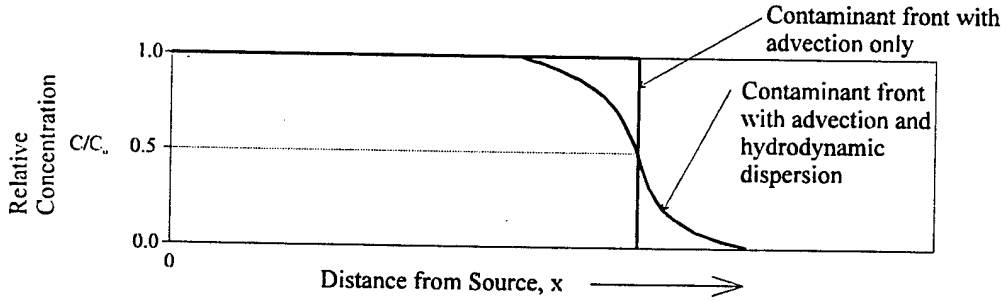



**Figure B.2.5** Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.

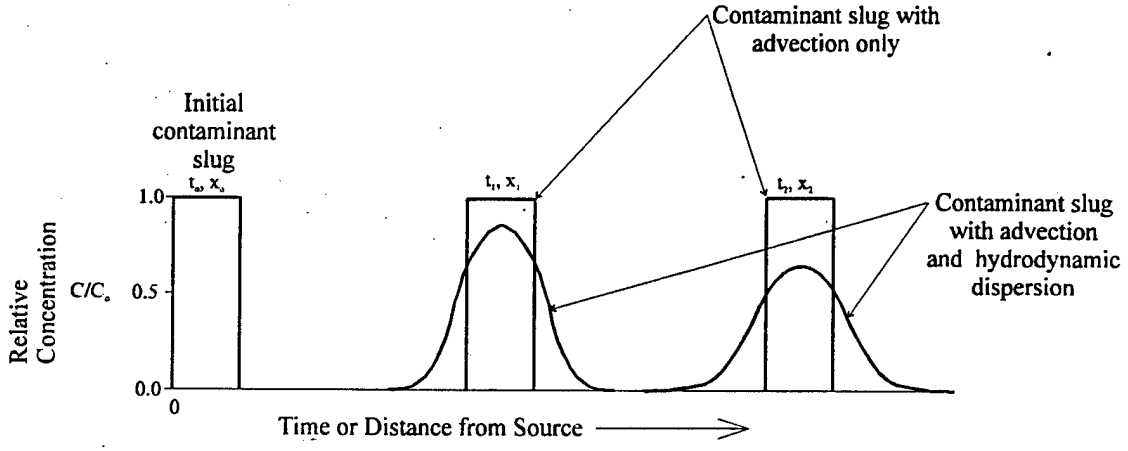



**Figure B.2.6** Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.

### B.2.2.2 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:

$$F = -D\frac{dC}{dx} \qquad \text{eq. B.2.4}$$

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:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad \text{eq. B.2.5}$$

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):

$$D^* = wD \qquad \text{eq. B.2.6}$$

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

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

### B.2.2.3 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):

$$D_x = \alpha_x v_x + D^* \qquad \text{eq. D.2.7}$$

Where: $D_X$ = longitudinal coefficient of hydrodynamic dispersion in the x direction [$L^2/T$]
$\alpha_X$ = 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. It is now commonly accepted (on the basis of empirical evidence) that as the scale of the plume or the system being studied increases, the dispersivity will also increase. Therefore, dispersivity is scale-dependent, but at a given scale, data compiled by Gelhar *et al.* (1985 and 1992) show that dispersivity may vary over three orders of magnitude. The data of Gelhar *et al.* (1992) are presented on Figure B.2.7.

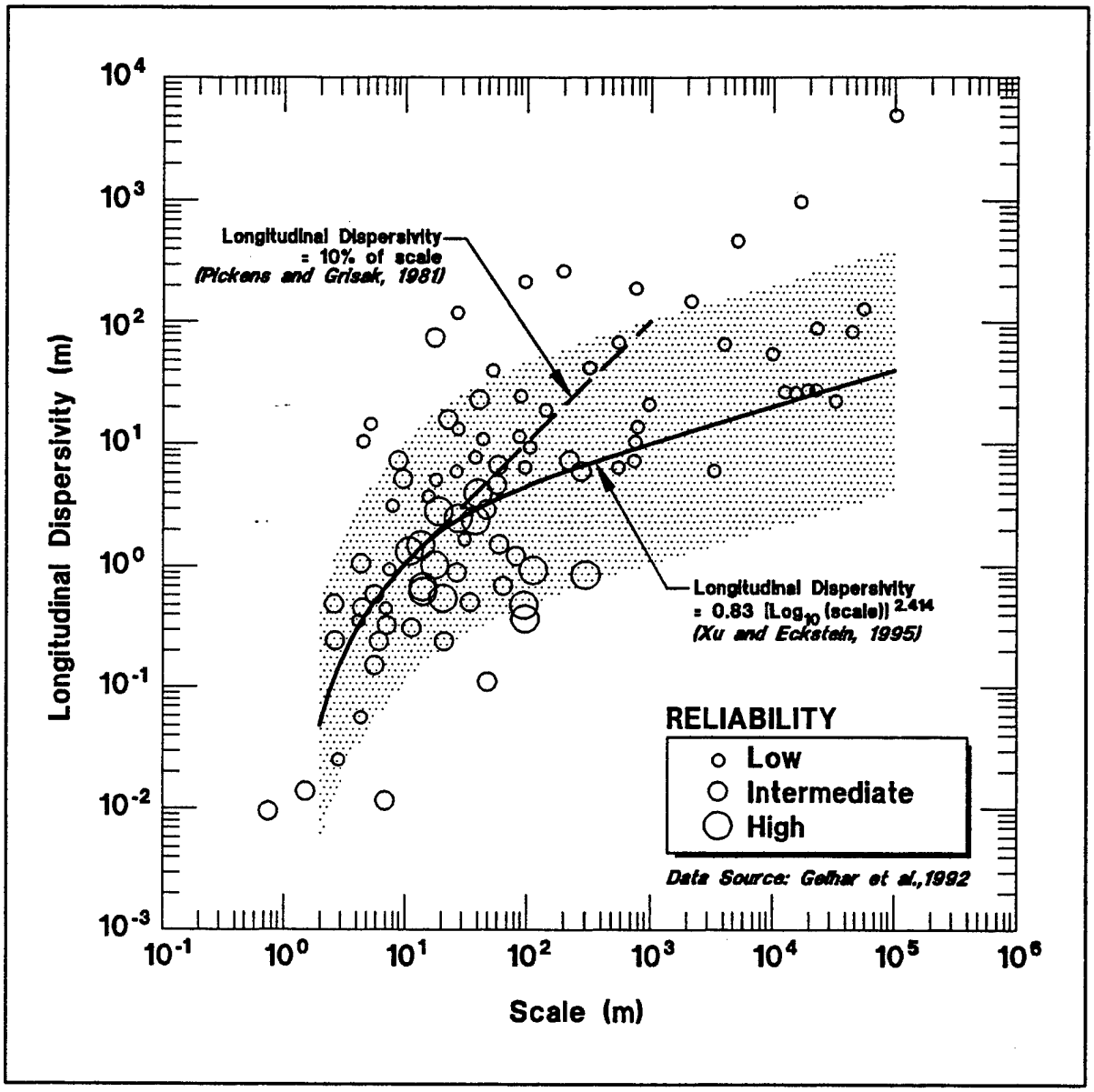



Figure B.2.7

Relationship Between Dispersivity and Scale

Source: Newell *et al.*, 1996

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Several approaches can be used to estimate longitudinal dispersivity, $\alpha_x$., on the field scale (i.e., macroscopic to megascopic scales). 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; Pickens and Grisak, 1981; Spitz and Moreno, 1996). This assumes that dispersivity varies linearly with scale. However, Xu and Eckstein (1995) evaluated the same data presented by Gelhar *et al.* (1992) and, by using a weighted least-squares method, developed the following relationship for estimating dispersivity:

$$\alpha_x = 0.83(Log_{10} L_P)^{2.414} \qquad \text{eq. B.2.8}$$

Where: $\alpha_X$ = longitudinal dispersivity [L]
$L_p$ = plume length [L]

Both relationships are shown on Figure B.2.7. In either case, the value derived for dispersivity will be an estimate at best, given the great variability in dispersivity for a given plume length. However, for modeling studies, an initial estimate is needed, and these relationships provide good starting points for a modeling study.

In addition to estimating longitudinal dispersivity, it may be necessary to estimate the transverse and vertical dispersivities ($\alpha_T$. and $\alpha_Z$., respectively) for a given site. Several empirical relationships between longitudinal dispersivity and transverse and vertical dispersivity have been described. Commonly, $\alpha_T$ is estimated as $0.1\alpha_x$. (based on data from Gelhar *et al.*, 1992), or as $0.33\alpha_x$. (ASTM, 1995; US EPA, 1986). Vertical dispersivity ($\alpha_Z$) may be estimated as $0.05\alpha_x$. (ASTM, 1995), or as $0.025\alpha_x$. to $0.1\alpha_x$. (US EPA, 1986).

Some solute transport modelers will start with an accepted literature value for the types of materials found in the aquifer matrix. After selecting initial dispersivity values, the contaminant transport model is calibrated by adjusting the dispersivities (along with other transport parameters, as necessary) 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 hydraulic parameters, including hydraulic conductivity, effective porosity, and dispersivity, are variable within the flow system (Anderson, 1979; Davis *et al.*,

1993), and other transport parameters such as retardation and biodegradation may not be well-defined.

### B.2.2.4 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:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.9}$$

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.

## B.2.3 SORPTION

Many organic contaminants, including chlorinated solvents and 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.2.8 and B.2.9 illustrate the effects of sorption on an advancing solute front.

Keep in mind that sorption is a reversible reaction and that at a given solute concentrations, some portion of the solute is partitioning to the aquifer matrix and some portion is also desorbing and reentering solution. As solute concentrations change, the relative amounts of contaminant that are sorbing and desorbing will change. For example, as solute concentrations decrease

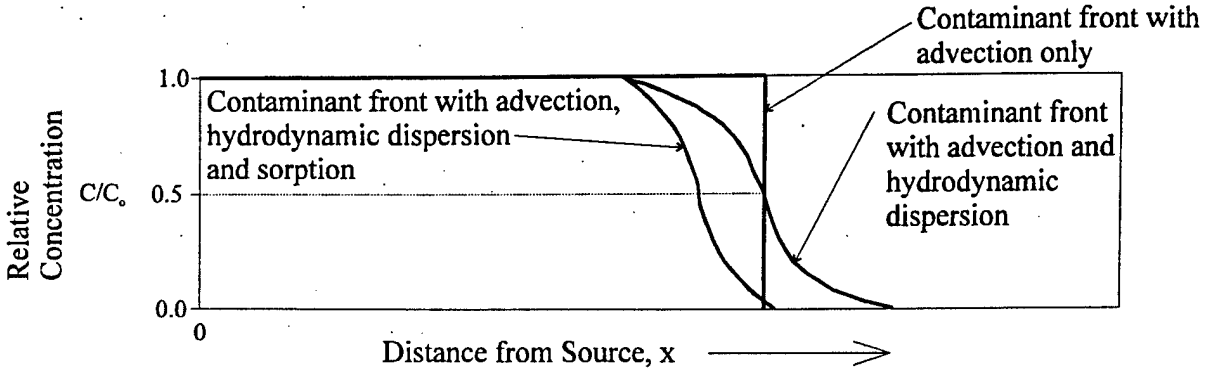



**Figure B.2.9** Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.

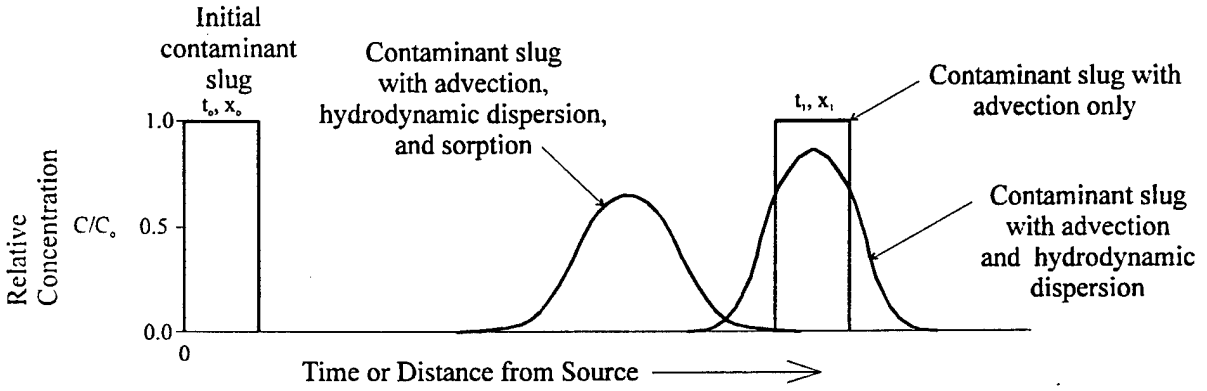



**Figure B.2.9** Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.

(perhaps due to plume migration or solute biodegradation and dilution), the amount of contaminant reentering solution will likely increase. The affinity of a given compound for the aquifer matrix will not be sufficient to permanently isolate it from groundwater, although for some compounds, the rates of desorption may be so slow that the loss of mass may be considered permanent for the time scale of interest. Sorption therefore does not permanently remove solute mass from groundwater; it merely retards migration. It is this slowing of contaminant migration that must be understood in order to effectively predict the fate of a dissolved contaminant.

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.2.3.1 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 organic contaminants.

### B.2.3.2 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.2.3.2.1 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):

$$C_a = \frac{KC_l b}{1 + KC_l} \qquad \text{eq. B.2.10}$$

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, $b$.

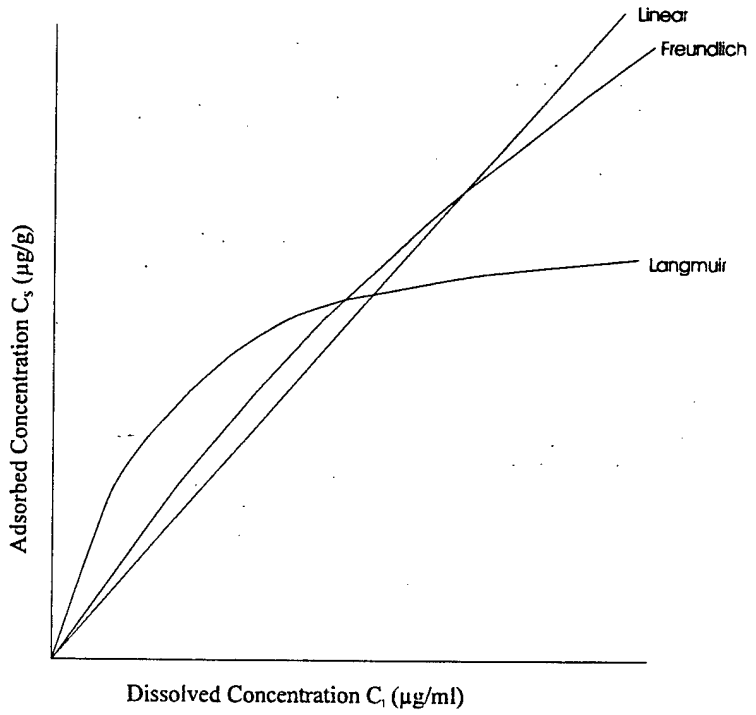



**Figure B.2.10** Characteristic adsorption isotherm shapes.

B.2.3.2.2 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):

$$C_a = K_d C_l^{1/n} \qquad \text{eq. B.2.11}$$

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):

$$C_a = K_d C_l \qquad \text{eq. B.2.12}$$

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.2.3.3 Distribution Coefficient

The most commonly used method for expressing the distribution of an organic compound 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:

$$K_d = \frac{C_a}{C_l} \qquad \text{eq. B.2.13}$$

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), Karickhoff *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)

$$f_{oc_c} = \frac{A_s}{200}\frac{1}{K_{ow}^{0.84}} \qquad \text{eq. B.2.14}$$

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.

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 $K_{oc}$:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{eq. B.2.15}$$

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):

$$K_{oc} = 1.724 K_{om} \qquad \text{eq. B.2.16}$$

### B.2.3.4 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:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. B.2.17}$$

Where: $R$ = coefficient of retardation [dimensionless]
$\rho_b$ = 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:

$$v_c = \frac{v_x}{R} \qquad \text{eq. B.2.18}$$

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.2.3.4.1 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.2.15. In effect, equation B.2.15 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.2.1 lists $K_{oc}$ values for selected chlorinated compounds, and Table B.2.2 lists $K_{oc}$ values for BTEX and trimethylbenzene.

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:

$$K_d = K_{oc} f_{oc} \qquad \text{eq. B.2.19}$$

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.

**Table B.2.1**
Values of Aqueous Solubility and $K_{oc}$ for selected chlorinated compounds

| Compound | Solubility (mg/L) | $K_{oc}$ (L/Kg) |
|---|---|---|
| Tetrachloroethene | 150[a] | 263[a] |
| Tetrachloroethene | | 359[b] |
| Tetrachloroethene | 1,503[c] | 209 - 238[c] |
| Trichloroethene | 1,100[a] | 107[a] |
| Trichloroethene | | 137[b] |
| Trichloroethene | 1,100[c] | 87 - 150[c] |
| 1,1-Dichloroethene | 2,250[a] | 64.6[a] |
| 1,1-Dichloroethene | | 80.2[b] |
| 1,1-Dichloroethene | 2,500[d] | 150[d] |
| *cis*-1,2-Dichloroethene | | 80.2[b] |
| *cis*-1,2-Dichloroethene | 3,500[c] | 49[c] |
| *trans*-1,2-Dichloroethene | 6,300[a] | 58.9[a] |
| *trans*-1,2-Dichloroethene | | 80.2[b] |
| *trans*-1,2-Dichloroethene | 6,300[c] | 36[c] |
| Vinyl Chloride | 1,100[a] | 2.45[a] |
| Vinyl Chloride | 2,763[d] | 0.4 - 56[d] |
| 1,1,1-Trichloroethane | 1,495[c] | 183[c] |
| 1,1,2-Trichloroethane | 4,420[e] | 70[e] |
| 1,1-Dichloroethane | 5,060[d] | 40[d] |
| 1,2-Dichloroethane | 8,520[c] | 33 to 152[c] |
| Chloroethane | 5,710[e] | 33 to 143[e] |
| Hexachlorobenzene | 0.006[f] | -- |
| 1,2-Dichlorobenzene | 156[c] | 272 - 1480[c] |
| 1,3-Dichlorobenzene | 111[g] | 293 to 31,600[g] |
| 1,4-Dichlorobenzene | 74 to 87[d] | 273 to 1833[d] |
| Chlorobenzene | 472[d] | 83 to 389[d] |
| Carbon Tetrachloride | 805[g] | 110[g] |
| Chloroform | 7,950[c] | <34[c] |
| Methylene Chloride | 13,000[c] | 48[c] |
| | | |
| | | |

[a] From Knox *et al.*, 1993
[b] From Jeng *et al.*, 1992; Temperature = 20°C
[c] From Howard, 1990; Temperature = 25°C
[d] From Howard, 1989; Temperature = 25°C
[e] From Howard, 1989; Temperature = 20°C
[f] ATSDR, 1990; Temperature = 20°C
[g] From Howard, 1990; Temperature = 20°C

## Table B.2.2

Values of Aqueous Solubility and $K_{oc}$ for BTEX and Trimethylbenzene Isomers

| 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

B.2.3.4.2 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.2.3 contains data from a hypothetical batch test. These data are plotted (Figure B.2.11) 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).

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).

**Table B.2.3**
**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

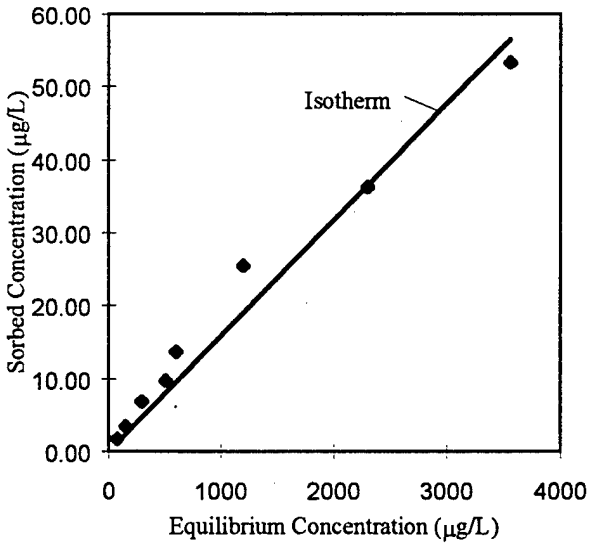



**Figure B.2.11** Plot of sorbed concentration vs. equilibrium concentration.

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.

### B.2.3.5 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:

$$R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} \qquad \text{eq. B.2.20}$$

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.

## B.2.4 VOLATILIZATION

While not a destructive attenuation mechanism, volatilization does remove contaminants from the groundwater system. In general, 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).

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):

$$C_a = HC_l \qquad \text{eq. B.2.21}$$

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 chlorinated and petroleum hydrocarbons range over several orders of magnitude. For petroleum hydrocarbons, Henry's Law constants (H) for the saturated aliphatics range from 1 to 10 atm $m^3$/mol @ 25°C, for the unsaturated and cyclo-aliphatics H range from 0.1 to 1 atm $m^3$/mol @ 25°C, and for the light aromatics (e.g., BTEX) H ranges from 0.007 to 0.02 atm $m^3$/mol @ 25°C (Lyman *et al.*, 1992). Values of Henry's Law constants for selected chlorinated solvents and the BTEX compounds are given in Table B.2.4. As indicated on the table, values of H for chlorinated compounds also vary over several orders of magnitude, although most are similar to those for BTEX compounds.

The physiochemical properties of chlorinated solvents and the BTEX compounds give them low Henry's Law constants, with the exception of vinyl chloride. Because of the small surface area of the groundwater flow system exposed to soil gas, volatilization of chlorinated solvents and 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. Moreover, Rivett (1995) observed that for plumes more than about 1 meter below the air-water interface, little, if any, solvent concentrations will be detectable in soil gas due to the downward groundwater velocity in the vicinity of the water table. This suggests that for portions of plumes more than 1 meter below the water table, very little, if any, mass will be lost due to volatilization. In addition, vapor transport across the capillary fringe can be very slow (McCarthy and Johnson, 1993), thus further limiting mass transfer rates. Because of this, the impact of volatilization on dissolved contaminant reduction can generally be neglected, except possibly in the case of vinyl chloride. However, Rivett's (1995) findings should be kept in mind even when considering volatilization as a mechanism for removal of vinyl chloride from groundwater.

**Table B.2.4**
Henry's Law Constants and Vapor Pressures for
Common Fuel Hydrocarbons and Chlorinated Solvents

| Compound | Vapor Pressure (mmHg @ 25°C) | Henry's Law Constant ($atm\text{-}m^3/mol$) |
|---|---|---|
| Benzene | 95 | 0.0054 |
| Ethylbenzene | 10 | 0.0066 |
| Toluene | 28.4 | 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 |
| Tetrachloroethene | 14 | 0.0153 |
| Trichloroethene | 57.8 | 0.0091 |
| 1,1-Dichloroethene | 591 | 0.018 |
| *cis*-1,2-Dichloroethene | 200 | 0.0037 |
| *trans*-1,2-Dichloroethene | 265 | 0.0072 |
| Vinyl Chloride | 2,580 | 1.22 |
| 1,1,1-Trichloroethane | 123.7 | 0.008 |
| 1,1,2-Trichloroethane | 30.3 | 0.0012 |
| 1,1-Dichloroethane | 227 | 0.0059 |
| 1,2-Dichloroethane | 78.7 | 0.00098 |
| Chloroethane | 766 | 0.0085 |
| Hexachlorobenzene | 0.0000109 | 0.00068 |
| 1,2-Dichlorobenzene | 1.47 | 0.0012 |
| 1,3-Dichlorobenzene | 2.3 | 0.0018 |
| 1,4-Dichlorobenzene | 1.76 | 0.0015 |
| Chlorobenzene | 11.9 | 0.0035 |
| Carbon Tetrachloride | 113.8 | 0.0304 |
| Chloroform | 246 | 0.00435 |
| Methylene Chloride | 434.9 | 0.00268 |

## B.2.5 RECHARGE

Groundwater recharge can be defined as the entry into the saturated zone of water made available at the water-table surface (Freeze and Cherry, 1979). In recharge areas, flow near the water table is generally downward. Recharge defined in this manner may therefore include not only precipitation that infiltrates through the vadose zone, but water entering the groundwater system due to discharge from surface water bodies (i.e., streams and lakes). Where a surface water body is in contact with or is part of the groundwater system, the definition of recharge above is stretched slightly. However, such bodies are often referred to as recharging lakes or

streams. Recharge of a water table aquifer has two effects on the natural attenuation of a dissolved contaminant plume. Additional water entering the system due to infiltration of precipitation or from surface water will contribute to dilution of the plume, and the influx of relatively fresh, electron-acceptor-charged water will alter geochemical processes and in some cases facilitate additional biodegradation.

Recharge from infiltrating precipitation is the result of a complex series of processes in the unsaturated zone. Description of these processes is beyond the scope of this discussion; however, it is worth noting that the infiltration of precipitation through the vadose zone brings the water into contact with the soil and thus may allow dissolution of additional electron acceptors and possibly organic soil matter (a potential source of electron donors). Infiltration therefore provides fluxes of water, inorganic species, and possibly organic species into the groundwater. Recharge from surface water bodies occurs when the hydraulic head of the body is greater than that of the adjacent groundwater. The surface water may be a connected part of the groundwater system, or it may be perched above the water table. In either case, the water entering the groundwater system will not only aid in dilution of a contaminant plume but it may also add electron acceptors and possibly electron donors to the groundwater.

An influx of electron acceptors will tend to increase the overall electron-accepting capacity within the contaminant plume. In addition to the inorganic electron acceptors that may be dissolved in the recharge (e.g., dissolved oxygen, nitrate, or sulfate), the introduction of water with different geochemical properties may foster geochemical changes in the aquifer. 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). Such a shift may be beneficial for biodegradation of compounds used as electron donors, such as fuel hydrocarbons or vinyl chloride. However, these shifts can also make conditions less favorable for reductive dehalogenation.

Evaluating the effects of recharge is typically difficult. The effects of dilution might be estimated if one has a detailed water budget for the system in question, but if a plume has a significant vertical extent, it cannot be known with any certainty what proportion of the plume mass is being diluted by the recharge. Moreover, because dispersivity, sorption, and biodegradation are often not well-quantified, separating out the effects of dilution may be very difficult indeed. Where recharge enters from precipitation, the effects of the addition of electron

acceptors may be qualitatively apparent due to elevated electron acceptor concentrations or differing patterns in electron acceptor consumption or byproduct formation in the area of the recharge. However, the effects of short-term variations in such a system (which are likely due to the intermittent nature of precipitation events in most climates) may not be easily understood. Where recharge enters from surface water, the influx of mass and electron acceptors is more steady over time. Quantifying the effects of dilution may be less uncertain, and the effects of electron acceptor replenishment may be more easily identified (though not necessarily quantified).

# SECTION B-3

# DESTRUCTIVE ATTENUATION MECHANISMS - BIOLOGICAL

Many anthropogenic organic compounds, including certain chlorinated solvents, can be degraded by both biological and abiotic mechanisms. Biological degradation mechanisms are discussed in this section; abiotic degradation mechanisms are discussed in Section B.4. Table B.3.1 summarizes the various biotic and abiotic mechanisms that result in the degradation of anthropogenic organic compounds. Biological degradation mechanisms tend to dominate in most groundwater systems, depending on the type of contaminant and the groundwater chemistry.

**Table B.3.1**
**Biologic and Abiotic Degradation Mechanisms for Various Anthropogenic Organic Compounds**

| Compound | Degradation Mechanism |
|---|---|
| PCE | Reductive dechlorination |
| TCE | Reductive dechlorination, cometabolism |
| DCE | Reductive dechlorination, direct biological oxidation |
| Vinyl Chloride | Reductive dechlorination, direct biological oxidation |
| TCA | Reductive dechlorination, hydrolysis, dehydrohalogenation |
| 1,2-DCA | Reductive dechlorination, direct biological oxidation |
| Chloroethane | Hydrolysis |
| Carbon Tetrachloride | Reductive dechlorination, cometabolism, abiotic |
| Chloroform | Reductive dechlorination, cometabolism |
| Methylene Chloride | Direct biological oxidation |
| Chlorobenzenes | Direct biological oxidation, reductive dechlorination, cometabolism |
| Benzene | Direct biological oxidation |
| Toluene | Direct biological oxidation |
| Ethylbenzene | Direct biological oxidation |
| Xylenes | Direct biological oxidation |
| 1,2-Dibromoethane | Reductive dehalogenation, hydrolysis, direct biological oxidation, and photolysis |

Many organic contaminants are biodegraded by microorganisms indigenous to the subsurface environment. During biodegradation, dissolved contaminants are ultimately transformed into

innocuous byproducts such as carbon dioxide, chloride, methane, and water. In some cases, intermediate products of these transformations may be more hazardous than the original compound; however, they may also be more easily degraded. Biodegradation of organic compounds dissolved in groundwater results in a reduction in contaminant concentration (and mass) and slowing of the contaminant front relative to the average advective groundwater flow velocity. Figures B.3.1 and B.3.2 illustrate the effects of biodegradation on an advancing solute front.

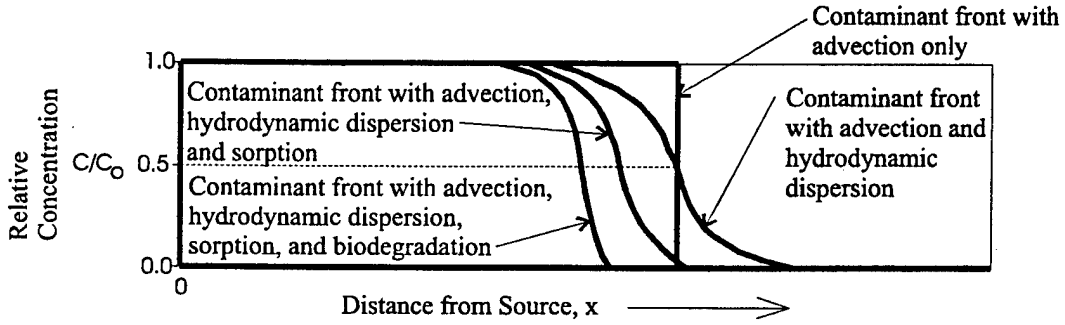



**Figure B.3.1** Breakthrough Curve in One Dimension Showing Plug Flow with Continuous Source Resulting from Advection Only; the Combined Processes of Advection and Hydrodynamic Dispersion; the Combined Processes of Advection, Hydrodynamic Dispersion, and Sorption; and the Combined Processes of Advection, Hydrodynamic Dispersion, Sorption, and Biodegradation

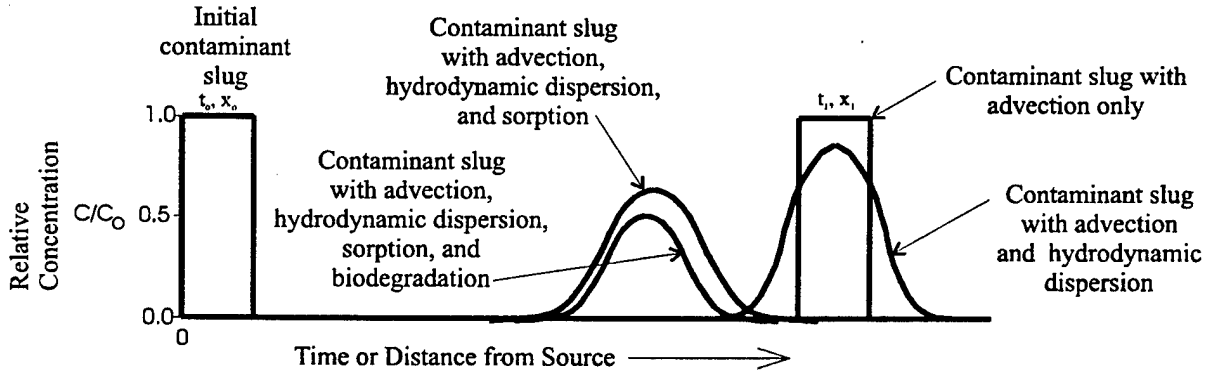



**Figure B.3.2** Breakthrough Curve in One Dimension Showing Plug Flow with Instantaneous Source Resulting from Advection Only; the Combined Processes of Advection and Hydrodynamic Dispersion; the Combined Processes of Advection, Hydrodynamic Dispersion, and Sorption; and the Combined Processes of Advection, Hydrodynamic Dispersion, Sorption, and Biodegradation

## B.3.1 OVERVIEW OF BIODEGRADATION

As recently as 1975 the scientific literature reported the subsurface/aquifer environment as devoid of significant biological activity. It is now known that soils and shallow sediments contain a large variety of microorganisms, ranging from simple prokaryotic bacteria and cyanobacteria to more complex eukaryotic algae, fungi, and protozoa. Over the past two decades, numerous laboratory and field studies have shown that microorganisms indigenous to the subsurface environment can degrade a variety of organic compounds, including components of gasoline, kerosene, diesel, jet fuel, chlorinated ethenes, chlorinated ethanes, the chlorobenzenes, and many other compounds (e.g., for fuels see 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; and Lovley *et al.*, 1995; and for chlorinated solvents see Brunner and Leisinger, 1978; Brunner *et al.*, 1980; Rittman and McCarty, 1980; Bouwer *et al.*, 1981; Miller and Guengerich, 1982; Roberts *et al.*, 1982; Bouwer and McCarty, 1983; Stucki *et al.*, 1983; Reineke and Knackmuss, 1984; Wilson and Wilson, 1985; Fogel *et al.*, 1986; Egli *et al.*, 1987; Vogel and McCarty, 1987; Vogel *et al.*, 1987; Bouwer and Wright, 1988; Little *et al.*, 1988; Freedman and Gossett, 1989; Sewell and Gibson, 1991; Chapelle, 1993; DeBruin *et al.*, 1992; Ramanand *et al.*, 1993; Vogel, 1994; Suflita and Townsend, 1995; Adriaens and Vogel, 1995; Bradley and Chapelle, 1996; Gossett and Zinder, 1996; Spain, 1996). Table B.3.2 presents a partial list of microorganisms known to degrade anthropogenic organic compounds.

Although we now recognize the ubiquitous nature and significance of subsurface microorganisms, the study of the microbial ecology and physiology of the subsurface, below the rhizosphere, is still in its infancy. However, great progress has been made at least in identifying, if not fully understanding, the numerous and diverse types of microbially-mediated contaminant transformations that can occur in the subsurface.

Chemothrophic organisms, such as humans and most microorganisms, obtain energy for growth and activity from physiologically coupling oxidation and reduction reactions and harvesting the chemical energy that is available. Under aerobic conditions (in the presence of molecular oxygen) humans and many bacteria couple the oxidation of organic compounds (food) to the reduction of oxygen (from the air). However in the absence of oxygen (anaerobic

**Table B.3.2**

Some Microorganisms Capable of Degrading Organic Compounds
(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 sp., P. putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, P. aeruginosa, 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 |
| Chlorinated Ethenes | *Dehalobacter restrictus, Dehalospirillum multivorans, Enterobacter agglomerans, Dehalococcus entheogenes* strain 195,*Desulfitobacterium sp.* strain PCE1, *Pseudomonas putida* (multiple strains), *P. cepacia* G4, *P. mendocina, Desulfobacterium sp., Methanobacterium sp., Methanosarcina sp.* strain DCM, *Alcaligenes eutrophus* JMP 134, *Methylosinus trichosporium OB3b, Escherichia coli, Nitorsomonas europaea, Methylocystis parvus* OBBP, *Mycobacterium sp., Rhodococcus erythopolis* | Moderate |
| Chlorinated Ethanes | *Desulfobacterium sp., Methanobacterium sp., Pseudomonas putida, Clostridium sp., C. sp.* strain TCAIIB, | Moderate |
| Chlorinated Methanes | *Acetobacterium woodii, Desulfobacterium sp., Methanobacterium sp., Pseudomonas sp.* strain KC, *Escherichia coli* K-12, *Clostridium sp., Methanosarcina sp., Hyphomicrobium sp.* strain DM2, | Moderate |
| Chlorobenzenes | *Alcaligenes sp.* (multiple strains), *Pseudomonas sp.*(multiple strains), *P. putida, Staphylococcus epidermis* | Moderate to high |

conditions), microorganisms may use other compounds as electron acceptors. Anaerobic microorganisms can obtain energy from a variety of electron donors such as natural organic carbon or many forms of anthropogenic carbon and electron acceptors such as nitrate, iron (III), sulfate, carbon dioxide, as well as many of the chlorinated solvents.

The introduction of oxidizable soluble organic contaminants into ground water initiates a series of complex responses by subsurface microorganisms. Field and laboratory research suggests that distinct, communities defined by the dominant electron acceptor develop which are spatially and

temporally separate. These communities are most likely ecologically defined by the flux of biologically available electron donors and acceptors. The biological processes of these communities are potentially useful as natural attenuation mechanisms, as the basis of new bioremediation technologies, and as indicators of the extent and severity of the release

As electron acceptors and nutrients are depleted by microbial activity during biodegradation of contaminants, the redox potential of contaminated aquifers decreases. This results in a succession of bacterial types adapted to specific redox regimes and electron acceptors. Metabolic byproducts of contaminant biodegradation also exert selective forces, either by presenting different carbon sources or by further modifying the physical and chemical environment of the aquifer. Like organic and inorganic colloids, microorganisms possess complex surface chemistry, and can themselves serve as mobile and immobile reactive sites for contaminants.

Under anaerobic conditions most organic compounds are degraded by groups of interacting microorganisms referred to as a consortium. In the consortium, individual types of organisms carry out different specialized reactions which, when combined, can lead to the complete mineralization of a particular compound. The metabolic interaction between organisms can be complex and may be so tightly linked under a given set of conditions that stable consortia can be mistakenly identified as a single species. There seems to be several advantages to the consortial system, including: 1) This system allows for the creation of microenvironments where certain types of organisms can survive in otherwise hostile conditions; 2) Reactions that are thermodynamically unfavorable can be driven by favorable reactions when they are metabolically linked within the consortium; and, 3) This system takes advantage of the diverse metabolic capabilities of microorganisms by allowing for the formation and enrichment of associations that can utilize an introduced substrate faster than a single species could evolve a novel complex enzyme pathway to degrade the same compound.

It appears that subsurface microbial communities contain the metabolic diversity required to utilize a wide variety of organic contaminants as a primary growth substrate in the presence of electron acceptors such as oxygen. Some pollutants, especially the highly oxidized chlorinated hydrocarbons, are not amenable to use as a primary growth substrate. Instead, these compounds are used as electron acceptors in reactions that rely on another source of carbon as a primary substrate or are degraded fortuitously via cometabolism. Thus, biodegradation of organic compounds in groundwater occurs via three mechanisms:

- Use of the organic compound as the primary growth substrate;
- Use of the organic compound as an electron acceptor; and

- Cometabolism.

The first two biodegradation mechanisms involve the microbial transfer of electrons from electron donors (primary growth substrate) to electron acceptors. This process can occur under aerobic or anaerobic conditions. Electron donors include natural organic material, fuel hydrocarbons, chlorobenzenes, and the less oxidized chlorinated ethenes and ethanes. Electron acceptors are elements or compounds that occur in relatively oxidized states. The most common naturally occurring electron acceptors in groundwater include dissolved oxygen, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide. In addition, the more oxidized chlorinated solvents such as PCE, TCE, DCE, TCA, DCA, and polychlorinated benzenes can act as electron acceptors under favorable conditions. Under aerobic conditions, dissolved oxygen is used as the terminal electron acceptor during aerobic respiration. Under anaerobic conditions, the electron acceptors listed above are used during denitrification, manganese (IV) reduction, iron (III) reduction, sulfate reduction, methanogenesis, or reductive dechlorination. Chapelle (1993) and Atlas (1988) discuss terminal electron accepting processes in detail.

The third biodegradation mechanism is cometabolism. During cometabolism the compound being degraded does not benefit the organism. Instead, degradation is brought about by a fortuitous reaction wherein an enzyme produced during an unrelated reaction degrades the organic compound.

As discussed in sections B.3.2, B.3.3, and B.3.4, biodegradation causes measurable changes in groundwater chemistry. Table B.3.3 summarizes these trends. 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 $N_2$ via denitrification or dissimilatory nitrate reduction, nitrate concentrations decrease. In anaerobic systems where iron (III) is the electron acceptor, it is reduced to iron (II) via iron (III) reduction, and iron (II) concentrations increase. In anaerobic systems where sulfate is the electron acceptor, it is reduced to $H_2S$ via sulfate reduction, and sulfate concentrations decrease. During aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction, total alkalinity will increase. In anaerobic systems where $CO_2$ is used as an electron acceptor, it is reduced by methanogenic bacteria during methanogenesis; and $CH_4$ is produced. In anaerobic systems where contaminants are being used as electron acceptors they are reduced to less chlorinated daughter products; in such a system, parent compound concentrations will decrease and daughter product concentrations will increase at first and then decrease as the daughter product is used as an electron acceptor or is oxidized.

**Table B.3.3**

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

| Analyte | Terminal Electron Accepting Process | Trend in Analyte Concentration During Biodegradation |
|---|---|---|
| Fuel Hydrocarbons | Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Methanogenesis | Decreases |
| Highly Chlorinated Solvents and Daughter Products | Reductive Dechlorination | Parent Compound Concentration Decreases, Daughter Products Increase Initially and Then May Decrease |
| Lightly Chlorinated Solvents | Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction (Direct Oxidation) | Compound Concentration Decreases |
| Dissolved Oxygen | Aerobic Respiration | Decreases |
| Nitrate | Denitrification | Decreases |
| Manganese (II) | Manganese (IV) Reduction | Increases |
| Iron (II) | Iron (III) Reduction | Increases |
| Sulfate | Sulfate Reduction | Decreases |
| Methane | Methanogenesis | Increases |
| Chloride | Reductive Dechlorination or Direct Oxidation of Chlorinated Compound | Increases |
| ORP | Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Methanogenesis | Decreases |
| Alkalinity | Aerobic Respiration, Denitrification, Iron (III) Reduction, and Sulfate Reduction | Increases |

As each subsequent electron acceptor is utilized, the groundwater becomes more reducing and the redox potential of the water decreases. Figure B.3.3 shows the typical ORP conditions for groundwater when different electron acceptors are used. The main force driving this change in ORP is microbially mediated oxidation-reduction reactions. ORP can be used as a crude indicator of which oxidation-reduction reactions may be operating at a site. The ORP determined in the field using an electrode 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.

## B.3.2 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS A PRIMARY GROWTH SUBSTRATE

Many organic compounds including natural organic carbon, fuel hydrocarbons, and the less oxidized chlorinated compounds such as DCE, 1,2-DCA, chlorobenzene, or vinyl chloride can be used as primary growth substrates (electron donor) for microbial metabolism. The following sections describe biodegradation of organic compounds through use as a primary substrate under both aerobic and anaerobic conditions.

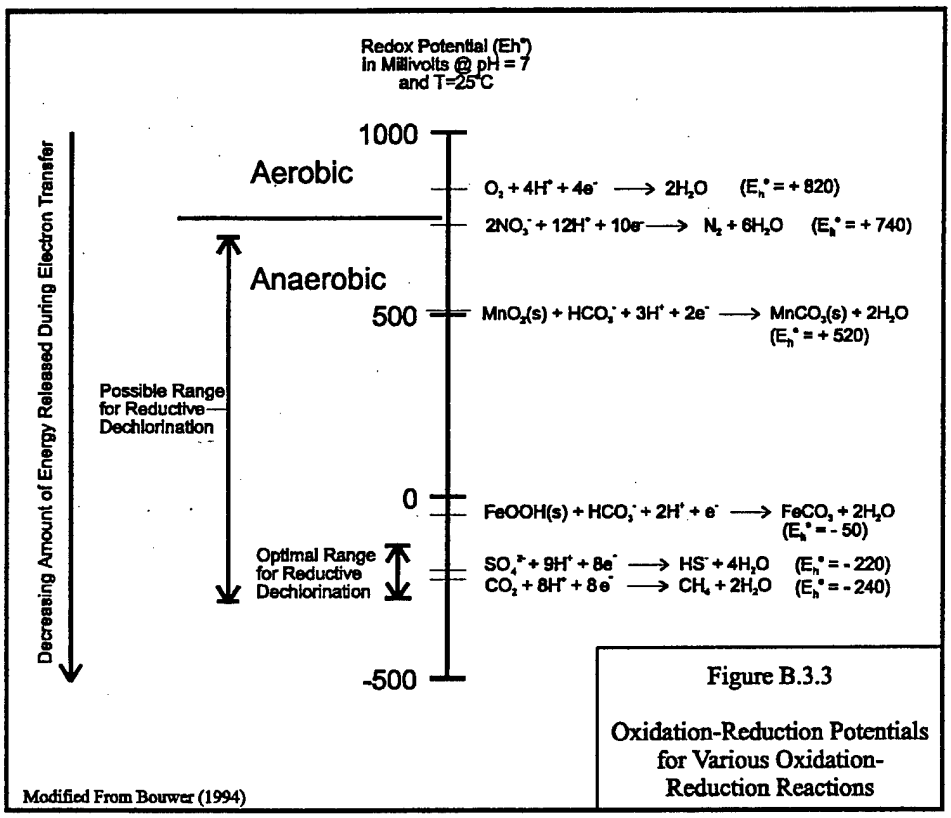



Figure B.3.3

Oxidation-Reduction Potentials for Various Oxidation-Reduction Reactions

### B.3.2.1 Aerobic Biodegradation of Primary Substrates

Biodegradation of organic compounds is often an aerobic process that occurs when indigenous populations of microorganisms are supplied with the oxygen and nutrients necessary to utilize organic carbon as an energy source. The biodegradation of fuel hydrocarbons occurs rapidly under aerobic conditions and is discussed in Wiedemeier *et al.* (1995). Some pollutants, especially the highly oxidized chlorinated hydrocarbons (i.e., those containing more chlorine substituents), are biologically recalcitrant under aerobic conditions. However, some of the less chlorinated ethenes and ethanes such as DCE, VC, and 1,2-DCA, and many of the chlorinated benzenes can be utilized as primary substrates and oxidized under aerobic conditions. During aerobic biodegradation (oxidation) of chlorinated solvents, the facilitating microorganism obtains energy and organic carbon from the degraded solvent.

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic biodegradation, and PCE the least. Of the chlorinated ethanes, 1,2-DCA is the most susceptible to aerobic biodegradation (chloroethane is more likely to abiotically hydrolyze to ethanol), while TCA, tetrachloroethane, and hexachloroethane are less so. Chlorinated benzenes with up to 4 chlorine atoms (i.e., chlorobenzene, dichlorobenzene, trichlorobenzene, and tetrachlorobenzene) also have

been shown to be readily biodegradable under aerobic conditions (Spain, 1996). Pentachlorobenzene and hexachlorobenzene are unlikely to be oxidized by microbial activity.

B.3.2.1.1 Aerobic Oxidation of Petroleum Hydrocarbons

Fuel hydrocarbons are rapidly biodegraded when they are utilized as the primary electron donor for microbial metabolism under aerobic conditions. Biodegradation of fuel hydrocarbons occurs naturally when sufficient oxygen (or other electron acceptors) and nutrients are available in the groundwater. The rate of natural biodegradation is generally limited by the lack of oxygen or other electron acceptors rather than by the lack of nutrients such as nitrogen or phosphorus. The rate of natural aerobic biodegradation in unsaturated soil and shallow aquifers is largely dependent upon the rate at which oxygen enters the contaminated media. Biodegradation of fuel hydrocarbons is discussed by Wiedemeier *et al.* (1995).

B.3.2.1.2 Aerobic Oxidation of Chlorinated Ethenes

In general, the highly chlorinated ethenes (e.g., PCE and TCE) are not likely to serve as electron donors or substrates for microbial degradation reactions. This is because the highly chlorinated compounds tend to be much more oxidized than many compounds present in a natural groundwater system.. Several microbes or microbial enrichments have been shown to be capable of TCE oxidation (Fogel *et al.*, 1986; Nelson et al., 1986; Little et al., 1988); however, as noted by Vogel (1994), no strong evidence for the oxidation of highly chlorinated solvents has been derived from actual hazardous waste sites.

Using microcosms from two different sites with no prior history of exposure to DCE, Klier *et al.* (1996) show that all three isomers of DCE (i.e., 1,1-DCE, I-1,2-DCE, and *trans*-1,2-DCE) can be biodegraded in aerobic systems. In these experiments, it was observed that *cis*-1,2-DCE degraded more rapidly than the other isomers. Hartmans et al. (1985) and Hartmans and de Bont (1992) show that vinyl chloride can be used as a primary substrate under aerobic conditions, with vinyl chloride apparently being directly mineralized to carbon dioxide and water. This has also been reported by Davis and Carpenter (1990). Aerobic biodegradation is rapid relative to other mechanisms of vinyl chloride degradation, especially reductive dehalogenation.

B.3.2.1.3 Aerobic Oxidation of Chlorinated Ethanes

Of the chlorinated ethanes, only 1,2-dichloroethane has been shown to be aerobically mineralized/oxidized. Stucki *et al.* (1983) and Janssen *et al.* (1985) show that 1,2-DCA can be used as a primary substrate under aerobic conditions. In this case, the bacteria transform 1,2-DCA to chloroethanol, which is then mineralized to carbon dioxide. Evidence of oxidation of chloroethane is scant, however, it appears to rapidly degrade via abiotic mechanisms (hydrolysis) and is thus less likely to undergo biodegradation.

B.3.2.1.4 Aerobic Oxidation of Chlorobenzenes

Chlorobenzene and polychlorinated benzenes (up to and including tetrachlorobenzene) have been shown to be biodegradable under aerobic conditions. Several studies have shown that bacteria are able to utilize chlorobenzene (Reineke and Knackmuss, 1984), 1,4-DCB (Reineke and Knackmuss, 1984; Schraa *et al.*, 1986; Spain and Nishino, 1987), 1,3-DCB (de Bont *et al.*, 1986), 1,2-DCB (Haigler *et al.*, 1988), 1,2,4-TCB (van der Meer *et al.*, 1987; Sander *et al.*, 1991), and 1,2,4,5-TeCB (Sander *et al.*, 1991) as primary growth substrates in aerobic systems. Nishino *et al.* (1994) note that aerobic bacteria able to grow on chlorobenzene have been detected at a variety of chlorobenzene-contaminated sites, but not at uncontaminated sites. Spain (1996) notes that this provides strong evidence that the bacteria are selected for their ability to derive carbon and energy from chlorobenzene degradation *in situ*.

The pathways for all of these reactions are similar, and are also similar to that of benzene (Chapelle, 1993; Spain, 1996). In general, the aerobic biodegradation involves hydroxylation of the chlorinated benzene to a chlorocatechol, followed by *ortho* cleavage of the benzene ring. This produces a muconic acid, which is dechlorinated, and the non-chlorinated intermediates are then metabolized. The only significant difference between this process and aerobic benzene degradation is the elimination of chlorine at some point in the pathway (Chapelle, 1993).

**B.3.2.2 Anaerobic Biodegradation of Primary Substrates**

Rapid depletion of dissolved oxygen caused by microbial respiration results in the establishment of anaerobic conditions in areas with high organic carbon concentrations. Certain requirements must be met in order for anaerobic (anoxic) bacteria to degrade organic compounds, including: absence of dissolved oxygen; availability of carbon sources (natural or anthropogenic), electron acceptors, and essential nutrients; and proper ranges of pH, temperature, salinity, and redox potential. When oxygen is absent, nitrate, manganese (IV), iron (III), sulfate, and carbon

dioxide can serve as terminal electron acceptors during oxidation of organic carbon. While there is a large body of evidence for anaerobic mineralization (oxidation) of fuel hydrocarbons, there is very little evidence of such transformations involving chlorinated compounds.

#### B.3.2.2.1 Anaerobic Oxidation of Petroleum Hydrocarbons

Biodegradation of fuel hydrocarbons will occur under anaerobic conditions in most, if not all, groundwater environments via denitrification, manganese (IV) reduction, iron (III) reduction, sulfate reduction, and methanogenesis. Biodegradation of fuel hydrocarbons is discussed by Wiedemeier *et al.* (1995), and many primary references are cited therein..

#### B.3.2.2.2 Anaerobic Oxidation of Chlorinated Ethenes

In general, due to the oxidized nature of polychlorinated ethenes, they are unlikely to undergo oxidation in groundwater systems. However, Bradley and Chapelle (1996) show that vinyl chloride (with only one chlorine substituent) can be directly oxidized to carbon dioxide and water via iron (III) reduction. Reduction of vinyl chloride concentrations in microcosms amended with iron (III)-EDTA closely matched the production of carbon dioxide. Slight mineralization was also noted in unamended microcosms. The rate of this reaction apparently depends on the bioavailability of the iron (III). At this time, it is not known if other workers have demonstrated other anaerobic mineralization reactions involving chlorinated ethenes.

#### B.3.2.2.3 Anaerobic Oxidation of Chlorinated Ethanes

During preparation of this protocol, no evidence of anaerobic oxidation of chlorinated ethanes was found; this does not necessarily indicate that such reactions have not been described. However, the lack of discussion of such transformations in surveys of chlorinated hydrocarbon biodegradation (e.g., Vogel et al., 1987; Semprini and McCarty, 1994; Vogel, 1994, Adriaens and Vogel, 1995; Spain, 1996) suggests that there has indeed been little, if any, work on this subject.

#### B.3.2.2.4 Anaerobic Oxidation of Chlorobenzenes

While aerobic mineralization of chlorobenzenes is similar to that of benzene, similar activity under anaerobic conditions has not been documented. As discussed above, there is little, if any, discussion of this topic in the literature.

## B.3.3 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS AN ELECTRON ACCEPTOR (REDUCTIVE DECHLORINATION)

Bouwer *et al.* (1981) were the first to show that halogenated aliphatic hydrocarbons could be biologically transformed under anaerobic conditions in the subsurface environment. Since that time, numerous investigators have shown that chlorinated compounds can degrade via reductive dechlorination under anaerobic conditions. Anaerobically, biodegradation of chlorinated solvents most often proceeds through a process called reductive dechlorination. During this process, the halogenated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a halogen atom is removed and replaced with a hydrogen atom. As an example, *Dehalobacter restrictus* was shown by Holliger (1992) to use tetrachloroethene as an electron acceptor during reductive dechlorination to produce *cis-1,2*-dichloroethene. Because chlorinated compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth in order for reductive dehalogenation to occur (Baek and Jaffe, 1989; Freedman and Gossett, 1989; Fathepure and Boyd, 1988; Bouwer, 1994). Potential carbon sources can include low molecular weight organic compounds (lactate, acetate, methanol, glucose, etc.), fuel hydrocarbons, byproducts of fuel degradation (e.g., volatile fatty acids), or naturally occurring organic matter.

In some situations, reductive dechlorination may be a cometabolic process, in that the reaction is incidental to normal metabolic functions and the organisms derive no benefit from the reaction. Such cometabolism typically results in slow, incomplete dechlorination (Gantzer and Wackett, 1991; Gossett and Zinder, 1996). More important, recent studies are discovering direct dechlorinators (typically isolated from contaminated subsurface environments or treatment systems) that use chlorinated ethenes as electron acceptors in reactions that provide growth and energy (e.g., Holliger *et al.*, 1992; Holliger *et al.*, 1993; Holliger and Schumacher, 1994; Neumann *et al.*, 1994; Krumholz, 1995; Maymo-Gatell *et al.*, 1995; Sharma and McCarty, 1996; Gerritse *et al.*, 1996). This process has been termed both *halorespiration* and *dehalorespiration*.

Biotic transformations of chlorinated solvents under anaerobic conditions generally are reductions that involve either hydrogenolysis or dihaloelimination (McCarty and Semprini, 1994). Hydrogenolysis occurs when a chlorine atom is replaced with hydrogen. Dihaloelimination occurs when two adjacent chlorine atoms are removed and a double bond is formed between the respective carbon atoms. The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination (hydrogenolysis).

Higher ratios of chlorine to carbon represent higher oxidation levels; highly chlorinated compounds are more oxidized than lesser chlorinated compounds and thus are less susceptible to oxidation. Thus, highly chlorinated compounds such as PCE, TCE, TCA, or HCB are more likely to undergo reductive reactions than oxidative reactions. During these reductive reactions, electrons are transferred to the chlorinated compound, and a chlorine atom is replaced with a hydrogen atom. As an example, consider the reductive dechlorination of PCE to TCE and then TCE to DCE, and finally DCE to vinyl chloride. Because of the relatively low oxidation state of VC, this compound more commonly undergoes aerobic biodegradation as a primary substrate than reductive dechlorination.

Reductive dechlorination processes result in the formation of intermediates which are more reduced than the parent compound. These intermediates are often more susceptible to oxidative bacterial metabolism than to further reductive anaerobic processes. Actual mechanisms of reductive dehalogenation are still unclear, and in some cases may be a form of cometabolism (Gantzer and Wackett, 1991; Adriaens and Vogel, 1995; Wackett, 1995). In addition, other factors that will influence the process include the type of electron donor and the presence of competing electron acceptors (Adriaens and Vogel, 1995; Suflita and Townsend, 1995), temperature, and substrate availability.

Recent evidence suggests that dechlorination is dependent upon the supply of hydrogen ($H_2$), which acts as the electron donor in many such reactions (Gossett and Zinder, 1996; Smatlak *et al.*, 1996). The hydrogen is produced as a result of the microbial degradation of a primary substrate (e.g., lactate, acetate, butyrate, ethanol, BTEX, or other such compounds). Bacteria that facilitate dechlorination compete with sulfate-reducers and methanogens for the $H_2$ produced in such a system. When degradation of the original substrate/electron donor rapidly yields high concentrations of $H_2$, the sulfate-reducers and methanogens appear to be favored over the dechlorinators. Conversely, when substrate degradation produces a steady supply of $H_2$ at low concentrations, the dechlorinators are favored (Gossett and Zinder, 1996; Smatlak *et al.*, 1996). Complete dechlorination is thus apparently favored when a steady, low-concentration supply of $H_2$ is produced through microbial degradation of substrates such as proprionate or benzoate (and, by extension from benzoate, the BTEX compounds) (Gossett and Zinder, 1996). Therefore, the type of substrate/electron donor can also play a role in how thoroughly a natural system is able to dechlorinate solvents.

One or more of the following generally is observed at a site where reductive dechlorination of alkenes is ongoing:

1) Ethene is being produced (even low concentrations are indicative of biodegradation);
2) Methane is being produced;
3) Iron II is being produced;
4) Hydrogen concentrations are between 1-4 nM; and
5) Dissolved oxygen concentrations are low.

### B.3.3.1 Reductive Dechlorination of Chlorinated Ethenes

PCE and TCE have been shown to undergo reductive dechlorination in a variety of anaerobic systems from different environments, with various electron donors/carbon sources (Table B.3.4) (Wilson, 1988; Sewell et al., 1991; Roberts et al, 1982). This is particularly true if the subsurface also contains other anthropogenic or native organic compounds that can serve as electron donors and whose utilization by subsurface bacteria will deplete any available oxygen. In general, reductive dechlorination of chlorinated ethenes occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. With sufficient quantities or appropriate types of electron donors (e.g., slow but steady $H_2$-production), the final end-product of anaerobic reductive dehalogenation can be ethene (Freedman and Gossett, 1989). Reductive dehalogenation of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in chloride.

Studies have shown that PCE and TCE can be anaerobically reduced to either 1,1-DCE, *cis*-1,2-DCE, or *trans*-1,2-DCE, all of which can be further transformed to vinyl chloride (Miller and Guengerich, 1982; Wilson and Wilson, 1985; Mayer *et al.*, 1988; Nelson, *et al.*, 1986; Henson *et al.*, 1989; Tsien *et al.*, 1989; Henry, 1991; McCarty, 1994; Wilson *et al.*, 1994). During reductive dehalogenation, all three isomers of DCE can theoretically be produced; however, Bouwer (1994) reports that *cis-1,2*-DCE is a more common intermediate than *trans-1,2*-DCE and that *1,1*-DCE is the least prevalent intermediate of the three DCE isomers. Vinyl chloride produced from dehalogenation of DCE may be subsequently reduced to innocuous products such as ethane or carbon dioxide. The removal of vinyl chloride occurs more readily under aerobic conditions, such as those encountered at the edge of the plume. Vinyl chloride may also be used as a primary substrate by aerobic organisms, as previously discussed.

**Table B.3.4**

**Sources, Donors, Acceptors, and Products of Reductive Dechlorinating Laboratory Systems**

| Reference | Source | Donor | Acceptor-Product |
|---|---|---|---|
| Bouwer & McCarty,1983 | Digester | Organic Material | PCE-TCE |
| Vogel & McCarty, 1985 | Bioreactor | Acetate | PCE-VC, $CO_2$ |
| Kleopfer *et al.*, 1985 | Soil | Soybean Meal | TCE-DCE |
| Barrio-Lage *et al.*, 1987 | Swamp Muck<br>Soil | Organic Material<br>Methanol (?) | PCE-VC<br>PCE-VC |
| Fathepure *et al.*, 1987 | Methanosarcina<br>DCB-1 | Methanol<br>3CB[a],Pyruvate,RF[b] | PCE-TCE<br>PCE-TCE |
| Baek & Jaffe, 1989 | Digester | Formate<br>Methanol | TCE-VC,CA[c]<br>TCE-VC,CA |
| Freedman & Gossett, 1989 | Digester | Methanol<br>Glucose<br>H2<br>Formate<br>Acetate | PCE-VC, Ethene<br>PCE-VC, Ethene<br>PCE-VC, Ethene<br>PCE-VC, Ethene<br>PCE-VC, Ethene |
| Scholz-Muramatsu *et al.*, 1990 | Bioreactor | Benzoate | PCE-DCE |
| Gibson & Sewell, 1990 | Aquifer | VFA[d] | PCE-DCE |
| Sewell & Gibson, 1990 | Aquifer | Toluene | PCE-DCE |
| Sewell *et al.*, 1991 | Aquifer<br>Landfill | VFA<br>VFA | PCE-DCE<br>PCE-VC |
| Lyon *et al.*, 1995 | Aquifer | Native Organic Matter | PCE-DCE |

a 3 Chlorobenzoate
b Rumen Fluid
c Chloroethane
d Volatile Fatty Acid

### B.3.3.2 Reductive Dechlorination of Chlorinated Ethanes

As with the ethenes, chlorinated ethanes will also undergo reductive dehalogenation in the subsurface via use as electron acceptors. Dechlorination of TCA has been described by Vogel and McCarty (1987) and Cox *et al.* (1995), but this pathway is complicated by the abiotic reactions that can affect TCA and its byproducts (Vogel, 1994).

### B.3.3.3 Reductive Dechlorination of Chlorobenzenes

For the highly chlorinated benzenes (e.g., hexachlorobenzene and pentachlorobenzene, as well as tetrachlorobenzene, and trichlorobenzene), reductive dechlorination is the most likely biodegradation mechanism (Holliger *et al.*, 1992; Ramanand *et al.*, 1993; Suflita and Townsend, 1995). As discussed by Suflita and Townsend (1995), reductive dehalogenation of aromatic compounds has been observed in a variety of anaerobic habitats, including aquifer materials, marine and freshwater sediments, sewage sludges, and soil samples; however, isolation of specific microbes capable of these reactions has been difficult. As with the chlorinated ethenes and ethanes, the chlorobenzenes are most likely acting as electron acceptors as other sources of carbon and energy are being utilized by microbes or microbial consortia (Suflita and Townsend, 1995). Evidence has been presented suggesting that oxidation of hydrogen using halogenated aromatics as electron acceptors may yield more energy than if more commonly available electron acceptors were used (Dolfing and Harrison, 1992).

As discussed previously, the actual mechanisms of reductive dehalogenation are not well understood. Further, reductive dehalogenation of chlorinated benzenes has not been as well-documented as for other chlorinated solvents. However, reductive dechlorination of chlorobenzenes has been documented more frequently in the past several years (e.g., Bosma *et al.*, 1988; Fathepure *et al.*, 1988; Fathepure and Vogel, 1991; Holliger *et al.*, 1992; Ramanand *et al.*, 1993). As with other chlorinated solvents, the reductive dehalogenation of chlorobenzenes is affected by the degree of chlorination of the compound. The more chlorinated aromatic compounds are typically more amenable to this reaction (Suflita and Townsend, 1995; Adriaens and Vogel, 1995), but as they are dechlorinated, the daughter products will become more resistant to further dehalogenation reactions (Fathepure *et al.*, 1988; Bosma *et al.*, 01988; Holliger *et al.*, 1992). The reductive dechlorination of chlorobenzenes is analogous to reactions involving chlorinated ethenes and ethanes in that such degradation will make them more amenable to aerobic biodegradation (Schraa, *et al.*, 1986; Spain and Nishino, 1987; Ramanand *et al.*, 1993)

## B.3.4 BIODEGRADATION OF ORGANIC COMPOUNDS VIA COMETABOLISM

When a chlorinated solvent is biodegraded through cometabolism, it serves as neither an electron acceptor nor a primary substrate in a biologically mediated redox reaction. Instead, the degradation of the compound is catalyzed by an enzyme cofactor that is fortuitously produced by organisms for other purposes. The best-documented cometabolism reactions involve catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrate (BTEX or other organic compounds). These oxygenases are typically nonspecific and

therefore fortuitously initiate oxidation of a variety of compounds, including many of the CAHs (McCarty and Semprini, 1994). The organism receives no known benefit from the degradation of the chlorinated solvent; in some cases the cometabolic degradation of the solvent may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). Chlorinated solvents are usually only partially transformed during cometabolic processes, with additional biotic or abiotic degradation generally required to complete the transformation (McCarty and Semprini, 1994).

Cometabolism is best documented for CAHs in aerobic environments; evidence of cometabolism of chlorobenzenes is scant, as is clear evidence of anaerobic cometabolism. In an aerobic environment many chlorinated organic compounds can only be degraded via cometabolism. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994; Adriaens and Vogel, 1995). Vogel (1994) further elaborates that the oxidation rate increases as the degree of chlorination decreases. Aerobic cometabolism of ethenes may be characterized by a loss of contaminant mass, the presence of intermediate degradation products (e.g., chlorinated oxides, aldehydes, ethanols, and epoxides), and the presence of other products such as chloride, carbon dioxide, carbon monoxide, and a variety of organic acids (Miller and Guengerich, 1982; McCarty and Semprini, 1994).

The lack of clear evidence for anaerobic cometabolism does not necessarily imply that such transformations do not occur; in some cases, reductive dechlorination may be a result of cometabolism (e.g., Gantzer and Wackett, 1991), depending upon the relationship between the microbes, substrates, contaminants, and other electron acceptors. However, as with aerobic cometabolism, anaerobic cometabolism will be slow relative to dehalorespiration and might not be distinguishable at the field scale (Gossett and Zinder, 1996).

Several groups of aerobic bacteria currently recognized as being capable of transforming TCE and other CAHs via cometabolism; these groups include:

- Methane Oxidizers (Methanotrophs) (Fogel *et al.*, 1986; Little *et al.*, 1989, Mayer *et al.*, 1988; Oldenhuis *et al.*, 1989; Tsien *et al.*, 1989; Henry and Grbic-Galic, 1990; Alvarez-Cohen and McCarty, 1991a,b; Henry and Grbic-Galic, 1991a,b; Lanzarone and McCarty, 1990; Oldenhuis *et al.*, 1991);
- Propane Oxidizers (Wackett *et al.*, 1989);
- Ethene Oxidizers (Henry, 1991);
- Toluene, Phenol, or Cresol Oxidizers (Nelson *et al.*, 1986, 1987, 1988; Wackett and Gibson, 1988; Folsom *et al.*, 1990; Harker and Kim, 1990);

- Ammonia Oxidizers (Arciero *et al.*, 1989; Vannelli *et al.*, 1990);
- Isoprene Oxidizers (Ewers *et al.*, 1991); and
- Vinyl Chloride Oxidizers (Hartmans and de Bont, 1992).

These bacteria all have catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrates and have the potential for initiating the oxidation of CAHs.

Cometabolism is not nearly as important a degradation mechanism for chlorinated solvents in the saturated zone as reductive dehalogenation. Due to the need for a substrate that may be present in limited concentrations, as well as the fortuitous nature of the reactions, rates of cometabolism are often slow enough that this process may not be detectable unless the system is stimulated with additional substrate mass. For a discussion of this topic, see McCarty and Semprini (1994) or Wackett (1995).

## B.3.5 THERMODYNAMIC CONSIDERATIONS

Electron transfer results in oxidation of the electron donor and reduction of the electron acceptor and the production of usable energy. The energy produced by these reactions is quantified by the Gibb's free energy of the reaction ($\Delta G_r$) which is given by:

$$\Delta G^{o}_{r} = \sum \Delta G^{o}_{f,\ products} - \sum \Delta G^{o}_{f,\ reactants} \qquad \text{eq. B.3.1}$$

Where: $\Delta G_r$ = Gibb's Free Energy of the Reaction at Standard State
$\Delta G_{f,\ products}$ = Gibb's Free Energy of Formation for Products at Standard State
$\Delta G_{f,\ reactants}$ = Gibb's Free Energy of Formation for the Reactants at Standard State

The $\Delta G_r$ defines the maximum useful energy change for a chemical reaction at a constant temperature and pressure. Table B.3.5 presents select electron acceptor and electron donor half-cell reactions and the calculated $\Delta G_r$ values. Table B.3.6 gives the Gibbs free energy of formation ($\Delta G_f$) for species used in these half-cell reactions. Table B.3.7 presents coupled oxidation-reduction reactions. In general, those reactions that yield the most energy tend to take precedence over less energy-yielding reaction. However, the calculated energy yield of processes involving anthropogenic organic compounds may not be reflected in the true energy yield of the metabolic process. Figure B.3.4 illustrates the expected sequence of microbially mediated redox reactions based on $\Delta G_r$. There is sufficient energy in the reaction of fuel hydrocarbons with chlorinated solvents to allow their use by microorganisms as physiological electron acceptors.

# Table B.3.5

## Electron Donor and Electron Acceptor Half Cell Reactions

| HALF-CELL REACTIONS | $\Delta G°_r$ (kcal/equiv)* | $\Delta G°_r$ (kJ/equiv)* | E° (V) | Eh (V) | pe | Conditions for Eh and pe § |
|---|---|---|---|---|---|---|
| ELECTRON-ACCEPTOR (REDUCTION) HALF CELL REACTIONS | | | | | | |
| $5e^- + 6H^+ + NO_3^- \Rightarrow 0.5N_2 + 3H_2O$<br>*Denitrification* | -28.7 | -120. | +1.24 | +0.708 | +12.0 | pH = 7<br>$\Sigma[N]=10^{-3}$ |
| $4e^- + 4H^+ + O_2 \Rightarrow 2H_2O$<br>*Aerobic Respiration* | -28.3 | -119. | +1.23 | +0.805 | +13.6 | pH = 7<br>$P_{O_2}$=0.21 atm |
| $2e^- + 4H^+ + \underline{MnO_2} \Rightarrow Mn^{2+} + 2H_2O$<br>*Pyrolusite Dissolution/Reduction* | -28.3 | -119 | +1.23 | +0.550 | +9.27 | pH = 7<br>$\Sigma[Mn]=10^{-5}$ |
| $CO_2 + e^- + H^+ + \underline{MnOOH} \Rightarrow MnCO_3 + H_2O$<br>*a Manganite Carbonation/Reduction* | -23.1 | -96.8 | +1.00 | +0.408 | +6.90 | pH = 8<br>$P_{CO_2}=10^{-2}$ |
| $e^- + H^+ + MnO_2 \Rightarrow \underline{MnOOH}$<br>*Pyrolusite Hydrolysis/Reduction* | -22.1 | -92.5 | +0.959 | +0.545 | +9.21 | pH = 7 |
| $e^- + 3H^+ + \underline{Fe(OH)_{3,amph.}} \Rightarrow Fe^{2+} + 2H_2O$<br>*Amorphous "Goethite" Dissolution/Reduction* | -21.5 | -89.9 | +0.932 | +0.163 | +2.75 | pH = 6<br>$\Sigma[Fe]=10^{-5}$ |
| $8e^- + 10H^+ + NO_3^- \Rightarrow NH_4^+ + 3H_2O$<br>*Nitrate Reduction* | -20.3 | -84.9 | +0.879 | +0.362 | +6.12 | pH = 7 |
| $2e^- + 2H^+ + NO_3^- \Rightarrow NO_2^- + H_2O$<br>*Nitrate Reduction* | -18.9 | -78.9 | +0.819 | +0.404 | +6.82 | pH = 7 |
| $e^- + 3H^+ + \underline{FeOOH} \Rightarrow Fe^{2+} + 2H_2O$<br>*"Ferric oxyhydroxide" Dissolution/Reduction* | -15.0 | -62.9 | +0.652 | -0.118 | -1.99 | pH = 6<br>$\Sigma$ [Fe]=$10^{-5}$ |
| $e^- + 3H^+ + \underline{Fe(OH)_{3,xline.}} \Rightarrow Fe^{2+} + 3H_2O$<br>*Crystallized "Goethite" Dissolution/Reduction* | -11.8 | -49.2 | +0.510 | -0.259 | -4.38 | pH = 6<br>$\Sigma$ [Fe]=$10^{-5}$ |
| $e^- + H^+ + CO_{2,g} + \underline{Fe(OH)_{3,amph.}} \Rightarrow \underline{FeCO_3} + 2H_2O$<br>*Amorphous "Goethite" Carbonation/Reduction* | -11.0 | -46.2 | +0.479 | -0.113 | -1.90 | pH = 8<br>$P_{CO_2}=10^{-2}$ atm |
| $8e^- + 9H^+ + SO^{2-}_4 \Rightarrow HS^- + 4H_2O$<br>*Sulfate Reduction* | -5.74 | -24.0 | +0.249 | -0.278 | -4.70 | pH = 8 |
| $8e^- + 10H^+ + SO^{2-}_4 \Rightarrow H_2S^o + 4H_2O$<br>*Sulfate Reduction* | -6.93 | -28.9 | +0.301 | -0.143 | -2.42 | pH = 6 |
| $8e^- + 8H^+ + CO_{2,g} \Rightarrow CH_{4,g} + 2H_2O$<br>*Methanogenesis* | -3.91 | -16.4 | +0.169 | -0.259 | -4.39 | pH = 7<br>$P_{CO_2}=10^{-2}$<br>$P_{CH_4}=10^{0}$ |
| $C_2Cl_4 + H^+ + 2e^- \Rightarrow C_2HCl_3 + Cl^-$<br>*PCE Reductive Dechlorination* | -14.79 | -61.9 | +0.642 | +0.553 | +9.35 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2HCl_3 + H^+ + 2e^- \Rightarrow C_2H_2Cl_2 + Cl^-$<br>*TCE Reductive Dechlorination* | -14.50 | -60.7 | +0.629 | +0.540 | +9.13 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_2Cl_2 + H^+ + 2e^- \Rightarrow C_2H_3Cl + Cl^-$<br>*c-DCE Reductive Dechlorination* | -12.12 | -50.7 | +0.526 | +0.437 | +7.39 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_3Cl + H^+ + 2e^- \Rightarrow C_2H_4 + Cl^-$<br>*VC Reductive Dechlorination* | -13.73 | -57.4 | +0.595 | +0.506 | +8.55 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_3Cl_4 + H^+ + 2e^- \Rightarrow C_2H_3Cl_3 + Cl^-$<br>*PCA Reductive Dechlorination* | -13.64 | -57.0 | +0.591 | +0.502 | +8.49 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_3Cl_3 + H^+ + 2e^- \Rightarrow C_2H_4Cl_2 + Cl^-$<br>*TCA Reductive Dechlorination* | -18.26 | -76.3 | +0.791 | +0.702 | +11.9 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_4Cl_2 + H^+ + 2e^- \Rightarrow C_2H_5Cl + Cl^-$<br>*DCA Reductive Dechlorination* | -17.34 | -72.5 | +0.751 | +0.662 | +11.2 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_6Cl_6 + H^+ + 2e^- \Rightarrow C_2HCl_5 + Cl^-$<br>*Hexachlorobenzene Reductive Dechlorination* | -13.91 | -58.1 | +0.602 | +0.513 | +8.67 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2HCl_5 + H^+ + 2e^- \Rightarrow C_2H_2Cl_4 + Cl^-$<br>*Pentachlorobenzene Reductive Dechlorination* | -11.53 | -48.2 | +0.500 | +0.411 | +6.95 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_2Cl_4 + H^+ + 2e^- \Rightarrow C_2H_3Cl_3 + Cl^-$<br>*Tetrachlorobenzene Reductive Dechlorination* | -8.45 | -35.3 | +0.366 | +0.277 | +4.68 | pH = 7<br>$[Cl^-]=10^{-4}$ |
| $C_2H_3Cl_3 + H^+ + 2e^- \Rightarrow C_2H_4Cl_2 + Cl^-$<br>*Trichlorobenzene Reductive Dechlorination* | -3.94 | -16.5 | +0.171 | +0.082 | +1.39 | pH = 7<br>$[Cl^-]=10^{-4}$ |

| HALF-CELL REACTIONS | $\Delta G^\circ_r$ (kcal/ equiv)* | $\Delta G^\circ_r$ (kJ/ equiv)* | $E^\circ$ (V) | Eh (V) | pe | Conditions for Eh and pe § |
|---|---|---|---|---|---|---|
| ELECTRON-DONOR (OXIDATION) HALF CELL REACTIONS | | | | | | |
| $12H_2O + C_6H_6 \Rightarrow 6CO_2 + 30H^+ + 30e^-$ *Benzene Oxidation* | +2.83 | +11.8 | -0.122 | +0.316 | +5.34 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $14H_2O + C_6H_5CH_3 \Rightarrow 7CO_2 + 36H^+ + 36e^-$ *Toluene Oxidation* | +2.96 | +12.4 | -0.128 | +0.309 | +5.22 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $16H_2O + C_6H_5C_2H_5 \Rightarrow 8CO_2 + 42H^+ + 42e^-$ *Ethylbenzene Oxidation* | +2.96 | +12.4 | -0.128 | +0.309 | +5.21 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $20H_2O + C_{10}H_8 \Rightarrow 10CO_2 + 48H^+ + 48e^-$ *Naphthalene Oxidation* | +2.98 | +12.5 | -0.130[a] | +0.309 | +5.22 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $18H_2O + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48H^+ + 48e^-$ *1,3,5-Trimethylbenzene Oxidation* | +3.07 | +12.8 | -0.133[a] | +0.303 | +5.12 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $18H_2O + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48H^+ + 48e^-$ *1,2,4-Trimethylbenzene Oxidation* | +3.07 | +12.9 | -0.134[a] | +0.302 | +5.11 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $4H_2O + C_2H_3Cl \Rightarrow 2CO_2 + 11H^+ + 10e^- + Cl^-$ *Vinyl Chloride Oxidation* | -0.55 | -2.30 | +0.024[a] | -0.455 | -7.69 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $12H_2O + C_6H_2Cl_4 \Rightarrow 6CO_2 + 26H^+ + 25e^- + 4Cl^-$ *Tetrachlorobenzene Oxidation* | -0.66 | -2.74 | +0.028 | -0.431 | -7.28 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $12H_2O + C_6H_3Cl_3 \Rightarrow 6CO_2 + 27H^+ + 26e^- + 3Cl^-$ *Trichlorobenzene Oxidation* | +0.42 | +1.77 | -0.018 | -0.475 | -8.02 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $12H_2O + C_6H_4Cl_2 \Rightarrow 6CO_2 + 28H^+ + 27e^- + 2Cl^-$ *Dichlorobenzene Oxidation* | +1.39 | +5.81 | -0.060 | -0.516 | -8.72 | pH = 7 $P_{CO_2}=10^{-2}$ |
| $12H_2O + C_6H_5Cl \Rightarrow 6CO_2 + 29H^+ + 28e^- + Cl^-$ *Chlorobenzene Oxidation* | +2.21 | +9.26 | -0.096[a] | +0.358 | +6.05 | pH = 7 $P_{CO_2}=10^{-2}$ |

NOTES:

* = $\Delta G^\circ_r$ 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.

[a] = $E^\circ$ calculated using the following equation; $E^\circ = \Delta G^\circ_r$ (J/nF) * $1.0365 \times 10^{-5}$ (VF/J) from Stumm and Morgan, 1981

**Table B.3.6**

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

| Species | State | $\Delta G^{\circ}_{f298.15}$ (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) |
| $CH_2O$, formaldehyde | 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) |
| $C_2Cl_4$, PCE | l | +1.1 | CRC Handbook (1990) |
| $C_2HCl_3$, TCE | l | +2.9 | CRC Handbook (1990) |
| $C_2H_2Cl_2$ 1,1-dichloroethene | l | +5.85 | Dean (1972) |
| $C_2H_2Cl_2$ cis-1,2-dichloroethene | l | 5.27 | CRC Handbook (1990) |
| $C_2H_2Cl_2$ trans-1,2-dichloroethene | l | +6.52 | CRC Handbook (1990) |
| $C_2H_4$ Ethene | g<br>aq, m=1 | +16.28<br>+19.43 | CRC Handbook (1990) |
| $C_2H_6$ Ethane | g<br>aq, m=1 | -7.68<br>-4.09 | CRC Handbook (1990) |
| HCl hydrochloric acid | aq, m=1 | -31.372 | CRC Handbook (1990)a |
| $C_2H_2Cl_4$, 1,1,2,2-PCA | l | -22.73 | Dean (1972) |
| $C_2H_3Cl_3$, 1,1,2-TCA | g | -18.54 | Dean (1972) |
| $C_2H_4Cl_2$, 1,2-DCA | g | -17.68 | Dean (1972) |
| $C_2H_5Cl_1$, Chloroethane | g | -14.47 | Dean (1972) |
| $C_{10}H_8$, naphthalene | l | +48.05 | Dean (1972) |
| $C_6H_3(CH_3)_3$, 1,3,5-TMB | l | +24.83 | Dean (1972) |
| $C_6H_3(CH_3)_3$, 1,2,4-TMB | l | +24.46 | Dean (1972) |
| $C_2H_3Cl$, Vinyl chloride | g | +12.4 | Dean (1972) |
| $C_6Cl_6$, Hexachlorobenzene | l | +0.502 | Dolfing (1992) |
| $C_6H_1Cl_5$, Pentachlorobenzene | l | +3.16 | Dolfing (1992) |
| $C_6H_2Cl_4$, 1,2,4,5-Tetrachlorobenzene | l | +5.26 | Dolfing (1992) |
| $C_6H_3Cl_3$, 1,2,4-Trichlorobenzene | l | +9.31 | Dolfing (1992) |
| $C_6H_4Cl_2$, 1,4-Dichlorobenzene | l | +14.28 | Dolfing (1992) |
| $C_6H_5Cl$, chlorobenzene | l | +21.32 | Dean (1972) |
| $C_{14}H_{10}$, phenanthrene | l | +64.12 | Dean (1972) |

## Table B.3.6 - Con't

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

| Species | State | $\Delta G^{\circ}_{f298.15}$ (kcal/mole) | Source |
|---|---|---|---|
| **Nitrogen Species** | | | |
| $NO_3^-$ | I | -26.61 | Dean (1972) |
| $N_2$ | g | 0 | std |
| $NO_2^-$ | I | -7.7 | Dean (1972) |
| $NH_4^+$ | aq | -18.97 | 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, ferric 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) |
| **Chloride Species** | | | |
| $Cl^-$ | aq | -31.37 | Dean (1972) |

NOTES:

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

# Table B.3.7

## Coupled Oxidation-Reduction Reactions

| Coupled Benzene Oxidation Reactions | $\Delta G^{\circ}_r$ (kcal/ mole) | $\Delta G^{\circ}_r$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $7.5O_2 + C_6H_6 \Rightarrow 6CO_{2,g} + 3H_2O$<br>*Benzene oxidation /aerobic respiration* | -765.34 | -3202 | 3.07:1 | 0.326:1 |
| $6NO_3 + 6H^+ + C_6H_6 \Rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g}$<br>*Benzene oxidation / denitrification* | -775.75 | -3245 | 4.77:1 | 0.210:1 |
| $30H^+ + 15\underline{MnO_2} + C_6H_6 \Rightarrow 6CO_{2,g} + 15Mn^{2+} + 18H_2O$<br>*Benzene oxidation / manganese reduction* | -765.45 | -3202 | 10.56:1 | 0.095:1 |
| $3.75\ NO_3^- + C_6H_6 + 7.5\ H^+ + 0.75\ H_2O \Rightarrow 6\ CO_2 + 3.75\ NH_4^+$<br>*Benzene oxidation / nitrate reduction* | -524.1 | -2193 | 2.98:1 | 0.336:1 |
| $60H^+ + 30\underline{Fe(OH)_{3,a}} + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$<br>*Benzene oxidation / iron reduction* | -560.10 | -2343 | 21.5:1 | 0.047:1 |
| $7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6CO_{2,g} + 3.75H_2S^{\circ} + 3H_2O$<br>*Benzene oxidation / sulfate reduction* | -122.93 | -514.3 | 4.61:1 | 0.217:1 |
| $4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2,g} + 3.75CH_4$<br>*Benzene oxidation / methanogenesis* | -32.40 | -135.6 | 0.77:1 | 1.30:1 |
| $15\ C_2H_2Cl_4 + C_6H_6 + 12\ H_2O\ 6\ CO_2 + 15\ C_2H_3Cl_3 + 15\ H^+ + 15\ Cl^-$<br>*Benzene oxidation / PCA reduction* | -374.56 | -1570 | 31.9:1 | 0.03:1 |
| $15\ C_2H_3Cl_3 + C_6H_6 + 12\ H_2O\ 6\ CO_2 + 15\ C_2H_4Cl_2 + 15\ H^+ + 15\ Cl^-$<br>*Benzene oxidation / TCA reduction* | -377.86 | -1580 | 25.4:1 | 0.04:1 |
| $15\ C_2H_4Cl_2 + C_6H_6 + 12\ H_2O\ 6\ CO_2 + 15\ C_2H_5Cl + 15\ H^+ + 15\ Cl^-$<br>*Benzene oxidation / DCA reduction* | -337.96 | -1410 | 18.8:1 | 0.05:1 |
| $15C_2Cl_4 + 12H_2O + C_6H_6 \Rightarrow 15C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$<br>*Benzene oxidation/ Tetrachloroethylene reductive dehalogenation* | -358.59 | -1500 | 31.8:1 | 0.03:1 |
| $15C_2HCl_3 + 12H_2O + C_6H_6 \Rightarrow 15C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$<br>*Benzene oxidation/ Trichloroethylene reductive dehalogenation* | -350.04 | -1465 | 25.2:1 | 0.04:1 |
| $15C_2H_2Cl_2 + 12H_2O + C_6H_6 \Rightarrow 15C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$<br>*Benzene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -278.64 | -1166 | 18.6:1 | 0.05:1 |
| $15C_2H_3Cl + 12H_2O + C_6H_6 \Rightarrow 15C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$<br>*Benzene oxidation/ Vinyl chloride reductive dehalogenation* | -327.37 | -1370 | 11.9:1 | 0.08:1 |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled Toluene Oxidation Reactions | $\Delta G^{\circ}_r$ (kcal/ mole) | $\Delta G^{\circ}_r$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $9O_2 + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 4H_2O$<br>*Toluene oxidation /aerobic respiration* | -913.76 | -3823 | 3.13:1 | 0.32:1 |
| $7.2NO_3^- + 7.2H^+ + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 7.6H_2O + 3.6N_{2,g}$<br>*Toluene oxidation / denitrification* | -926.31 | -3875 | 4.85:1 | 0.21:1 |
| $36H^+ + 18\underline{MnO_2} + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 18Mn^{2+} + 22H_2O$<br>*Toluene oxidation / manganese reduction* | -913.89 | -3824 | 10.74:1 | 0.09:1 |
| $72H^+ + 36\underline{Fe(OH)_{3,a}} + C_6H_5CH_3 \Rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$<br>*Toluene oxidation / iron reduction* | -667.21 | -2792 | 21.86:1 | 0.05:1 |
| $9H^+ + 4.5SO_4^{2-} + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 4.5H_2S^o + 4H_2O$<br>*Toluene oxidation / sulfate reduction* | -142.86 | -597.7 | 4.7:1 | 0.21:1 |
| $5H_2O + C_6H_5CH_3 \Rightarrow 2.5CO_{2,g} + 4.5CH_4$<br>*Toluene oxidation / methanogenesis* | -34.08 | -142.6 | 0.78:1 | 1.28:1 |
| $18\ C_2H_2Cl_4 + C_6H_5CH_3 + 14\ H_2O\ 7\ CO_2 + 18\ C_2H_3Cl_3 + 18H^+ + 18Cl^-$<br>*Toluene oxidation / PCA reduction* | -1383 | -5781 | 32.5:1 | 0.03:1 |
| $18\ C_2H_3Cl_3 + C_6H_5CH_3 + 14\ H_2O\ 7\ CO_2 + 18\ C_2H_4Cl_2 + 18H^+ + 18Cl^-$<br>*Toluene oxidation / TCA reduction* | -1391 | -5814 | 25.8:1 | 0.04:1 |
| $18\ C_2H_4Cl_2 + C_6H_5CH_3 + 14\ H_2O\ 7\ CO_2 + 18\ C_2H_5Cl + 18\ H^+ + 18\ Cl^-$<br>*Toluene oxidation / DCA reduction* | -1343 | -5614 | 19.2:1 | 0.05:1 |
| $18C_2Cl_4 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2HCl_3 + 7CO_2 + 18H^+ + 18Cl^-$<br>*Toluene oxidation/ Tetrachloroethylene reductive dehalogenation* | -425.66 | -1781 | 32.4:1 | 0.03:1 |
| $18C_2HCl_3 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_2Cl_2 + 7CO_2 + 18H^+ + 18Cl^-$<br>*Toluene oxidation/ Trichloroethylene reductive dehalogenation* | -415.40 | -1738 | 25.7:1 | 0.04:1 |
| $18C_2H_2Cl_2 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_3Cl + 7CO_2 + 18H^+ + 18Cl^-$<br>*Toluene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -329.72 | -1380 | 18.9:1 | 0.05:1 |
| $18C_2H_3Cl + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_4 + 7CO_2 + 18H^+ + 18Cl^-$<br>*Toluene oxidation/ Vinyl chloride reductive dehalogenation* | -388.22 | -1624 | 12.1:1 | 0.08:1 |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled Ethylbenzene Oxidation reactions | $\Delta G°_r$ kcal/ mole | $\Delta G°_r$ kJ/ mole | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $10.5O_2 + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 5H_2O$<br>*Ethylbenzene oxidation /aerobic respiration* | -1066.13 | -4461 | 3.17:1 | |
| $8.4NO_3^- + 8.4H^+ + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 9.2H_2O + 4.2N_{2,g}$<br>*Ethylbenzene oxidation / denitrification* | -1080.76 | -4522 | 4.92:1 | |
| $46H^+ + 22\underline{MnO_2} + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 22Mn^{2+} + 28H_2O$<br>*Ethylbenzene oxidation / manganese reduction* | -1066.27 | -4461 | 11.39:1 | |
| $84H^+ + 42\underline{Fe(OH)_{3,a}} + C_6H_5C_2H_5 \Rightarrow 8CO_2 + 42Fe^{2+} + 110H_2O$<br>*Ethylbenzene oxidation / iron reduction* | -778.48 | -3257 | 22.0:1 | |
| $10.5H^+ + 5.25SO_4^{2-} + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 5.25H_2S^\circ + 5H_2O$<br>*Ethylbenzene oxidation / sulfate reduction* | -166.75 | -697.7 | 4.75:1 | |
| $5.5H_2O + C_6H_5C_2H_5 \Rightarrow 2.75CO_{2,g} + 5.25CH_4$<br>*Ethylbenzene oxidation / methanogenesis* | -39.83 | -166.7 | 0.79:1 | |
| $21C_2Cl_4 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2HCl_3 + 8CO_2 + 21H^+ + 21Cl^-$<br>*Ethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation* | -496.67 | -2078 | 32.8:1 | |
| $21C_2HCl_3 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_2Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$<br>*Ethylbenzene oxidation/ Trichloroethylene reductive dehalogenation* | -484.70 | -2028 | 26.0:1 | |
| $21C_2H_2Cl_2 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_3Cl + 8CO_2 + 21H^+ + 21Cl^-$<br>*Ethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -384.74 | -1610 | 19.2:1 | |
| $21C_2H_3Cl + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_4 + 8CO_2 + 21H^+ + 21Cl^-$<br>*Ethylbenzene oxidation/ Vinyl chloride reductive dehalogenation* | -452.99 | -1895 | 12.3:1 | |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled m-Xylene Oxidation Reactions | $\Delta G^{\circ}_r$ (kcal/ mole) | $\Delta G^{\circ}_r$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $10.5O_2 + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 5H_2O$<br>*m-Xylene oxidation /aerobic respiration* | -1063.25 | -4448 | 3.17:1 | |
| $8.4NO_3^- + 8.4H^+ + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 9.2H_2O + 4.2N_{2,g}$<br>*m-Xylene oxidation / denitrification* | -1077.81 | -4509 | 4.92:1 | |
| $46H^+ + 22\underline{MnO_2} + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 22Mn^{2+} + 28H_2O$<br>*m-Xylene oxidation / manganese reduction* | -1063.39 | -4449 | 11.39:1 | |
| $84H^+ + 42\underline{Fe(OH)_{3,s}} + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 42Fe^{2+} + 110H_2O$<br>*m-Xylene oxidation / iron reduction* | -775.61 | -3245 | 22:1 | |
| $10.5H^+ + 5.25SO_4^{2-} + C_6H_4(CH_3)_2 \Rightarrow 8CO_{2,g} + 5.25H_2S^{\circ} + 5H_2O$<br>*m-Xylene oxidation / sulfate reduction* | -163.87 | -685.6 | 4.75:1 | |
| $5.5H_2O + C_6H_4(CH_3)_2 \Rightarrow 2.75CO_{2,g} + 5.25CH_4$<br>*m-Xylene oxidation / methanogenesis* | -36.95 | -154.6 | 0.79:1 [a] | |
| $21C_2Cl_4 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2HCl_3 + 8CO_2 + 21H^+ + 21Cl^-$<br>*m-Xylene oxidation/ Tetrachloroethylene reductive dehalogenation* | -493.79 | -2066 | 32.8:1 | |
| $21C_2HCl_3 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_2Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$<br>*m-Xylene oxidation/ Trichloroethylene reductive dehalogenation* | -481.82 | -2016 | 26.0:1 | |
| $21C_2H_2Cl_2 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_3Cl + 8CO_2 + 21H^+ + 21Cl^-$<br>*m-Xylene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -381.86 | -1598 | 19.2:1 | |
| $21C_2H_3Cl + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_4 + 8CO_2 + 21H^+ + 21Cl^-$<br>*m-Xylene oxidation/ Vinyl chloride reductive dehalogenation* | -450.11 | -1883 | 12.3:1 | |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled Naphthalene Oxidation Reactions | $\Delta G^{\circ}_{r}$ (kcal/ mole) | $\Delta G^{\circ}_{r}$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $12O_2 + C_{10}H_8 \Rightarrow 10CO_2 + 4H_2O$<br>*Naphthalene oxidation /aerobic respiration* | -1217.40 | -5094 | 3.00:1 | |
| $9.6NO_3^- + 9.6H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 8.8H_2O + 4.8N_{2,g}$<br>*Naphthalene oxidation / denitrification* | -1234.04 | -5163 | 4.65:1 | |
| $24MnO_2 + 48H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 24Mn^{2+} + 28H_2O$<br>*Naphthalene oxidation / manganese reduction* | -1217.57 | -5094 | 16.31:1 | |
| $48Fe(OH)_{3,a} + 96H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 48Fe^{2+} + 124H_2O$<br>*Naphthalene oxidation / iron reduction* | -932.64 | -3902 | 40.13:1 | |
| $6SO_4^{2-} + 12H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 6H_2S^{\circ} + 4H_2O$<br>*Naphthalene oxidation / sulfate reduction* | -196.98 | -824.2 | 4.50:1 | |
| $8H_2O + C_{10}H_8 \Rightarrow 4CO_2 + 6CH_4$<br>*Naphthalene oxidation / methanogenesis* | -44.49 | -186.1 | 1.13:1 | |
| $24C_2Cl_4 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2HCl_3 + 10CO_2 + 24H^+ + 24Cl^-$<br>*Naphthalene oxidation/ Tetrachloroethylene reductive dehalogenation* | -566.59 | -2371 | 31.1:1 | |
| $24C_2HCl_3 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_2Cl_2 + 10CO_2 + 24H^+ + 24Cl^-$<br>*Naphthalene oxidation/ Trichloroethylene reductive dehalogenation* | -552.91 | -2313 | 24.6:1 | |
| $24C_2H_2Cl_2 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_3Cl + 10CO_2 + 24H^+ + 24Cl^-$<br>*Naphthalene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -438.67 | -1835 | 18.2:1 | |
| $24C_2H_3Cl + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_4 + 10CO_2 + 24H^+ + 24Cl^-$<br>*Naphthalene oxidation/ Vinyl chloride reductive dehalogenation* | -516.67 | -2162 | 11.6:1 | |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled 1,3,5-Trimethylbenzene Oxidation Reactions | $\Delta G^{\circ}_{r}$ (kcal/ mole) | $\Delta G^{\circ}_{r}$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $12O_2 + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O$<br>*1,3,5-Trimethylbenzene oxidation /aerobic respiration* | -1213.29 | -5076 | 3.20:1 | |
| $9.6NO_3^- + 9.6H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 10.8H_2O + 4.8N_{2,g}$<br>*1,3,5-Trimethylbenzene oxidation / denitrification* | -1229.93 | -5146 | 4.96:1 | |
| $24MnO_2 + 48H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 30H_2O + 24Mn^{2+}$<br>*1,3,5-Trimethylbenzene oxidation / manganese reduction* | -1213.46 | -5077 | 17.40:1 | |
| $48Fe(OH)_{3,a} + 96H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48Fe^{2+} + 126H_2O$<br>*1,3,5-Trimethylbenzene oxidation / iron reduction* | -928.53 | -3885 | 42.80:1 | |
| $6SO_4^{2-} + 12H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O + 6H_2S^{\circ}$<br>*1,3,5-Trimethylbenzene oxidation / sulfate reduction* | -192.87 | -807.0 | 4.80:1 | |
| $6H_2O + C_6H_3(CH_3)_3 \Rightarrow 3CO_2 + 6CH_4$<br>*1,3,5-Trimethylbenzene oxidation / methanogenesis* | -40.39 | -169.0 | 0.90:1 | |
| $24C_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2HCl_3 + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,3,5-Trimethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation* | -562.48 | -2353 | 33.2:1 | |
| $24C_2HCl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_2Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,3,5-Trimethylbenzene oxidation/ Trichloroethylene reductive dehalogenation* | -548.80 | -2296 | 26.3:1 | |
| $24C_2H_2Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,3,5-Trimethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -434.56 | -1818 | 19.4:1 | |
| $24C_2H_3Cl + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4 + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,3,5-Trimethylbenzene oxidation/ Vinyl chloride reductive dehalogenation* | -512.56 | -2145 | 12.4:1 | |

# Table B.3.7 - Con't

## Coupled Oxidation-Reduction Reactions

| Coupled 1,2,4-Trimethylbenzene Oxidation Reactions | $\Delta G^{\circ}_r$ (kcal/ mole) | $\Delta G^{\circ}_r$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $12O_2 + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O$<br>*1,2,4-Trimethylbenzene oxidation /aerobic respiration* | -1212.92 | -5075 | 3.20:1 | |
| $9.6NO_3^- + 9.6H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 10.8H_2O + 4.8N_{2,g}$<br>*1,2,4-Trimethylbenzene oxidation / denitrification* | -1229.56 | -5144 | 4.96:1 | |
| $24\underline{MnO_2} + 48H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 30H_2O + 24Mn^{2+}$<br>*1,2,4-Trimethylbenzene oxidation / manganese reduction* | -1213.09 | -5076 | 17.4:1 | |
| $48\underline{Fe(OH)}_{3,a} + 96H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48Fe^{2+} + 126H_2O$<br>*1,2,4-Trimethylbenzene oxidation / iron reduction* | -928.16 | -3883 | 42.8:1 | |
| $6SO_4^{2-} + 12H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O + 6H_2S^{\circ}$<br>*1,2,4-Trimethylbenzene oxidation / sulfate reduction* | -192.50 | -805.4 | 4.80:1 | |
| $6H_2O + C_6H_3(CH_3)_3 \Rightarrow 3CO_2 + 6CH_4$<br>*1,2,4-Trimethylbenzene oxidation / methanogenesis* | -40.02 | -167.4 | 0.90:1 | |
| $24C_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2HCl_3 + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,2,4-Trimethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation* | -562.11 | -2352 | 33.2:1 | |
| $24C_2HCl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_2Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,2,4-Trimethylbenzene oxidation/ Trichloroethylene reductive dehalogenation* | -548.43 | -2295 | 26.3:1 | |
| $24C_2H_2Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,2,4-Trimethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -434.19 | -1817 | 19.4:1 | |
| $24C_2H_3Cl + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4 + 9CO_2 + 24H^+ + 24Cl^-$<br>*1,2,4-Trimethylbenzene oxidation/ Vinyl chloride reductive dehalogenation* | -512.19 | -2143 | 12.4:1 | |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled Chlorobenzene Oxidation Reactions | $\Delta G^{\circ}_{r}$ (kcal/ mole) | $\Delta G^{\circ}_{r}$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $7O_2 + C_6H_5Cl \Rightarrow 6CO_2 + H^+ + 2H_2O + Cl^-$ *Chlorobenzene oxidation /aerobic respiration* | -731.62 | -3061 | 2.00:1 | |
| $5.6NO_3^- + 4.6H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 4.8H_2O + 2.8N_{2,g} + Cl^-$ *Chlorobenzene oxidation / denitrification* | -741.33 | -3102 | 3.10:1 | |
| $14\underline{MnO_2} + 27H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 16H_2O + 14Mn^{2+} + Cl^-$ *Chlorobenzene oxidation / manganese reduction* | -731.72 | -3062 | 10.9:1 | |
| $28\underline{Fe(OH)_{3,a}} + 55H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 72H_2O + 28Fe^{2+} + Cl^-$ *Chlorobenzene oxidation / iron reduction* | -565.51 | -2366 | 26.8:1 | |
| $3.5SO_4^{2-} + 6H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 2H_2O + 3.5H_2S^{\circ} + Cl^-$ *Chlorobenzene oxidation / sulfate reduction* | -136.38 | -570.6 | 3.00:1 | |
| $5H_2O + C_6H_5Cl \Rightarrow 2.5CO_2 + 3.5CH_4 + H^+ + Cl^-$ *Chlorobenzene oxidation / methanogenesis* | -47.43 | -198.4 | 0.80:1 | |
| $14C_2Cl_4 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Tetrachloroethylene reductive dehalogenation* | -351.99 | -1473 | 20.7:1 | |
| $14C_2HCl_3 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Trichloroethylene reductive dehalogenation* | -344.01 | -1439 | 16.4:1 | |
| $14C_2H_2Cl_2 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ cis-Dichloroethylene reductive dehalogenation* | -277.37 | -1161 | 12.1:1 | |
| $14C_2H_3Cl + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Vinyl chloride reductive dehalogenation* | -322.87 | -1351 | 7.75:1 | |

## Table B.3.7 - Con't

### Coupled Oxidation-Reduction Reactions

| Coupled Vinyl Chloride Oxidation Reactions | $\Delta G^{\circ}_{r}$ (kcal/ mole) | $\Delta G^{\circ}_{r}$ (kJ/ mole) | Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate | Mass of Primary Substrate Utilized per mass of Electron Acceptor Utilized or Metabolic Byproduct Produced |
|---|---|---|---|---|
| $2.5O_2 + C_2H_3Cl \Rightarrow 2CO_2 + H_2O + H^+ + Cl^-$ *Vinyl Chloride oxidation /aerobic respiration* | -288.98 | -1209 | 1.29:1 | |
| $2NO_3^- + H^+ C_2H_3Cl \Rightarrow 2CO_2 + 2H_2O + Cl^- + N_{2,g}$ *Vinyl Chloride oxidation / denitrification* | -292.44 | -1224 | 2.00:1 | |
| $5\underline{MnO_2} + 9H^+ + C_2H_3Cl \Rightarrow 2CO_2 + 6H_2O + 5Mn^{2+} + Cl^-$ *Vinyl Chloride oxidation / manganese reduction* | -289.01 | -1209 | 7.02:1 | |
| $10\underline{Fe(OH)_{3,a}} + 19H^+ + C_6H_3(CH_3)_3 \Rightarrow 2CO_2 + 10Fe^{2+} + 26H_2O + Cl^-$ *Vinyl Chloride oxidation / iron reduction* | -229.65 | -960.9 | 17.3:1 | |
| $1.25SO_4^{2-} + 1.5H^+ + C_2H_3Cl \Rightarrow 2CO_2 + H_2O + 1.25H_2S^{\circ} + Cl^-$ *Vinyl Chloride oxidation / sulfate reduction* | -76.40 | -319.7 | 1.94:1 | |
| $1.5H_2O + C_2H_3Cl \Rightarrow .75CO_2 + 1.25CH_4 + H^+ + Cl^-$ *Vinyl Chloride oxidation / methanogenesis* | -44.62 | -186.7 | 0.44:1 | |
| $5C_2Cl_4 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2HCl_3 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Tetrachloroethylene reductive dehalogenation* | -153.39 | -641.8 | 13.4:1 | |
| $5C_2HCl_3 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_2Cl_2 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Trichloroethylene reductive dehalogenation* | -150.54 | -629.9 | 10.6:1 | |
| $5C_2H_2Cl_2 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_3Cl + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ cis-Dichloroethylene reductive dehalogenation* | -126.74 | -530.3 | 7.82:1 | |

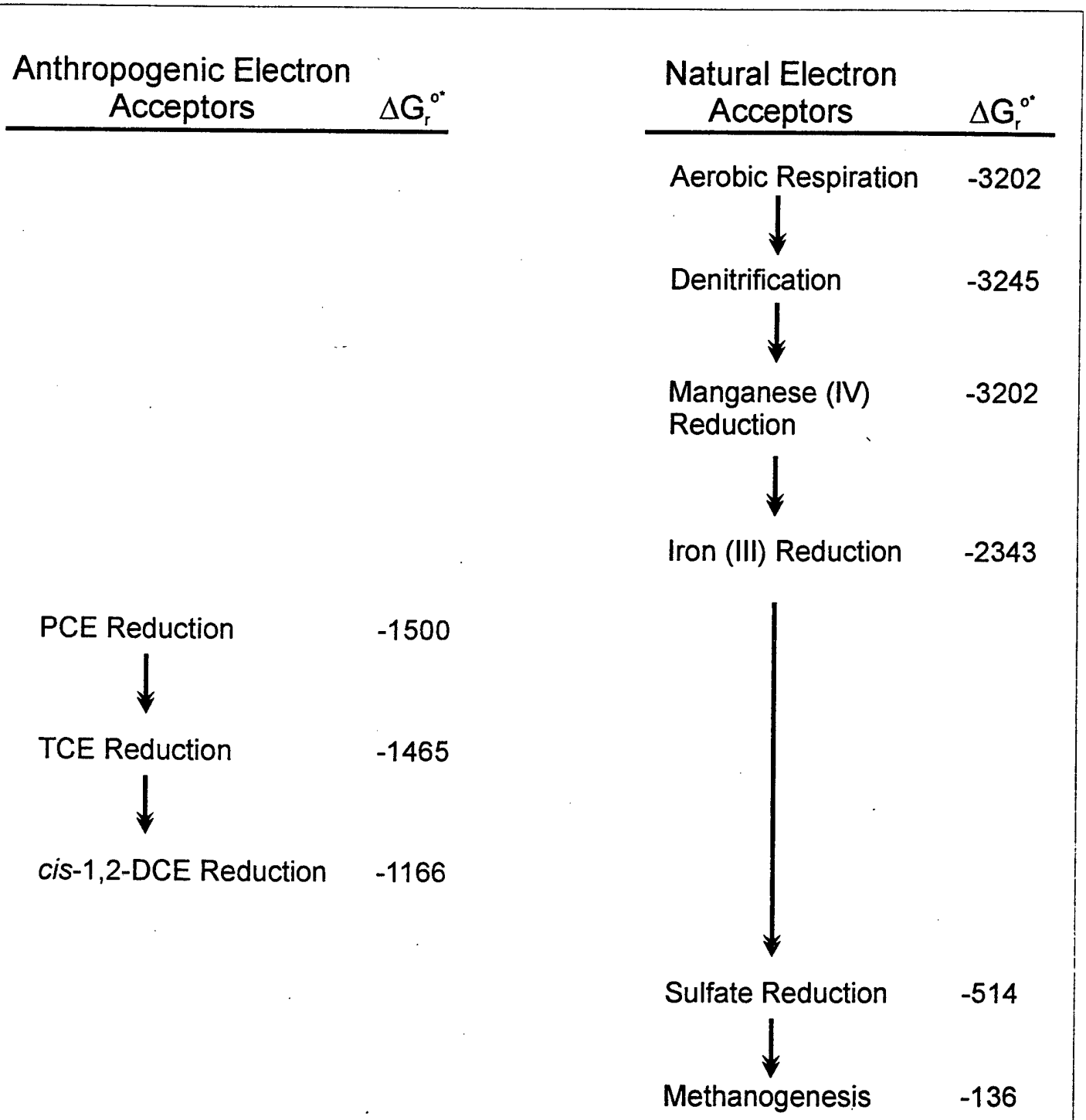



Figure B.3.4

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

d:\chlorinated_protocol\append-b\figures\B3-4.cdr

## B.3.6 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION WITH RETARDATION AND BIODEGRADATION

The advection-dispersion equation is obtained by adding a biodegradation term to equation B.2.20. In one dimension, this is expressed as:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.3.2}$$

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]
$\lambda$ = 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-4

# DESTRUCTIVE ATTENUATION MECHANISMS - ABIOTIC

Chlorinated solvents dissolved in groundwater may also be degraded by abiotic mechanisms, although the reactions are typically not complete and often result in the formation of an intermediate that may be at least as toxic as the original contaminant. The most common reactions affecting chlorinated compounds are hydrolysis (a substitution reaction) and dehydrohalogenation (an elimination reaction). Other possible reactions include oxidation and reduction reactions. Butler and Barker (1996) note that no abiotic oxidation reactions involving typical halogenated solvents have been reported in the literature. They also note that reduction reactions (which include hydrogenolysis and dihaloelimination) are commonly microbially mediated, although some abiotic reduction reactions have been observed.

As Butler and Barker (1996) note, attributing changes in either the presence or absence of halogenated solvents or the concentrations of halogenated solvents to abiotic processes is usually difficult. For example, microbial activity is generally required to produce reducing conditions that favor reductive dehalogenation. If such activity is taking place, chlorinated solvents may be undergoing both biotic and abiotic degradation, and discerning the relative contribution of each mechanism on the field scale, if possible, would be very difficult. As another example, Butler and Barker (1996) note that to substantiate that hydrolysis is occurring, the presence of non-halogenated breakdown products such as acids and alcohols should be established. In general, these products are more easily biodegraded that their parent compounds and can be difficult to detect. Field evidence of this nature has yet to be collected to demonstrate hydrolysis of halogenated solvents (Butler and Barker, 1996).

Given the difficulties of demonstrating abiotic degradation on the field scale, it may not be practical to demonstrate that such processes are occurring and to quantitatively evaluate the contributions of those reactions (i.e., separately from biotic processes). If biodegradation is occurring at a site, the loss of contaminant mass due to that process may dwarf the mass lost to abiotic reactions, ruling out a cost-effective evaluation of abiotic degradation. However, while the rates of abiotic degradation may be slow relative to biotic mechanisms, the contribution of these mechanisms may still play a significant role in natural attenuation, depending on site conditions (e.g., a site with a slow solute transport velocity or a long distance to the nearest

receptor). Vogel (1994) describes data patterns that may result from varying combinations of biotic and abiotic degradation of chlorinated solvents. Moreover, because some of the byproducts of these reactions are chlorinated compounds that may be more easily or less easily degraded than the parent, the contributions of abiotic mechanisms may need to be considered when evaluating analytical data from a site.

## B.4.1 HYDROLYSIS AND DEHYDROHALOGENATION

As discussed by Butler and Barker (1996), hydrolysis and dehydrohalogenation reactions are the most thoroughly studied abiotic attenuation mechanisms. In general, the rates of these reactions are often quite slow within the range of normal groundwater temperatures, with half-lives of days to centuries (Vogel *et al.*, 1987; Vogel, 1994). Therefore, most information about the rates of these reactions is extrapolated from experiments run at higher temperatures so that the experiments could be performed within a practical time frame.

### B.4.1.2 Hydrolysis

Hydrolysis is a substitution reaction in which an organic molecule reacts with water or a component ion of water, and a halogen substituent is replaced with a hydroxyl ($OH^-$) group. The hydroxyl substitution typically occurs at the halogenated carbon. This leads initially to the production of alcohols. If the alcohols are halogenated, additional hydrolysis to acids or diols may occur. Also, the addition of a hydroxyl group to a parent molecule may make the daughter product more susceptible to biodegradation, as well as more soluble (Neely, 1985). Non-alcohol products have also been reported by Vogel *et al.* (1987) and Jeffers *et al.* (1989), but they are apparently products of competing dehydrohalogenation reactions.

The likelihood that a halogenated solvent will undergo hydrolysis depends in part on the number of halogen substituents. More halogen substituents on a compound will decrease the chance for hydrolysis reactions to occur (Vogel *et al.*, 1987), and will therefore decrease the rate of the reaction. In addition, bromine substituents are more susceptible to hydrolysis than chlorine substituents (Vogel *et al.*, 1987). 1,2-Dibromoethane is one compound that is subject to significant hydrolysis reactions under natural conditions. Locations of the halogen substituent on the carbon chain may also have some effect on the rate of reaction. The rate also may increase with increasing pH; however, a rate dependence upon pH is typically not observed below a pH of 11 (Mabey and Mill, 1978; Vogel and Reinhard, 1986). Rates of hydrolysis may also be increased by the presence of clays, which can act as catalysts (Vogel *et al.*, 1987). Hydrolysis rates can

generally be described using first-order kinetics, particularly in solutions in which water is the dominant nucleophile (Vogel *et al.*, 1987). However, this oversimplifies what is typically a much more complicated relationship (Neely, 1985). As noted in the introduction to this Appendix, reported rates of environmentally significant hydrolysis reactions involving chlorinated solvents are typically the result of extrapolation from experiments performed at higher temperatures (Mabey and Mill, 1978; Vogel, 1994).

Hydrolysis of chlorinated methanes and ethanes has been well-demonstrated in the literature. Vogel (1994) reports that monohalogenated alkanes have half-lives on the order of days to months, while polychlorinated methanes and ethanes have half-lives that may range up to thousands of years for carbon tetrachloride. As the number of chlorine atoms increases, dehydrohalogenation may become more important (Jeffers *et al.*, 1989). Butler and Barker (1996) note that chlorinated ethenes do not undergo significant hydrolysis reactions (i.e., the rates are slow). Butler and Barker also reported that they were unable to find any studies on hydrolysis of vinyl chloride. A listing of half-lives for abiotic hydrolysis and dehydrohalogenation of some chlorinated solvents is presented on Table B.4.1. Note that no distinctions are made in the table as to which mechanism is operating; this is consistent with the references from which the table has been derived (Vogel *et al.*, 1987; Butler and Barker, 1996).

One common chlorinated solvent for which abiotic transformations have been well-studied is 1,1,1-TCA. 1,1,1-TCA may be abiotically transformed to acetic acid through a series of substitution reactions, including hydrolysis. In addition, 1,1,1-TCA may be reductively dehalogenated to form 1,1- DCA) and then chloroethane (CA), which is then hydrolyzed to ethanol (Vogel and McCarty, 1987) or dehydrohalogenated to vinyl chloride (Jeffers *et al.*, 1989). Rates of these reactions have been studied by several parties, and these rates are summarized in Table B.4.1.

### B.4.1.2 Dehydrohalogenation

Dehydrohalogenation is an elimination reaction involving halogenated alkanes in which a halogen is removed from one carbon atom, followed by the subsequent removal of a hydrogen atom from an adjacent carbon atom. In this two-step reaction, an alkene is produced. Although the oxidation state of the compound decreases due to the removal of a halogen, the loss of a hydrogen atom increases it. This results in no external electron transfer, and there is no net change in the oxidation state of the reacting molecule (Vogel *et al.*, 1987). Contrary to the patterns observed for hydrolysis, the likelihood that dehydrohalogenation will occur increases

with the number of halogen substituents. It has been suggested that under normal environmental conditions, monohalogenated aliphatics apparently do not undergo dehydrohalogenation, and these reactions are apparently not likely to occur (March, 1985; Vogel *et al.*, 1987). However, Jeffers *et al.* (1989) report on the dehydrohalogenation of CA to VC. Polychlorinated alkanes have been observed to undergo dehydrohalogenation under normal conditions and extremely basic conditions (Vogel *et al.*, 1987). As with hydrolysis, bromine substituents are more reactive with respect to dehydrohalogenation.

**Table B.4.1**
Approximate Half-Lives of Abiotic Hydrolysis and
Dehydrohalogenation Reactions involving Chlorinated Solvents

| Compound | Half-Life (years) | Products |
|---|---|---|
| Chloromethane | no data | |
| Methylene Chloride (Dichloromethane) | 704[a/] | |
| Trichloromethane (Chloroform) | 3500[a], 1800[b] | |
| Carbon Tetrachloride | 41[b] | |
| Chloroethane | 0.12[c] | ethanol |
| 1,1-Dichloroethane | 61[b] | |
| 1,2-Dichloroethane | 72[b] | |
| 1,1,1-Trichloroethane | 1.7[a], 1.1[b]<br>2.5[d] | acetic acid<br>1,1-DCE |
| 1,1,2-Trichloroethane | 140[b], 170[a] | 1,1-DCE |
| 1,1,1,2-Tetrachloroethane | 47[b], 380[a] | TCE |
| 1,1,2,2-Tetrachloroethane | 0.3[e]<br>0.4[b], 0.8[a] | 1,1,2-TCA<br>TCE |
| Tetrachloroethene | 0.7[f]*, 1.3 x 10[6 b] | |
| Trichloroethene | 0.7[f]*, 1.3 x 10[6 b] | |
| 1,1-Dichloroethene | 1.2 x 10[8 b] | |
| 1,2-Dichloroethene | 2.1 x 10[10 b] | |

[a] From Mabey and Mill, 1978
[b] From Jeffers *et al.*, 1989
[c] From Vogel *et al.*, 1987
[d] From Vogel and McCarty, 1987
[e] From Cooper *et al.*, 1987
[f] From Dilling *et al.*, 1975
* Butler and Barker (1996) indicate that these values may reflect experimental difficulties and that the longer half-life [as calculated by Jeffers et al. (1989)] should be used.

Dehydrohalogenation rates may also be approximated using pseudo-first-order kinetics. Once again, this is not truly a first-order reaction, but such approximations have been used in the literature to quantify the reaction rates. The rates will not only depend upon the number and types of halogen substituent, but also on the hydroxide ion concentration. Under normal pH conditions (i.e., near a pH of 7), interaction with water (acting as a weak base) may become more

important (Vogel *et al.*, 1987). Transformation rates for dehydrohalogenation reactions is presented in Table B.4.1. 1,1,1-TCA is also known to undergo dehydrohalogenation (Vogel and McCarty, 1987). In this case, TCA is transformed to 1,1-DCE, which is then reductively dehalogenated to VC. The VC is then either reductively dehalogenated to ethene or consumed as a substrate in an aerobic reaction and converted to $CO_2$. In a laboratory study, Vogel and McCarty (1987) reported that the abiotic conversion of 1,1,1-TCA to 1,1-DCE has a rate constant of about 0.04 $year^{-1}$. It was noted that this result was longer than indicated in previous studies, but that experimental methods differed. Jeffers *et al.* (1989) reported on several other dehydrohalogenation reactions; in addition to 1,1,1-TCA and 1,1,2-TCA both degrading to 1,1-DCE, the tetrachloroethanes and pentachloroethanes degrade to TCE and PCE, respectively. Rates of these reactions are included in Table B.4.1. As noted previously, Jeffers *et al.* (1989) also report that CA may degrade to VC, but no information on rates was encountered during the literature search for this Appendix.

## B.4.2 REDUCTION REACTIONS

Two abiotic reductive dechlorination reactions that may operate in the subsurface are hydrogenolysis and dihaloelimination. Hydrogenolysis is the simple replacement of a chlorine (or another halogen) by a hydrogen, while dihaloelimination is the removal of two chlorines (or other halogens) accompanied by the formation of a double carbon-carbon bond. Butler and Barker (1996) review work by Criddle *et al.* (1986), Jafvert and Wolfe (1987), Reinhard *et al.* (1990), and Acton (1990) and this review suggests that while these reactions are thermodynamically possible under reducing conditions, they often do not take place in the absence of biological activity, even if such activity is only indirectly responsible for the reaction. While not involved in a manner similar to that for cometabolism, microbes may produce reductants that facilitate such reactions in conjunction with minerals in the aquifer matrix, as has been suggested by work utilizing aquifer material from the Borden test site (Reinhard *et al.*, 1990). Moreover, the reducing conditions necessary to produce such reactions are most often created as a result of microbial activity. It is therefore not clear if some of these reactions are truly abiotic, or if because of their reliance on microbial activity to produce reducing conditions or reactants, they should be considered to be a form of cometabolism.

In some cases, truly abiotic reductive dechlorination has been observed; however, the conditions that favor such reactions may not occur naturally. For example, Gillham and O'Hannesin (1994) describe reductive dehalogenation of chlorinated aliphatics using zero-valent iron, in which the iron serves as an electron donor in an electrochemical reaction. However, this

is not a natural process. Wang and Tan (1990) reported reduction of TCE to ethene and carbon tetrachloride to methane during a platinum-catalyzed reaction between elemental magnesium and water. Given that the metals involved in these reactions are unlikely to occur naturally in the reduced forms used in the aforementioned work, such processes are not likely to contribute to natural attenuation of chlorinated solvents.

# APPENDIX C

# DATA INTERPRETATION AND CALCULATIONS

# TABLE OF CONTENTS - APPENDIX C

C-1 INTRODUCTION ..... C1-1

C-2 PREPARATION OF GEOLOGIC BORING LOGS, HYDROGEOLOGIC SECTIONS, AND MAPS ..... C2-1
C.2.1 PREPARATION OF LITHOLOGIC LOGS ..... C2-1
C.2.2 PREPARATION OF HYDROGEOLOGIC SECTIONS ..... C2-1
C.2.3 REVIEW OF TOPOGRAPHIC MAPS AND PREPARATION OF POTENTIOMETRIC SURFACE MAPS AND FLOW NETS ..... C2-2
C.2.3.1 Review of Topographic Maps ..... C2-2
C.2.3.2 Preparation of Potentiometric Surface Maps ..... C2-4
C.2.3.3 Preparation of Flow Nets ..... C2-5
C.2.3.4 Preparation of Contaminant Isopach Maps ..... C2-7
C.2.3.5 Preparation of Contaminant and Daughter Product Isopleth Maps ..... C2-15
C.2.3.6 Preparation of Electron Donor, Inorganic Electron Acceptor, and Metabolic Byproduct Contour (Isopleth) Maps ..... C2-18

C-3 NATURAL ATTENUATION CALCULATIONS ..... C3-1
C.3.1 CALCULATING HYDRAULIC PARAMETERS ..... C3-1
C.3.1.1 Hydraulic Conductivity ..... C3-1
C.3.1.2 Transmissivity ..... C3-4
C.3.1.3 Hydraulic Head and Gradient ..... C3-4
C.3.1.4 Total Porosity (n) and Effective Porosity ($n_e$) ..... C3-8
FIGURE C.3.4 POROSITY ..... C3-10
C.3.1.5 Linear Groundwater Flow Velocity (Seepage or Advective Velocity) ..... C3-11
C.3.1.6 Coefficient of Retardation and Retarded Contaminant Transport Velocity C3-11
C.3.2 CONTAMINANT SOURCE TERM CALCULATIONS ..... C3-16
C.3.2.1 Direct Measurement of Dissolved Contaminant Concentrations in Groundwater in Contact with NAPL ..... C3-20
C.3.2.2 Equilibrium Partitioning Calculations ..... C3-21
C.3.2.3 Mass Flux Calculations ..... C3-24
C.3.3 CONFIRMING AND QUANTIFYING BIODEGRADATION ..... C3-28
C.3.3.1 Isopleth maps ..... C3-28
C.3.3.2 Data Set Normalization ..... C3-29
C.3.3.3 Calculating Biodegradation Rates ..... C3-36

C.3.4 DESIGN, IMPLEMENTATION, AND INTERPRETATION OF MICROCOSM STUDIES ..... C3-43
C.3.4.1 Overview ..... C3-43
C.3.4.2 When to Use Microcosms ..... C3-45
C.3.4.3 Application of Microcosms ..... C3-45
C.3.4.4 Selecting Material for Study ..... C3-45
C.3.4.5 Geochemical Characterization of the Site ..... C3-47
C.3.4.6 Microcosm Construction ..... C3-50
C.3.4.7 Microcosm Interpretation ..... C3-52
C.3.4.8 The Tibbetts Road Case Study ..... C3-52
C.3.4.9 Summary ..... C3-61

## FIGURES

| No. | Title | Page |
|---|---|---|
| C.2.1 | Example Hydrogeologic Section | C2-3 |
| C.2.2 | Example Groundwater Elevation Map | C2-6 |
| C.2.3 | Example Flow Net | C2-8 |
| C.2.4 | Example Mobile LNAPL Isopach (A) and Contaminant Isopleth (B) Maps | C2-9 |
| C.2.5 | Measured (Apparent) *versus* Actual LNAPL Thickness | C2-11 |
| C.2.6 | Type Curve for LNAPL Baildown Test | C2-14 |
| C.2.7 | Total BTEX, Chlorinated Solvents, and Daughter Products | C2-16 |
| C.2.8 | BTEX, Electron Acceptors, and Metabolic Byproducts | C2-17 |
| C.3.1 | Range of Hydraulic Conductivity Values | C3-3 |
| C.3.2 | Hydraulic Head | C3-6 |
| C.3.3 | Groundwater Elevation Map | C3-8 |
| C.3.4 | Range of Porosity Values | C3-10 |
| C.3.5 | Tibbetts Road Study Site | C3-53 |
| C.3.6 | TCE Microcosm Results | C3-55 |
| C.3.7 | Benzene Microcosm Results | C3-56 |
| C.3.8 | Toluene Microcosm Results | C3-57 |

## TABLES


| No. | Title | Page |
|---|---|---|
| C.2.1 | Typical values for $h_{aw}^{c}\big\|_{dr}$ | C2-12 |
| C.2.2 | Surface Tensions for Various Compounds | C2-13 |
| C.2.3 | Results of Example Baildown Test | C2-15 |
| C.3.1 | Representative Values of Hydraulic Conductivity for Various Sediments and Rocks | C3-2 |
| C.3.2 | Representative Values of Dry Bulk Density, Total Porosity, and Effective Porosity for Common Aquifer Matrix Materials | C3-9 |
| C.3.3 | Representative Values of Total Organic Carbon for Common Sediments | C3-15 |
| C.3.4 | Example Retardation Calculations for Select Compounds | C3-16 |
| C.3.5 | Representative First-order Biodegradation Rate Constants | C3-38 |
| C.3.6 | Geochemical Parameters | C3-49 |
| C.3.7 | Contaminants and Daughter Products | C3-50 |
| C.3.8 | Concentrations of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms | C3-58 |
| C.3.9 | First-order Rate Constants for Removal of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms | C3-59 |
| C.3.10 | Concentrations of Contaminants and Metabolic By-products in Monitoring Wells along Segments in the Plume used to Estimate Field-scale Rate Constants | C3-60 |
| C.3.11 | First-order Rate Constants in Segments of the Tibbetts Road Plume | C3-61 |
| C.3.12 | Comparison of First-order Rate Constants in a Microcosm Study, and in the Field at the Tibbetts Road NPL Site | C3-62 |

# SECTION C-1

# INTRODUCTION

Successful documentation of natural attenuation requires interpretation of site-specific data to define the groundwater flow system, refine the conceptual model, quantify rates of contaminant attenuation, and model the fate and transport of dissolved contaminants. Tasks to be completed include preparation of lithologic logs, hydrogeologic sections, potentiometric surface maps and flow nets, contaminant isopach and isopleth maps, electron acceptor and metabolic byproduct isopleth maps, and calculation of hydraulic parameters, retardation coefficients, and biodegradation rate constants. The rate and amount of partitioning of organic compounds from mobile and residual nonaqueous-phase liquid (NAPL) into groundwater should also be determined to allow estimation of a source term. Completion of these tasks permits refinement of the conceptual model and is necessary to successfully support remediation by natural attenuation.

This appendix consists of three sections, including this introduction. Section C-2 discusses preparation of geologic boring logs, hydrogeologic sections, and maps. Section C-3 covers intrinsic remediation calculations, including hydraulic parameter calculations, contaminant source term calculations, confirming and quantifying biodegradation, and designing, implementing, and interpreting microcosm studies.

# SECTION C-2

# PREPARATION OF GEOLOGIC BORING LOGS, HYDROGEOLOGIC SECTIONS, AND MAPS

The first step after completion of site characterization field activities is to prepare geologic boring logs, hydrogeologic sections, water table elevation (or potentiometric surface) maps, flow nets, and maps depicting contaminant concentrations, electron acceptor and metabolic byproduct concentrations, and mobile NAPL thickness. The construction of these items is discussed in the following sections.

## C.2.1 PREPARATION OF LITHOLOGIC LOGS

Lithologic logs should be prepared using field data. Whenever possible, these logs should contain descriptions of the aquifer matrix, 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 significant observations such as visible fuel or fuel odor. It is also important to correlate the results of volatile organic compound (VOC) screening using 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 pathways may be limited to stratigraphic units less than 6 inches thick.

## C.2.2 PREPARATION OF HYDROGEOLOGIC SECTIONS

Lithologic logs should be used in conjunction with water level data to prepare a minimum of two hydrogeologic sections for the site. One section should be oriented parallel to the direction of groundwater flow, and one section should be oriented perpendicular to the direction of groundwater flow. Both sections should be drawn to scale. Hydrogeologic sections are an integral part of the conceptual model and are useful in identifying preferential contaminant migration pathways and in modeling the site.

At a minimum, hydrogeologic sections should contain information on the relationships between hydrostratigraphic units at the site, including the location and distribution of transmissive *vs.* non-transmissive units, the location of the water table relative to these units, and the location(s) of the contaminant source(s). Figure C.2.1 is an example of a completed hydrogeologic section.

## C.2.3 REVIEW OF TOPOGRAPHIC MAPS AND PREPARATION OF POTENTIOMETRIC SURFACE MAPS AND FLOW NETS

Determining the direction of groundwater flow and the magnitude of hydraulic gradients is important because these parameters influence the direction and rate of contaminant migration. Groundwater flow directions are represented by a three-dimensional set of equipotential lines and orthogonal flow lines. If a plan view (potentiometric surface, or water table elevation, map) or a two-dimensional cross-section is drawn to represent a flow system, the resultant equipotential lines and flow lines constitute a flow net. A flow net can be used to determine the distribution of hydraulic head, the groundwater velocity distribution, groundwater and solute flow paths and flow rates, and the general flow pattern in a groundwater system.

### C.2.3.1 Review of Topographic Maps

Groundwater flow is strongly influenced by the locations of groundwater divides and by recharge from and discharge to surface water bodies such as rivers, streams, lakes, and wetlands. Topographic highs generally represent divergent flow boundaries (divergent groundwater divide), and topographic lows such as valleys or drainage basins typically represent convergent flow boundaries (convergent groundwater divide). In addition, the configuration of the water table is typically a subtle reflection of the surface topography in the area. However, topography is not always indicative of subsurface flow patterns and should not be depended upon unless confirmed by head data. In order to place the local hydrogeologic flow system within the context of the regional hydrogeologic flow system, it is important to have an understanding of the local and regional topography. Included in this must be knowledge of the locations of natural and manmade surface water bodies. This information can generally be gained from topographic maps published by the United States Geological Survey.

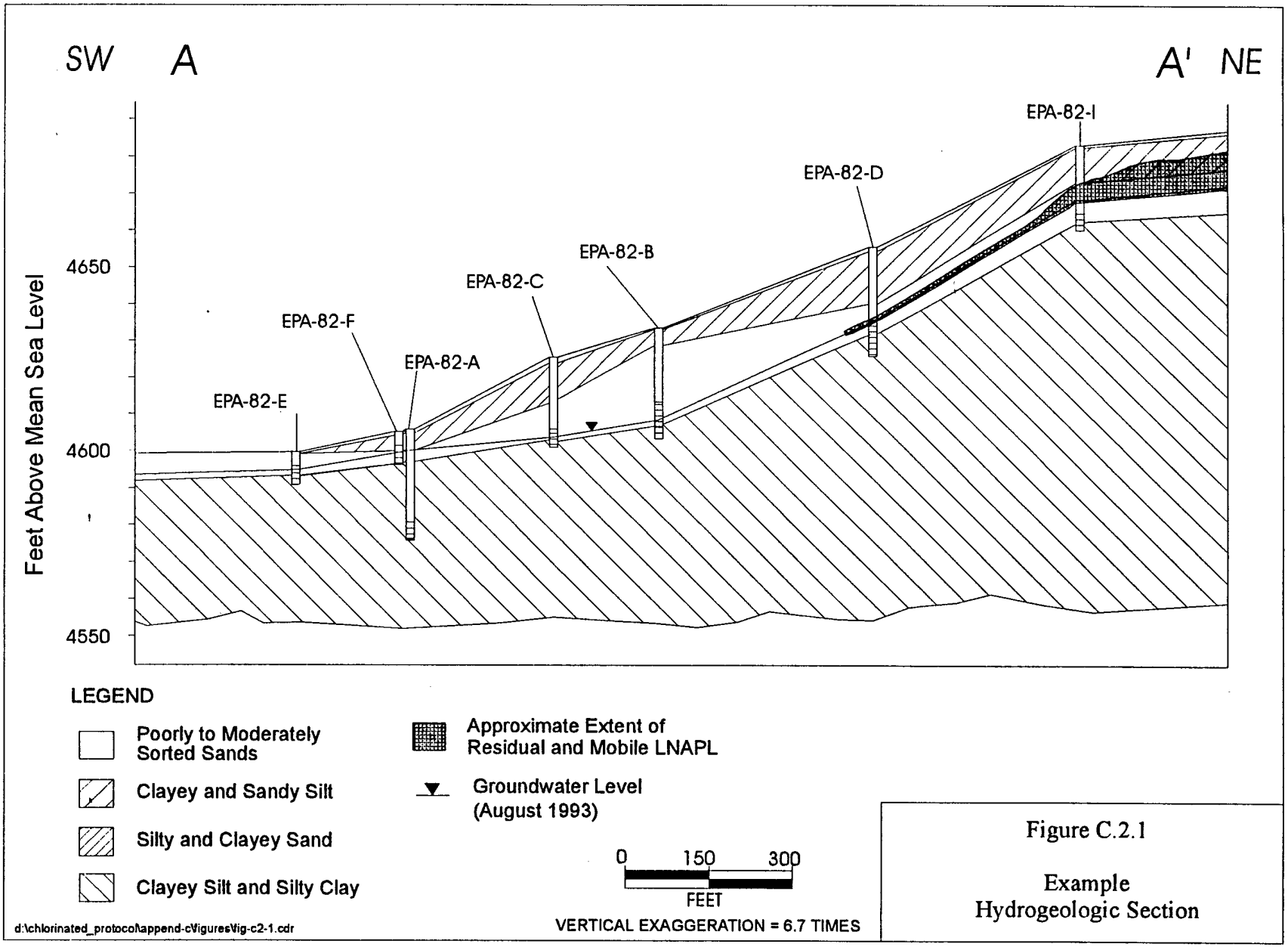



Figure C.2.1

Example
Hydrogeologic Section

### C.2.3.2 Preparation of Potentiometric Surface Maps

A potentiometric surface map is a two-dimensional graphical representation of equipotential lines shown in plan view. Water table elevation maps are potentiometric surface maps drawn for water table (unconfined) aquifers. Potentiometric surface maps for water table aquifers show where planes of equal potential intersect the water table. A potentiometric surface map should be prepared from water level measurements and surveyor's data. These maps are used to estimate the direction of plume migration and to calculate hydraulic gradients. To document seasonal variations in groundwater flow, separate potentiometric surface maps should be prepared using quarterly water level measurements taken over a period of at least 1 year.

The data used to develop the potentiometric surface map should be water level elevation data (elevation relative to mean sea level) from piezometers/wells screened in the same relative position within the same hydrogeologic unit. For example, wells that are screened at the water table can be used for the same potentiometric surface map. Wells screened in different hydrogeologic units or at different relative positions within the same water table aquifer cannot be used to prepare a potentiometric surface map. Where possible, a potentiometric surface map should be prepared for each hydrogeologic unit at the site. In recharge areas, wells screened at various elevations cannot all be used to prepare the same potentiometric surface map because of strong downward vertical gradients. Likewise, wells screened at various elevations in discharge areas such as near streams, lakes, or springs, should not all be used because of the strong upward vertical gradients.

When preparing a potentiometric surface map, the locations of system boundaries should be kept in mind; particularly the site features that tend to offset the shape of the contours on the map. Such features include topographic divides, surface water bodies, and pumping wells.

In addition to, and separately from, preparation of a potentiometric surface map, water level measurements from wells screened at different depths can be used to determine any vertical hydraulic gradients. It is important to have a good understanding of vertical hydraulic gradients because they may have a profound influence on contaminant migration.

In areas with measurable mobile LNAPL, a correction must be made for the water table deflection caused by the LNAPL. The following relationship, based on Archimedes' Principle, provides a correction factor that allows the water table elevation to be adjusted for the effect of floating LNAPL.

$$CDTW = MDTW - \frac{\rho_{lnapl}}{\rho_w}(PT) \qquad \text{eq. C.2.1}$$

Where: $CDTW$ = corrected depth to water [L]
$MDTW$ = measured depth to water [L]
$\rho_{lnapl}$ = density of the LNAPL [M/L$^3$]
$\rho_w$ = density of the water, generally 1.0 [M/L$^3$]
$PT$ = measured LNAPL thickness [L]

Using the corrected depth to water, the corrected groundwater elevation, CGWE, is given by:

$$CGWE = \text{Datum Elevation} - CDTW \qquad \text{eq. C.2.2}$$

Corrected groundwater elevations should be used for potentiometric surface map preparation. Figure C.2.2 is an example of a groundwater elevation map for an unconfined aquifer. Water table elevation data used to prepare this map were taken from wells screened across the water table.

### C.2.3.3 Preparation of Flow Nets

Where an adequate three-dimensional database is available, flow nets can be constructed to facilitate the interpretation of the total hydraulic head distribution in the aquifer. This will help determine potential solute migration pathways. The simplest groundwater flow system is one that is homogeneous and isotropic. This type of hydrogeologic setting serves as a simple basis for describing the basic rules of flow net construction, despite the fact that homogeneous, isotropic media rarely occur in nature. Regardless of the type of geologic media, the basic rules of flow net construction must be applied, and necessary modifications must be made throughout the procedure to account for aquifer heterogeneity or anisotropic conditions. Water level data for flow net construction should come from multiple sets of nested wells (two or more wells at the same location) at various depths in the aquifer. The fundamental rules of flow net construction and the important properties of flow nets are summarized as follows:

- Flow lines and equipotential lines intersect at 90-degree angles if the permeability is isotropic;
- The geometric figures formed by the intersection of flow lines and equipotential lines must approximate squares or rectangles;
- Equipotential lines must meet impermeable boundaries at right angles (impermeable boundaries are flow lines); and

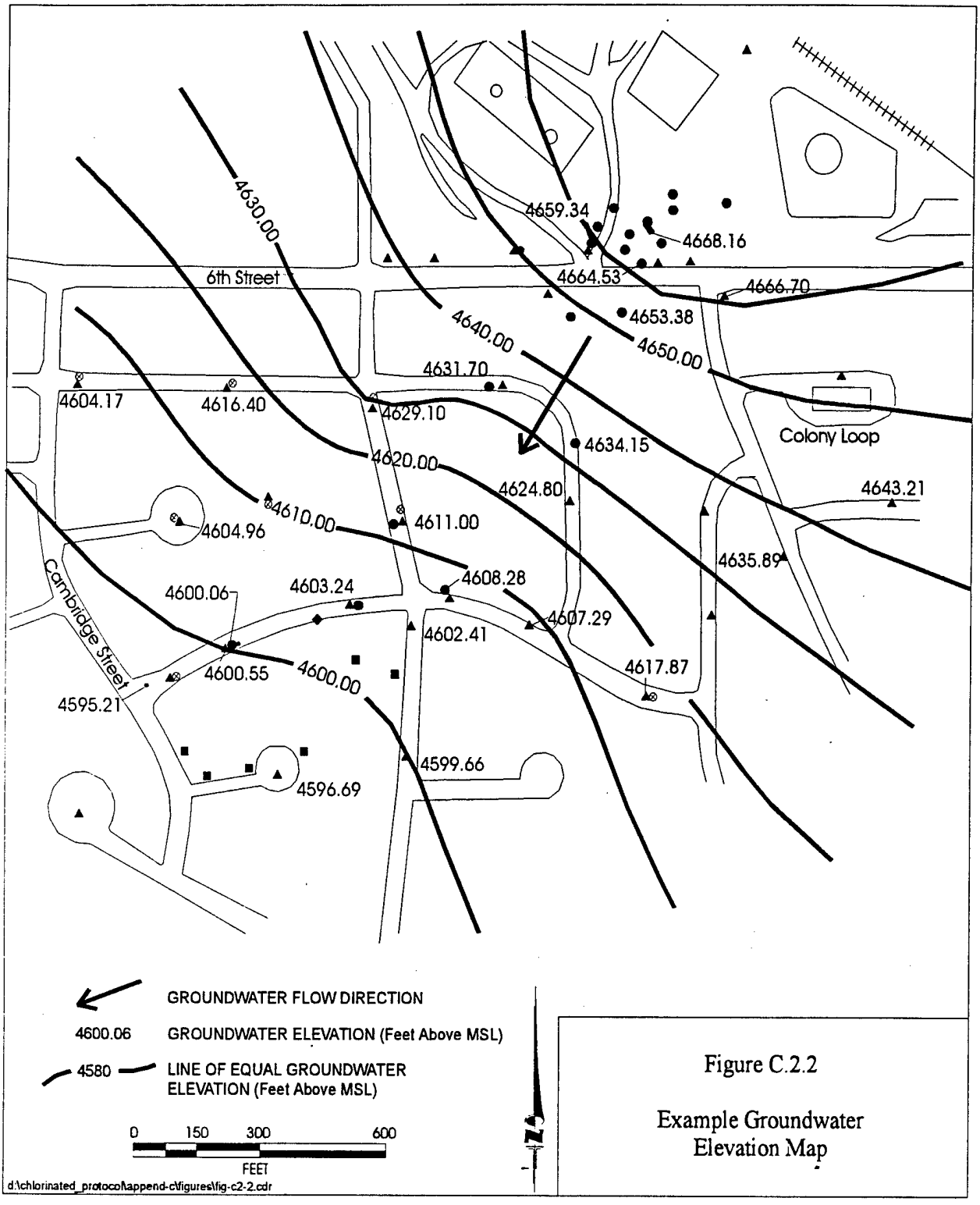



Figure C.2.2

Example Groundwater Elevation Map

- Equipotential lines must be parallel to constant-head boundaries (constant-head boundaries are equipotential lines).

Trial-and-error sketching is generally used to construct a flow net. Flow net sketching can be sufficiently accurate if constructed according to the basic rules outlined above. A relatively small number of flow lines (three to five) generally are sufficient to adequately characterize flow conditions. Flow nets should be superimposed on the hydrogeologic sections. Figure C.2.3 is an example of a completed flow net. This figure shows groundwater flow patterns in both recharge and discharge areas.

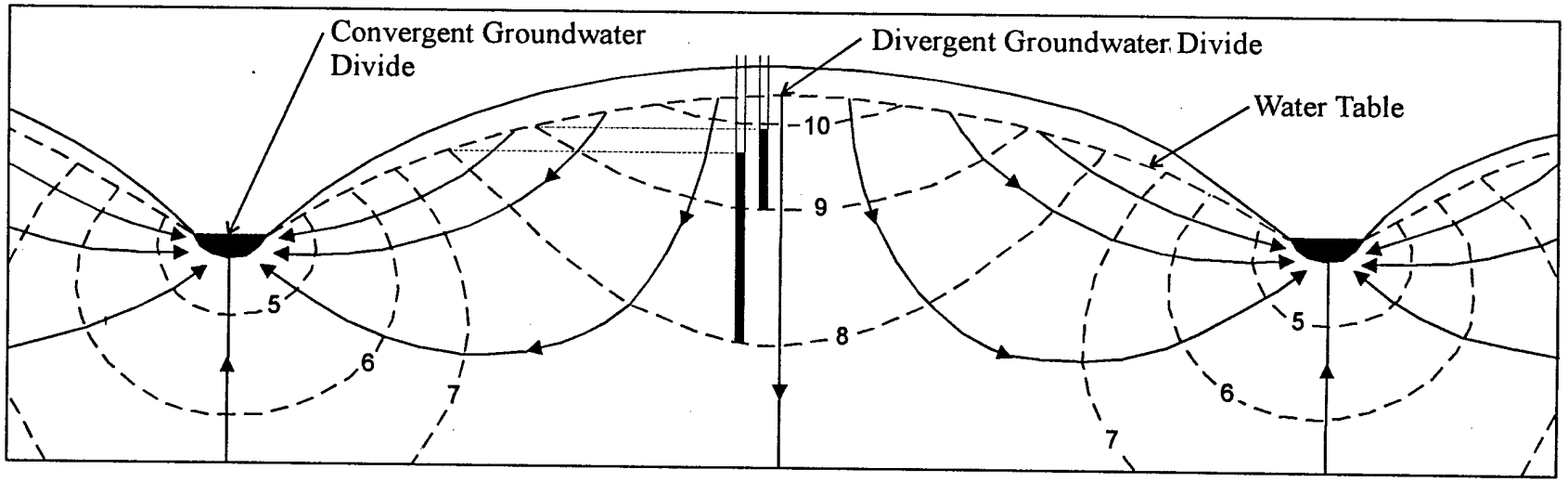
### C.2.3.4 Preparation of Contaminant Isopach Maps

If NAPL is present at the site, isopach maps showing the thickness and distribution of NAPL should be prepared. Two maps should be prepared: one for mobile NAPL, and one for residual NAPL. Such isopach maps allow estimation of the distribution of NAPL in the subsurface and aid in fate and transport model development by identifying the boundary of the NAPL. Because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of fuel and water, LNAPL thickness observations made in monitoring points are only an estimate of the actual volume of mobile LNAPL in the aquifer. To determine the actual NAPL thickness it is necessary to collect and visually analyze soil samples. LNAPL thickness data also should be used to correct for water table deflections caused by the mobile LNAPL. This process is described in Section C.2.2.3.2.

Isopach maps are prepared by first plotting the measured NAPL thickness on a base map prepared using surveyor's data. Lines of equal NAPL thickness (isopachs) are then drawn and labeled. Each data point must be honored during contouring. Figure C.2.4 is an example of a completed isopach map. This figure also contains an example of an isopleth map.

#### C.2.3.4.1 Relationship Between Apparent and Actual LNAPL Thickness

It is well documented that LNAPL thickness measurements taken in groundwater monitoring wells are not indicative of actual LNAPL thicknesses in the formation (de Pastrovich *et al.*, 1979; Blake and Hall, 1984; Hall *et al.*, 1984; Hampton and Miller, 1988; Hughes *et al.*, 1988; Abdul *et al.*, 1989; Testa and Paczkowski, 1989; Farr *et al.*, 1990; Kemblowski and Chiang, 1990; Lehnard and Parker, 1990; Mercer and Cohen, 1990; Ballestero *et al.*, 1994; Huntley *et al.*, 1994a and 1994b). These authors note that the measured thickness of LNAPL in a monitoring well is




Flow Line

Equipotential Line

10 Total Head (meters)

Modified from Hubbert (1940)

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Figure C.2.3

Example Flow Net

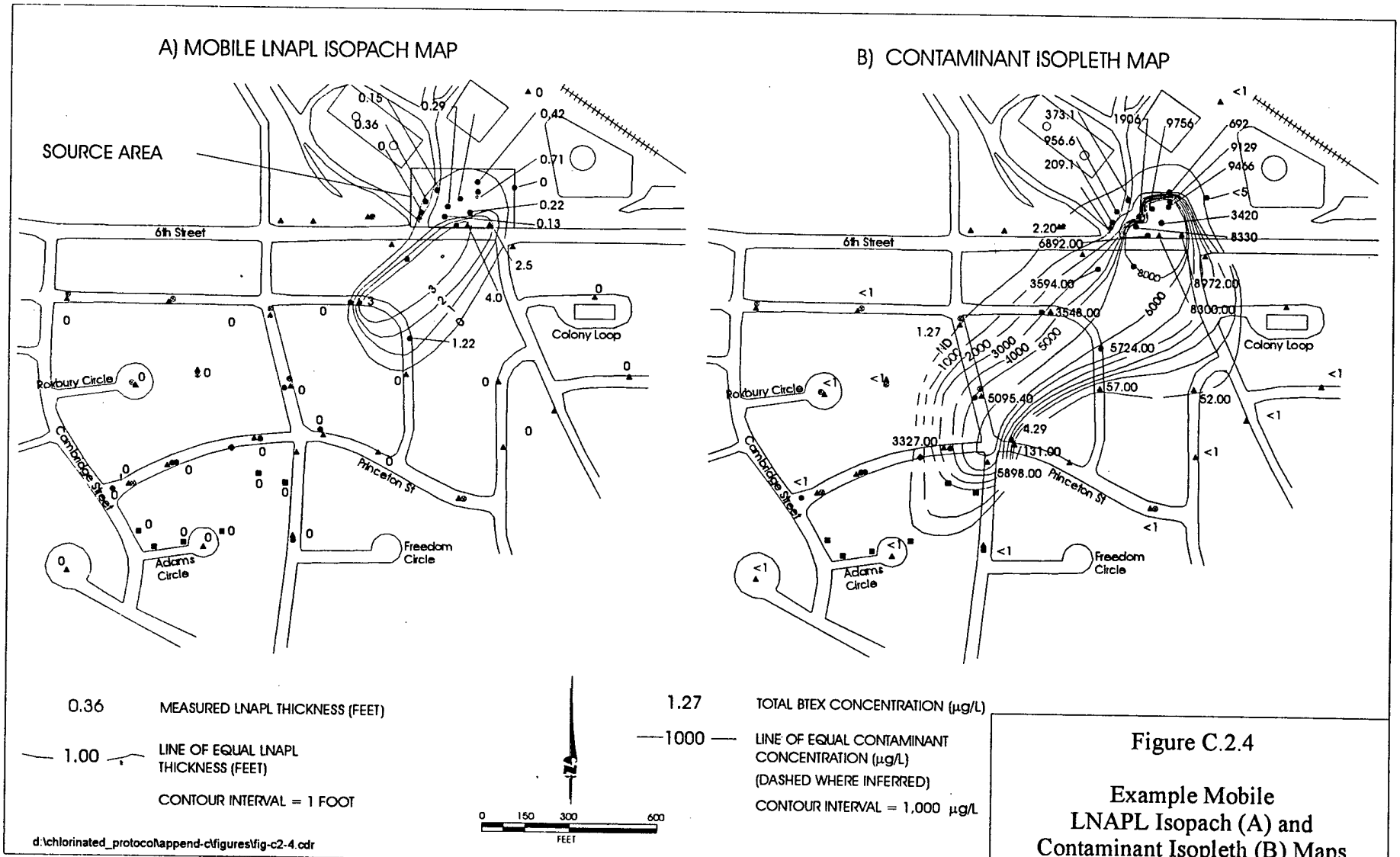



Figure C.2.4

Example Mobile LNAPL Isopach (A) and Contaminant Isopleth (B) Maps

greater that the true LNAPL thickness in the aquifer and, according Mercer and Cohen (1990), measured LNAPL thickness in wells is typically 2 to 10 times greater than the actual LNAPL thickness in the formation. The difference between actual and measured LNAPL thickness occurs because mobile LNAPL floating on the water table flows into the well (if the top of well screen is above the base of the LNAPL) and depresses the water table. Figure C.2.5 is a schematic that illustrates this relationship. The equation for correcting depth to groundwater caused by LNAPL in the well is given in Section C.2.2.3.1. Empirical relationships relating measured LNAPL thickness to actual LNAPL thickness are presented below. Also presented below are test methods that can be used to determine actual LNAPL thickness.

*C.2.3.4.1.1 Empirical Relationships*

There are several empirical methods available to estimate the actual thickness of mobile LNAPL in the subsurface based on LNAPL thicknesses measured in a groundwater monitoring well. Such empirical relationships are, at best, approximations because many factors influence the relationship between measured and apparent LNAPL thickness, including (Mercer and Cohen, 1990):

- Capillary fringe height depends on grain size and is hysteretic with fluid level fluctuations.
- LNAPL can become trapped below the water table as the water table rises and falls.
- The thickness of LNAPL is ambiguous because the interval of soil containing mobile LNAPL is not 100-percent saturated with LNAPL.

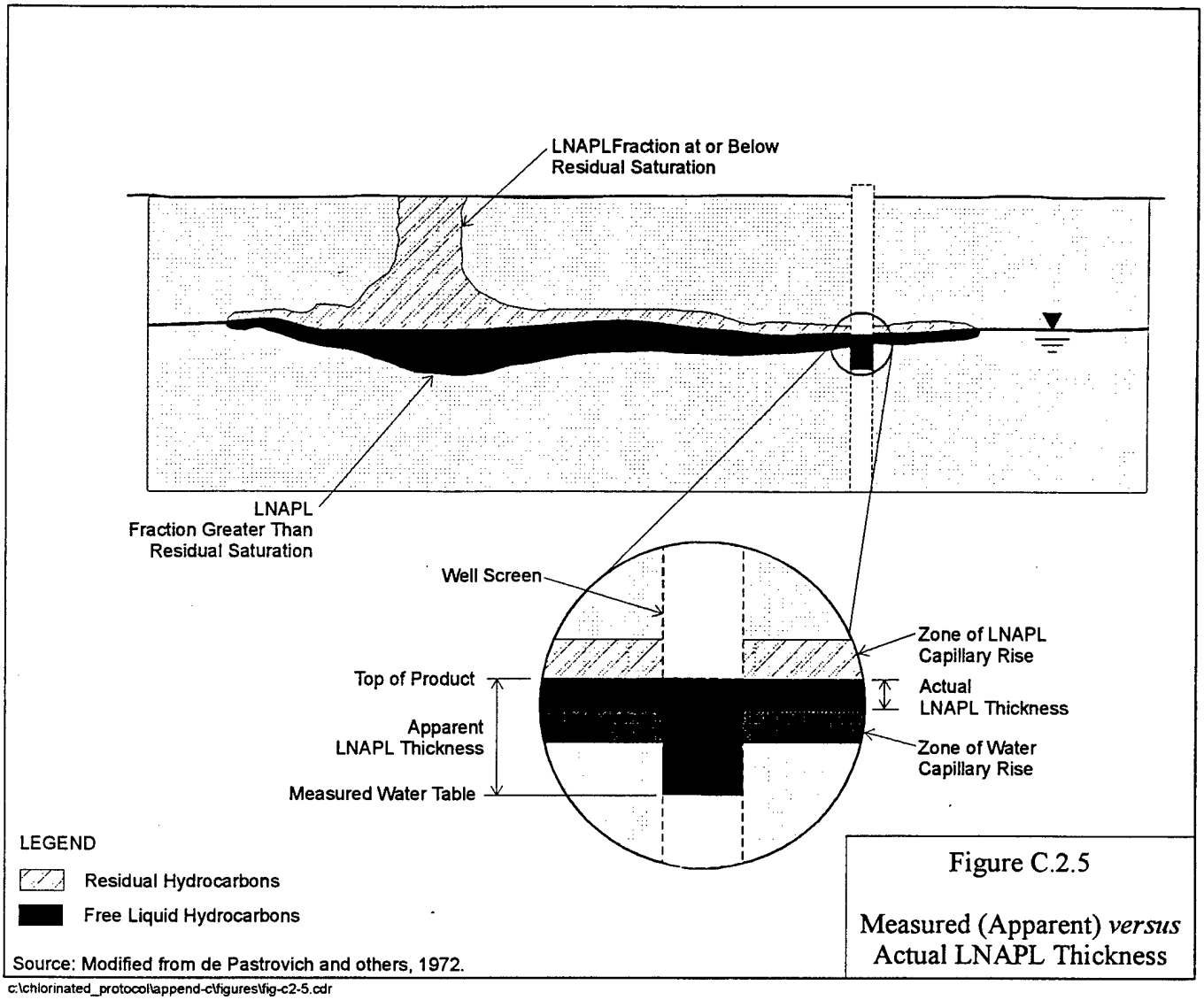
Some empirical methods for determining actual LNAPL thickness are described below.

Method of de Pastrovich *et al.* (1979)

Hampton and Miller (1988) conducted laboratory experiments to examine the relationship between the actual thickness of LNAPL in a formation, $h_f$, and that measured in a monitoring well, $h_m$. Based on their research, Hampton and Miller (1988) suggest using the following relationship (developed by de Pastrovich *et al.* in 1979) to estimate LNAPL thickness:

$$h_f \approx \frac{h_m(\rho_w - \rho_{lnapl})}{\rho_{lnapl}} \qquad \text{eq. C.2.3}$$

Where: $h_f$ = actual thickness of LNAPL in formation
$h_m$ = measured LNAPL thickness in well
$\rho_w$ = density of water (1.0 gm/cm$^3$ for pure water)
$\rho_{lnapl}$ = density of LNAPL (See Table C.3.9)




Source: Modified from de Pastrovich and others, 1972.

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Figure C.2.5

Measured (Apparent) *versus* Actual LNAPL Thickness

Method of Kemblowski and Chiang (1990)

Another empirical relationship was proposed by Kemblowski and Chiang (1990) to estimate actual LNAPL thickness based on measured LNAPL thickness. This relationship is given by:

$$h_o = H_o - 2.2h_{aw}^c\Big|_{dr} \qquad \text{eq. C.2.4}$$

Where: $h_o$ = equivalent thickness of LNAPL in the formation (volume of oil per unit area of aquifer, divided by porosity).
$H_o$ = measured LNAPL thickness in well
$h_{aw}^c\Big|_{dr}$ = capillary height of air-water interface assuming water is being displaced by oil (typical values are given in Table C.2.1)

This method assumes equilibrium conditions, water drainage, and oil imbibition.

**Table C.2.1**

Typical values for $h_{aw}^c\Big|_{dr}$ (Bear, 1972)

| Aquifer Matrix | $h_{aw}^c\Big\|_{dr}$ (cm) | $h_{aw}^c\Big\|_{dr}$ (ft) |
|---|---|---|
| Coarse Sand | 2-5 | 0.066-0.16 |
| Sand | 12-35 | 0.39-1.15 |
| Fine Sand | 35-70 | 1.14-2.30 |
| Silt | 70-150 | 2.30-4.92 |
| Clay | >200-400 | >6.56-13.12 |

Method of Lehnard and Parker (1990)

Another empirical relationship was proposed by Lehnard and Parker (1990) to estimate actual LNAPL thickness based on measured LNAPL thickness. This relationship is given by:

$$D_o = \frac{\rho_{ro}\beta_{ao}H_o}{\beta_{ao}\rho_{ro} - \beta_{ow}(1-\rho_{ro})} \qquad \text{eq. C.2.5}$$

Where: $D_o$ = actual thickness of LNAPL in formation
$H_o$ = measured LNAPL thickness in well
$\rho_{ro}$ = specific gravity of LNAPL (density of oil/density of water)
$\beta_{ao} = \frac{\sigma_{aw}}{\sigma_{ao}}$ = Air-oil scaling factor

$\beta_{ow} = \frac{\sigma_{aw}}{\sigma_{ow}}$ = Oil-water scaling factor

$\sigma_{aw}$ = surface tension of uncontaminated water (72.75 dynes/cm @ 20°C)
$\sigma_{ao}$ = surface tension of LNAPL [25 dynes/cm @ 20°C for JP-4, Table C.2.2]
$\sigma_{ow} = \sigma_{aw} - \sigma_{ao}$ = interfacial tension between water and LNAPL (47.75dynes/cm @ 20°C)

It is important to note that this method includes the capillary thickness of the hydrocarbon, and is therefore likely to be an overestimate.

**Table C.2.2**

Surface Tensions for Various Compounds

| Compound | Surface Tension @ 20°C (dyne/cm) |
|---|---|
| JP-4 | 25[a/] |
| Gasoline | 19-23 [a/] |
| Pure Water | 72.75[b/] |

a/ Martel (1987).
b/ CRC Handbook (1956).

*C.2.3.4.1.2 LNAPL Baildown Test*

The LNAPL baildown test is applicable in areas where the hydrocarbon/water interface is below the potentiometric surface, and the recharge rate of hydrocarbon into the well is slow (Hughes *et al.*, 1988).

Baildown Test Procedure (From Hughes *et al.*, 1988):

1) Gauge the well and calculate the corrected potentiometric surface elevation using equations C.2.1 and C.2.2.

2) Rapidly bail the hydrocarbon from the well.

3) Gauge the well again, and if the thickness of the hydrocarbon is acceptable (0.1 to 1 foot), calculate the potentiometric surface elevation. The potentiometric surface elevation thus calculated should be within 0.005 foot of the value calculated in step 1. If it is, then continue to step 4; if it is not, repeat steps 2 and 3.

4) Record the top of the LNAPL surface in the well as it recharges until the well is fully recharged.

5) Plot the elevation of the top of LNAPL in the well *vs.* time since bailing ceased.

6) The true thickness of the mobile LNAPL layer ($T_f$) is the distance from the inflection point to the top of the hydrocarbon under static conditions (Figure C.2.6). Thus, $T_f$ is picked directly off the plot. Table C.2.3 is an example of the results of this procedure.

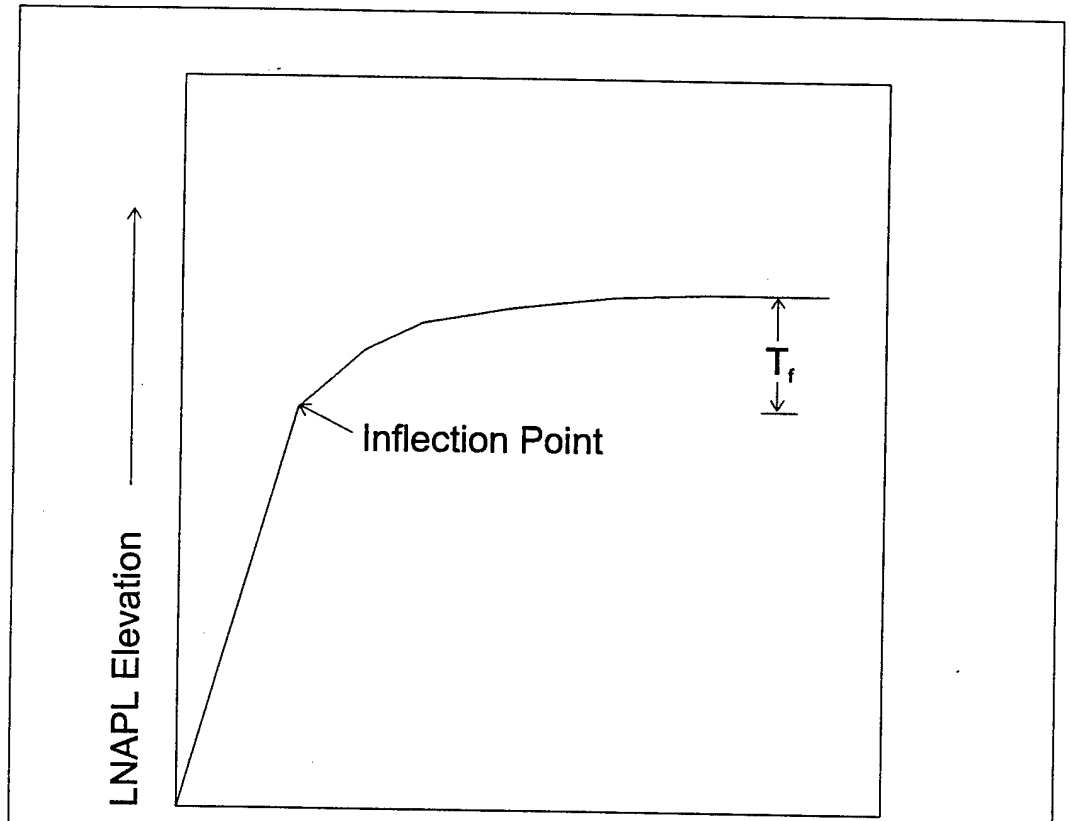



Figure C.2.6

Type Curve for LNAPL Baildown Test

**Table C.2.3**
Results of Example Baildown Test
(Modified from Hughes *et al.*, 1988)

| Well | $T_w$ (ft)[a/] | $T_f$ (ft) | Exaggeration ($T_w/T_f$) |
|---|---|---|---|
| ROW-143 | 4.97 | 0.61 | 8.1:1 |
| ROW-189 | 12.5 | 0.29 | 43.0:1 |
| ROW-129 | 0.94 | 0.0[b/] | N/A |

a/ $T_w$ = LNAPL thickness initially measured in the well
b/ Capillary oil only

Hughes *et al.* (1988) also present a recharge method that involves pumping the mobile LNAPL until steady-state conditions are achieved, and then letting the well fully recharge.

### C.2.3.5 Preparation of Contaminant and Daughter Product Isopleth Maps

Isopleth maps should be prepared for all chlorinated solvents of concern and their daughter products and for total BTEX if present. For example, if trichloroethene and BTEX were released (as is typical for fire training areas), then maps of dissolved trichloroethene, dichloroethene, vinyl chloride, ethene, and total BTEX concentrations should be prepared. Isopleth maps allow interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant isopleth maps allow contaminant concentrations to be gridded and used for input into a solute transport model.

Isopleth maps are prepared by first plotting the concentration of the contaminant on a base map prepared using surveyor's data. Lines of equal contaminant concentration (isopleths) are then drawn and labeled. It is important to ensure that each data point is honored during contouring, unless some data are suspect. Figures C.2.4, C.2.7, and C.2.8 contain examples of contaminant isopleth maps.

Dissolved BTEX concentrations are determined through groundwater sampling and laboratory analysis. From these data, isopleth maps for each of the BTEX compounds and for total dissolved BTEX should be made. Dissolved BTEX concentrations are transferred to the fate and transport model grid cells by overlaying the isopleth map onto the model grid.

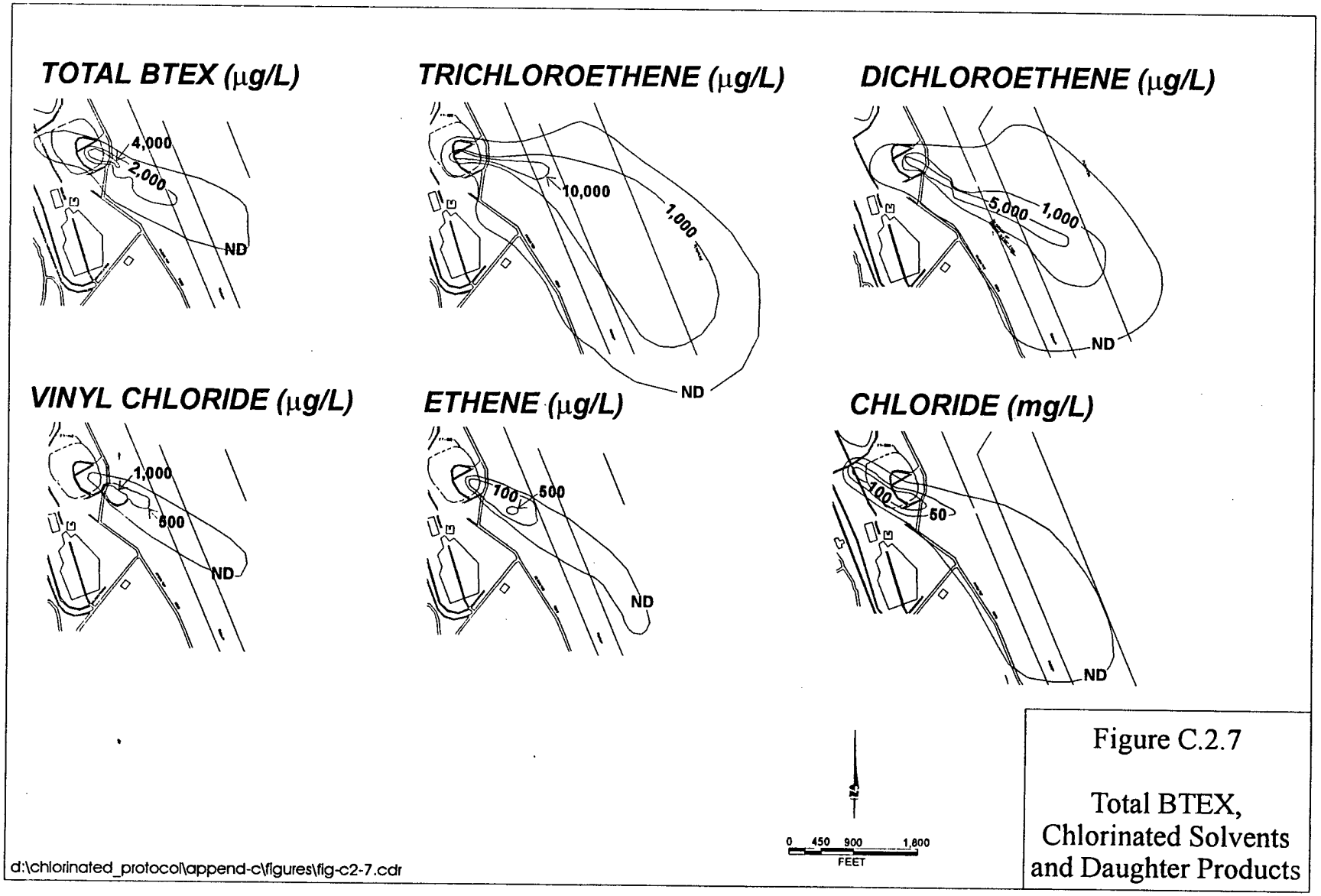



Figure C.2.7

Total BTEX, Chlorinated Solvents and Daughter Products

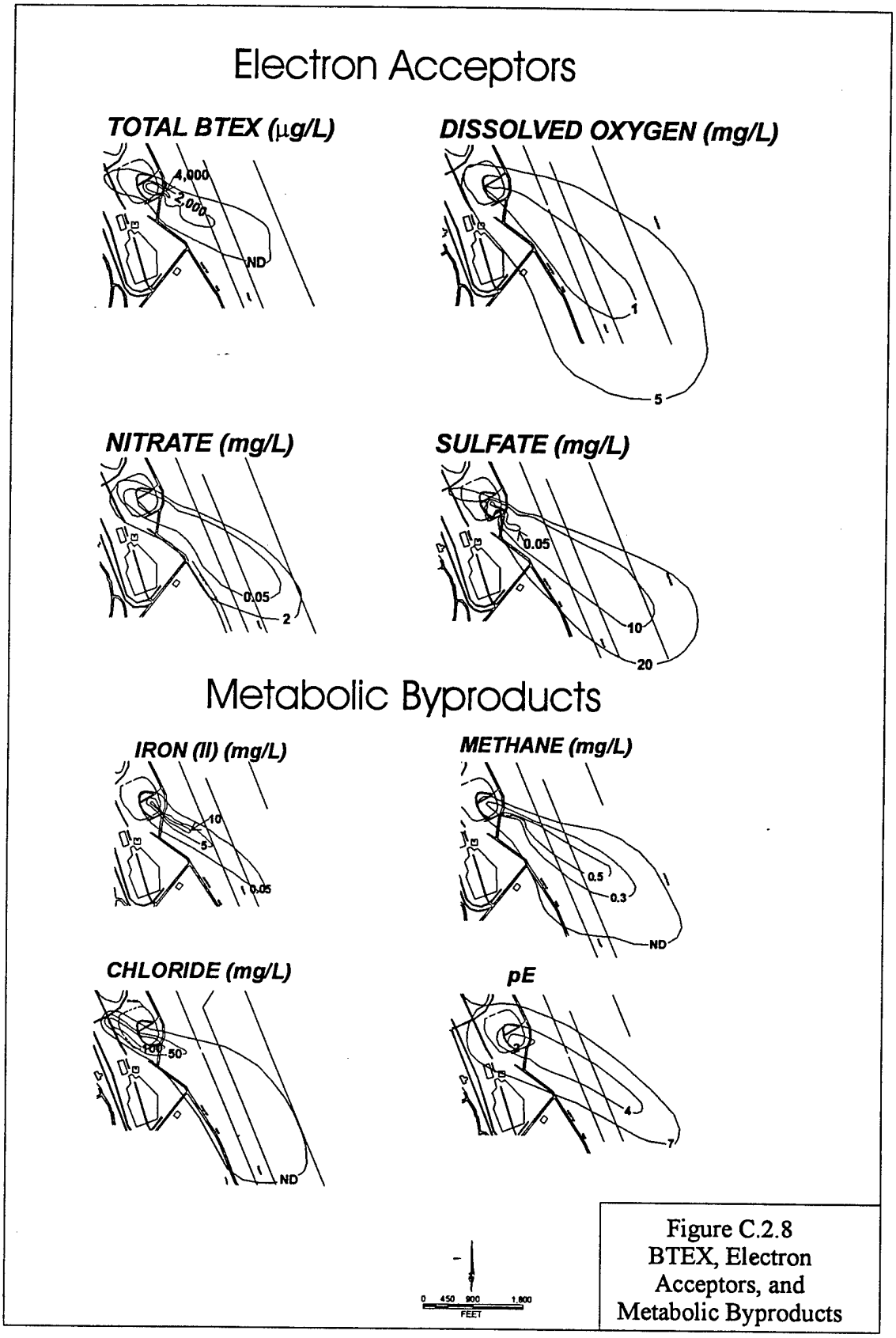



Figure C.2.8
BTEX, Electron Acceptors, and Metabolic Byproducts

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### C.2.3.6 Preparation of Electron Donor, Inorganic Electron Acceptor, and Metabolic Byproduct Contour (Isopleth) Maps

Isopleth maps should be prepared for any organic compound that can be used as an electron donor. Examples of such compounds include natural organic carbon, petroleum hydrocarbons, (e.g., BTEX, napthalene, landfill leachate, etc.). These maps are used to provide visible evidence that biodegradation could occur or is occurring. Isopleth maps also should be prepared for dissolved oxygen, nitrate, manganese (II), iron (II), sulfate, methane, and chloride. These maps are used to provide visible evidence that biodegradation is occurring. The electron acceptor and metabolic byproduct isopleth maps can be used to determine the relative importance of each of the terminal electron-accepting processes (TEAPs).

Isopleth maps are prepared by first plotting the concentration of the electron donor, electron acceptor, or metabolic byproduct on a base map prepared using surveyor's data. Lines of equal concentration (isopleths) are then drawn and labeled. It is important to ensure that each data point is honored during contouring, unless some data are suspect.

#### C.2.3.6.1 Inorganic Electron Acceptor Isopleth Maps

Electron acceptor isopleth maps allow interpretation of data on the distribution of dissolved oxygen, nitrate, and sulfate in the subsurface. Isopleth maps for these compounds provide a visual indication of the relationship between the contaminant plume and the electron acceptors and the relative importance of each TEAP. Dissolved oxygen concentrations below background levels in areas with high organic carbon concentrations are indicative of aerobic respiration. Nitrate concentrations below background in areas with high organic carbon concentrations are indicative of denitrification. Sulfate concentrations below background in areas with high organic carbon concentrations are indicative of sulfate reduction.

Figure C.2.7 gives examples of completed isopleth maps for dissolved oxygen, nitrate, and sulfate. This figure also contains the total BTEX (electron donor) isopleth map for the same period. Comparison of the total BTEX isopleth map and the electron acceptor isopleth maps shows that there is a strong correlation between areas with elevated organic carbon and depleted electron acceptor concentrations. The strong correlation indicates that the electron acceptor demand exerted during the metabolism of BTEX has resulted in the depletion of soluble inorganic electron acceptors. These relationships provide strong evidence that biodegradation is occurring via the processes of aerobic respiration, denitrification, and sulfate reduction.

C.2.3.6.2 Metabolic Byproduct Isopleth Maps

Metabolic byproduct maps should be prepared for manganese (II), iron (II), methane, and chloride. The manganese (II) map is prepared in lieu of an electron acceptor isopleth map for manganese (IV) because the amount of bioavailable amorphous or poorly crystalline manganese (IV) in an aquifer matrix is extremely hard to quantify. The iron (II) map is prepared in lieu of an electron acceptor isopleth map for iron (III) because the amount of bioavailable amorphous or poorly crystalline iron (III) in an aquifer matrix is extremely hard to quantify. Iron (II) concentrations above background levels in areas with BTEX contamination are indicative of anaerobic iron (III) reduction. Methane concentrations above background levels in areas with BTEX contamination are indicative of methanogenesis, another anaerobic process. Biodegradation of chlorinated solvents tends to increase the chloride concentration found in groundwater. Thus, chloride concentrations inside the contaminant plume generally increase to concentrations above background. This map will allow visual interpretation of chloride data by showing the relationship between the contaminant plume and chloride. During biodegradation, the oxidation-reduction potential of groundwater is lowered. Thus, the oxidation-reduction potential (or pE) inside the contaminant plume generally decreases to levels below background.

Figure C.2.8 gives examples of completed isopleth maps for iron (II), methane, chloride, and pE. This figure also contains the total BTEX (electron donor) isopleth map for the same period. Comparison of the total BTEX isopleth map and the metabolic byproduct isopleth maps and comparison of Figures C.2.7 and C.2.8 shows that there is a strong correlation between areas with elevated organic carbon and elevated metabolic byproduct concentrations. These relationships provide strong evidence that biodegradation is occurring via the processes of iron (III) reduction, methanogenesis, and reductive dechlorination.

# SECTION C-3

# NATURAL ATTENUATION CALCULATIONS

Several calculations using site-specific data must be made in order to document the occurrence of natural attenuation and successfully implement the natural attenuation 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 and Figure 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**

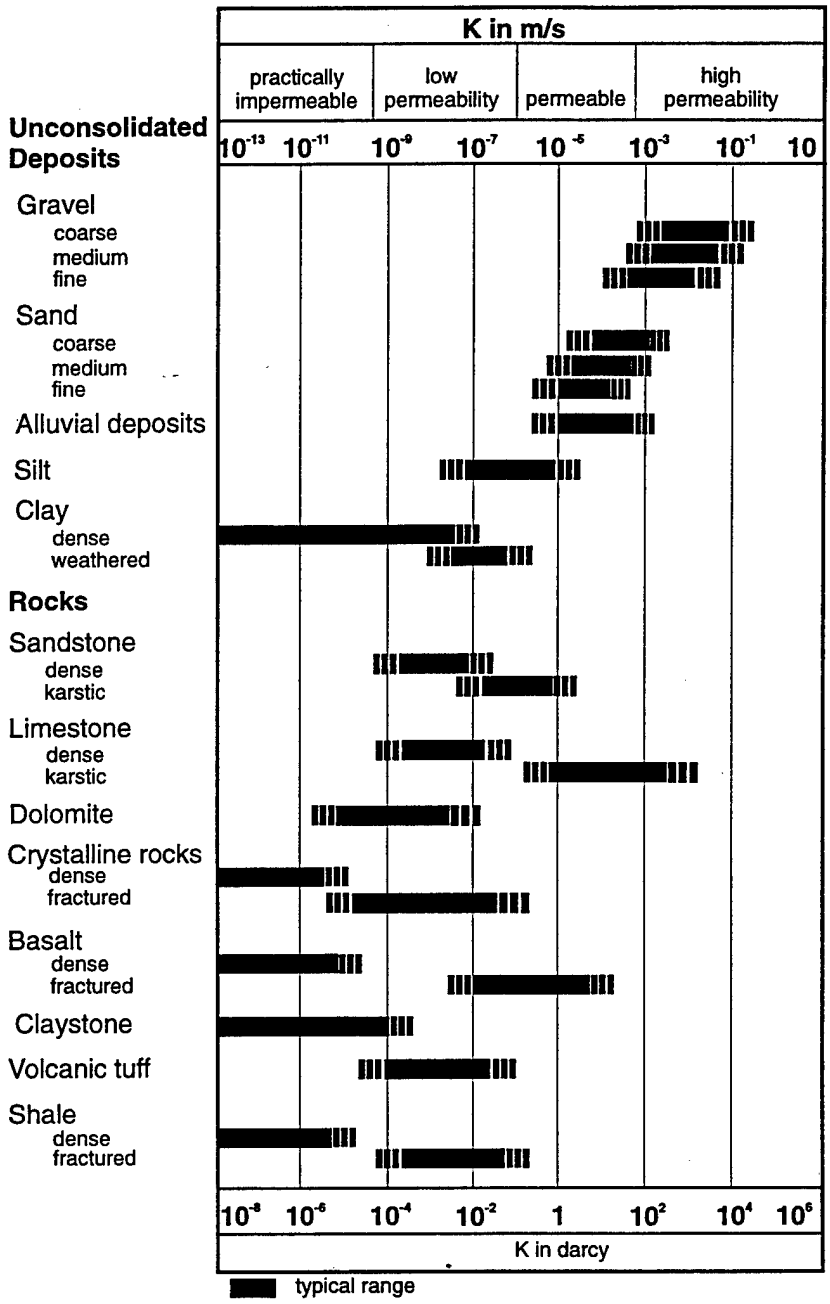
Representative Values of Hydraulic Conductivity for Various Sediments and Rocks
(From Domenico and Schwartz, 1990)

| 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




Source: Spitz and Moreno, 1996.

Figure C.3.1

Range of Hydraulic Conductivity Values

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.3.2):

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

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
$\rho$ = 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

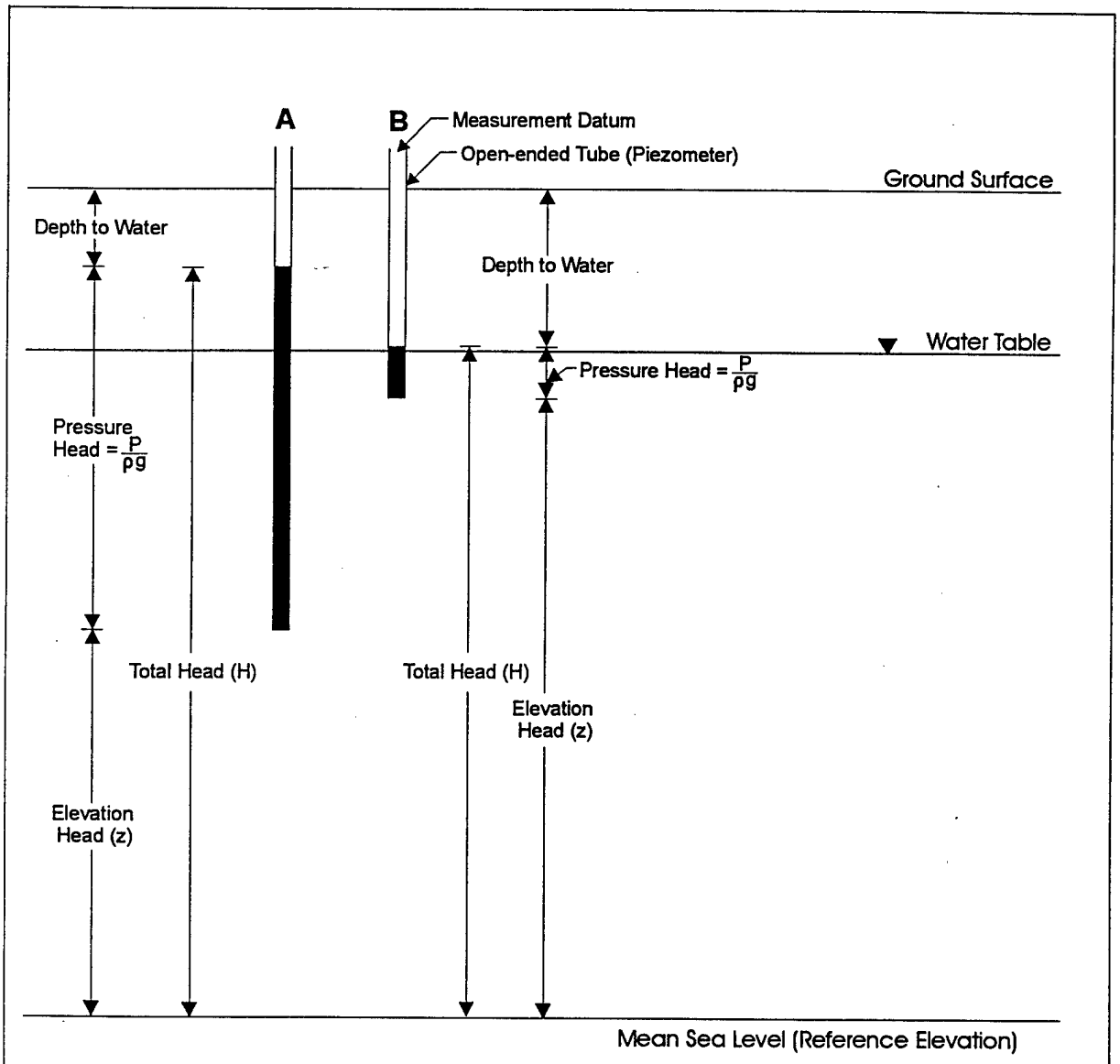



Figure C.3.2

Hydraulic Head

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or is a well screened across the water table. Figure C.3.2 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.3.2) 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.3.3, calculate the hydraulic gradient between points A and B. Assume that all wells are screened across the water table.

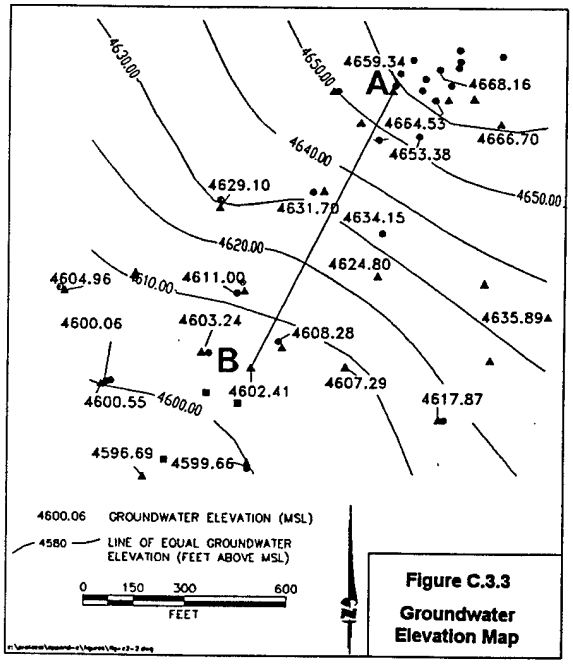



Figure C.3.3
Groundwater Elevation Map

**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:

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

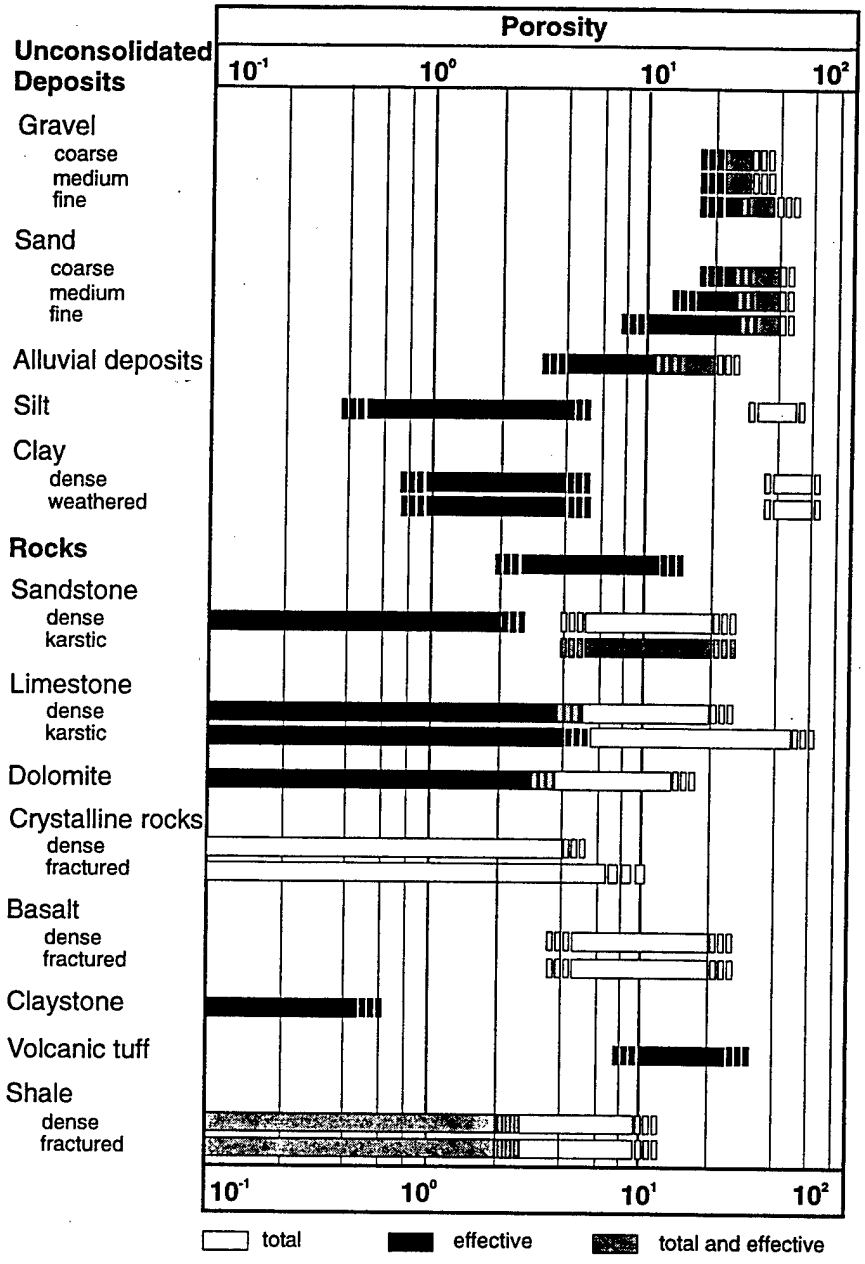
Where: $n_e$ = effective porosity [dimensionless]
$n$ = total porosity [dimensionless]
$S$ = specific retention (unconfined) or storativity (confined) [dimensionless]

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, and these values are also summarized on Figure C.3.4. 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 |




Source: Spitz and Moreno, 1996.

Figure C.3.4

Range of Porosity Values

### 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 $1.7 \times 10^{-1}$ 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
$\rho_b$ = 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 natural attenuation. 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 contaminant plume.

C.3.1.6.1 Bulk Density

The bulk density of a soil, $\rho_b$, 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: $\rho_b$ = 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: $\rho_b$ = bulk density
$n$ = total porosity
$\rho_s$ = density of grains comprising the aquifer

The bulk density is always less than the particle density, $\rho_s$; for example, if pores constitute half the volume, then $\rho_b$ is half of $\rho_s$. 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, $\rho_b$ can be as high as 1.81 gm/cm$^3$. In aggregated loams and clayey soils, $\rho_b$ 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 trichloroethene.

**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 chlorinated solvents and BTEX are obtained from Tables B.2.1 and B.2.2, respectively, and are listed in Table C.3.4.

For trichloroethene the most conservative (i.e., that value giving the highest solute velocity) is $K_{oc}$ = 87 L/kg, and (using equation C.3.13):

$$K_d = \left(87\frac{L}{kg}\right)(0.007) = 0.61\frac{L}{kg}$$

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

$$v_c = \frac{1.9\frac{m}{day}}{1+\frac{\left(1.6\frac{kg}{L}\right)\left(0.61\frac{L}{kg}\right)}{0.4}} = 0.55\frac{m}{day}$$

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 Select 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 |
| Tetrachloroethene | 209 | 0.007 | 1.463 | 1.60 | 0.40 | 6.85 | 1.90 | 0.28 |
| Trichloroethene | 87 | 0.007 | 0.609 | 1.60 | 0.40 | 3.44 | 1.90 | 0.55 |
| cis-1,2-Dichloroethene | 49 | 0.007 | 0.343 | 1.60 | 0.40 | 2.37 | 1.90 | 0.80 |
| Vinyl Chloride | 2.5 | 0.007 | 0.0175 | 1.60 | 0.40 | 1.07 | 1.90 | 1.78 |
| 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 represent a continuing source of groundwater contamination. NAPLs may be made up of one compound, or more likely, a mixture of compounds. Concentrations of dissolved contaminants and the lifetime of NAPL source areas and associated groundwater plumes are ultimately determined by the rate at which contaminants dissolve from the NAPL. When sufficient quantities of NAPL are present, the unsaturated zone may initially be saturated with NAPL, and the NAPL may migrate under the influence of gravity. After a period of time the NAPL may drain from the pores under the influence of gravity, leaving a thin coating of NAPL. Depending on the surface area of the subsurface materials, 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. In residual zones, NAPL will be present in immobile blobs or ganglia that may occupy 10 percent or less of the pore space (Feenstra and Guiguer, 1996). If the NAPL is at saturation and is mobile within and among the

pores of the aquifer matrix, the NAPL is referred to as mobile NAPL. Mobile NAPL may occupy as much as 50 to 70 percent of the pore space and can reduce flow through these zones.

In the unsaturated zone, dissolution from residual or mobile NAPL into downward-migrating precipitation (recharge) will occur, as well as migration and dissolution of vapors. In the saturated zone, dissolution of contaminants from residual NAPL occurs as groundwater flows through the residual zone. Dissolution from mobile NAPL mostly takes place along the tops, bottoms, or lateral margins of the NAPL bodies, because groundwater (or recharge) flow through the NAPL is restricted. Because the distribution of residual NAPL results in a greater surface area of product in contact with groundwater and does not restrict groundwater velocities, concentrations of contaminants entering groundwater will typically be closer to the compounds' equilibrium solubilities than in the case of mobile NAPL bodies. The equilibrium solubility of the compound(s) of interest will depend on the composition of the NAPL (i.e., the molar fraction of the NAPL represented by the compound).

In general, residual and mobile NAPL may be present above or below the water table, but direct dissolution will only occur when NAPL is at or below the capillary fringe. In either case, quantifying the flux of contamination entering groundwater from above or below the water table is a difficult proposition. The processes governing dissolution from NAPLs are complex and depend upon many variables (Feenstra and Guiguer, 1996). Among these variables (in the saturated zone) are the shape of a mobile NAPL body, the contact area between the NAPL and the groundwater, the velocity of the groundwater moving through or past the NAPL, the effect of residual NAPL on the effective porosity of the contact zone, the solubility of the compounds of interest, the relative fractions of the compounds in the NAPL, the diffusion coefficients of the compounds, and the effects of other compounds present in the NAPL. This will be further complicated by any processes in the vadose zone (e.g., volatilization, dissolution from residual NAPL into recharge, or dissolution of vapors into recharge) that also will add contaminant mass to groundwater. Further, as the mass of the NAPL body changes over time, the rate of dissolution will also change. Clearly, given the number of variables that affect the transfer of contaminant mass to groundwater, it is difficult to accurately estimate the flux of contaminants into groundwater. Depending on the intended use of the flux estimate, differing approaches can be used.

If one desires to estimate a source term for a contaminant fate and transport model, one can attempt to estimate the mass loading rate use that estimate as an input parameter. However, this often does not yield model concentrations (dissolved) that are similar to observed concentrations.

As a result, the source in the model often becomes a calibration parameter (Mercer and Cohen, 1990; Spitz and Moreno, 1996). This is because the effects of the source (i.e., the dissolved contaminant plume) are easier to quantify than the actual flux from the source. The frequent need for such a "black box" source term has been borne out during modeling associated with evaluations of natural attenuation of fuel hydrocarbons [following the AFCEE technical protocol (Wiedemeier *et al.*,1995d)] at over 30 US Air Force sites. Use of other methods to calculate source loading for those models often produced model concentrations that differed from observed concentrations by as much as an order of magnitude. From the model, the flux estimate then can be used for estimating source lifetimes or other such calculations.

For other purposes, one can estimate flux using several methods, as summarized by Feenstra and Guiguer (1996). For bodies of mobile LNAPL, this is more practical, because the area of NAPL in contact with groundwater can be estimated from plume/pool dimensions. Where most NAPL is residual, the surface area can be highly variable, and cannot be measured in the field. Laboratory studies to understand and quantify mass transfer from residual NAPL in porous media are in the early stages, and when such mass transfer is modeled, surface area is a calibration parameter with great uncertainty (Abriola, 1996). Most methods of estimating NAPL dissolution rates require an estimate of the contact area, and therefore will contain a great deal of uncertainty. This is one of the main reasons why for purposes of modeling, the "black box" source term is more commonly used.

One reason practitioners want to estimate mass transfer rates is to provide a basis for estimating contaminant source lifetimes, which can affect regulatory decisions and remedial designs. To determine how long it will take for a dissolved contaminant plume to fully attenuate, it is necessary to estimate how fast the contaminants are being removed from the NAPL. In general, it is difficult to estimate cleanup times, so conservative estimates should be made based on NAPL dissolution rates. Predicting the cleanup time for sites with mobile NAPL is especially difficult because residual NAPL will remain after the recoverable mobile NAPL has been removed. Of course, this is all complicated by the many factors that affect dissolution rates as discussed above. Moreover, most methods do not account for changing dissolution rates as a result of NAPL volume loss (and subsequent surface area decrease), preferential partitioning from mixed NAPLs, and the change in porosity (and therefore groundwater velocity) resulting from NAPL dissolution. Finally, the mass of the NAPL present in the subsurface must also be estimated, lending further uncertainty to any calculation of source lifetime.

There are several ways to quantify the mass loading rate from a body of mobile or residual NAPL. Feenstra and Guiguer (1996) present a good summary of some common methods. As noted above, transfer rates calculated from these methods are all dependent upon several parameters, many of which cannot be measured or derived from the literature. This is especially true for residual NAPL. Johnson and Pankow (1992) present a method for estimating dissolution rates from pools of NAPL which contact groundwater over an area that is essentially two-dimensional. Many other dissolution models may be available; however, as noted before, the experimental evidence to support dissolution models is really just starting to be collected. Despite these limitations, some of these models can prove useful, and a selected few are presented (in limited detail) in the following subsections.

If estimating mass flux rates is less important, one can use direct measurement or equilibrium concentration calculations to estimate contaminant source area concentrations. The first method involves directly measuring the concentration of dissolved contaminants in groundwater near the NAPL plume. The second method involves the use of partitioning calculations. These approaches are described in the following sections. This type of data can be useful if it can be demonstrated that the source is not capable of introducing concentrations of compounds of concern that exceed regulatory limits, or that with slight weathering the same results can be expected. Source area concentrations, whether measured or calculated, also may be used to provide calibration targets for transport models in which a "black box" source term is used.

If contaminant concentrations in the residual and mobile NAPL 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 natural attenuation less feasible and will reduce the chance of implementation. In order for natural attenuation 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 NAPL recovery, soil vapor extraction, bioventing, or bioslurping. Because natural weathering processes can be fairly slow, especially in systems where the NAPL dissolves slowly or is inhibited from volatilizing or biodegrading, it will generally be necessary to implement engineered remedial solutions to remove the NAPL or reduce the total mass of residual and dissolved NAPL.

A discussion of estimating source terms for sites contaminated solely with fuel hydrocarbons is presented by Wiedemeier *et al.* (1995d). In general, estimating dissolution rates of individual compounds from fuels is simpler than estimating rates of dissolution from other NAPL mixtures

because there is a great deal of experimental evidence regarding partitioning and equilibrium solubilities of individual compounds from common fuel mixtures. Methods presented in the following subsections can use incorporate such data to reduce some of the uncertainty in source term calculations.

Typical uses of chlorinated solvents (e.g.., degreasing or parts cleaning) and past disposal practices that generally mixed different waste solvents or placed many types of waste solvents in close proximity have resulted in complex and greatly varying NAPL mixtures being released at sites. For mixtures containing other compounds (e.g., either DNAPLs containing multiple chlorinated compounds, or fuel LNAPLs containing commingled chlorinated compounds), the equilibrium solubility of the individual compounds of interest must first be calculated, then that information can be used in the common mass transfer rate calculations. Except in the case of pure solvent spills, therefore, the estimation of dissolution rates is then further complicated by this need to estimate equilibrium solubilities from the mixture.

Because this work focuses largely on saturated-zone processes, vadose zone dissolution processes will not be discussed in any detail. However, this discussion will provide a starting point for estimating source terms for groundwater contaminant fate and transport modeling, as well as for estimating source and plume lifetimes. As a starting point, two basic methods of estimating or measuring equilibrium dissolved contaminant concentrations in the vicinity of NAPL bodies are presented. In addition, methods for estimating fluxes summarized by Feenstra and Guiguer (1996) and presented by Johnson and Pankow (1992) will be briefly summarized.

### 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 near a NAPL plume. The first method involves collecting groundwater samples from near a NAPL lens in monitoring wells. The second method involves collecting samples of mixed NAPL and water from monitoring wells.

#### C.3.2.1.1 Collecting Groundwater Samples From Near the NAPL

This method involves carefully sampling groundwater beneath a floating LNAPL lens or near a DNAPL lens. One way of collecting a groundwater sample from beneath a lens of floating LNAPL or above/adjacent to a DNAPL body involves using a peristaltic pump. For LNAPL, 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. For DNAPL, the tube would be cut to reach 1 to 2 feet above the NAPL. Another useful technique for obtaining such samples 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 NAPL can be used to collect water samples from beneath or above the NAPL.

C.3.2.1.2 Collecting Mixed Groundwater/NAPL Samples

This method involves collecting a sample of groundwater and NAPL 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 above or below 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 for LNAPL. Two or three samples should be collected from different monitoring wells containing NAPL at the site. This test should only be done when it is not possible to collect a discrete sample from above or below the NAPL.

### C.3.2.2 Equilibrium Partitioning Calculations

NAPL present at a site represents a continuing source of contamination because chlorinated solvents, BTEX, and other compounds will partition from the NAPL into the groundwater. In such cases, it is generally necessary to estimate the dissolved concentration of contaminants 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 at the time the groundwater or NAPL samples are collected. Such calculations allow a crude estimation of the impact of continuing sources of contamination on dissolved contaminant 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 contaminant concentrations 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

contaminant concentrations in groundwater above regulatory standards. Such partitioning calculations should be confirmed with a LTM program.

On the other hand, if partitioning calculations indicate that continued dissolution will produce contaminant concentrations exceeding regulatory guidelines, further work will be needed. The contaminant concentrations calculated by equilibrium methods will clearly not provide mass flux estimates that can be used in modeling; again, the "black box" methods will be more useful. Moreover, there is no estimation of the actual mass flux across the entire body of NAPL, and therefore source lifetimes and weathering rates cannot be estimated directly from partitioning data. More advanced calculations, such as those that will be discussed in later sections, are then required, keeping in mind that greater uncertainties will be introduced.

When found in the saturated zone, residual NAPL is extremely difficult to remove. Maximum contaminant concentrations resulting from such partitioning will occur when the groundwater and NAPL reach equilibrium. Assuming that equilibrium is reached gives the most conservative modeling results.

C.3.2.2.1 Equilibrium Partitioning of Contaminants from Mobile NAPL into Groundwater

Because most NAPLs will be a mixture of compounds, the solubilities of those compounds will be lower than the solubility of the individual compound (which is what is most commonly found in the literature). For an organic NAPL mixture, the dissolved concentration of each compound (in equilibrium with the mixture) can be approximated by:

$$C_{sat,m} = X_m C_{sat,p} \qquad \text{eq. C.3.14}$$

Where: $C_{sat,m}$ = Solubility of compound from mixture
$X_m$ = Mole fraction of compound in the mixture
$C_{sat,p}$ = solubility of pure compound

This equilibrium concentration may also be referred to as the effective solubility of the compound from the mixture. Experimental evidence (Banerjee, 1984; Broholm and Feenstra, 1995) have suggested that eq. C.3.14 produces reasonable approximations of effective solubilities for mixtures of structurally similar compounds, and that the relationship works best for binary mixtures of similar compounds. For other mixtures, the error is greater due to the complex solubility relationships created; however, the method is appropriate for many environmental studies for which there are many other uncertainties (Feenstra and Guiguer, 1996).

For complex mixtures (e.g., multiple identified and unidentified solvents, or mixed fuels and solvents), it will be necessary to estimate the weight percent and an average molecular weight of the unidentified fraction of the NAPL before the calculation can be completed. In doing so, it should be remembered that increasing the average molecular weight for the unidentified fraction will produce greater estimated effective solubilities for the identified contaminants. A higher molecular weight for the unidentified fraction will result in a lower mole fraction for that fraction and therefore higher mole fractions (and solubilities) for the known compounds. Feenstra and Guiguer (1996) provide an example of these calculations for a mixture of chlorinated and nonchlorinated compounds.

In the case of fuel hydrocarbon mixtures, experimental partitioning data has been collected and used to develop individual-compound solubility calculations, largely because fuel mixtures are somewhat consistent in their makeup. 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:

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

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$^3$]

A summary of values of $K_{fw}$ for BTEX and trimethylbenzenes (TMB) in jet fuel and gasoline are presented by Wiedemeier *et al.* (1995d), along with the relationships relating $K_{fw}$ to the aqueous solubility of a pure compound in pure water, S, which can be used to estimate $K_{fw}$ for compounds for which there is no experimental data.

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:

$$C_w = \frac{C_f}{K_{fw}} \qquad \text{eq. C.3.16}$$

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. Further discussion and example calculations for this method are presented by Wiedemeier *et al.* (1995d).

### C.3.2.3 Mass Flux Calculations

In general, the rate of mass transfer from a NAPL can be given as the product of a mass transfer coefficient, a concentration difference, and a contact area. As Feenstra and Guiguer (1996) note, the driving force for mass transfer is the concentration difference across a boundary layer between the NAPL and the groundwater. The concentration difference can be approximated using the effective solubility of a compound (eq. C.3.14) and either the measured concentration of the compound in groundwater adjacent to the NAPL, or a calculated (theoretical) groundwater concentration. However, the contact area and the mass transfer coefficient incorporate a great deal of uncertainty and are typically calibration parameters for modeling dissolution, as discussed previously.

Once these parameters have been estimated, one can use them in a variety of models. In general, models for dissolution of NAPL in porous media either assume local equilibrium between phases, or assume that dissolution is a first-order process governed by the variables discussed above (Feenstra and Guiguer, 1996). Abriola and Pinder (1985a and 1985b), Baehr and Corapcioglu (1987), and Kaluarachchi and Parker (1990) developed two-dimensional NAPL migration models that account for dissolution using the local equilibrium assumption (LEA). As noted by Abriola (1996), these studies generally were computer modeling studies for which follow-up laboratory work is ongoing and uncovering additional factors to consider. For single-component NAPLs, models utilizing a first-order reaction have been developed by Miller *et al.* (1990), Powers *et al.* (1992), Brusseau (1992), Guiguer (1993), and Guiguer and Frind (1994). For multi-component NAPLs, a model developed by Shiu *et al.* (1988) and Mackay *et al.* (1991) may be of use.

Due to approximate nature of flux calculations and the inherent uncertainty in those calculations, we have chosen to omit a detailed discussion of such efforts. The numerical modeling using LEA methods is beyond the scope of this work, and may not be practical for use at most sites. Instead, we will present a brief review of ideas presented by Feenstra and Guiguer (1996) and Johnson and Pankow (1992) in order to illustrate some of the concepts involved in estimating flux terms. Should further detail or other methods be desired, both of those works provide excellent background and references to start with, including many of the works referenced in this discussion of source term calculations.

C.3.2.3.1 General Mass Transfer Models

Using concepts from the field of chemical engineering, Feenstra and Guiguer (1996) note that for a single-component NAPL, simple dissolution of the compound may be described by:

$$N = K_c(C_w - C_{sat}) \qquad \text{eq. C.3.17}$$

Where: $N$ = flux of the species of interest ($M/L^2T$)
$K_c$ = mass transfer coefficient (L/T)
$C_w$ = concentration of compound in bulk aqueous phase ($M/L^3$)
$C_{sat}$ = concentration of compound at NAPL-water interface (taken as the solubility of the compound) ($M/L^3$)

The mass transfer coefficient may be calculated various ways, but in all cases, the diffusivity of the species of interest is a factor. Feenstra and Guiguer (1996) present three methods for determining a mass transfer coefficient.

In a porous media, the mass transfer rate per volume of porous medium can be defined by multiplying the mass flux by the ratio of NAPL surface contact area to the unit volume of porous medium, yielding:

$$N^* = \lambda(C_w - C_{sat}) \qquad \text{eq. C.3.18}$$

Where: $N^*$ = flux of the species of interest per unit volume of porous medium ($M/L^2T$)
$\lambda$ = lumped mass transfer coefficient (L/T)
$C_w$ = concentration of compound in bulk aqueous phase ($M/L^3$)
$C_{sat}$ = concentration of compound at NAPL-water interface (taken as the solubility of the compound) ($M/L^3$)

The lumped mass transfer coefficient is the product of $K_c$ and the ratio of the NAPL surface contact area and the unit volume of the porous media. This can further be extended for multicomponent NAPLs :

$$N_m^* = \lambda_m(C_{w,m} - C_{sat,m}) \qquad \text{eq. C.3.19}$$

Where: $N_m^*$ = flux of component $m$ per unit volume of porous medium ($M/L^2T$)
$\lambda_m$ = lumped mass transfer coefficient for component $m$ (L/T)
$C_{w,m}$ = concentration of component $m$ in bulk aqueous phase ($M/L^3$)

$C_{sat,m}$ = concentration of component *m* at NAPL-water interface (calculated using eq. C.3.14) ($M/L^3$)

Further complicating all of these relationships is the fact that as dissolution continues, $\lambda_m$ will vary over time as the amount of NAPL changes. This can be accounted by using the following first-order relation:

$$N_m = S_w \lambda_m (C_{sat,m} - C_{w,m}) \qquad \text{eq. C.3.20}$$

Where:
$N_m$ = flux of component *m* per unit volume of porous medium ($M/L^2T$)
$S_w$ = average fraction of pore volume occupied by water
$\lambda_m$ = lumped mass transfer coefficient for component *m* (L/T)
$C_{w,m}$ = concentration of component *m* in bulk aqueous phase ($M/L^3$)
$C_{sat,m}$ = concentration of component *m* at NAPL-water interface (calculated using eq. C.3.14)) ($M/L^3$)

Again, it bears repeating that on the field scale, measurement of many of the parameters used for these calculations is not possible, and therefore great uncertainty is introduced. Source terms calculated using these or any other methods should be presented in that light, and if used for solute transport modeling, should be accompanied with a sensitivity analysis.

C.3.2.3.2 Nonequilibrium Partitioning Model of Johnson and Pankow (1992)

The steady-state, two-dimensional dissolution of contaminants 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):

$$v_x \frac{\partial C}{\partial x} = D_z \frac{\partial^2 C}{\partial z^2} \qquad x,z > 0 \qquad \text{eq. C.3.21}$$

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):

$$M_a = C_e n_e \sqrt{\frac{4 D_z v_x}{\pi L}} \qquad \text{eq. C.3.22}$$

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):

$$D_z = D_e + v_x \alpha_z \qquad \text{eq. C.3.23}$$

Where: $D_e$ = effective molecular diffusivity (corrected for porosity and tortuosity)
$\alpha_z$ = 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 $1 \times 10^{-5}$ $cm^2/sec$ (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).

## 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 Data Set Normalization

In order to accurately calculate biodegradation rates, measured contaminant concentrations must be normalized for the effects of dispersion, dilution, and sorption. A convenient way to do this is to use compounds or elements associated with the contaminant plume that are relatively unaffected or predictably affected by biologic processes occurring within the aquifer. At sites where commingled fuel hydrocarbon and chlorinated solvent plumes are present, the trimethylbenzene isomers, which can be biologically recalcitrant under some geochemical conditions have proven useful when estimating biodegradation rates for BTEX and chlorinated solvents. At sites where TMB data are not available, the chloride produced as a result of biodegradation or the carbon nucleus of the chlorinated compound can be used as a tracer.

Measured tracer and contaminant concentrations from a minimum of two points along a flow path can be used to estimate the amount of contaminant remaining at each point if biodegradation had been the only attenuation process operating to reduce contaminant concentrations. The fraction of contaminant remaining as a result of all attenuation processes can be computed from the measured contaminant concentrations at two adjacent points. The fraction of contaminant remaining as a result of non-destructive attenuation mechanisms only, can be estimated from the tracer concentrations at the same two points, because an ideal tracer is affected by non-destructive attenuation mechanisms to the same degree as the contaminant of interest and is not affected by biologic processes. The following equation uses these assumptions to solve for the estimated downgradient contaminant concentration if biodegradation had been the only attenuation process operating between two points ($i$ and $i$-1) along the flow path:

$$C_{i,corr} = C_{i-1,corr}\left(\frac{C_i}{C_{i-1}}\right)\left(\frac{T_{i-1}}{T_i}\right) \qquad \text{eq. C.3.24}$$

where: $C_{i,corr}$=corrected contaminant concentration at point $i$

$C_{i\text{-}1,corr}$=corrected contaminant concentration at point $i$-1. (If point $i$-1 is the first or most upgradient point, $C_{i\text{-}1,corr}$ is equivalent to the observed contaminant concentration.)

$C_i$=observed contaminant concentration at point $i$

$C_{i-1}$=observed contaminant concentration at point $i$-1

$T_i$=observed tracer concentration at point $i$

$T_{i-1}$=observed tracer concentration at point $i$-1

This equation can be used to estimate the theoretical contaminant concentration resulting from biodegradation alone for every point along a flow path on the basis of the measured contaminant concentration at the origin and the contaminant/tracer ratios between consecutive points along the flow path. This series of normalized concentrations can then be used to estimate a first-order rate of biodegradation as described in Section C.3.3.3.1.1. If, rather than for a series of points, an estimate of the biodegradation rates between only two points (A and B) is desired equation C.3.24 simplifies to:

$$C_{B,corr} = C_B\left(\frac{T_A}{T_B}\right) \qquad \text{eq. C.3.25}$$

C.3.3.2.1 Normalization Using Organic Compounds as Tracers

A convenient way of estimating biodegradation rate constants is to use compounds present in the dissolved contaminant plume that that are biologically recalcitrant. 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) are generally present in sufficient quantities in fuel mixtures to be readily detectable when dissolved in groundwater. In addition, the TMB isomers are fairly recalcitrant to biodegradation under anaerobic conditions; however, the TMB isomers do not make good tracers under aerobic conditions (because they are readily biodegraded in aerobic environments). The degree of recalcitrance of TMB is site-specific, and the use of this compound as a tracer must be evaluated on a case-by-case basis. Nevertheless, if any TMB mass is lost to biodegradation, equation C.3.24 will be conservative because the calculated mass losses and the attenuation rate constants calculated on the basis of those losses will be lower than the actual losses and attenuation rates (see also Section C.3.3.2.4.1). Another compound of potential use as a conservative tracer is tetramethylbenzene; however, detectable dissolved tetramethylbenzene concentrations are generally less common than detectable dissolved TMB concentrations.

An ideal tracer would have Henry's Law and soil sorption coefficients identical to the contaminant of interest; however, TMB is more hydrophobic than BTEX, chlorinated ethenes,

and chlorinated ethanes, resulting in a higher soil sorption coefficient. This causes preferential sorption of TMB, and an increase in the coefficient of retardation for dissolved TMB in the aquifer. Therefore, for these compounds it is advisable to modify equation C.3.24, to account for the difference in contaminant and tracer velocity resulting from the higher soil sorption and consequent retardation of TMB. Without this modification, using TMB as a tracer can be so conservative that estimated biodegradation rates can be negative.

When the tracer migrates at a velocity that is significantly slower than the compound of interest, it is more important to evaluate contaminant and tracer concentrations after equal travel times rather than equal travel distances, as assumed in equation C.3.24. The equal time assumption ensures that both the contaminant and tracer are more equally affected by dilution/dispersion and sorption, which are the two dominant non-destructive attenuation mechanisms in most systems. The ratio of tracer velocity to contaminant velocity can be used to switch from equal travel distances to equal travel times as follows:

$$\frac{V_t}{V_c} = \left(\frac{V_{gw}}{R_t}\right) / \left(\frac{V_{gw}}{R_c}\right) = \frac{R_c}{R_t} \qquad \text{eq. C.3.26}$$

Where: $V_t$=Velocity of tracer
$V_c$=Velocity of contaminant
$V_{gw}$=Velocity of groundwater
$R_t$=Coefficient of retardation for the tracer
$R_c$=Coefficient of retardation for the contaminant

The fraction of tracer lost over the time required for the contaminant to travel between points $i$-1 and $i$ is represented by the expression $R_c/R_t(1-T_i/T_{i-1})$ which is the product of the fraction of tracer lost between travel points and the ratio of retardation factors. Therefore, the fraction of tracer remaining is $1-R_c/R_t(1-T_i/T_{i-1})$. As discussed earlier in this section, the fraction of contaminant remaining after biodegradation is equivalent to the fraction of contaminant remaining as a result of all attenuation processes divided by the fraction of tracer remaining as a result of only non-destructive attenuation processes. Therefore, the corrected concentration at point $i$ can be represented by the following equation:

$$C_{i,corr} = C_{i-1,corr}\left(\frac{C_i}{C_{i-1}}\right)\left(\frac{1}{\left(1-\frac{R_c}{R_t}\left(1-\frac{T_i}{T_{i-1}}\right)\right)}\right) \qquad \text{eq. C.3.27}$$

where: $C_{i,corr}$=corrected contaminant concentration at point *i*

$C_{i-1,corr}$=corrected contaminant concentration at point *i*-1. (If point *i*-1 is the first or most upgradient point, $C_{i-1,corr}$ is equivalent to the observed contaminant concentration.)

$C_i$=observed contaminant concentration at point *i*

$C_{i-1}$=observed contaminant concentration at point *i*-1

$T_i$=observed tracer concentration at point *i*

$T_{i-1}$=observed tracer concentration at point *i*-1

Note: This assumes that $R_t/R_c + T_i/T_{i-1} > 1$.

When $R_c$ is equivalent to $R_t$, this equation reduces to equation C.3.24.

C.3.3.2.2 Normalization Using Inorganics as Tracers

Inorganic compounds also can serve as tracers for the contaminant of interest as long as their presence is in some way associated (either directly or indirectly) with the dissolved contaminant plume. For may chlorinated solvent plumes, the sum of ionic chloride and organic chloride associated with the solvents can be considered a conservative tracer. Note that the following discussion assumes that the background chloride concentration is negligible in comparison to the source area concentration of total chloride plus chlorine. If background chloride is more than approximately 10 percent of the total source area chloride plus chlorine concentration, then background concentrations will need to be accounted for prior to performing the tracer normalization.

Total chlorine can easily be calculated by multiplying the measured concentration of a chlorinated organic compound by the mass fraction of chlorine in the molecule, then summing that quantity for all the chlorinated organic compounds represented in the plume. The stoichiometry for chlorinated ethenes follows in the following paragraphs.

As PCE is reduced to ethene, 4 moles of chloride are produced:

$$C_2Cl_4 \rightarrow C_2H_4 + 4Cl^-$$

On a mass basis, the ratio of chloride produced to PCE degraded is given by:

| | | |
|---|---|---|
| Molecular weights: | PCE | 2(12.011) + 4(35.453) = 165.83 gm |
| | Chloride | 4(35.453) = 141.81 gm |

Mass Ratio of Chloride to PCE = 141.81:165.83 = 0.86:1

Similarly, as TCE is reduced to ethene, 3 moles of chloride are produced:

$$C_2Cl_3H \rightarrow C_2H_4 + 3Cl^-$$

On a mass basis, the ratio of chloride produced to TCE degraded is given by:

| | | |
|---|---|---|
| Molecular weights: | TCE | 2(12.011) + 3(35.453) + 1(1.01)= 131.39 gm |
| | Chloride | 3(35.453) = 106.36 gm |

Mass Ratio of Chloride to TCE = 106.36:131.39 = 0.81:1

Likewise, as DCE is reduced to ethene, 2 moles of chloride are produced:

$$C_2Cl_2H_2 \rightarrow C_2H_4 + 2Cl^-$$

On a mass basis, the ratio of chloride produced to DCE degraded is given by:

| | | |
|---|---|---|
| Molecular weights: | DCE | 2(12.011) + 2(35.453) + 2(1.01)= 96.95 gm |
| | Chloride | 2(35.453) = 70.9 gm |

Mass Ratio of Chloride to DCE = 70.9:96.95 = 0.73:1

As VC is reduced to ethene, 1 mole of chloride is produced

$$C_2ClH_3 \rightarrow C_2H_4 + Cl^-$$

On a mass basis, the ratio of chloride produced to VC degraded is given by:

| | | |
|---|---|---|
| Molecular weights: | VC | 2(12.011) + 1(35.453) + 3(1.01)= 62.51 gm |
| | Chloride | 1(35.453) = 35.453 gm |

Mass Ratio of Chloride to VC = 35.453:62.51 = 0.57:1

Therefore, the amount of total chloride plus chlorine for a PCE spill undergoing reductive dechlorination would be estimated as:

$$Cl_{Total} = 0.86(PCE) + 0.81(TCE) + 0.73(DCE) + 0.57(VC) \qquad \text{eq. C.3.28}$$

The approach is illustrated in the data set from the fire protection training pit plume at Plattsburgh AFB. At location A near the source of the plume (see map --) in August 1995, the concentrations of chloride, TCE, total DCE, and vinyl chloride were 63, 25.3, 51.4, and 0 mg/L, respectively. This results in an up-gradient tracer concentration of

| | | |
|---|---|---|
| Chloride | | 63 mg/L |
| TCE chlorine | + | (0.809)(25.3 mg/L) |
| DCE chlorine | + | (0.731)(51.4 mg/L) |
| Vinyl chloride chlorine | + | (0.567)(0.0 mg/L) |
| Total chloride plus chlorine | = | 121 mg/L |

At downgradient location B, in August 1995, the concentrations of chloride, TCE, total DCE, and vinyl chloride were 48, 0.002, 15.0, and 0.90 mg/L, respectively. This results in a down gradient concentration of

| | | |
|---|---|---|
| Chloride | | 48 mg/L |
| TCE chlorine | + | (0.809)(0.002 mg/L) |
| DCE chlorine | + | (0.731)(15 mg/L) |
| Vinyl chloride chlorine | + | (0.567)(0.90 mg/L) |
| Total chloride plus chlorine | = | 59 mg/L |

The computed series of total chloride plus chlorine concentrations can be used with equation C.3.24 to estimate a normalized data set for contaminant concentrations.

C.3.3.2.3 Normalization Using Total Ethenes as a Tracer

A third tracer method that can be used with chlorinated solvent plumes involves tracking the carbon core of the chlorinated compounds in relation to chlorine. During reductive dechlorination the source chlorinated solvent undergoes successive transformations involving the replacement of a chlorine atom by a hydrogen atom; however, the carbon core of both the parent and daughter compound remain unchanged (i.e., no carbon bonds are broken). The carbon core is subject to

the same non-destructive attenuation mechanisms that act on the larger chlorinated molecule, but it is unaffected by biologically mediated reductive dechlorination. For this reason, tracking the carbon core of dissolved chlorinated solvents can serve as a theoretically perfect "tracer" for biodegradation via reductive dechlorination. Because biodegradation processes other than reductive dechlorination may operate on lower-molecular weight chlorinated solvents (e.g., DCE and VC), the total biodegradation rate may be higher than estimated by this tracer method for reductive dechlorination alone. The following discussion focuses on the application of this technique to chlorinated ethenes; however, this technique can be applied to any chain of chlorinated compounds and daughter products (such as chlorinated ethanes or chlorinated benzenes) that can be reductively dechlorinated.

In order to use the carbon core of the chlorinated source and daughter compounds as a "tracer" for reductive dechlorination, the molar concentrations of carbon and chlorine must be calculated for each point along a flow path. For chlorinated ethenes, the molar carbon concentration is calculated by multiplying the number of carbon atoms per molecule of chlorinated ethene (2) by the sum of the molar concentrations for PCE, TCE, DCE, VC, and ethene:

$$Mc_i = 2\,(M_{PCE,i} + M_{TCE,i} + M_{DCE,i} + M_{VC,i} + M_{Ethene,i}) \qquad \text{eq. C.3.29}$$

Where: $Mc_i$ = molar carbon concentration
$M_{PCE,i}$ = molar concentration of PCE at point $i$
$M_{TCE,i}$ = molar concentration of TCE at point $i$
$M_{DCE,i}$ = molar concentration of DCE at point $i$
$M_{VC,i}$ = molar concentration of VC at point $i$
$M_{Ethene,i}$ = molar concentration of ethene at point $i$

The total organic chlorine is defined as the sum of the products of molar concentration and chlorine atoms per molecule for each source and daughter compound. For the chlorinated ethenes, the number of chlorine atoms per molecule are 4 for PCE, 3 for TCE, 2 for DCE, 1 for VC, and 0 for ethene:

$$TOX_i = (M_{PCE,i}*4) + (M_{TCE,i}*3) + (M_{DCE,i}*2) + M_{VC,i} \qquad \text{eq. C.3.30}$$

Where: $TOX_i$ = molar organic chlorine concentration

Using equation C.3.24 substituting $Mc$ for tracer concentrations and $TOX$ for observed contaminant concentrations, yields the theoretical total CAH concentrations at downgradient

locations if reductive dechlorination had been the only natural attenuation process operating along the flow path. The same process can be used to determine the theoretical chlorine equivalents. The normalized CAH concentrations are useful for comparison to other techniques; the normalized molar chlorine concentrations simplify visualization of the reductive dechlorination rate. Either the normalized total CAH concentrations or normalized molar chlorine concentrations can be used to calculate identical first-order rates for dechlorination. Remember that a rate for reductive dechlorination is considered a lower-bound estimate for the total biodegradation rate.

**Example C.3.5: Normalizing Total CAH Data Along a Flow Path**

Given the observed concentrations of PCE, TCE, DCE, VC, ethene, TMB, Chloride, and dissolved oxygen provided in Table C.3.? for five points (A through E) that form a line parallel to the direction of groundwater flow, calculate normalized data sets for total CAH using the TMB, chloride, and carbon core methods to normalize for non-destructive attenuation processes.

**Table C.3.?**

To be provided in future revisions

**Solution:**

To be provided in future revisions.

### C.3.3.3 Calculating Biodegradation Rates

Several methodologies, including first- and second-order approximations, may be used to estimate the rate of biodegradation of chlorinated compounds when they are being used to oxidize other organic compounds. Use of the first-order approximation can be appropriate to estimate biodegradation rates for chlorinated compounds where the rate of biodegradation is assumed to be controlled solely by the concentration of the contaminant. However, the use of a first-order approximation may not be appropriate when more than one substrate is limiting microbial degradation rates or when microbial mass is increasing or decreasing. In such cases a second- or higher-order approximation may provide a better estimate of biodegradation rates.

C.3.3.2.2 First-Order Decay

As with a large number of processes, the change in a solute's concentration in groundwater over time often can be described using a first-order rate constant. A first-order approximation, if appropriate, has the advantage of being easy to calculate and simplifying fate and transport modeling of complex phenomenon. 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 normalized data set 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 with respect to BTEX biodegradation. Table C.3.5 lists representative first-order decay rate constants for chlorinated compounds.

*C.3.3.2.4.1 Use of a Normalized Data Set*

In order to ensure that observed decreases in contaminant concentrations can be attributed to biodegradation, measured contaminant concentrations must be corrected for the effects of advection, dispersion, dilution from recharge, and sorption, as described in Section C.3.3.2 using equation C.3.24. The corrected concentration of a compound is the concentration that would be expected at one point (B) located downgradient from another point (A) if the processes of dispersion, dilution from recharge, volatilization, and sorption had not been occurring between points A and B.

## Table C.3.5

Representative First-Order Biodegradation Rate Constants

| Compound | First-order Biodegradation Rate Constant ($day^{-1}$) | Notes | Reference |
|---|---|---|---|
| PCE | 0.00068 to 0.00079 | PCE to TCE; field-scale | Ellis *et al.*, 1996 |
| | 0.02 | microcosm | Parson *et al.*, 1984 |
| | 0.054 | anaerobic | Bouwer and McCarty, 1983 |
| | | | |
| TCE | 0.00082 to 0.0047 | field-scale | Weaver *et al.*, 1996 |
| | 0.0005 | field-scale dechlorination rate | Swanson *et al.*, 1996 |
| | 0.002 to 0.006 | field-scale | Gorder *et al.*, 1996 |
| | 0.0001 to 0.003 | microcosm | Wilson *et al.*, 1991 |
| | 0.0033 to 0.0038 | field-scale | Ehlke *et al.*, 1994 |
| | 0.00088 | field-scale | Benker *et al.*, 1994 |
| | 0.0019 | field-scale | Lee *et al.*, 1995 |
| | 0.0030 | field-scale | Cox *et al.*, 1995 |
| | 0.0033 to 0.0049 | microcosm | Haston *et al.*, 1994 |
| | 0.0049 | microcosm | Wilson *et al.*, 1990 |
| | 0.010 | microcosm | Wilson *et al.*, 1996 |
| | 0.0011 to 0.0016 | field-scale | Wilson *et al.*, 1996 |
| | 0.00063 to 0.0035 | field-scale | Wiedemeier *et al.*, 1996c |
| | 0.00045 to 0.00079 | TCE to DCE; field-scale | Ellis *et al.*, 1996 |
| | 0.0006 to 0.0007 | field-scale | Dupont *et al.*, 1996 |
| | 0.0077 to 0.021 | microcosm | Barrio-Lage et al., 1987 |
| | 0.29 | anaerobic microcosm | Fogel *et al.*, 1986 |
| | 0.0078 | anaerobic microcosms | Wilson *et al.*, 1986 |
| | | | |
| DCE | 0.00016 to 0.0025 | field-scale | Wiedemeier *et al.*, 1996c |
| | 0.00068 to 0.0014 | DCE to VC; field-scale | Ellis *et al.*, 1996 |
| | | | |
| 1,2-DCE | 0.009 | microcosm | Wilson *et al.*, 1986 |
| | 0.29 | microcosm | Fogel *et al.*, 1986 |
| | | | |
| *cis*-1,2-DCE | 0.00071 to 0.0090 | field-scale | Weaver *et al.*, 1996 |
| | 0.0005 | field-scale dechlorination rate | Swanson *et al.*, 1996 |
| | 0.0014 to 0.0044 | field-scale | Ehlke *et al.*, 1994 |
| | 0.0024 | field-scale | Cox *et al.*, 1995 |
| | 0.0085 to 0.026 | microcosm | Wilson *et al.*, 1991 |
| | 0.0012 to 0.0018 | field-scale | Wilson et al., 1996 |
| | 0.002 to 0.0078 | anaerobic; scale not specified | Barbee, 1994* |
| | | | |
| *trans*-1,2-DCE | 0.009 | | Tabak *et al.*, 1981 |
| | 0.005 | microcosm | Wilson *et al.*, 1982 |
| | | | |

**Table C.3.5** (continued)
Representative First-Order Biodegradation Rate Constants

| Compound | First-order Biodegradation Rate Constant ($day^{-1}$) | Notes | Reference |
|---|---|---|---|
| VC | 0.00041 to 0.0071 | field-scale | Weaver *et al.*, 1996 |
| | 0.0085 | field-scale | Cox *et al.*, 1995 |
| | 0.012 | aerobic microcosm | Davis and Carpenter, 1990 |
| | 0.00003 | anaerobic microcosm | Barrio-Lage *et al.*, 1990 |
| | 0.00038 to 0.0013 | field-scale | Wiedemeier *et al.*, 1996c |
| | 0.00086 to 0.0010 | VC to ethene; field-scale | Ellis *et al.*, 1996 |
| | | | |
| TCA | 0.0099 | anaerobic microcosm | Parsons *et al.*, 1985 |
| | | | |
| 1,1,1-TCA | 1.98 | anaerobic microcosm | Bouwer and McCarty., 1983 |
| | 0.0033 to 0.0035 | anaerobic microcosm | Klecka *et al.*, 1990 |
| | >0.69 | TCA to 1,1-DCA; anaerobic microcosm | Vogel and McCarty, 1987 |
| | | | |
| 1,1-DCA | <<0.12 | 1,1-DCA to CA in microcosm | Vogel and McCarty, 1987 |
| | 0.0044 | microcosm | Wilson *et al.*, 1982 |
| | 0.0048 to 0.011 | microcosm | Henson *et al.*, 1989 |
| | | | |
| 1,2-DCA | 0.0019 to 0.0069 | microcosm | Henson *et al.*, 1989 |
| | | | |
| CT | 0.025 to 0.1 | anaerobic; scale not specified | Barbee, 1994* |
| | | | |
| CF | 0.042 | | Parson *et al.*, 1984 |
| | 0.0062 to 0.25 | anaerobic microcosms | Saunders and Maltby, 1996 |
| | | | |
| Chlorobenzene | 0.0059 | | Wilson *et al.*, 1983 |
| | 0.0029 | | Wilson *et al.*, 1982 |
| | | | |
| DCB | 0.0059 to 0.011 | field-scale; anaerobic | Stauffer *et al.*, 1994 |
| | | | |

The biodegradation rate can be estimated between any two points (A and B) of a normalized data set (where point A is upgradient of point B) by substituting the normalized concentration at point A, $C_{A,corr}$, for $C_0$, and the normalized concentration at point B, $C_{B,corr}$, for C in equation C.3.42. The resulting relationship is expressed as:

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

Where: $C_{B,corr}$ = normalized contaminant concentration at downgradient point B (from eq. C.3.25)
$C_{A,corr}$ = normalized contaminant concentration at upgradient point A (from eq. C.3.25). Note that if point A if the first point in the normalized data set, then $C_A = C_{A,corr}$
$\lambda$ = first-order biological decay rate (first-order rate constant) [1/T]
t = time of contaminant travel between points A and B

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:

$$\lambda = -\frac{\ln\left(\frac{C_{B,corr}}{C_{A,corr}}\right)}{t} \qquad \text{eq. C.3.34}$$

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]

The simplest way to determine the first-order rate constant from an entire set of normalized data is to make a log-linear plot of normalized contaminant concentrations 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 normalized data, x is the downgradient contaminant travel time 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.3.6: First-Order Decay Rate Constant Calculation Using Normalized Data Set**

Calculate first-order decay rate constants for total CAHs using each of the normalized data sets computed for example C.3.5. The site has an average gradient of ???, an average hydraulic conductivity of ???, an assumed effective porosity of ???, an average organic carbon content of ???, and an estimated soil/water partitioning coefficient for CAH of ???.

**Solution:**

The solution will be completed in future revisions.

An accurate first-order biological decay rate can be calculated only if it can be shown that biodegradation is a first-order process. Normalized contaminant concentrations must first be plotted on log-linear paper to ensure that biodegradation is a first order process.

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. Using the data presented above, the average retarded contaminant velocity at the site is ?? 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.?. Dissolved oxygen was observed in points D and E used in this example; therefore, anaerobic processes are prevalent only between points A, B, and C.

*C.3.3.2.2.2 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: $\lambda$ = first-order biological decay rate
$v_c$ = retarded contaminant velocity in the x-direction
$\alpha_x$ = 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.3.7: First-Order Rate Constant Calculation Using Method of Buscheck and Alcantar (1995)**

Calculate first-order decay rate constant for total CAH, TCE, and DCE using the data provided for example C.3.5. The site has an average gradient of ???, an average hydraulic conductivity of ???, an assumed effective porosity of ???, an average organic carbon content of ???, an estimated longitudinal dispersivity of ??, and an estimated soil/water partitioning coefficient for CAH of ???.

**Solution:**

The solution will be completed in future revisions.

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. Using linear regression, the ratio k/v is determined and entered into equation C.3.?. 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.?? and the biodegradation rate constant, $\lambda$, is calculated. 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.3.3.2.2.3 Comparison of First-Order Methods*

To be provided in future revisions.

## 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, or 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.

Microcosm studies are often used to provide a third line of evidence. The potential for biodegradation of the contaminants of interest can be confirmed by the use of microcosms, through comparison of removals in the living treatments with removals in the controls. Microcosm studies also permit an absolute mass balance determination based on biodegradation of the contaminants of interest. Further, the appearance of daughter products in the microcosms can be used to confirm biodegradation of the parent compound.

### C.3.4.2 When to Use Microcosms

There are two fundamentally different applications of microcosms. They are frequently used in a qualitative way to illustrate the important processes that control the fate of organic contaminants. They are also used to estimate rate constants for biotransformation of contaminants that can be used in a site-specific transport and fate model of a plume of contaminated groundwater. This paper only discusses microcosms for the second application.

Microcosms should be used when there is no other way to obtain a rate constant for attenuation of contaminants, in particular, when it is impossible to estimate the rate of attenuation from data from monitoring wells in the plume of concern. There are situations where it is impossible to compare concentrations in monitoring wells along a flow path due to legal or physical impediments. In many landscapes, the direction of groundwater flow (and water table elevations in monitoring wells) can vary over short periods of time due to tidal influences or changes in barometric pressure. The direction of groundwater flow may also be affected by changes in the stage of a nearby river or pumping wells in the vicinity. These changes in groundwater flow direction do not allow simple snap-shot comparisons of concentrations in monitoring wells because of uncertainties in identifying the flow path. Rate constants from microcosms can be used with average flow conditions to estimate attenuation at some point of discharge or point of compliance.

### C.3.4.3 Application of Microcosms

The primary objective of microcosm studies is to obtain rate constants applicable to average flow conditions. These average condition can be determined by continuous monitoring of water table elevations in the aquifer being evaluated. The product of the microcosm study and the continuous monitoring of water table elevations will be a yearly or seasonal estimate of the extent of attenuation along average flow paths. Removals seen at field scale can be attributed to biological activity. If removals in the microcosms duplicate removal at field scale, the rate constant can be used for risk assessment purposes.

### C.3.4.4 Selecting Material for Study

Prior to choosing material for microcosm studies, the location of major conduits of groundwater flow should be identified and the geochemical regions along the flow path should be determined. The important geochemical regions for natural attenuation of chlorinated aliphatic hydrocarbons are regions that are actively methanogenic; regions that exhibit sulfate

reduction and iron reduction concomitantly; and regions that exhibit iron reduction alone. The pattern of biodegradation of chlorinated solvents varies in different regions. Vinyl chloride tends to accumulate during reductive dechlorination of TCE or PCE in methanogenic regions (Weaver *et al.*, 1995; Wilson *et al.*, 1995); it does not accumulate to the same extent in regions exhibiting iron reduction and sulfate reduction (Chapelle, 1996). In regions showing iron reduction alone, vinyl chloride is consumed but dechlorination of PCE, TCE, or DCE may not occur (Bradley and Chapelle, 1996). Core material from each geochemical region in major flow paths represented by the plume must be acquired, and the hydraulic conductivity of each depth at which core material is acquired must be measured. If possible, the microcosms should be constructed with the most transmissive material in the flow path.

Several characteristics of groundwater from the same interval used to collect the core material should be determined. These characteristics include temperature, redox potential, pH, and concentrations of oxygen, sulfate, sulfide, nitrate, ferrous iron, chloride, methane, ethane, ethene, total organic carbon, and alkalinity. The concentrations of compounds of regulatory concern and any breakdown products for each site must be determined. The groundwater should be analyzed for methane to determine if methanogenic conditions exist and for ethane and ethene as daughter products. A comparison of the groundwater chemistry from the interval where the cores were acquired to that in neighboring monitoring wells will demonstrate if the collected cores are representative of that section of the contaminant plume.

Reductive dechlorination of chlorinated solvents requires an electron donor to allow the process to proceed. The electron donor could be soil organic matter, low molecular weight organic compounds (lactate, acetate, methanol, glucose, etc.), $H_2$, or a co-contaminant such as landfill leachate or petroleum compounds (Bouwer, 1994; Sewell and Gibson, 1991; Klecka *et al.*, 1996). In many instances, the actual electron donor(s) may not be identified.

Several characteristics of the core material should also be evaluated. The initial concentration of the contaminated material (on a mass per mass basis) should be identified prior to construction of the microcosms. Also, it is necessary to know if the contamination is present as a nonaqueous phase liquid (NAPL) or in solution. A total petroleum hydrocarbon (TPH) analysis will determine if any hydrocarbon-based oily materials are present. The water-filled porosity is a parameter generally used to extrapolate rates to the field. It can be calculated by comparing wet and dry weights of the aquifer material.

To insure sample integrity and stability during acquisition, it is important to quickly transfer the aquifer material into a jar, exclude air by adding groundwater, and seal the jar without headspace. The material should be cooled during transportation to the laboratory. Incubate

the core material at the ambient groundwater temperature in the dark before the construction of microcosms.

At least one microcosm study per geochemical region should be completed. If the plume is over one kilometer in length, several microcosm studies per geochemical region may need to be constructed.

### C.3.4.5 Geochemical Characterization of the Site

The geochemistry of the subsurface affects behavior of organic and inorganic contaminants, inorganic minerals, and microbial populations. Major geochemical parameters that characterize the subsurface encompasses (1) pH; (2) ORP; (3) alkalinity; (4) physical and chemical characterization of the solids; (5) temperature; (6) dissolved constituents, including electron acceptors; and (7) microbial processes. The most important of these in relation to biological processes are redox potential, alkalinity, concentration of electron acceptor, and chemical nature of the solids.

Alkalinity: Field indications of biologically active portions of a plume may be identified by increased alkalinity, compared to background wells, from carbon dioxide due to biodegradation of the pollutants. Increases in both alkalinity and pH have been measured in portions of an aquifer contaminated by gasoline undergoing active utilization of the gasoline components (Cozzarelli *et al.*, 1995). Alkalinity can be one of the parameters used when identifying where to collect biologically active core material.

pH: Bacteria generally prefer a neutral or slightly alkaline pH level with an optimum pH range for most microorganisms between 6.0 and 8.0; however, many microorganisms can tolerate a pH range of 5.0 to 9.0. Most groundwaters in uncontaminated aquifers are within these ranges. Natural pH values may be as low as 4.0 or 5.0 in aquifers with active oxidation of sulfides, and pH values as high as 9.0 may be found in carbonate-buffered systems (Chapelle, 1993). However, pH values as low as 3.0 have been measured for groundwaters contaminated with municipal waste leachates which often contain elevated concentrations of organic acids (Baedecker and Back, 1979). In groundwaters contaminated with sludges from cement manufacturing, pH values as high as 11.0 have been measured (Chapelle, 1993).

ORP: The ORP of groundwater is a measure of electron activity that indicates the relative ability of a solution to accept or transfer electrons. Most redox reactions in the subsurface are microbially catalyzed during metabolism of native organic matter or contaminants. The only elements that are predominant participants in aquatic redox processes are carbon, nitrogen,

oxygen, sulfur, iron, and manganese (Stumm and Morgan, 1981). The principal oxidizing agents in groundwater are oxygen, nitrate, sulfate, manganese (IV), and iron (III). Biological reactions in the subsurface both influence and are affected by the redox potential and the available electron acceptors. The redox potential changes with the predominant electron acceptor, with reducing conditions increasing through the sequence oxygen, nitrate, iron, sulfate, and carbonate. The redox potential decreases in each sequence, with methanogenic (carbonate as the electron acceptor) conditions being most reducing. The interpretation of redox potentials in groundwaters is difficult (Snoeyink and Jenkins, 1980). The potential obtained in groundwaters is a mixed potential that reflects the potential of many reactions and cannot be used for quantitative interpretation (Stumm and Morgan, 1981). The approximate location of the contaminant plume can be identified in the field by measurement of the redox potential of the groundwater.

To overcome the limitations imposed by traditional redox measurements, recent work has focused on the measurement of molecular hydrogen to accurately describe the predominant *in situ* redox reactions (Chapelle *et al.*, 1995; Lovley *et al.*, 1994; Lovley and Goodwin, 1988). The evidence suggests that concentrations of $H_2$ in groundwater can be correlated with specific microbial processes, and these concentrations can be used to identify zones of methanogenesis, sulfate reduction, and iron reduction in the subsurface (Chapelle, 1996).

Electron Acceptors: Measurement of the available electron acceptors is critical in identifying the predominant microbial and geochemical processes occurring *in situ* at the time of sample collection. Nitrate and sulfate are found naturally in most groundwaters and will subsequently be used as electron acceptors once oxygen is consumed. Oxidized forms of iron and manganese can be used as electron acceptors before sulfate reduction commences. Iron and manganese minerals solubilize coincidently with sulfate reduction, and their reduced forms scavenge oxygen to the extent that strict anaerobes (some sulfate reducers and all methanogens) can develop. Sulfate is found in many depositional environments, and sulfate reduction may be very common in many contaminated groundwaters. In environments where sulfate is depleted, carbonate becomes the electron acceptor with methane gas produced as an end product.

Temperature: The temperature at all monitoring wells should be measured to determine when the pumped water has stabilized and is ready for collection. Below approximately 30 feet, the temperature in the subsurface is fairly consistent on an annual basis. Microcosms should be stored at the average *in situ* temperature. Biological growth can occur over a wide

range of temperatures, although most microorganisms are active primarily between 10°C and 35°C (50°F to 95°F).

Chloride: Reductive dechlorination results in the accumulation of inorganic chloride. In aquifers with a low background of inorganic chloride, the concentration of inorganic chloride should increase as the chlorinated solvents are degraded. The sum of the inorganic chloride plus the contaminant being degraded should remain relatively consistent along the groundwater flow path.

Tables C.3.6 and C.3.7 list the geochemical parameters, contaminants, and daughter products that should be measured during site characterization for natural attenuation. The tables include the analyses that should be performed, the optimum range for natural attenuation of chlorinated solvents, and the interpretation of the value in relation to biological processes.

**Table C.3.6**

**Geochemical Parameters**

| Analysis | Range | Interpretation |
|---|---|---|
| Redox Potential | <50 millivolt against Ag/AgCl | Reductive pathway possible |
| Sulfate | <20 mg/L | Competes at higher concentrations with reductive pathway |
| Nitrate | <1 mg/L | Competes at higher concentrations with reductive pathway |
| Oxygen | <0.5 mg/L | Tolerated, toxic to reductive pathway at higher concentrations |
| Oxygen | >1 mg/L | Vinyl chloride oxidized |
| Iron (II) | >1 mg/L | Reductive pathway possible |
| Sulfide | >1 mg/L | Reductive pathway possible |
| Hydrogen | >1 nM | Reductive pathway possible, vinyl chloride may accumulate |
| Hydrogen | <1 nM | Vinyl chloride oxidized |
| pH | 5 < pH < 9 | Tolerated range |

### C.3.4.6 Microcosm Construction

During construction of the microcosms, it is best if all manipulations take place in an anaerobic glovebox. These gloveboxes exclude oxygen and provide an environment where the integrity of the core material may be maintained, since many strict anaerobic bacteria are sensitive to oxygen. Stringent aseptic precautions not necessary for microcosm construction. It is more important to maintain anaerobic conditions of the aquifer material and solutions added to the microcosm bottles.

**Table C.3.7**
**Contaminants and Daughter Products**

| Analysis | Interpretation |
|---|---|
| PCE | Material spilled |
| TCE | Material spilled or daughter product of PCE |
| 1,1,1-TCA | Material spilled |
| *cis*-1,2-DCE | Daughter product of TCE |
| *trans*-1,2-DCE | Daughter product of TCE |
| Vinyl Chloride | Daughter product of dichloroethylenes |
| Ethene | Daughter product of vinyl chloride |
| Ethane | Daughter product of ethene |
| Methane | Ultimate reductive daughter product |
| Chloride | Daughter product of organic chlorine |
| Carbon Dioxide | Ultimate oxidative daughter product |
| Alkalinity | Results from interaction of carbon dioxide with aquifer minerals |

The microcosms should have approximately the same ratio of solids to water as the *in situ* aquifer material, with a minimum or negligible headspace. Most bacteria in the subsurface are attached to the aquifer solids. If a microcosm has an excess of water, and the contaminant is primarily in the dissolved phase, the bacteria must consume or transform a great deal more

contaminant to produce the same relative change in the contaminant concentration. As a result, the kinetics of removal at field scale will be underestimated in the microcosms.

A minimum of three replicate microcosms for both living and control treatments should be constructed for each sampling event. Microcosms sacrificed at each sampling interval are preferable to microcosms that are repetitively sampled. The compounds of regulatory interest should be added at concentrations representative of the higher concentrations found in the geochemical region of the plume being evaluated. The compounds should be added as a concentrated aqueous solution. If an aqueous solution is not feasible, dioxane or acetonitrile may be used as solvents. Avoid carriers that can be metabolized anaerobically, particularly alcohols. If possible, use groundwater from the site to prepare dosing solutions and to restore water lost from the core barrel during sample collection.

For long term microcosm studies, autoclaving is the preferred method for sterilization. Nothing available to sterilize core samples works perfectly. Mercuric chloride is excellent for short term studies (weeks or months). However, mercuric chloride complexes to clays, and control may be lost as it is sorbed over time. Sodium azide is effective in repressing metabolism of bacteria that have cytochromes, but is not effective on strict anaerobes.

The microcosms should be incubated in the dark at the ambient temperature of the aquifer. It is preferable that the microcosms be incubated inverted in an anaerobic glovebox. Anaerobic jars are also available that maintain an oxygen-free environment for the microcosms. Dry redox indicator strips can be placed in the jars to assure that anoxic conditions are maintained. If no anaerobic storage is available, the inverted microcosms can be immersed in approximately two inches of water during incubation. Teflon-lined butyl rubber septa are excellent for excluding oxygen and should be used if the microcosms must be stored outside an anaerobic environment.

The studies should last from one year to eighteen months. The residence time of a plume may be several years to tens of years at field scale. Rates of transformation that are slow in terms of laboratory experimentation may have a considerable environmental significance. A microcosm study lasting only a few weeks to months may not have the resolution to detect slow changes that are of environmental significance. Additionally, microcosm studies often distinguish a pattern of sequential biodegradation of the contaminants of interest and their daughter products.

### C.3.4.7 Microcosm Interpretation

As a practical matter, batch microcosms with an optimal solids/water ratio, that are sampled every two months in triplicate, for up to eighteen months, can resolve biodegradation from abiotic losses with a detection limit of 0.001 to 0.0005 per day. Rates determined from replicated batch microcosms are found to more accurately duplicate field rates of natural attenuation than column studies. Many plumes show significant attenuation of contamination at field calibrated rates that are slower than the detection limit of microcosms constructed with that aquifer material. Although rate constants for modeling purposes are more appropriately acquired from field-scale studies, it is reassuring when the rates in the field and the rates in the laboratory agree.

The rates measured in the microcosm study may be faster than the estimated field rate. This may not be due to an error in the laboratory study, particularly if estimation of the field-scale rate of attenuation did not account for regions of preferential flow in the aquifer. The regions of preferential flow may be determined by use of a downhole flow meter or by other methods for determining hydraulic conductivity in one- to two-foot sections of the aquifer.

Statistical comparisons can determine if removals of contaminants of concern in the living treatments are significantly different from zero or significantly different from any sorption that is occurring. Comparisons are made on the first-order rate of removal, that is, the slope of a linear regression of the natural logarithm of the concentration remaining against time of incubation for both the living and control microcosm. These slopes (removal rates) are compared to determine if they are different, and if so, extent of difference that can be detected at a given level of confidence.

### C.3.4.8 The Tibbetts Road Case Study

The Tibbetts Road Superfund Site in Barrington, N.H., a former private home, was used to store drums of various chemicals from 1944 to 1984. The primary groundwater contaminants in the overburden and bedrock aquifers were benzene and TCE, with respective concentrations of 7,800 $\mu$g/L and 1,100 $\mu$g/L. High concentrations of arsenic, chromium, nickel, and lead were also found.

Material collected at the site was used to construct a microcosm study evaluating the removal of benzene, toluene, and TCE. This material was acquired from the most contaminated source at the site, the waste pile near the origin of Segment A (Figure C.3.5). Microcosms were incubated for nine months. The aquifer material was added to 20-mL

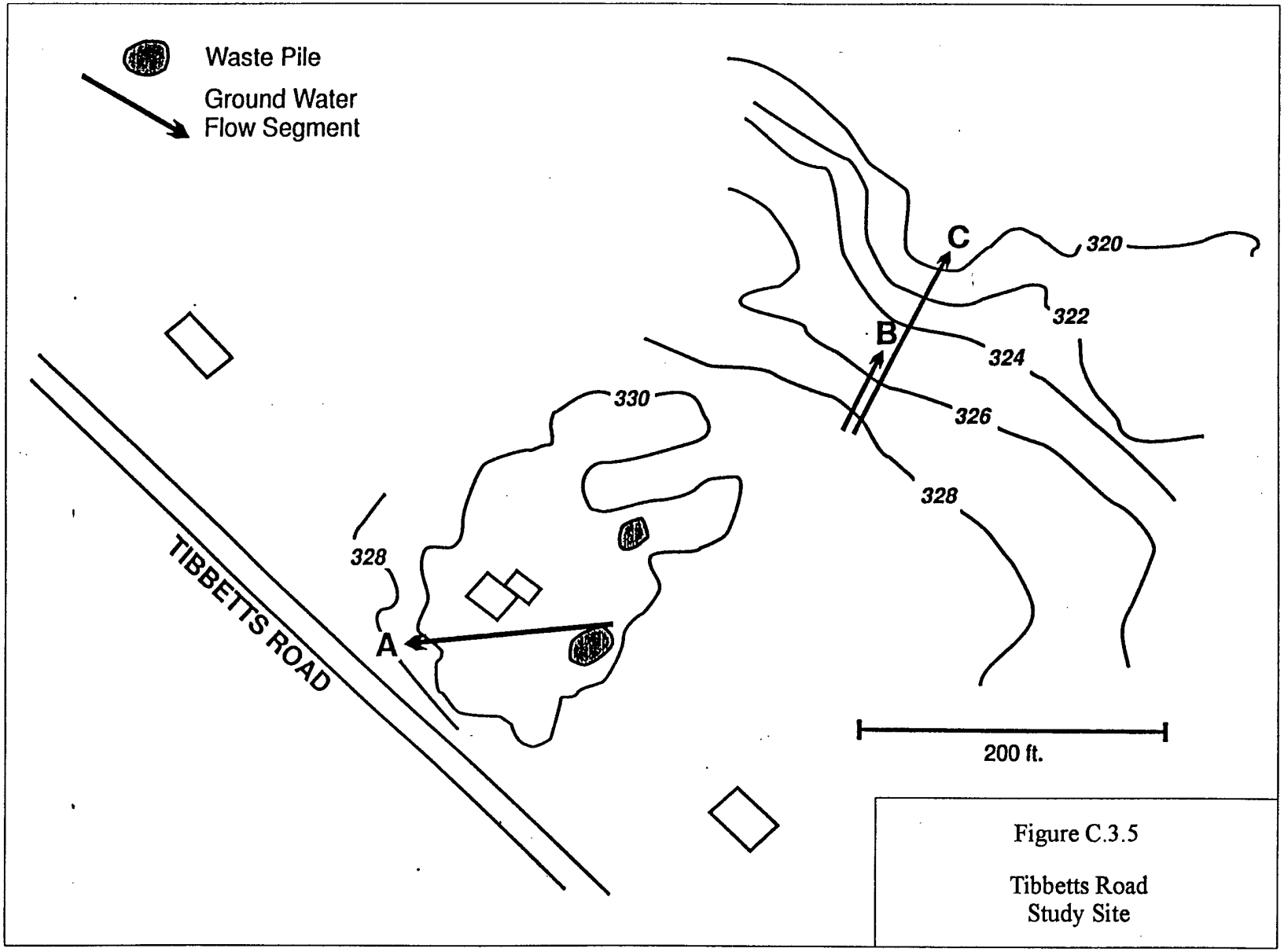



Figure C.3.5

Tibbetts Road
Study Site

headspace vials, dosed with 1 mL of spiking solution, capped with a Teflon-lined, gray butyl rubber septa, and sealed with an aluminum crimp cap. Controls were prepared by autoclaving the material used to construct the microcosms overnight. Initial concentrations for benzene, toluene, and TCE were, respectively, 380 μg/L, 450 μg/L, and 330 μg/L. The microcosms were thoroughly mixed by vortexing, then stored inverted in the dark at the ambient temperature of 10°C.

The results (Figures C.3.6, C.3.7, and C.3.8; Table C.3.8) show that significant biodegradation of both petroleum aromatic hydrocarbons and the chlorinated solvent had occurred. Significant removal in the control microcosms also occurred for all compounds. The data exhibited more variability in the living microcosms than in the control treatment, which is a pattern that has been observed in other microcosm studies. The removals observed in the controls are probably due to sorption; however, this study exhibited more sorption than typically seen.

The rate constants determined from the microcosm study for the three compounds are shown in Table C.3.9. The appropriate rate constant to be used in a model or a risk assessment would be the first-order removal in the living treatment minus the first-order removal in the control, in other words the removal that is in excess of the removal in the controls.

The first-order removal in the living and control microcosms was estimated as the linear regression of the natural logarithm of concentration remaining in each microcosm in each treatment against time of incubation. Student's t-distribution with *n-2* degrees of freedom was used to estimate the 95% confidence interval. The standard error of the difference of the rates of removal in living and control microcosms was estimated as the square root of the sum of the squares of the standard errors of the living and control microcosms, with *n-4* degrees of freedom (Glantz, 1992).

Table C.3.10 presents the concentrations of organic compounds and their metabolic products in monitoring wells used to define line segments in the aquifer for estimation of field-scale rate constants. Wells in this aquifer showed little accumulation of *trans*-1,2-DCE; 1,1-DCE; vinyl chloride; or ethene, although removals of TCE and *cis*-1,2-DCE were extensive. This can be explained by the observation (Bradley and Chapelle, 1996) that iron-reducing bacteria can rapidly oxidize vinyl chloride to carbon dioxide. Filterable iron accumulated in groundwater in this aquifer.

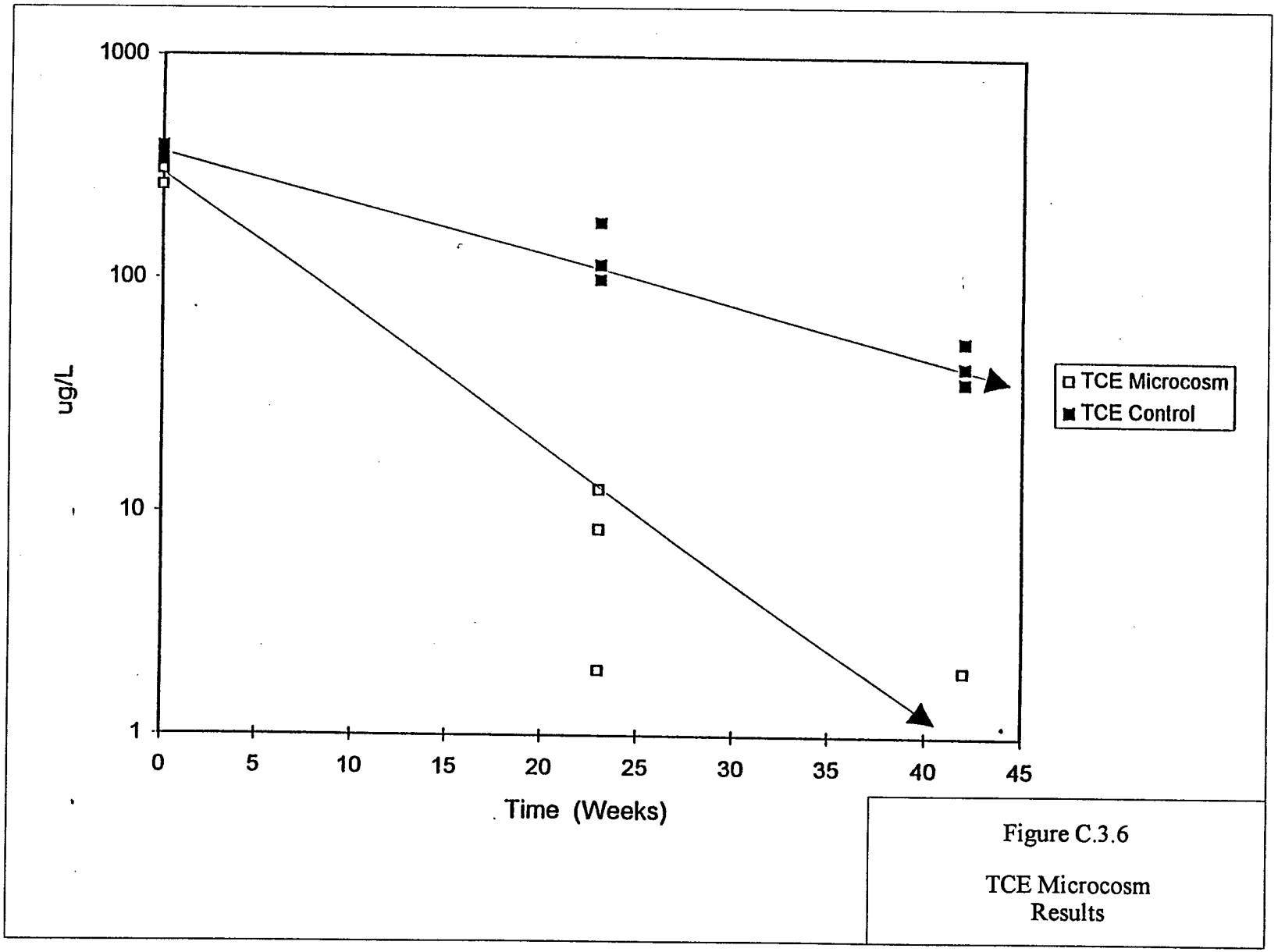



Figure C.3.6

TCE Microcosm Results

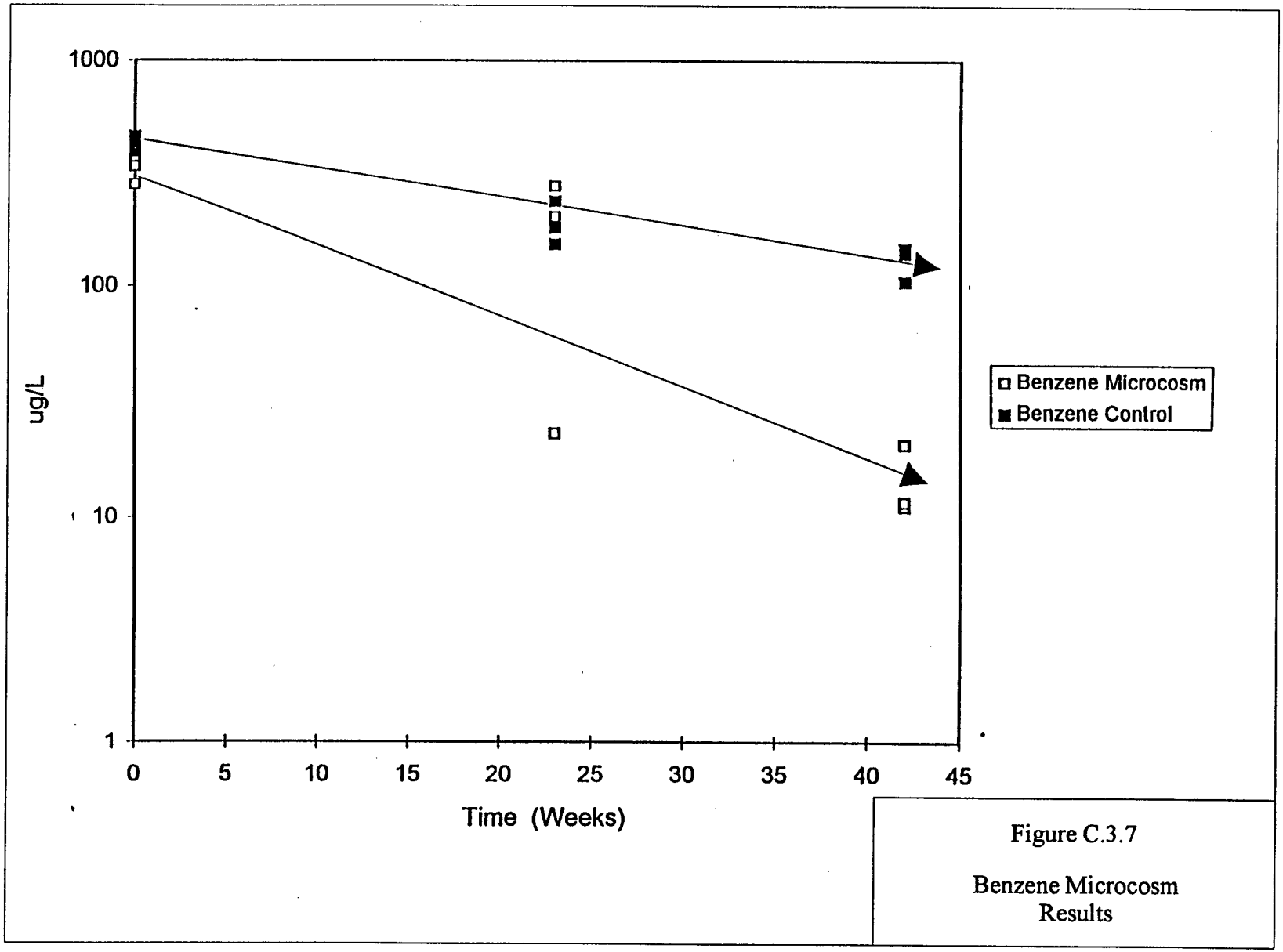



Figure C.3.7

Benzene Microcosm Results

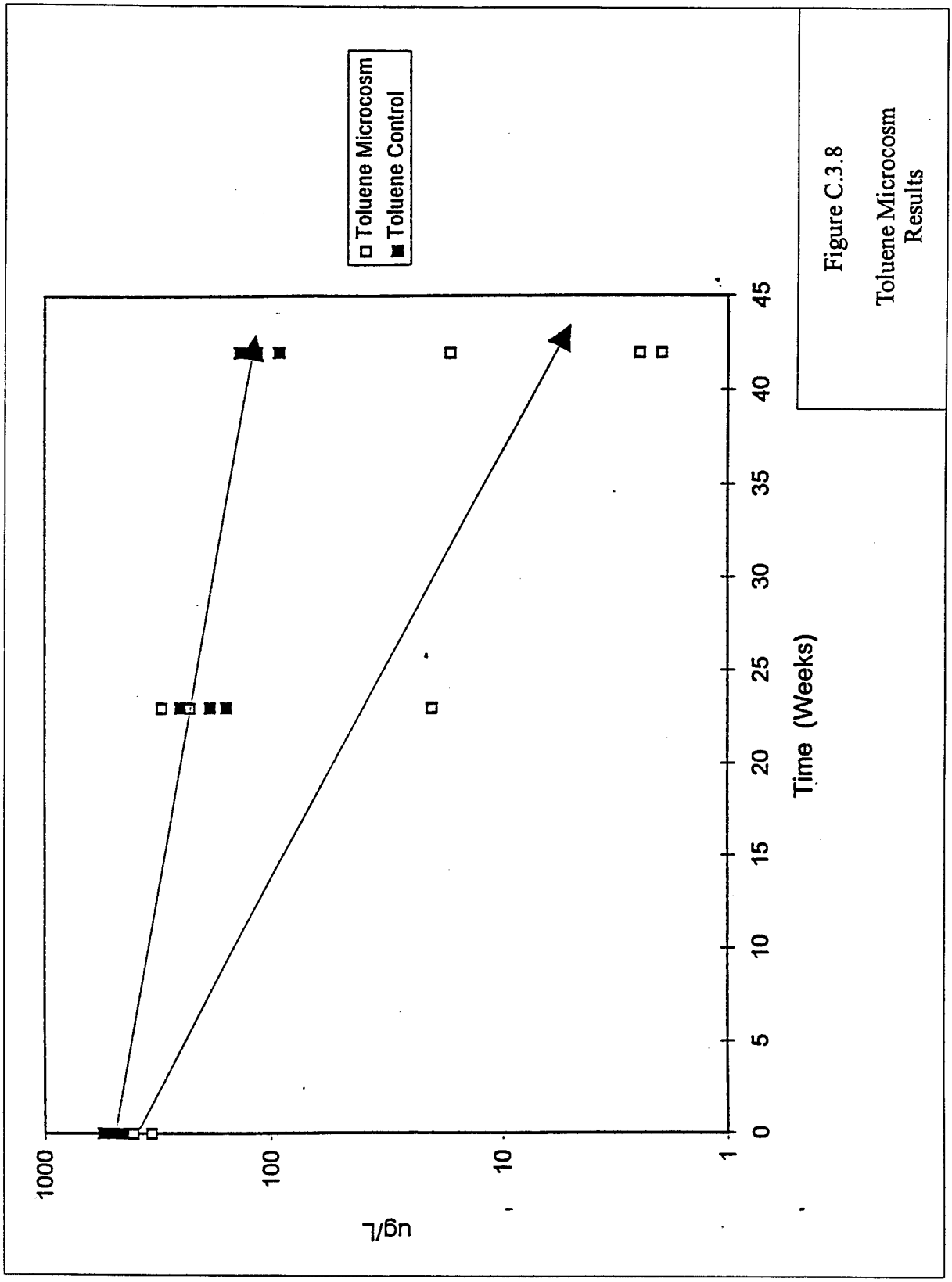



Figure C.3.8
Toluene Microcosm
Results

## Table C.3.8

## Concentrations of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms

| Compound | Time Zero Microcosms | Time Zero Controls | Week 23 Microcosms | Week 23 Controls | Week 42 Microcosms | Week 42 Controls |
|---|---|---|---|---|---|---|
| TCE | 328 | 337 | 1 | 180 | 2 | 36.3 |
| | 261 | 394 | 12.5 | 116 | 2 | 54.5 |
| | 309 | 367 | 8.46 | 99.9 | 2 | 42.3 |
| Mean ± Standard Deviation | 299 ± 34.5 | 366 ± 28.5 | 7.32 ± 5.83 | 132 ± 42.4 | 2.0 ± 0.0 | 44.4 ± 9.27 |
| | | | | | | |
| Benzene | 366 | 396 | 201 | 236 | 11.1 | 146 |
| | 280 | 462 | 276 | 180 | 20.5 | 105 |
| | 340 | 433 | 22.8 | 152 | 11.6 | 139 |
| Mean ± Standard Deviation | 329 ± 44.1 | 430 ± 33.1 | 167 ± 130 | 189 ± 42.8 | 14.4 ± 5.29 | 130 ± 21.9 |
| | | | | | | |
| Toluene | 443 | 460 | 228 | 254 | 2 | 136 |
| | 342 | 557 | 304 | 185 | 2.5 | 92 |
| | 411 | 502 | 19.9 | 157 | 16.6 | 115 |
| Mean ± Standard Deviation | 399 ± 51.6 | 506 ± 48.6 | 184 ± 147 | 199 ± 49.9 | 7.03 ± 8.29 | 114 ± 22.0 |

## Table C.3.9

**First-order Rate Constants for Removal of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms**

| Parameter | Living Microcosms | Autoclaved Controls | Removal Above Controls |
|---|---|---|---|
| | First-order Rate of Removal (per year) | | |
| TCE | 6.31 | 2.62 | 3.69 |
| 95% Confidence Interval | ± 2.50 | ± 0.50 | ± 2.31 |
| Minimum Rate Significant at 95% Confidence | | | 1.38 |
| | | | |
| Benzene | 3.87 | 1.51 | 2.36 |
| 95% Confidence Interval | ± 1.96 | ± 0.44 | ± 1.83 |
| Minimum Rate Significant at 95% Confidence | | | 0.53 |
| | | | |
| Toluene | 5.49 | 1.86 | 3.63 |
| 95% Confidence Interval | ± 2.87 | ± 0.45 | ± 2.64 |
| Minimum Rate Significant at 95% Confidence | | | 0.99 |

## Table C.3.10

**Concentrations of Contaminants and Metabolic By-products in Monitoring Wells along Segments in the Plume used to Estimate Field-scale Rate Constants**

| Parameter | Segment A | | Segment B | | Segment C | |
|---|---|---|---|---|---|---|
| Monitoring Well | 80S | 79S | 70S | 52S | 70S | 53S |
| | Upgradient | Down-gradient | Up-gradient | Down-gradient | Up-gradient | Down-gradient |
| | ----------($\mu$g/liter)---------- | | | | | |
| TCE | 200 | 13.7 | 710 | 67 | 710 | 3.1 |
| *cis*-1,2-DCE | 740 | 10.9 | 220 | 270 | 220 | 2.9 |
| *trans*-1,2-DCE | 0.41 | <1 | 0.8 | 0.3 | 0.8 | <1 |
| 1,1-DCE | 0.99 | <1 | <1 | 1.6 | <1 | <1 |
| Vinyl Chloride | <1 | <1 | <1 | <1 | <1 | <1 |
| Ethene | <4 | <4 | 7 | <4 | 7 | <4 |
| Benzene | 510 | 2.5 | 493 | 420 | 493 | <1 |
| Toluene | 10000 | <1 | 3850 | 900 | 3850 | <1 |
| *o*-Xylene | 1400 | 8.4 | 240 | 71 | 240 | <1 |
| *m*-Xylene | 2500 | <1 | 360 | 59 | 360 | <1 |
| *p*-Xylene | 1400 | 22 | 1100 | 320 | 1100 | <1 |
| Ethylbenzene | 1300 | 0.7 | 760 | 310 | 760 | <1 |
| Methane | 353 | 77 | 8 | 3 | 8 | <2 |
| Iron | | | | | | 27000 |

The extent of attenuation from well to well listed in Table C.3.10, and the travel time between wells in a segment (Figure C.3.4) were used to calculate first-order rate constants for each segment (Table C.3.11). Travel time between monitoring wells was calculated from site-specific estimates of hydraulic conductivity and from the hydraulic gradient. In the area sampled for the microcosm study, the estimated Darcy flow was 2.0 feet per year. With an

estimated porosity in this particular glacial till of 0.1, this corresponds to a plume velocity of 20 feet per year.

### C.3.4.9 Summary

Table C.3.12 compares the first-order rate constants estimated from the microcosm studies to the rate constants estimated at field scale. The agreement between the independent estimates of rate is good; indicating that the rates can appropriately be used in a risk assessment. The rates of biodegradation documented in the microcosm study could easily account for the disappearance of trichloroethylene, benzene, and toluene observed at field scale. The rates estimated from the microcosm study are several-fold higher than the rates estimated at field scale. This may reflect an underestimation of the true rate in the field. The estimates of plume velocity assumed that the aquifer was homogeneous. No attempt was made in this study to correct the estimate of plume velocity for the influence of preferential flow paths. Preferential flow paths with a higher hydraulic conductivity than average would result in a faster velocity of the plume, thus a lower residence time and faster rate of removal at field scale.

**Table C.3.11**

**First-order Rate Constants in Segments of the Tibbetts Road Plume**

| Flow Path Segments in Length and Time of Groundwater Travel | | | |
|---|---|---|---|
| | **Segment A**<br>**130 feet = 6.5 years** | **Segment B**<br>**80 feet = 4.0 years** | **Segment C**<br>**200 feet = 10 years** |
| **Compound** | **First-order Rate Constants in Segments ( per year)** | | |
| TCE | 0.41 | 0.59 | 0.54 |
| *cis*-1,2-DCE | 0.65 | produced | 0.43 |
| Benzene | 0.82 | 0.04 | >0.62 |
| Toluene | >1.42 | 0.36 | >0.83 |
| *o*-Xylene | 0.79 | 0.30 | >0.55 |
| *m*-Xylene | >1.20 | 0.45 | >0.59 |
| *p*-Xylene | 0.64 | 0.31 | >0.70 |
| Ethylbenzene | 1.16 | 0.22 | >0.66 |

## Table C.3.12

## Comparison of First-order Rate Constants in a Microcosm Study, and in the Field at the Tibbetts Road NPL Site

| Parameter | Microcosms Corrected for Controls | | Field Scale | | |
|---|---|---|---|---|---|
| | Average Rate | Minimum Rate Significant at 95% Confidence | Segment A | Segment B | Segment C |
| | ----------First-order Rate (per year)---------- | | | | |
| Trichloroethylene | 3.69 | 1.38 | 0.41 | 0.59 | 0.54 |
| Benzene | 2.36 | 0.53 | 0.82 | 0.04 | >0.62 |
| Toluene | 3.63 | 0.99 | >1.42 | 0.36 | >0.83 |

# APPENDIX D

# MODELING THE FATE AND TRANSPORT OF CONTAMINANTS DISSOLVED IN GROUNDWATER

# TABLE OF CONTENTS - APPENDIX D


INTRODUCTION ..... D1-1

D.1.1 MATHEMATICAL EXPRESSIONS USED TO DESCRIBE SOLUTE TRANSPORT AND REMEDIATION BY NATURAL ATTENUATION ..... D1-2

D.1.1.1 One-Dimensional Reactive Solute Transport ..... D1-2

D.1.1.2 Two-Dimensional Reactive Solute Transport ..... D1-3

D.1.1.3 Three-Dimensional Reactive Solute Transport ..... D1-4

D.1.2 ANALYTICAL VERSUS NUMERICAL MODELS AND MODEL SELECTION ..... D1-4

D.1.3 IS A MODEL REALLY NECESSARY? ..... D1-10

MODEL DEVELOPMENT AND IMPLEMENTATION ..... D2-1

D.2.1 DATA COLLECTION ..... D2-1

D.2.2 CONCEPTUAL MODEL ..... D2-2

D.2.3 SELECTION OF ANALYTICAL SOLUTION OR NUMERICAL CODE ..... D2-3

D.2.4 MODEL SETUP ..... D2-5

D.2.4.1 Model Domain ..... D2-6

D.2.4.2 Discretization ..... D2-6

D.2.4.2.1 Model Grid Orientation and Spacing ..... D2-7

D.2.4.2.2 Time Discretization ..... D2-8

D.2.4.3 Initial Conditions ..... D2-9

D.2.4.3.1 Groundwater Flow ..... D2-10

D.2.4.3.2 Solute Transport ..... D2-10

D.2.4.4 Boundary Conditions ..... D2-11

D.2.4.4.1 First-Type Boundary Condition (Dirichlet, Specified-Head or -Concentration) ..... D2-15

D.2.4.4.1.1 Groundwater Flow (Specified-Head Boundary) ..... D2-15

D.2.4.4.1.2 Solute Transport (Specified-Concentration) ..... D2-16

D.2.4.4.2 Second-Type Boundary Condition (Neumann, Specified-Flux) ..... D2-17

D.2.4.4.2.1 Groundwater Flow (Specified-Flux) ..... D2-17

D.2.4.4.2.2 Solute Transport (Specified Concentration Gradient) ..... D2-19

D.2.4.4.3 Third-Type Boundary Condition (Cauchy, Variable-Flux) ..... D2-20

D.2.4.4.3.1 Groundwater Flow (Head-Dependent Flux Boundary) ..... D2-20

D.2.4.4.3.2 Solute Transport (Concentration-Dependent Concentration Gradient) ..... D2-21

D.2.5 MODEL CALIBRATION ..... D2-21
D.2.5.1 Groundwater Flow Calibration ..... D2-23
D.2.5.2 Calibrating the Model to Contaminant Distribution ..... D2-24
D.2.6 SENSITIVITY ANALYSIS ..... D2-26
D.2.7 PREDICTION ..... D2-27
D.2.8 MODEL DOCUMENTATION AND REPORTING ..... D2-28
D.2.9 POST-MODEL MONITORING, VERIFICATION, AND ADJUSTMENT .. D2-28
D.2.9.1 Monitoring Networks ..... D2-30
D.2.9.1.1 Long-Term Monitoring Wells ..... D2-31
D.2.9.1.2 Point-of-Compliance Wells ..... D2-31

ANALYTICAL SOLUTE TRANSPORT MODELS ..... D3-1
D.3.1 INITIAL AND BOUNDARY CONDITIONS FOR ANALYTICAL SOLUTE TRANSPORT MODELS ..... D3-2
D.3.1.1 Upgradient (Inflow) Boundary Conditions ..... D3-2
D.3.1.2 Downgradient (Outflow) Boundary Conditions ..... D3-3
D.3.1.3 Lateral and Vertical Boundary Conditions ..... D3-3
D.3.2 ONE-DIMENSIONAL ANALYTICAL MODELS ..... D3-4
D.3.2.1 Semi-infinite System with Constant Source ..... D3-5
D.3.2.2 Semi-infinite System with Decaying Source ..... D3-8
D.3.3 TWO-DIMENSIONAL ANALYTICAL MODELS ..... D3-9
D.3.3.1 Continuous Source ..... D3-10
D.3.4 THREE-DIMENSIONAL ANALYTICAL MODELS ..... D3-10
D.3.4.1 Continuous Source ..... D3-11
D.3.4.2 Decaying Source ..... D3-12
D.3.5 COMPUTER APPLICATIONS FOR ANALYTICAL MODELING ..... D3-13

NUMERICAL MODELS ..... D4-1
D.4.1 OVERVIEW OF NUMERICAL MODELS ..... D4-1
D.4.2 APPLICABLE MODEL CODES ..... D4-2

## FIGURES


| No. | Title | Page |
|---|---|---|
| D.1.1 | Decision Process for Model Selection | D1-9 |
| D.2.1 | Graphical Presentation of Conceptual Models | D2-4 |
| D.2.2 | Examples of Flow Model Boundary Conditions | D2-13 |
| D.2.3 | Examples of Transport Boundary Conditions | D2-14 |
| D.2.4 | Example Plot of Calibrated versus Observed Heads | D2-25 |
| D.2.5 | Example Table of Contents | D2-29 |


## TABLES


| No. | Title | Page |
|---|---|---|
| D.2.1 | Common Designations for Several Important Boundary Conditions | D2-11 |
| D.3.1 | Analytical Models Commonly used to Simulate Solute Transport | D3-2 |
| D.3.2 | Overview of Upgradient Boundary Conditions used to Simulate the Addition of Contaminants to a Hydrogeologic System | D3-3 |
| D.3.3 | Table of Error Functions | D3-6 |
| D.3.4 | Listing of Analytical Solute Transport Models | D3-14 |
| D.4.1 | Listing of Numerical Groundwater Flow and Solute Transport Models | D4-4 |

# SECTION D-1

# INTRODUCTION

A solute fate and transport model (possibly coupled with a groundwater flow model) provides the user with a tool that is useful for many aspects of an evaluation of natural attenuation. Prediction of the migration and degradation of a dissolved contaminant plume using a solute transport model is often an important component of the natural attenuation demonstration. This is the most common use of models for this type of study. However, models can also be used to synthesize, interpret, and present available data and in turn, guide any additional data collection that must be performed in order to verify remediation by natural attenuation. Some models can also be used to evaluate the effects of other remedial actions (e.g., source removal, source reduction, pump-and-treat, or hydraulic containment) on their own or in conjunction with natural attenuation.

A model, whether it is used for solute fate and transport, groundwater flow, or both, consists of several components. As enumerated by Spitz and Moreno (1996), these components are:

- the natural system for which the model is designed;
- a conceptual model as an idealized representation of the natural system;
- a mathematical model representing controlling mechanisms in mathematical terms;
- solution of the mathematical model;
- calibration of the solution by adjusting simulated to observed responses of the natural system;
- validation of the accuracy of the model predictions; and
- simulations based on the calibrated solution of the conceptual model.

In general, any modeling effort will contain some or all of these components, depending on the type of study, the available data, and the type of model being used. Material in this appendix will briefly focus on some of these topics, with the intent to provide a overall understanding of these concepts in the context of their application to a demonstration of remediation by natural attenuation.

In order for a model to adequately predict the fate and transport of a dissolved contaminant plume, it must be capable of modeling solute transport under the influence of advection, dispersion, sorption, and biodegradation. In many cases, the model must also be able to simulate the groundwater flow field in which contaminants are transported. Models used to simulate groundwater flow and solute transport can be classified according to the mathematical technique used to solve the governing partial differential equations. Analytical solutions and numerical solutions are the two mathematical techniques used to solve the advective-dispersive transport 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 the merits of analytical and numerical models and some suggestions regarding model selection. Finally, consideration is given to whether or not a model is necessary to successfully implement remediation by natural attenuation at a given site.

## D.1.1 MATHEMATICAL EXPRESSIONS USED TO DESCRIBE SOLUTE TRANSPORT AND REMEDIATION BY NATURAL ATTENUATION

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 and 1979; Domenico and Schwartz, 1990; Bedient *et al.*, 1994; Segol, 1994). No discussion of groundwater flow equations will be presented here. This information can be found in the aforementioned texts, as well as those by Strack (1989) and Spitz and Moreno (1996).

### D.1.1.1 One-Dimensional Reactive Solute Transport

The one-dimensional partial differential equation describing transient solute transport with first-order decay of the solute 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
$\lambda$ = first-order decay rate constant

This is a parabolic partial differential equation. The decay rate may be used to simulate any process that is observed to be reducing solute concentrations in a manner that approximates first-order decay, such as biodegradation, radioactive decay, or hydrolysis). 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
$\lambda$ = 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:

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

### 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
$\lambda$ = 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 groundwater flow and/or solute transport can be solved analytically or numerically. The type of model selected to simulate site conditions will depend on the results of data review and conceptual model development. Analytical methods (models) provide exact, closed-form solutions, and numerical methods (models) provide approximate solutions. Analytical models are the simplest to set up and solve, allowing the user to evaluate many scenarios in a relatively short time. Numerical methods are more efficient for those systems that are too complex for analytical methods. Analytical models are restricted in the nature of the problems for which they can be used, and for some transport problems they may become so complex and unwieldy that the use of numerical methods may be more efficient. As suggested, numerical methods can be used for more complex systems. Theoretically there are no limits on the characteristics of the hydrogeological system and the properties of the solute(s) that

can be simulated using a numerical model code. There are, however, practical limits on the ways in which the system and any reactions within it can be represented.

As a result, groundwater flow and 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 groundwater flow and/or contaminant fate and transport. Such a balance will depend on the nature of the hydrogeologic system being simulated, the available data, and the intended use of the model results. As an example, a simple analytical model will, in many cases, provide the appropriate information with much less effort than would be required to produce a numerical model. Spitz and Moreno (1996) note that:

> *Whenever possible, the model user should give preference to analytical solutions over numerical modeling. A large number of groundwater problems can be greatly simplified and solved analytically without substantial loss of accuracy. There is no systematic approach for simplifying a given groundwater problem and for selecting the appropriate analytical solution. In fact, it depends entirely on the capability of the model user to visualize the investigated problem and to judge professionally if a chosen analytical method is consistent with the hydrogeological controls. If the deviation between reality and the conceptual model is recognized and its impact properly estimated, analytical solutions can be beneficial.*

In addition to arguing for the use of analytical models where appropriate, his passage also illustrates the balance that must be achieved between the "art" of selecting a solution method and adequately representing the system in a simple and straightforward manner and the science of evaluating and utilizing the site data to produce a model with results that are defensible and consistent with the available data.

Subsurface groundwater flow and/or 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.

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, an 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. Several analytical solute transport models are 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 or underestimate the spread of contamination. By making assumptions that will ensure the model will overpredict contaminant concentrations and travel distances (or at least not underpredict them), the model predictions will be 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 remediation by natural attenuation.

Numerical solutions provide approximate solutions to the advection-dispersion equation. Numerical models are less burdened by simplifying assumptions and are capable of addressing more complicated problems. Unlike analytical models, numerical models allow subsurface heterogenieties and varying aquifer parameters to be simulated, as well as transient simulations (i.e., one or more properties or conditions change over time), if the requisite data are available. In numerical models, the continuous problem domain is replaced by a discretized domain. The resolution of the results provided by a model depends on the degree of discretization (in the model) of the groundwater system under investigation. Many of the assumptions required for the analytical solutions are not necessary when numerical techniques are used to solve the governing solute transport equation. However, a greater amount of site-specific data is needed to implement a numerical model, and the 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. Several well-documented and widely accepted numerical model codes are available for modeling the fate and transport of CAHs and fuel hydrocarbons dissolved in groundwater under the influences of advection, dispersion, sorption, and biodegradation. Specific numerical fate and transport models are described in Section D-4.

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. Most numerical groundwater flow and transport model codes fall into one of the following four model types:

- finite difference;
- finite element;
- random walk; and
- method of characteristics (MOC).

These differing methods have been developed to address the multitude of problems presented by the number of physical and chemical processes that can affect groundwater flow and dissolved contaminant transport. Excellent descriptions of these methods may be found in the texts by Anderson and Woessner (1992) and Spitz and Moreno (1996).

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. In addition, the user should avoid making the problem more complex than necessary. Spitz and Moreno (1996) note that:

> *Solutions to groundwater problems do not necessarily require the most sophisticated model. In each case the most appropriate model is the one that addresses the investigated problem with as little effort as necessary to represent the real system. The model should be simple enough to facilitate model efforts but not too simple so as to exclude features dominant to the investigated groundwater problem.*

Success in solute fate and transport modeling depends upon 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. Keep in mind that any numerical model code or analytical solution selected for a demonstration of remediation by natural attenuation should be properly validated through sufficient previous application at a variety of field sites.

There is one final caveat that should be considered before deciding what type of model to use, as well as at all times during the modeling process. This concern has been articulated quite well by Spitz and Moreno (1996), who state that:

> *Transport models for advection and dispersion are at a mature stage of development and are applied with success to two- and three-dimensional transport problems. Transport modeling of chemically reacting contaminants, however, achieves only fair success if adsorption is linear. Besides large demands on computing power, uncertainties in describing complex reactions and difficulties in obtaining reliable field data limit modeling success. Transport predictions are more sensitive to a lack of field data than flow prognoses. Although the final objective of a model analysis is predictive, transport predictions in an absolute sense are impossible to achieve, even with the best models.*

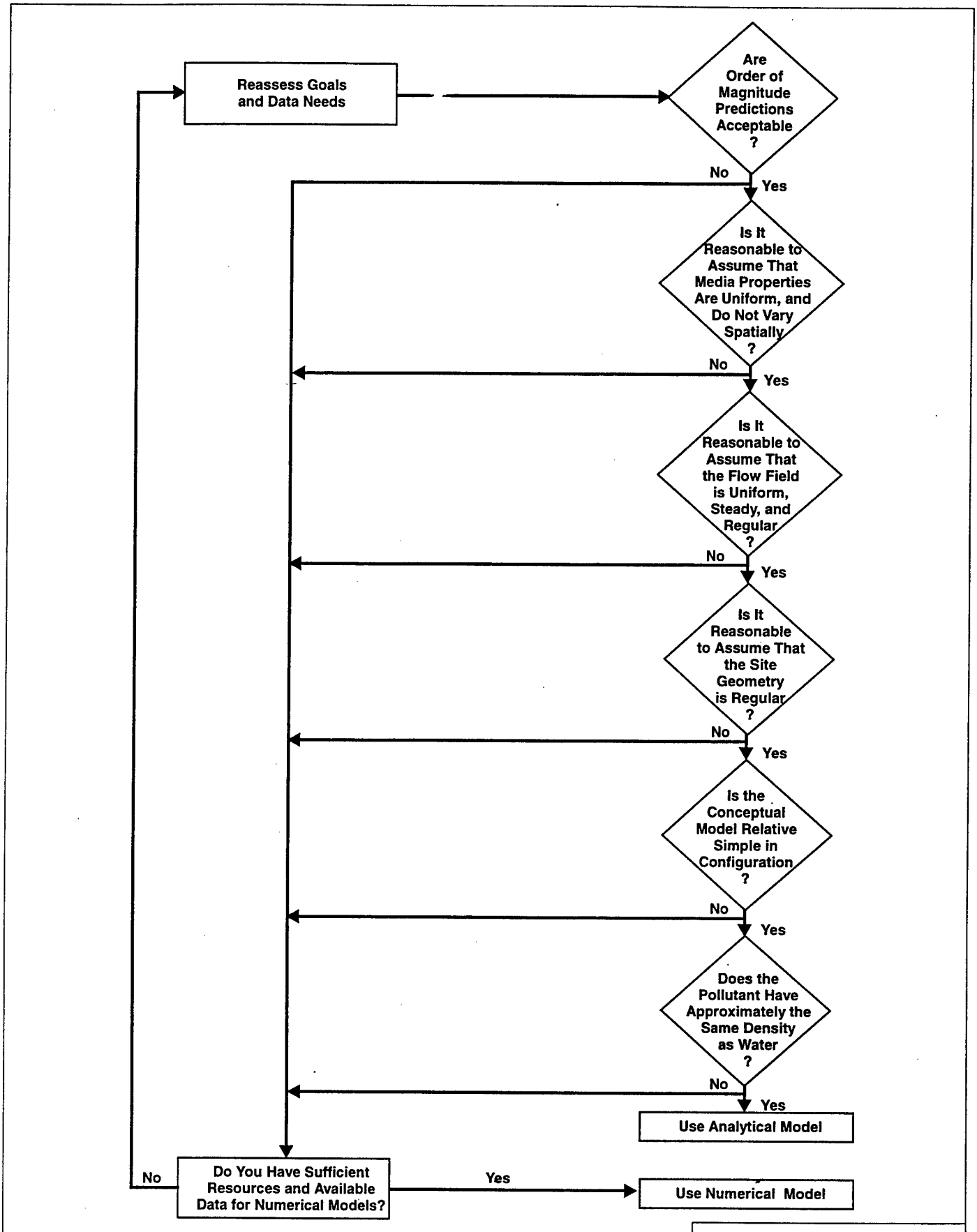



Figure D.1.1
Decisions Process for
Model Selection

figd-1-1.cdr nap 8/6/96

This is not to say that models are not useful or meaningful. Models are a powerful tool; however, as this passage implies, they do not provide definitive answers. With a good sense of the limitations imposed by the simplifying assumptions inherent in the models and the available data, the modeler and/or the model user should be able to apply the model and/or its results (as a tool) to reach reasonable conclusions and apply those conclusions appropriately. Failure to understand and work within the limitations of a particular model and data set will lead to erroneous conclusions that will hinder the application of remediation by natural attenuation.

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 contaminant 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 contaminant plume.

### D.1.3 IS A MODEL REALLY NECESSARY?

Two questions will invariably arise during a demonstration of remediation by natural attenuation. 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 natural attenuation is unable to provide plausible and defensible answers to these questions, it is unlikely that natural attenuation 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.

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 contaminant 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.

# 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. For further explanation and discussion of the theory and practice of modeling, the texts by Bear (1972 and 1979), Strack (1989), and Segol (1994) are recommended for the topic of analytical models, while the texts by Anderson and Woessner (1992) and Spitz and Moreno (1996) are recommended for the topic of numerical modeling.

## D.2.1 DATA COLLECTION

Data collection is a critical component of model development. Field data are necessary to produce model input, as well as to specify the problem to be addressed and to delineate the system to be simulated. Without adequate data, the quality and utility of the model results will be doubtful. Among the data required to complete a groundwater model (analytical or numerical), are the following:

- Hydraulic conductivity for all hydrogeologic units of concern;
- Initial hydraulic head distribution;
- Flow direction(s);
- Effective porosity for all hydrogeologic units of concern;
- Coefficient(s) of hydrodynamic dispersion;
- Coefficient(s) 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 (precipitation infiltration, evapotranspiration, pumpage from wells, discharges to surface water, etc.);

- Definition of physical and chemical boundary conditions; and
- Rates of chemical reactions, particularly biodegradation.

This is by no means an exhaustive list; some of the data are necessary for any model, some are useful only for certain types of model, and some data not listed above may be needed for specific model applications or codes. Also, some of the data listed above may need to be manipulated before use in a model. Ideally, collection and evaluation of data should be a dynamic process that takes place in conjunction with the formulation and calibration of the model. This would allow the investigator to determine what additional data could be collected to improve the model. Unfortunately, this is not always possible in practice. Because of the vastly different soil sorption coefficients and biodegradation mechanisms for each of the constituents of concern, specific attention should be paid to the assignment of these parameters.

Collection of field data for a model to evaluate natural attenuation is discussed in Appendix A, and premodeling calculations are discussed in Appendix C. As discussed in Appendix C, data that cannot be derived from field measurements can be taken from the literature, with appropriate caveats.

### D.2.2 CONCEPTUAL MODEL

The first step specifically related to the actual process of modeling is development of the conceptual model. A conceptual model is simply an idealization of the groundwater flow and contaminant transport system based on the available geological, hydrological, climatological, contaminant, 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. The conceptual model presents the current understanding of site conditions and the hydrogeologic system. 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 natural attenuation demonstration, the preliminary conceptual model should be refined.

Successful conceptual model development involves:

- Definition of the problem to be solved;
- Designing the conceptual model;
- 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 and, if necessary, to determine what additional data needs to be collected to allow adequate representation of site conditions.

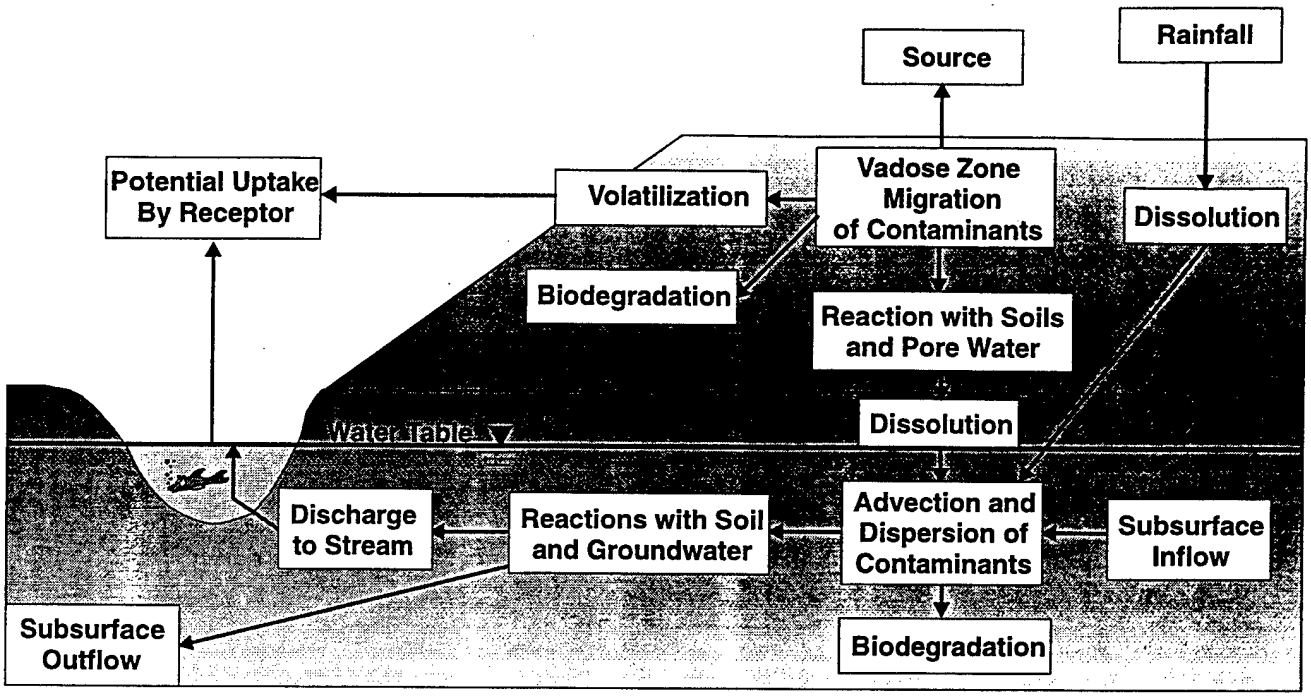
A conceptual model may be expressed in many ways, with different approaches suited for different groundwater systems and model objectives. In addition to a verbal description or a table listing model features, graphical methods are useful for describing a conceptual model. Suitable graphical methods include:

- a flow chart indicating interactions between elements of the problem;
- a hydrogeological cross-section labeled with key processes; and
- a three-dimensional diagram summarizing site conditions.

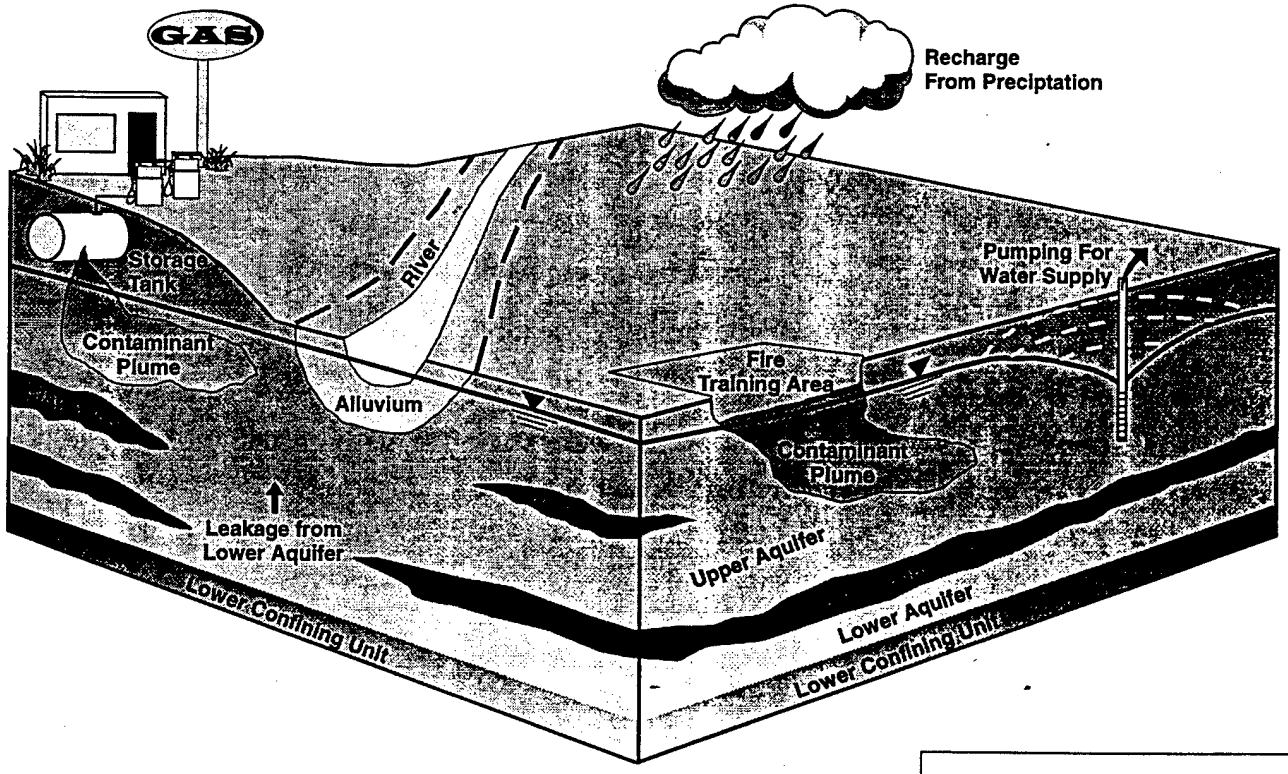
Figure D.2.1 shows two examples of graphical methods with which a conceptual model can be described. For verbal or graphical methods, the description of the conceptual model may be simple or complex, depending upon the type of model and the available data. Of course, any other method that suitably expresses the conceptual model would also be appropriate. The imagination of the modeler and the demands of the specific modeling task are the only limits on this process.

## D.2.3 SELECTION OF ANALYTICAL SOLUTION OR NUMERICAL CODE

Selection of the analytical solution or model code is a step in which the modeler looks at the conceptual model and the available data and uses his/her professional judgment to select the most appropriate code. This process is not always a rational one; non-scientific considerations may weigh significantly on the ultimate decision. Some of the general considerations for deciding between analytical or numerical methods are presented in Section D.1.2, but there are other criteria to consider once one has collected data and formulated a conceptual model.




PROCESSES IN CROSS-SECTION




THREE-DIMENSIONAL SCHEMATIC

Figure D.2.1
Graphic Presentation
of Conceptual Models

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Spitz and Moreno (1996) outline three types of criteria that the modeler can use in selecting a model code or analytical solution. First, the user should consider the model objectives (i.e., what is the ultimate purpose of the modeling effort?). If only general or very approximate results are needed, the user might select an analytical method or a very simple numerical code. The more specific and detailed the results must be, the more likely it is that the selected method will require a sophisticated numerical model code. Second, the user should use technical criteria. In this case, the user determines if the chosen model(s) is capable of adequately representing the dominant flow and transport processes at the site. Finally, if a model meets the objectives and technical criteria, implementation criteria can be used to further narrow the choice. These criteria include considerations such as how well-documented and reviewed the model is, the degree to which the solutions have been verified and applied to similar sites, available technical support, computer hardware requirements, and if the model has a good track record of acceptability to reviewing or regulatory agencies.

These criteria can be summarized into three key questions:

- Can the model adequately simulate site conditions?
- Can the model satisfy the objectives of the study?
- Is the model verified and peer-reviewed, well documented, and reasonably well field-tested?

The most appropriate choice is often a compromise between the first two considerations, particularly because study objectives typically include time limits and financial constraints. This is one of the points where a modeler's experience and judgment may play an important role.

### D.2.4 MODEL SETUP

The combined steps of model setup and model calibration make up over half of the total work in a modeling effort. Model setup includes selecting the model domain, discretizing the data in space and time, and assembling the discretized data in a form suitable for input to the numerical code or analytical solution. Choice of the domain and discretization will affect the resolution of the model and will also directly affect the cost of the modeling effort.

In general, analytical model setup can be accomplished much more quickly than for numerical models. Analytical modeling can be performed using commonly available spreadsheets, mathematical analysis programs such as MathCAD®, or codes written expressly for analytical modeling (e.g., BIOSCREEN, AT123D, SOLUTE, or PRINCE®). Because analytical solutions

are algebraic expressions, input into these models is very straightforward and usually consists of entering the parameter values in appropriate locations. Note that for computer codes, input and/or results may be entered or presented in a discretized manner because the code solves the equations at a given number of points. Because of the simplicity of analytical model input, most of the remaining discussion of model setup will be directed towards numerical modeling. Where appropriate, analytical model setup will also be discussed.

### D.2.4.1 Model Domain

Selection of the model domain will not only determine what portion of the system of interest will be modeled, but can also affect the amount of computational effort required. Clearly, the model domain should cover the entire area within which the contaminant plume may travel and, if necessary, the domain should also include any receptors of concern. If necessary, velocity calculations or analytical models could be used to estimate potential travel distances. Domain boundaries will ideally coincide with natural groundwater boundaries such as rivers, lakes, groundwater divides, or aquifer boundaries. These boundaries should be distant from the area of concern (i.e., the part of the model in which transport will be modeled) to prevent boundary effects from affecting the solution. Where possible, the domain should be oriented so that the primary transport direction will be parallel to a model axis. This will reduce the potential effects of numerical dispersion. Finally, the domain should be an area for which adequate data is available, and the domain size should be selected to minimize the computational effort required to perform the simulation. Of course, compromise among these considerations will often be required and may result in less-than-ideal configurations in some respects.

For analytical models, choosing a domain size is often less important. Many models assume an infinite or semi-infinite aquifer, and will solve for the appropriate unknowns at specified points. However, for some software packages, the user does have to specify a domain in which the solutions are calculated at a fixed number of points. In this case, the user should again consider the potential travel distance of the plume over the time period of interest and specify the domain accordingly. Location of the points where a solution is desired will depend on where solute concentration information is desired.

### D.2.4.2 Discretization

In a numerical model, both time and space are divided into discretized elements for which solutions to the groundwater flow and solute transport equations are approximated. Spatial

discretization is accomplished by replacing the continuous hydrogeologic domain with a discretized domain consisting of an array of nodes and associated blocks or elements (a model grid). Temporal discretization involves defining time periods for which model calculations are made. In the case of a steady-state model, time is not discretized. However, because transport solutions nearly always involve a time element, groundwater flow models are typically the only part of a model that may be steady-state. Selection of the time steps and model grid spacing are important steps in model design because both of these factors will strongly influence the numerical results. Ideally, the modeler will be able to use small grid spacing and time steps so that the numerical approximation better represents the partial differential equation (Anderson and Woessner, 1992). Spitz and Moreno (1996) suggest that to produce the optimal discretization the modeler should try to:

- enhance the model solution stability and convergence;
- increase the model resolution;
- minimize numerical dispersion; and
- minimize computational requirements for memory, storage, and run-time.

How each of these goals is met will depend on the available data, the limitations of the model code, and the computer hardware available to the modeler. Compromise between these goals and the available resources (time, hardware, software, and personnel) will often dictate the resulting model discretization. Some general guidelines will be presented herein, but for more through discussions of these topics, modeling texts such as those by Anderson and Woessner (1992) or Spitz and Moreno (1996).

D.2.4.2.1 Model Grid Orientation and Spacing

Spatial discretization of a model domain is controlled by the grid orientation and spacing (cell size). Grid orientation is often controlled by large-scale hydrologic, geologic, or hydrogeologic features and will therefore not necessarily coincide with primary compass directions or property boundaries. The optimum orientation, as noted in the discussion of the model domain, will have the primary directions of flow and/or transport parallel to the grid axes. This may follow naturally when the grid is aligned parallel to natural features of the system. In the case of finite-element models, orientation will be accommodated by the spacing of the nodes and the shape of the elements because there is more flexibility in the grid shape and orientation. Where the system is known to be anisotropic, the primary directions of the hydraulic conductivity tensor will control the grid orientation.

Numerous factors must be considered when selecting the size of grid cells to be used. There is a trade-off between grid spacing, grid alignment, 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 should be designed so that it is large enough that the solute plume will not intersect a model boundary. Otherwise, the solution routine used in the code should be able to handle such occurrences without producing an unstable solution.

Cell size can also affect the model by introducing numerical dispersion that is dependent on the relationship between the grid spacing and the contaminant velocity. Several considerations for grid spacing that will minimize numerical dispersion are discussed by Spitz and Moreno (1996), and a few of these are discussed here. For example, the cell size divided by the dispersivity (known as the Peclet number) should be no larger than 2, but this criterion is often relaxed where lower predictive accuracy is acceptable or where other constraints prevent optimization of this factor. In addition, to minimize problems with convergence of the numerical solution, the cell aspect ratios (i.e., the ratio of the x-dimension to the y-dimension of the cells) should be between 1:10 and 10:1. Finally, another rule-of-thumb is that the smoothness of the discretization (i.e., the difference in size of adjacent cells) should be such that the dimensions of cells are neither less than half nor twice as great as those of the adjacent cells. This will also minimize convergence problems.

D.2.4.2.2 Time Discretization

In numerical models, two types of time intervals that are used for arriving at solutions: time steps and stress periods. Time steps are required for transient calculations, and are the discrete time periods in which calculations are made. Their function is roughly analogous to that of the model grid, in that they allow the model to represent a continuous time domain by producing solutions for multiple discrete points. In general, the shorter the time step, the more closely the model will approximate the analytical solution. Time steps that are too small will require excessive computation time and memory, while time steps that are too large may introduce numerical dispersion or cause instability. In order to minimize numerical dispersion and maximize numerical stability, the modeler should strive for a Courant number (the product of the advective velocity and the time step, divided by the smallest cell dimension) that is less than 1. Essentially,

this implies that transport of a particle across a cell should take place over more than one time step.

Stress periods are intervals in which boundary conditions and stresses are constant and between which the boundary conditions and stresses change. Stress periods do not affect the model calculations, so they only need to represent actual time periods within which all boundary conditions and stresses are constant. However, stress periods can affect the selection of time steps. To avoid numerical dispersion, improve model stability, and allow more rapid solution convergence, time steps during changes in boundary conditions or stresses (i.e., at the beginning of stress periods) should be shorter.

### D.2.4.3 Initial Conditions

Initial conditions are used to describe conditions such as the distribution of heads and concentrations at the instant a numerical 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, but doing so can save computational time. Initial conditions for a transient run are best derived from the results of a steady-state flow simulation or a transient transport simulation (imposed on either a transient of steady-state flow simulation) (Anderson and Woessner, 1992; Spitz and Moreno, 1996). Doing so will provide a mass-balanced starting point that will also be consistent with the model hydrologic inputs and parameters. For transport modeling, Spitz and Moreno (1996) warn that:

> *Specification of an observed concentration distribution (e.g., and interpreted plume based on observed concentrations) as initial conditions for a transient transport simulation often leads to erroneous predictions because a field program rarely measures the highest concentrations and differing interpolations would lead to widely varying predictions. Therefore it is better to use estimated source terms as a starting point for the transport model, even if the source is not well defined. These sources can be used to calibrate the transport model, and to predict the starting conditions for subsequent model runs.*

The following sections briefly describe the mathematical representation of initial conditions. Again, for more thorough descriptions and discussions, the texts by Anderson and Woessner (1992) and Spitz and Moreno (1996) are recommended.

D.2.4.3.1 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.2.4.3.2 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. As noted before, this distribution is best derived from a simulation (where possible). For analytical transport modeling, equation D.2.3 is the only initial condition that can be used. Analytical models are not truly transient, but they are able to provide solute concentrations at a given location and time.

### D.2.4.4 Boundary Conditions

In defining the model area, the modeler must separate the area of interest from the surrounding system. Boundary conditions describe the interaction between the system being modeled and its surroundings or, for transport models, the loading of contaminant mass into the system. Proper design of model boundary conditions is therefore of great importance in numerical model implementation. Boundary conditions are used to include the effects of the 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 system. In effect, the boundaries of the model tell the area immediately inside the boundaries what to expect from the outside world. The solution of any differential equation requires specification of the conditions at the periphery of the system. Model boundaries are thus 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.

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 | $\frac{\partial H}{\partial n} + cH = f(x,y,z,t)$ | $\frac{\partial C}{\partial n} + cC = f(x,y,z,t)$ |

In flow models, boundary conditions are ideally used to specify actual hydrogeologic boundaries to the system, such as streams, lakes, confining units, groundwater divides, or any geologic feature that may bound a system. Also, the boundaries may also be defined as areas

where properties (e.g., flux) are known and can be defined. Figure D.2.2 illustrates different types of boundary conditions for flow models. When using a numerical flow 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.

In transport models, boundary conditions are used to specify contaminant sources such as NAPL bodies, dissolved mass entering through recharge, injection wells, surface water bodies, and leaking structures. Figure D.2.3 illustrates transport boundary conditions. Definition and quantification of such sources and representation of them in the model is an important part of the modeling process. Leaky structures, injection wells, and dissolved mass in recharge are often represented as specified-flux boundaries using the associated concentrations. Sources such as NAPL bodies may be represented as specified-concentration boundaries (limited by solubility constraints or observed maximum concentrations) or as specified-flux boundaries (for which the chemical dissolution rate must be known or estimated). However, in most cases, only the effects of the source are measured, not the source characteristics. The source must therefore be represented as a "black box" that produces appropriate concentrations or fluxes at selected points in the model. The source may be misrepresented under such a scenario, but there is often little choice in the matter.

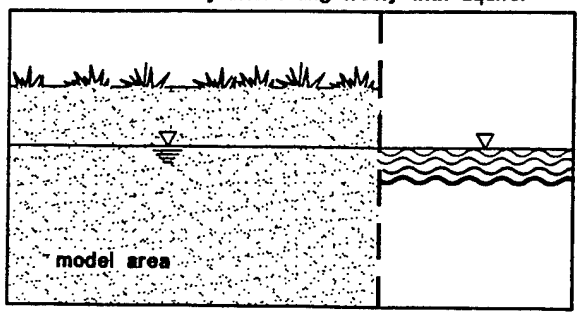
For coupled numerical flow and transport models, it is generally a good idea to make the modeled area large enough so that boundaries of the flow model can be placed far enough away from the plume that they will have minimal impact on the transport solution. This may not be possible in all cases, such as where the plume is near a surface water body. In some 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.

For analytical transport problems, one of the three types of transport boundary conditions will always be applied as a contaminant source. The solutions used in the analytical models are typically calculated using the assumption that the remaining boundaries are an infinite distance away from the source so that they do not affect the calculation of solute concentrations.

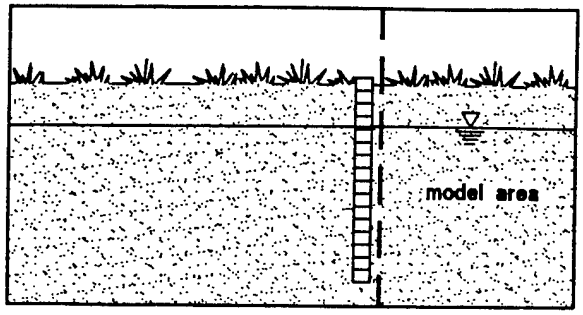
The following sections provide mathematical descriptions of boundary conditions used in flow and solute transport modeling. For more rigorous discussions and explanations of model

## SPECIFIED HEAD OR FIRST TYPE OR DIRICHLET'S CONDITION

Surface water body interacting freely with aquifer

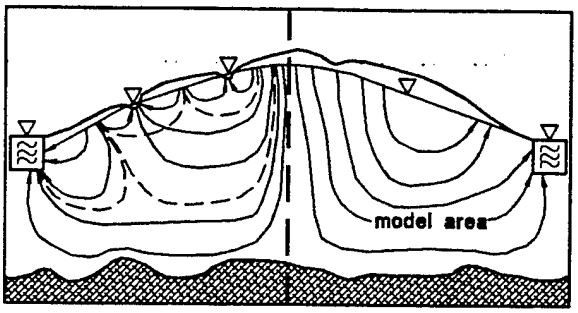



Measured groundwater head

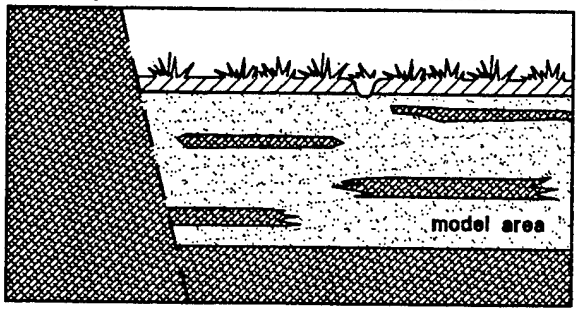



## SPECIFIED FLUX OR SECOND TYPE OR NEUMANN'S CONDITION

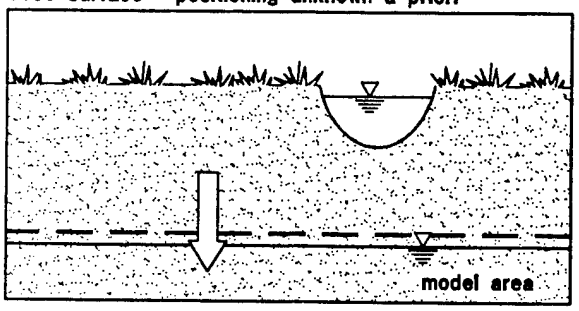
Groundwater divide or streamlines imposing no-flux conditions



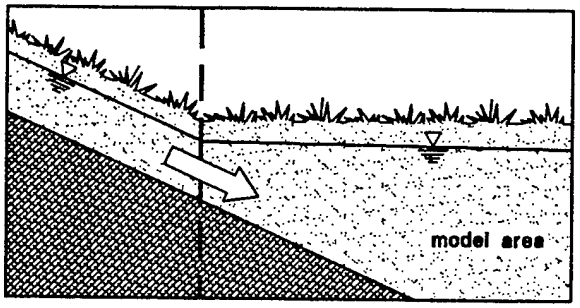

Fault imposing no-flux or fixed flux conditions




Free surface - positioning unknown a priori

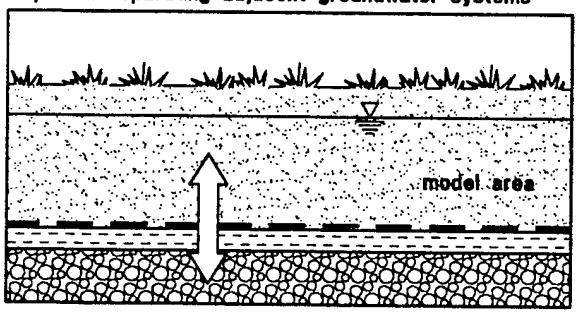



Subsurface inflow or outflow

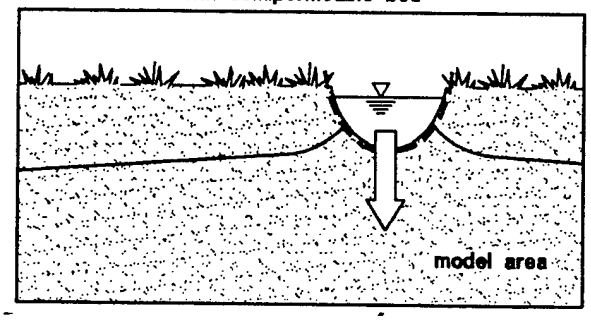



## HEAD-DEPENDENT FLUX OR THIRD TYPE OR CAUCHY'S CONDITION

Aquitard separating adjacent groundwater systems




Surface water with semipermeable bed




— — — Model boundary

Source: Spitz and Moreno, 1996

Figure D.2.2
Examples of
Flow Model Boundary
Conditions

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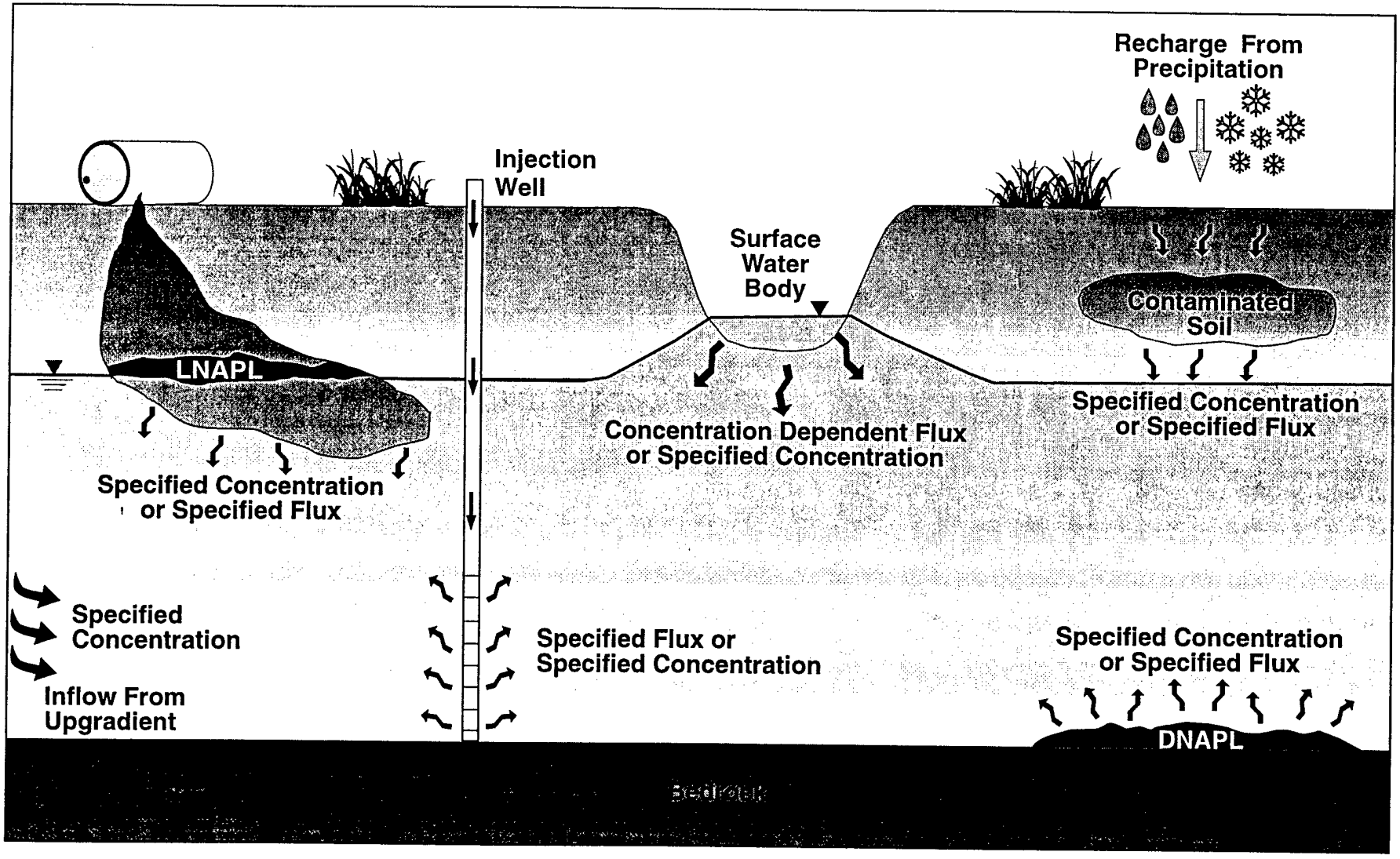



Figure D.2.3
Examples of Transport
Boundary Conditions

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boundary conditions, refer to Bear (1972 and 1979), Strack (1989), and Segol (1994) are for the topic of analytical models, and Anderson and Woessner (1992) and Spitz and Moreno (1996) for numerical models.

D.2.4.4.1 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.2.4.4.1.1 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 may be used to model the interaction between surface water bodies and groundwater, assuming the surface water body freely interacts with the aquifer. 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).

Another way the specified head boundary condition is used is for those cases where a model boundary, for whatever reason, does not coincide with a physical boundary. For example, one or more of the nearest physical hydrogeologic boundaries for the modeled system may be far away from the area of interest, and incorporating them would make the model domain larger than feasible. In this case, the modeler may then specify heads at one or more of the model boundaries on the basis of measured or projected head data. When doing this, the modeler should take care to ensure that these boundaries are far enough away from the area of interest that the do not affect the model calculations in that area.

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.,

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

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.2.4.4.1.2 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 dense nonaqueous-phase liquid (LNAPL) spill. The maximum contaminant concentration in groundwater in contact with the DNAPL is dictated by the partitioning relationships described in Section C.3.2.2. In reality, such a system is rare. The NAPL is subjected to weathering though the processes of dissolution, and biodegradation. Because of this, most contaminant source areas should be modeled as decaying sources; however, use of constant-concentration boundaries to simulate sources for periods without appropriate source or solute data is often used as part of the "black box" approach discussed in Section D.2.4.4.

D.2.4.4.2 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 across the boundary, and is equated to the normal derivative of head or concentration with respect to the direction perpendicular to the flow boundary.

*D.2.4.4.2.1 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.2.4.4.2.2 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.2.4.4.3 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.2.4.4.3.1 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. The flux across the semiconfining bed in this case 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

This relationship could also be used when the modeled area is a confined aquifers, but the overlying confining unit is leaky and the leakance across the unit is controlled by the head of the overlying aquifer.

*D.2.4.4.3.2 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.2.5 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 adjustment of key model input 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. Parameters should be varied within measured ranges, historical ranges, or ranges presented in the relevant literature, except possibly for those outside the area for which data is available. The range of values over which the data are varied will also depend on the uncertainty of the data. 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, source strengths, and biodegradation rates. As part of the calibration process, the modeler will also perform an error analysis in an attempt to quantify how well the model approximates the natural system and to identify any sources of excess differences between measured and modeled values. An error analysis in its most basic form is simply the comparison of measured and simulated values.

Calibration is necessary to account for the uncertain data and for any unknown, unrepresented, or unmeasured conditions or processes. It is possible to allow a computer code to perform the calibration (i.e., to solve what is known as the inverse problem), but this requires not only specification of the known data, but the also the statistical uncertainty associated with the data. Often the data or other resources do not allow such a procedure, so most modelers resort to the trial-and-error method of calibration. In this method the modeler uses his/her experience and judgment in conjunction with the available data to reach a solution that meets whatever criteria are specified for calibration. This implies that a certain amount of experience is needed for modeling in this manner (as well as for automated calibration). However, even with limited experience, a modeler may be able to calibrate a model in a reasonable and efficient manner with good guidance, either from a peer or from the texts that have been repeatedly referenced throughout this appendix. Even for the experienced modeler, these texts can provide useful, objective, and structured procedures for calibrating a model and evaluating that calibration.

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 to confirm 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 transport parameters (and hydraulic parameters, if results indicate the need to do so) in a trial-and-error fashion until the simulated contaminant 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 entering either a groundwater velocity or a gradient, a flow direction, and one reference head 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 contaminant plume approximates observed field values at specific locations or times.

### D.2.5.1 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 could be compared with only one set of data or a set of mean water levels over a selected period (Anderson and Woessner, 1992). 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 solute transport velocities. Other parameters that may be adjusted during flow model calibration include recharge, evapotranspiration, and hydraulic boundary conditions. However, most uncertainty will lie in the magnitude and variation in hydraulic conductivity or transmissivity and therefore variation of the values of those parameters will likely be relied on the most in order to calibrate a groundwater flow model.

The root mean squared (RMS) error is one method commonly used to express the average difference between simulated and measured heads (i.e., it is an error analysis tool). 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)

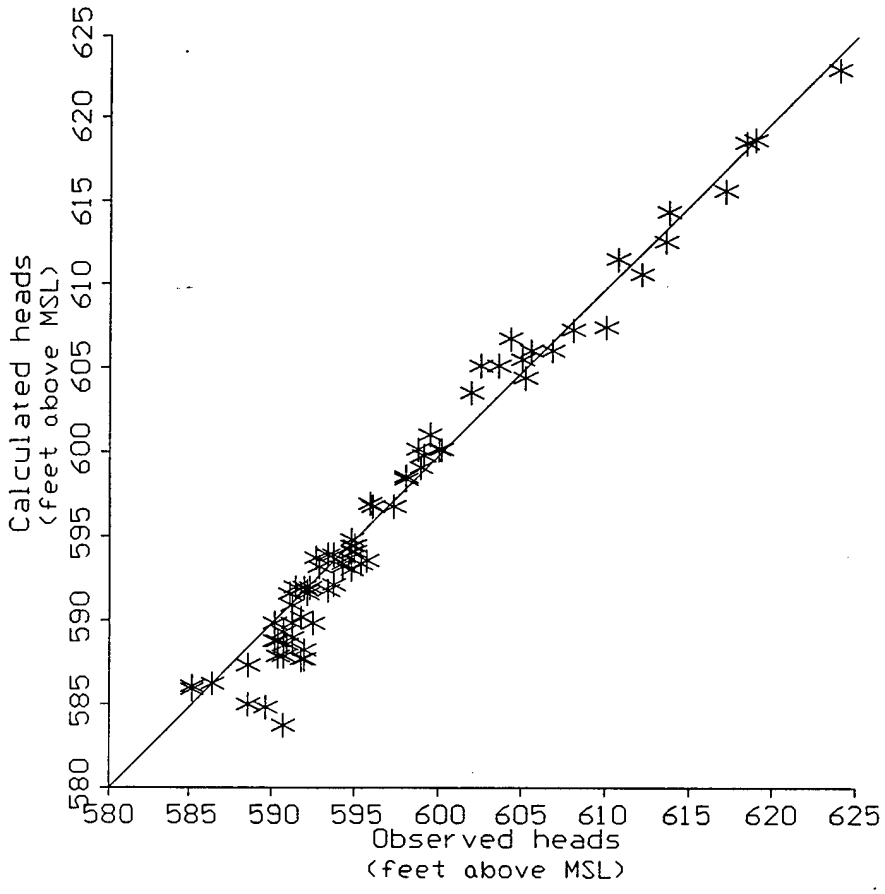
$RMS$ = Root mean square error [L]

$\Delta H_T$ = Total head change over model domain [L]

Another qualitative method of checking the calibrated model head distribution and performing an error analysis 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.2.4 is an example of such a plot.

### D.2.5.2 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. A strategy should be developed in order to determine if the model needs to be calibrated for single or multiple analytes.




Mean error: -0.716 Mean abs. err: 1.32 RMS error: 1.815

Figure D.2.4

Example
Plot of Calibrated Heads
vs. Observed Heads

Model input parameters affecting the distribution and concentration of the simulated contaminant plume should be modified so that model predictions match dissolved contaminant concentrations. To do this, model runs are made using the calibrated hydraulic parameters with available contaminant plume data. If the contaminant distribution is known at two different times, the plume may be calibrated over time, keeping in mind the uncertainty associated with the source term. Plume calibration is achieved by varying the source terms, decay coefficients, the coefficient of retardation, the effective porosity, and dispersivity until the contaminant plume is calibrated reasonably well to the existing plume in terms of migration distance, configuration, contaminant concentrations, and contaminant concentration changes in the plume area. As noted in Section D.2.4.4, the source terms are typically a significant source of uncertainty in the input and variation of the source terms is often a significant part the calibration process.

The calibration processes for analytical models and numerical models follow the same general steps as those outlined here. However, analytical models will only incorporate the transport portion of the calibration, with the flow component represented by a groundwater or contaminant velocity. Of course, calibration of an analytical model is less involved due to the simpler nature of the analytical models.

### D.2.6 SENSITIVITY ANALYSIS

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 and identify any additional field data that may need to be collected.

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 systematically 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. At a

minimum, the sensitivity analyses must involve varying these model input parameters over the range of plausible values used during calibration.

The results of sensitivity analyses can be shown graphically, in table format, or simply written in the text. For simple numerical models or analytical models, a paragraph or two describing the changes made and how the results differed from the calibrated model may suffice. More complex models will require many different runs for the sensitivity analysis, and tables or pictures are more useful for presenting the greater amount of information that is generated. As an example, one could display modeled contaminant concentrations versus distance along the centerline of the plume for different runs in which the same parameter is varied. This manner of displaying data is useful for plumes that are elongate and fairly symmetric because the figures allow easy visualization of the changes in contaminant 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 will allow the modeler to determine what input values to use so that the prediction scenarios are conservative.

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.2.7 PREDICTION

After the solute transport model has been calibrated and the sensitivity analyses have been performed and interpreted, 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. Assumptions made in this step should be made clear so that the entity that will ultimately use the results will understand this part of the model. As an example, assumptions about the contaminant source and how it may change

over time should be made clear. As needed, multiple scenarios can be simulated to evaluate actions such as source removal or source reduction, or to evaluate a range of possible conditions. While the model predictions will yield specific values such as contaminant concentrations at specific times and locations, the modeler should make it clear that the reliability of the values is heavily dependent upon the model assumptions and the uncertainty of the available data. The modeler's interpretation of the uncertainty in the predictions and how best to use them should be included with the prediction results.

### D.2.8 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 and why 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 taken from literature), the process used to interpolate the data spatially, how the model was calibrated, and what types of sensitivity/uncertainty analyses were performed. Model set-up and results should be presented graphically unless the model is simple or an analytical model with a limited number of solution points. Figure D.2.5 gives an example table of contents from a report that was used to successfully implement intrinsic remediation at a site contaminated with fuel hydrocarbons and chlorinated solvents. Appendices E and F present examples of such reports.

### D.2.9 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 model to be verified (or validated). Verification is the process of demonstrating that the model is an adequate representation of the natural system, by using it to successfully predict data other than those used for the calibration. Ideally, a model will be verified before predictions are made, but in practice the constraints of data, time, and money will often rule out this step. However, a calibrated but unverified model can be used to make predictions as long as a careful sensitivity analysis is performed and evaluated.

1 INTRODUCTION
- 1.1 SCOPE AND OBJECTIVES
- 1.2 FACILITY BACKGROUND

2 SITE CHARACTERIZATION ACTIVITIES

3 PHYSICAL CHARACTERISTICS OF THE STUDY AREA
- 3.1 SURFACE FEATURES
- 3.2 REGIONAL GEOLOGY AND HYDROGEOLOGY
- 3.3 SITE GEOLOGY AND HYDROGEOLOGY
  - 3.3.1 Lithology and Stratigraphic Relationships
  - 3.3.2 Groundwater Hydraulics
- 3.4 CLIMATOLOGICAL CHARACTERISTICS

4 NATURE AND EXTENT OF CONTAMINATION AND EVIDENCE FOR BIODEGRADATION
- 4.1 CONTAMINANT SOURCES AND SOIL CHEMISTRY
  - 4.1.1 Mobile Nonaqueous-Phase Contamination
  - 4.1.2 Residual Nonaqueous-Phase Contamination
  - 4.1.3 Total Organic Carbon in Soil
- 4.2 OVERVIEW OF CONTAMINANT BIODEGRADATION
- 4.3 DISTRIBUTION OF CONTAMINANTS AND DAUGHTER PRODUCTS DISSOLVED IN GROUNDWATER
- 4.4 ADDITIONAL EVIDENCE FOR CONTAMINANT BIODEGRADATION
  - 4.4.1 Additional Indicators of Dehalogenation
  - 4.4.2 Electron Donors, Electron Acceptors, and Byproducts
  - 4.4.3 Additional Geochemical Indicators
- 4.5 CALCULATION OF BIODEGRADATION RATES

5 GROUNDWATER MODEL
- 5.1 GENERAL OVERVIEW, MODEL SELECTION, AND MODEL DESCRIPTION
- 5.2 CONCEPTUAL MODEL DESIGN AND ASSUMPTIONS
- 5.3 INITIAL MODEL SETUP
  - 5.3.1 Grid Design and Boundary Conditions
  - 5.3.2 Groundwater Elevations and Gradients
  - 5.3.3 Contaminant Concentrations
- 5.4 MODEL CALIBRATION
  - 5.4.1 Flow Model Calibration
  - 5.4.2 Transport Model Calibration
- 5.5 SENSITIVITY ANALYSIS
- 5.6 MODEL RESULTS (PREDICTIONS)
  - 5.6.1 Continuation of Calibrated Conditions (Model 1)
  - 5.6.2 Source Removal (Model 2)
  - 5.6.3 Decreasing Source (Model 3)
- 5.7 CONCLUSIONS AND DISCUSSION

6 COMPARATIVE ANALYSIS OF REMEDIAL ALTERNATIVES
- 6.1 REMEDIAL ALTERNATIVE EVALUATION CRITERIA
- 6.2 FACTORS INFLUENCING ALTERNATIVES DEVELOPMENT
- 6.3 BRIEF DESCRIPTION OF REMEDIAL ALTERNATIVES
- 6.4 EVALUATION OF ALTERNATIVES
- 6.5 RECOMMENDED REMEDIAL APPROACH

7 LONG-TERM MONITORING PLAN
- 7.1 MONITORING NETWORKS
  - 7.1.1 Long-Term Monitoring Wells
  - 7.1.2 Point-of-Compliance Wells-
- 7.2 GROUNDWATER SAMPLING
  - 7.2.1 Analytical Protocol
  - 7.2.2 Sampling Frequency

Figure D.2.5

Example Table of Contents

There are several ways to verify a model. Typical ways a model may be verified include (Spitz and Moreno, 1996):

- using a model calibrated to steady-state conditions or a subset of the transient data to successfully predict transient data or a separate transient data set;
- using the model to successfully predict data not used in the calibration process (e.g. concentrations of solutes not considered during calibration);
- comparing model predictions with the results of other models of the similar situation (possibly using a different code or solution technique); and
- checking that data collected after model calibration and implementation supports the predictions made by the model.

If verification data do not agree with what the model predicted, then the model should be recalibrated using the new data. The last method is used frequently due to data constraints on using other methods, and the fact that it generally requires the least amount of additional work. It is the most practical and persuasive method, but requires that modeling and fieldwork be conducted together over some period of time. Fortunately, this method ties in neatly with the LTM component of a natural attenuation demonstration.

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 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 remediation by natural attenuation can be implemented.

### D.2.9.1 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 contaminant plume to verify the results of the solute transport model and to ensure that natural attenuation is occurring at rates sufficient to minimize 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 contaminant exceeding state, federal, or risk-based 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 those parameters required for regulatory compliance.

D.2.9.1.1 Long-Term Monitoring Wells

In at least four locations, groundwater wells within, upgradient, and downgradient of the observed contaminant plume should be used to monitor the effectiveness of natural attenuation in reducing total contaminant mass and minimizing contaminant migration at the site. At least one of these wells should be placed in the anaerobic zone, one should be placed in the aerobic zone, and another well is typically placed downgradient from the aerobic 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.2.9.1.2 Point-of-Compliance Wells

Three POC monitoring wells should be installed downgradient from the leading edge of the contaminant plume. The purpose of the POC wells is to verify that no contaminated groundwater exceeding state, federal, or risk-based 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 solutions presented in this section. Models based on these solutions are 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. 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 | $C(0,t) = C_o$, $0<t\leq t_o$<br>$C(0,t) = 0$, $t>t_o$ |
| 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 | $v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = v_x C_o$, $0<t\leq t_o$<br>$v_x C - D_x \left.\frac{\partial C}{\partial x}\right\|_{x=0} = 0$, $t>t_o$ |

$t_o$ = 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 the 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 chlorinated compounds can commonly be approximated as a first-order process.

### 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

$\lambda$ = 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 | $K := (3.15)\frac{m}{day}$ |
| Hydraulic gradient | $I := 0.02\frac{m}{m}$ |
| Effective porosity | $n_e := 0.25$ |
| Total porosity | $n := 0.35$ |
| Longitudinal dispersivity | $\alpha_x := 30 m$ |
| Initial Contaminant Concentration | $C_o := 12\frac{mg}{liter}$ |

Retardation Coefficient Calculation

| | |
|---|---|
| Contaminant Decay Rate | $\lambda := 0.01\frac{1}{day}$ |
| Soil sorption coefficient | $K_{oc} := 79\frac{mL}{gm}$ |
| Particle mass density (for quartz) | $\rho_s := 2.65\frac{gm}{cm^3}$ |
| Bulk density | $\rho_b := \rho_s(1-n)$ $\rho_b = 1.722\frac{gm}{cm^3}$ |
| Organic carbon content | $f_{oc} := 0.8\%$ |
| Retardation coefficient | $R := 1 + \frac{\rho_b K_{oc} f_{oc}}{n_e}$ $R = 5.354$ |

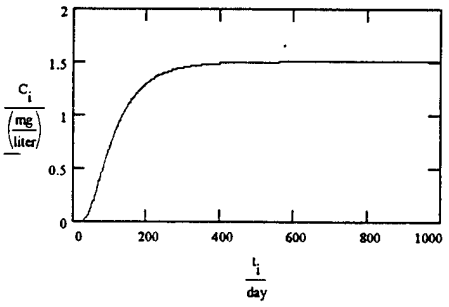
Groundwater Hydraulics Calculations

Groundwater velocity (pore-water) $v_x := \frac{K \cdot I}{n_e}$ $v_x = 0.252\frac{m}{day}$ Retarded Contaminant velocity $v_c := \frac{v_x}{R}$ $v_c = 0.047\frac{m}{day}$

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

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

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




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

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

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

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

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, $\lambda$, is not equal to the decay rate for the source, $\gamma$:

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

Where:

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

and

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

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

$\lambda$ = first-order decay rate constant for dissolved contaminant

$\gamma$ = 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:

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

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

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.

## 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 chlorinated 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:

$$W\left(u, \frac{r}{B}\right) \approx \sqrt{\frac{\pi B}{2r} \exp\left(-\frac{r}{B}\right) erfc\left(-\frac{\frac{r}{B} - 2u}{2\sqrt{u}}\right)} \qquad \text{eq. D.3.11}$$

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 chlorinated 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:

$$C(x,y,z,t) = \frac{C_o}{8} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet erfc\left[\frac{x - t\frac{v_x}{R}\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}}{2\sqrt{\alpha_x \frac{v_x}{R} t}}\right] \qquad \text{eq. D.3.12}$$

$$\bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\}$$

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
$\lambda$ = 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
$\gamma$ = 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:

$$C(x,y,z,t) = \frac{C_o e^{-\gamma t}}{8} \bullet \exp\left\{\frac{x}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}\right)\right\} \bullet erfc\left[\frac{x - t\frac{v_x}{R}\sqrt{1+\frac{4\lambda R\alpha_x}{v_x}}}{2\sqrt{\alpha_x \frac{v_x}{R} t}}\right] \quad \text{eq. D.3.15}$$

$$\bullet \left\{erf\left[\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right]\right\} \bullet \left\{erf\left[\frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right] - erf\left[\frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\right]\right\}$$

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
$\gamma$ = first-order decay rate constant for contaminant source
$\lambda$ = 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.

## D.3.5 COMPUTER APPLICATIONS FOR ANALYTICAL MODELING

Depending upon the needs, resources, and skills of the modeler, analytical modeling can be performed using commonly available spreadsheets, mathematical analysis applications such as MathCAD®, or codes written expressly for analytical modeling. Use of spreadsheets requires the most effort on behalf of the modeler, owing to the need to set up the sheet, enter the appropriate equations, and format the output. Mathematical analysis applications also require the user to enter the equations, but entering the equations and formatting the input and output can be much simpler and more intuitive than in a spreadsheet. However, once set up, both methods provide the modeler with a template that can be used repeatedly. For specific analytical modeling codes, the methods of input vary, as do the methods of displaying output. In general, though, these codes require the least amount of effort on behalf of the user.

A wide range of analytical solute transport modeling software is available. A partial list of codes is presented in Table D.3.4. Some of the codes are proprietary, and some are public domain. Proprietary codes often have graphical interfaces for processing input and output, resulting in a greater cost. Depending on the needs of the user, these extra costs may well be worth the time and labor for preparing and input and output that may be saved by using such a program. Other codes may be available; this is by no means an exhaustive list.

**Table D.3.4**

Listing of Analytical Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| AGU-10 | Analytical flow, advective solute transport, advective-dispersive transport, and advective-dispersive transport with decay of source and solute. Based on American Geophysical Union's Water Resources Monograph 10 (Javandel *et al.*, 1984) | IGWMC; documentation includes AGU Monograph 10 |
| AT123D | Based on analytical solution for transient one-, two-, or three-dimensional transport in a homogeneous isotropic aquifer with uniform regional flow. Allows for retardation, dispersion, and first-order decay, with differing source configurations and boundary conditions. Has a shell for pre- and post-processing. Authored by G.T. Yeh of Oak Ridge National Laboratories. | IGWMC |
| ONE-D | A package of five analytical solutions of the one-dimensional advective-dispersive transport equation with adsorption, dispersion, and first-order-decay options; also includes a zero-order production term. Written by M.T. van Genuchten and W.J. Alves of the US Department of Agriculture's Salinity Laboratory. | IGWMC |
| PLUME, PLUME2D | Analytical models for calculating point concentrations of solutes. Includes advection, dispersion, retardation, and first-order decay. Source terms can be varied over time (in discrete intervals). Written by P.K.M. van der Heijde of the IGWMC. | IGWMC |

**Table D.3.4** (concluded)

Listing of Analytical Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| PRINCE | A proprietary package of ten analytical solute transport and flow models, widely referred to as the Princeton Analytical Models. Seven solute transport models allow calculation of concentrations and breakthrough curves for one-, two-, and three-dimensional problem domains. Advection, dispersion, retardation, and first-order decay all can be simulated, along with a wide range of source terms (including multiple sources in two and three dimensions). A self-contained package with graphical user interface for pre- and post-processing. | Waterloo Hydrogeologic Software or IGWMC |
| SOLUTE | A menu-driven set of five different programs that provide the user with nine different types of analytical solute transport models. The nine models include one-, two-, and three-dimensional solutions with differing boundary conditions and options for retardation and first-order decay. Displays output graphically; output can also be used with other utilities for post-processing. Authored by M.S. Beljin and P.K.M. van der Heijde of IGWMC. | IGWMC |
| USGS-SOL | Analytical solutions describing advective-dispersive transport, as well as first-order decay and retardation. Includes one-, two-, and three-dimensional models with a limited number of boundary conditions. No pre-processor is provided, and the user must set up their own input files. Output can be sent to a file for use in other post-processors. Originally prepared by E.J. Wexler of the USGS. | IGWMC |
| WALTON35 | A set of 35 analytical and numerical models for a variety of groundwater flow and solute transport problems. Input is interactive, and results can be saved to a file. Prepared by W.C. Walton in conjunction with the IGWMC. | IGWMC |

# SECTION D-4

# NUMERICAL MODELS

## D.4.1 OVERVIEW OF NUMERICAL MODELS

Numerical models provide inexact (relative to analytical methods) 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. Numerical model codes can be used to simulate complex hydrogeologic systems or contaminant transport affected by multiple reactions for which rates or properties may vary spatially. Heterogeneous and anisotropic hydrologic systems can be modeled using numerical models, as can transient flow systems (i.e., systems in which stresses, parameters, or boundary conditions affecting or controlling groundwater flow change over time). Another advantage of numerical models is that most codes are more flexible in allowing simulation of contaminant sources that vary over time, allowing more straightforward simulation of scenarios including source reduction through weathering or through engineered solutions. Section D-2 of this Appendix includes a more detailed discussion of specific topics relevant to numerical flow and transport modeling.

Success in groundwater solute fate and transport modeling using numerical methods depends upon 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 understand the limitations of the solution methods and to and present model predictions that are reasonable within those limitations. When using a numerical transport model (and an associated flow model, if applicable), remember that implementation of a numerical model is much more complex than implementation of an analytical model, and generally requires at a minimum the supervision of an experienced hydrogeologist who is familiar with the model code. Also keep in mind the caveats regarding numerical flow and transport modeling that were presented in Section D.1.2. Keep in

mind that any numerical model code or analytical solution selected for a demonstration of remediation by natural attenuation should be properly validated through sufficient previous application at a variety of field sites.

## 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). A great variety of numerical codes are available for simulating groundwater flow and solute transport under the influence of these processes. Some include both flow and transport, while others are either flow or transport models alone, but which may be combined (i.e., flow fields from a flow model are incorporated into a transport model). The selection of a code will ultimately depend upon the user's needs, the available data, the sophistication of the desired predictions, the sophistication of the user's computer hardware, and the limitations of the available model codes.

Some codes are available for simulating the reactant-limited transport of solutes, but these codes are intended largely for simulating transport and biodegradation of petroleum compounds. The reaction is limited to a single instantaneous reaction of the solute with a superimposed dissolved oxygen plume, in which the petroleum compound is destroyed in one step because it is a substrate or electron donor. There are several codes designed specifically for the simulation of reactant-limited solute transport influenced by biodegradation. These include: Bioplume II, Bioplume III, BioTrans©, and Bio1D©. Except for Bioplume III, these codes are readily available. Bioplume III is under development for AFCEE and should be released in 1997.

Ideally, a model for simulating natural attenuation of chlorinated solvents would be able to track the degradation of a parent compound through its daughter products and allow the user to specify differing decay rates for each step of the process. This may be referred to as a reactive transport model, in which transport of a solute may be tracked while it reacts, its properties change due to those reactions, and the rates of the reactions change as the solute properties change. Moreover, the model would also be able to track the reaction of those other compounds that react with or are consumed by the processes affecting the solute of interest (e.g., electron donors and acceptors). At this time, researchers at Battelle Pacific Northwest Laboratories have initiated development of a code to address some of these issues (Sun *et al.*, 1996), called RT3D (for Reactive Transport in Three Dimensions). RT3D is being designed to describe multispecies

transport and reactions, including attenuation of chlorinated compounds and their daughter products, and fate of solid-phase species. Also included are modules for aerobic, instantaneous BTEX reactions (similar to Bioplume II) and multiple-electron-acceptor, kinetically-limited BTEX reactions (similar to Bioplume III). However, widespread release of RT3D may not be accomplished until about the year 2000.

A wide range of other codes that can be used to evaluate contaminant transport with biodegradation is currently available. In these codes, biodegradation reaction rates are typically controlled by a first-order rate constant, rather than by the availability of the reactants. Nonetheless, with appropriately calculated rate constants, these codes often are the most suitable means with which fate and transport of chlorinated solvents dissolved in groundwater may be simulated. Table D.4.1 presents a partial listing of numerical model codes that may be used for simulating the fate and transport of contaminants dissolved in groundwater. Of these codes, the combination of MODFLOW and MT3D may be one of the most commonly used, especially given the number of proprietary software packages that are designed around those programs. Table D.4.1 is not a thorough review of available codes; rather, this overview is to illustrate the variety of readily available codes for personal computers that may be useful in evaluating the natural attenuation of contaminants dissolved in groundwater.

**Table D.4.1**

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| AQUA | Two-dimensional, transient groundwater flow and transport. Aquifer may be heterogeneous and anisotropic, Can simulate advection, dispersion, linear sorption, and decay. A proprietary code with interactive/graphical interface. | Scientific Software Group |
| ASM | Aquifer Simulation Model for two-dimensional modeling of groundwater flow and solute transport. Uses random-walk method for solute transport, and can simulate advection, dispersion, linear sorption, and decay. Aquifer can be heterogeneous and anisotropic. Menu-driven, graphical interface. A proprietary program prepared by W. Kinzelbach (University of Heidelberg) and R. Rausch (University of Stuttgart). | IGWMC |
| BIO1D® | A one-dimensional model for simulation of biodegradation and sorption of hydrocarbons. Transport of substrates and electron acceptors is considered, assuming a uniform flow field. Several reaction options are available for biodegradation and sorption. Has a pre-processor and display graphics. A proprietary code developed at GeoTrans, Inc. | GeoTrans, Inc.; IGWMC |
| Bioplume II | A two-dimensional model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first-order decay, linear sorption, advection, and dispersion. Aquifer may be heterogeneous and anisotropic. Based on the USGS two-dimensional MOC model (including a finite-difference flow model) by Konikow and Bredehoeft (1978). Oxygen limited biodegradation is a reactive transport process. A public-domain code with a menu-driven preprocessor and limited post-processing abilities. Developed by Rifai *et al.* (1989) at Rice University. | IGWMC |

**Table D.4.1** (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| Bioplume III | Successor to Bioplume II. Two-dimensional model for reactive transport of multiple hydrocarbons under the influence of advection, dispersion, sorption, first-order decay, and reactant-limited biodegradation. Development commissioned by AFCEE. Anticipated release in late 1996. Will have interactive, graphical pre- and post-processing capabilities. | AFCEE (currently under development) |
| BioTrans® | A proprietary two-dimensional finite element transport code requiring flow velocity data from another code (e.g., MODFLOW). Models transport of multiple species under the influence of advection, dispersion, sorption, first-order decay, and oxygen-limited biodegradation. Allows internal computation of source terms due to dissolution of NAPL. Graphical, interactive user interface with pre- and post-processing capabilities. Prepared by Environmental Systems and Technologies, Inc. | Environmental Systems and Technologies, Inc. |
| FEMSEEP | A set of programs for solving steady-state and transient groundwater flow and solute transport problems in simplified two- and three-dimensional systems. Transport under the influence of advection, dispersion, linear sorption, and first-order decay may be simulated using finite element methods. A proprietary program with graphical and menu-driven user interfaces and pre- and post-processing capabilities. Prepared by D. Meiri of FEMSEEP Software, Inc. | FEMSEEP Software, Inc.; IGWMC |

**Table D.4.1** (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| FEMWATER, FEMWASTE | Finite-element flow (FEMWATER) and transport (FEMWASTE) models. FEMWATER can simulate variably saturated conditions in two and three dimensions. FEMWASTE can simulate transport in one, two, and three dimensions. The system may be heterogeneous and anisotropic, and the code can account for advection, dispersion, first-order decay, and 3 types of sorption. Public domain codes developed by researchers at Oak Ridge, National Laboratories. Some proprietary versions of FEMWATER are available; they are based on the Department of Defense's Groundwater Modeling System (GMS) modeling and data management package. | Oak Ridge National Laboratories, NTIS, distributors of proprietary GMS programs. |
| FLONET®, FLOTRANS® | Two-dimensional steady-state groundwater flow (FLONET) and transient solute transport (FLOTRANS) models for cross-sectional problems. FLOTRANS is an extension of FLONET that can simulate transport under the influence of advection, dispersion, linear sorption, and first-order decay. A proprietary program with an interactive graphical user interface and extensive pre- and post-processing capabilities. Developed by Waterloo Hydrogeologic Software, Inc. | IGWMC; Waterloo Hydrogeologic Software, Inc. |
| FTWORK | A block-centered finite-difference model for one, two, and three-dimensional flow and transport. The transport model includes advection, dispersion, first-order decay, and two types of sorption (linear and non-linear equilibrium). A public domain code that may be acquired with a proprietary (IGWMC) textual and menu-driven preprocessor and post-processor. Originally developed by Faust *et al.* (1990) at GeoTrans, Inc. | IGWMC; GeoTrans, Inc. |

**Table D.4.1** (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| HST3D | Program for simulating groundwater flow and associated heat and solute transport in three dimensions. Solute transport is for a single solute with advection, dispersion, linear sorption, and first-order decay. A public-domain code with no pre- and post-processors. Prepared by K.L. Kipp of the USGS. | IGWMC |
| MOC, USGS2D-MOC | A two-dimensional model for simulation of groundwater flow and non-conservative solute transport. Derived from the original model developed by Konikow and Bredehoeft (1978). The latest version (March 1995) simulates transport under the influence of advection, dispersion, first-order decay, reversible equilibrium-controlled sorption, and reversible equilibrium-controlled ion exchange. The flow model is a finite-difference model, while transport is simulated using MOC methods. A public-domain code with an interactive preprocessor. | IGWMC |
| MODFLOW | A block-centered finite-difference code for steady-state and transient simulation of groundwater flow in two and three dimensions. Consists of a main program and a large number of subroutines (modules) that are used to simulate a wide variety of boundaries and stresses on the hydrogeologic system. Originally coded by McDonald and Harbaugh (1988) of the USGS. Possibly the most widely used flow model in the US and Canada, MODFLOW can be used to generate flow fields that may be coupled with a wide variety of transport models (e.g., MT3D, BioTrans®, or RAND3D). The popularity of MODFLOW is also evidenced by the great number of proprietary pre- and post-processing programs that are available. MODFLOW is a public-domain code, although it is typically acquired in conjunction with a pre-/post-processing package. | USGS; IGWMC; in addition, many companies have developed pre- and post-processing programs with a wide variety of capabilities and features. |

**Table D.4.1** (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| MODFLOWP | An extension of MODFLOW that includes a package that uses nonlinear regression techniques to estimate model parameters under constraints given by the modeler. Model input includes statistics for analyzing the parameter estimates and the model to quantify the reliability of the resulting model, to suggest changes in model construction, and to compare results of models constructed in different ways. Prepared by M.C. Hill of the USGS. Requires a user with advanced skills. | USGS; IGWMC |
| MT3D | A three-dimensional transport model for simulation of advection, dispersion, linear or non-linear sorption, and first-order decay of a single species. Uses a modular structure similar to that of MODFLOW. Intended for use with any block-centered finite-difference flow model, such as MODFLOW, on the assumption that concentration changes will not affect the flow field. MT3D uses one of three methods (all based on MOC) for solution of the transport equation. Prepared by C. Zheng (for S.S. Papadopulos & Associates, Inc.), MT3D is available in public-domain and proprietary versions. Proprietary versions are typically the most advanced in terms of pre- and post-processing capabilities. | S.S. Papadopulos & Associates, Inc.; IGWMC; many versions available from many companies with pre- and post-processing programs with a wide variety of capabilities and features. Often coupled with MODFLOW in such codes. Public domain version may be acquired from USEPA. |
| RANDOM WALK | A code for simulation of two-dimensional groundwater flow and solute transport. Flow is simulated using either analytical solutions or a version of the PLASM finite-difference model (Prickett and Lonnquist, 1971). Transport is simulated using particle-tracking methods coupled with the random-walk technique for dispersion. The model also handles first-order decay, linear sorption, and zero-order production. A public domain code originally produced at the Illinois State Water Survey (Prickett *et al.*, 1981). The IGWMC version includes pre- and post-processing utilities. | IGWMC |

**Table D.4.1** (continued)

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| RAND3D | A three-dimensional version of the random walk algorithm developed by Prickett *et al.* (1981). RAND3D is designed to be coupled with MODFLOW input files for calculation of velocity vector files that are used to run the code. May be used for transient simulation of advection, dispersion, linear sorption, and zero-order, first-order, or variable-order-decay. Code has some pre- and post-processing capabilities. A proprietary code prepared by D. Koch of Engineering Technologies Associates and T.A. Prickett. | IGWMC |
| RT3D | A modification of MT3D, under development by researchers at Washington State University and Pacific Northwest National Laboratory. RT3D (Reactive Transport in Three Dimensions) is being designed to describe multispecies transport and reactions, including attenuation of chlorinated compounds and their daughter products, and fate of solid-phase species. Also included are modules for aerobic, instantaneous BTEX reactions (similar to Bioplume II) and multiple-electron-acceptor, kinetically-limited BTEX reactions (similar to Bioplume III). | Under Development |
| SUTRA | A code for simulating two-dimensional fluid movement and transport of energy or dissolved substances. May be used for saturated systems or variably saturated systems in profile view. Can simulate advection, dispersion, sorption, and first-order decay. A public-domain code originally prepared by C.I. Voss of the USGS. IGWMC version has a graphical post-processor. | IGWMC; USGS |

**Table D.4.1** (concluded)

Listing of Numerical Groundwater Flow and Solute Transport Models

| Model Code Name | Capabilities | Distributor |
|---|---|---|
| SWICHA | A three-dimensional finite-element code for simulating steady-state and transient flow and transport in confined (fully saturated) aquifers. Transport includes advection, dispersion, sorption, and first-order decay. A public domain code with no pre- or post-processing capabilities. Authored by B. Lester of GeoTrans, Inc. | IGWMC |
| SWIFT, SWIFT/486 | A fully three-dimensional finite-difference model for simulating flow and transport of fluid, heat, and solutes in porous and fractured media. Includes linear and nonlinear sorption, dispersion, diffusion, and decay, as well as dissolution, leaching, and dual porosity. An advanced code developed at Sandia National Laboratories (Reeves and Cranwell, 1981); now in the custody of GeoTrans, Inc. Public domain and proprietary versions of the code are available through IGWMC. | IGWMC |
| SWMS_2D | A two-dimensional model for simulating water and solute movement in variably saturated media. Includes dispersion, linear sorption, zero-order production, and first-order decay. A public domain code prepared by researchers at the US Salinity Lab. No pre- or post-processing utilities. | IGWMC |
| TARGET | A code for simulating two- and three-dimensional flow and transport under a wide variety of conditions. Can simulate advection, dispersion, diffusion, sorption, and first-order decay. A proprietary code prepared by workers at Dames & Moore, Inc. Has been used for a wide variety of applications. | Dames & Moore, Inc. |

# APPENDIX E

# NATURAL ATTENUATION OF CHLORINATED ALIPHATIC HYDROCARBONS AT PLATTSBURGH AIR FORCE BASE, NEW YORK

# NATURAL ATTENUATION OF CHLORINATED ALIPHATIC HYDROCARBONS AT PLATTSBURGH AIR FORCE BASE, NEW YORK

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## INTRODUCTION

Activities at a former fire training area (Site FT-002) at Plattsburgh Air Force Base (AFB) in New York resulted in contamination of shallow soils and groundwater with a mixture of chlorinated solvents and fuel hydrocarbons. Groundwater contaminants include trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), vinyl chloride, and benzene, toluene, ethylbenzene, and xylenes (BTEX). Table 1 contains contaminant data for selected wells at the site.

Table 1
Analytical Data, Plattsburgh Air Force Base

| Point | Date | Distance From Source (feet) | TMB (µg/L) | BTEX (µg/L) | TCE (µg/L) | Total DCE* (µg/L) | Vinyl Chloride (µg/L) | Methane (µg/L) | Ethene (µg/L) | Chloride (mg/L) | Dissolved Oxygen (mg/L) | Nitrate (mg/L) | Iron (II) (mg/L) | Sulfate (mg/L) | Hydrogen (nanomolar) | TOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Aug-95 | 0 | 1,757 | 16,790 | 25,280 | 51,412 | 0 | 1,420 | <0.001 | 63 | 0.1 | 0.2 | 4.0 | 5.5 | 6.70 | 80 |
| | May-96 | | 828 | 6,598 | 580 | 12,626 | 0 | 1,600 | <0.001 | 82 | 0.5 | 0.0 | 45.6 | 1.0 | 2.00 | 94 |
| B | Aug-95 | 970 | 491 | 3,060 | 2 | 14,968 | 897 | 305 | 35.00 | 48 | 0.5 | 0.2 | 15.3 | 0.0 | 1.66 | 30 |
| | May-96 | | 463 | 4,198 | 1 | 9,376 | 1,520 | 339 | 13.00 | 43 | 0.1 | 0.0 | 16.0 | 0.0 | 1.40 | 31 |
| C | Aug-95 | 1,240 | 488 | 3,543 | 3 | 10,035 | 1,430 | 1,010 | 182.00 | 46 | 0.4 | 0.2 | 13.8 | 0.0 | NA | 21 |
| | May-96 | | 509 | 3,898 | 1 | 10,326 | 1,050 | 714 | 170.00 | 57 | 0.2 | 0.0 | 19.3 | 0.0 | 11.13 | 24 |
| D | Aug-95 | 2,050 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | May-96 | | 9 | 89 | 0 | 1,423 | 524 | 617 | 4.00 | 14 | 0.2 | 0.1 | 2.5 | 1.5 | NA | 14 |
| E | Aug-95 | 2,560 | 0 | 40 | 24 | 2,218 | 8 | 3,530 | <0.001 | 20 | 0.9 | 0.3 | 0.7 | 0.5 | NA | 8 |
| | May-96 | | 0 | 40 | 17 | 1,051 | 12 | 1,800 | <0.001 | 18 | 0.1 | 0.0 | 0.0 | 1.0 | 0.81 | 8 |
| F | Aug-95 | 3,103 | 0 | 2 | 1 | 226 | 5 | 115 | <0.001 | 3 | 0.4 | 10.4 | 0.0 | 14.7 | 0.22 | NA |
| | May-96 | | 0 | 2 | 0 | 177 | 4 | 44 | <0.001 | 3 | 0.2 | 9.5 | 0.1 | 14.4 | 0.25 | NA |

* Greater than 99 percent of DCE is *cis*- 1,2-DCE
NA = Not analyzed
Point A=MW-02-108, B=MW-02-310, C=84DD, D=84DF, E=34PLTW12, F=35PLTW13

Contaminant plumes formed by chlorinated aliphatic hydrocarbons (CAHs) dissolved in groundwater can exhibit three types of behavior based on the amount and type of primary substrate present in the aquifer. Type 1 behavior occurs where anthropogenic carbon such as BTEX or landfill leachate is being utilized as the primary substrate for microbial degradation. Such plumes typically are anaerobic, and the reductive dechlorination of highly chlorinated CAHs introduced into such a system can be quite rapid. Type 2 behavior occurs in areas that are characterized by high natural organic carbon concentrations and anaerobic conditions. Under these conditions, microorganisms utilize the natural organic carbon as a primary substrate and, if redox conditions are favorable, highly chlorinated CAHs introduced into this type of system will be reductively dechlorinated. Type 3 behavior occurs in areas characterized by .low natural organic carbon concentrations, low anthropogenic carbon concentrations, and aerobic or weakly reducing conditions. Biodegradation of CAHs via reductive dechlorination will not occur under these conditions. However, biodegradation of the less chlorinated compounds, such as vinyl chloride can occur via oxidation.

Plattsburgh AFB is located in northeastern New York State, approximately 26 miles south of the Canadian border and 167 miles north of Albany, New York. Site FT-002 is located in the northwest corner of the base and is approximately 700 feet wide and 800 feet long. The site is located on a land surface that slopes gently eastward toward the confluence of the Saranac and the Salmon Rivers, which is located approximately 2 miles east of the

site. Site FT-002 was used to train base and municipal fire-fighting personnel from the mid- to late-1950s until the site was permanently closed to fire training activities in May 1989. Figure 1 is a map of the site.

Four distinct stratigraphic units underlie the site: sand, clay, till, and carbonate bedrock. Figure 2 shows three of the four stratigraphic units at the site. The sand unit consists of well-sorted, fine- to medium-grained sand with a trace of silt and generally extends from ground surface as much as 90 feet below ground surface (bgs) in the vicinity of the site. A 7-foot-thick clay unit has been identified on the eastern side of the site. The thickness of the clay on the western side of the site has not been determined. A 30- to 40-foot-thick clay till unit is also present from 80 to 105 feet bgs in the vicinity of the site. Bedrock is located approximately 105 feet bgs.

## GROUNDWATER HYDRAULICS

The depth to groundwater in the sand aquifer ranges from 45 feet bgs on the west side of the site to zero on the east side of the runway, where groundwater discharges to a swamp (Figure 2). Groundwater flow at the site is to the southeast. The average gradient is approximately 0.010 foot per foot (ft/ft). Hydraulic conductivity of the upper sand aquifer was measured using constant drawdown tests and rising head tests. Hydraulic conductivity values for the unconfined sand aquifer underlying the site range from 0.059 to 90.7 feet per day (ft/day). The average hydraulic conductivity for the site is 11.6 ft/day. Freeze and Cherry (1979) give a range of effective porosity for sand of 0.25 to 0.50. Effective porosity was assumed to be 0.30. Using the horizontal gradient of 0.010 ft/ft, the average hydraulic conductivity value of 11.6 ft/day, and an effective porosity of 0.30 yields an average advective groundwater velocity for the unconfined sand aquifer of 0.39 ft/day, or approximately 142 ft/year. Because of low background total organic carbon concentrations at the site, retardation is not considered to be an important transport parameter.

## GROUNDWATER AND LNAPL CHEMISTRY

*Contaminants*

Figure 1 shows the approximate distribution of light non-aqueous phase liquid (LNAPL) at the site. This LNAPL is a mixture of jet fuel and waste solvents that partitions BTEX and TCE to groundwater. Analysis of this LNAPL shows that the predominant chlorinated solvents are PCE and TCE; dichloroethene (DCE) and vinyl chloride are not present in measurable concentrations. For the most part, groundwater beneath and downgradient from the LNAPL is contaminated with dissolved fuel-related compounds and solvents consistent with those identified in the LNAPL. The most notable exceptions are the presence of *cis*-1,2-DCE and vinyl chloride, which, because of their absence in the LNAPL, probably were formed by reductive dechlorination of TCE.

The dissolved BTEX plume currently extends approximately 2,000 feet downgradient from the site, and has a maximum width of about 500 feet. Total dissolved BTEX concentrations as high as 17 milligrams per liter (mg/L) have been observed in the source area. Figure 3 shows the extent of BTEX dissolved in groundwater. As indicated on this map, dissolved BTEX contamination is migrating to the southeast in the direction of groundwater flow. Five years of historical data for the site shows that the dissolved BTEX plume is at steady-state equilibrium and is no longer expanding.

Detectable concentrations of dissolved TCE, DCE, and vinyl chloride currently extend approximately 4,000 feet downgradient from FT-002. Concentrations of TCE, DCE, and vinyl chloride as high as 25 mg/L, 51 mg/L and 1.5 mg/L, respectively, have been observed at the site. As stated previously, no DCE was detected in the LNAPL plume at the site and greater than 99 percent of the DCE found in groundwater is the *cis*-1,2-DCE isomer. Figure 3 shows the extents of CAH compounds dissolved in groundwater at the site. As indicated on this map, contamination is migrating to the southeast in the direction of groundwater flow. Five years of historical data for the site shows that the dissolved CAH plume is at steady-state equilibrium and is no longer expanding.

*Indicators of Biodegradation*

Figure 4 shows the distribution of electron acceptors used in microbially mediated oxidation-reduction reactions. Electron acceptors displayed in this figure include dissolved oxygen, nitrate, and sulfate. There is a strong correlation between areas with elevated BTEX concentrations and areas with depleted dissolved oxygen, nitrate, and sulfate. The absence of these compounds in contaminated groundwater suggests that aerobic respiration, denitrification, and sulfate reduction are working to biodegrade fuel hydrocarbons at the site.

Background dissolved oxygen, nitrate, and sulfate concentrations are on the order of 10 mg/L, 10 mg/L, and 25 mg/L, respectively.

Figure 5 shows the distribution of metabolic byproducts produced by microbially mediated oxidation-reduction reactions that biodegrade fuel hydrocarbons. Metabolic byproducts displayed in this figure include iron (II) and methane. There is a strong correlation between areas with elevated BTEX concentrations and areas with elevated iron (II) and methane. The presence of these compounds in concentrations above background in contaminated groundwater suggests that iron (III) reduction and methanogenesis are working to biodegrade fuel hydrocarbons at the site. Background iron (II) and methane concentrations are <0.05 mg/L and <0.001 mg/L, respectively. The pE of groundwater is shown in Figure 5. Areas of low pE correspond to areas with contamination. This is an indication that biologically mediated oxidation-reduction reactions are occurring in the area with groundwater contamination.

The distribution of chloride in groundwater is shown in Figure 3. This figure also compares measured concentrations of total BTEX and CAHs in the groundwater with chloride. There is a strong correlation between areas with contamination and areas with elevated chloride concentrations relative to measured background concentrations. The presence of elevated concentrations of chloride in contaminated groundwater suggests that TCE, DCE, and vinyl chloride are being biodegraded. Background chloride concentrations at the site are approximately 2 mg/L. The distribution of ethene in groundwater is shown in Figure 3. This figure also compares measured concentrations of total BTEX and CAHs in the groundwater with ethene. There is a strong correlation between areas with contamination and areas with elevated ethene concentrations relative to measured background concentrations. The presence of elevated concentrations of ethene in contaminated groundwater suggests that TCE, DCE, and vinyl chloride are being biodegraded. Background ethene concentrations at the site are <0.001 mg/L.

Dissolved hydrogen concentrations can be used to determine the dominant terminal electron-accepting process in an aquifer. Table 2 presents the range of hydrogen concentrations for a given terminal electron-accepting process. Much research has been done on the topic of using hydrogen measurements to delineate terminal electron-accepting processes (Lovley and Goodwin, 1988; Lovley *et al.*, 1994; and Chapelle *et al.*, 1995). Table 1 presents hydrogen data for the site.

Table 2

Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

| Terminal Electron Accepting Process | Hydrogen Concentration (nanomoles per liter, nM) |
|---|---|
| Denitrification | < 0.1 |
| Iron (III) Reduction | 0.2 to 0.8 |
| Sulfate Reduction | 1 to 4 |
| Methanogenesis | > 5 |

## BIODEGRADATION RATE CONSTANT CALCULATIONS

Apparent biodegradation rate constants were calculated using the method presented in Wiedemeier *et al.*, (1995 and 1996) for trimethylbenzene. A modified version of this method that takes into account the production of chloride during biodegradation also was used to calculate approximate biodegradation rates. Table 3 presents the results of these rate constant calculations.

## PRIMARY SUBSTRATE DEMAND FOR REDUCTIVE DECHLORINATION

In order for reductive dechlorination to occur, a carbon source that can be used as a primary substrate must be present in the aquifer. This carbon substrate can be in the form of anthropogenic carbon (e.g., fuel hydrocarbons) or native organic material.

Table 3
Approximate First-Order Biodegradation Rate Constants

| Compound | Correction Method | A - B 0 - 970 ft (1/year) | B - C 970 - 1,240 ft (1/year) | C - E 1,240 - 2,560 ft (1/year) |
|---|---|---|---|---|
| TCE | Chloride | 1.27 | 0.23 | -0.30 |
| | TMB | 1.20 | 0.52 | N/A |
| | Average | 1.24 | 0.38 | -0.30 |
| DCE | Chloride | 0.06 | 0.60 | 0.07 |
| | TMB | 0.00 | 0.90 | N/A |
| | Average | 0.03 | 0.75 | 0.07 |
| VC | Chloride | 0.00 | 0.14 | 0.47 |
| | TMB | 0.00 | 0.43 | N/A |
| | Average | 0.00 | 0.29 | 0.47 |
| BTEX | Chloride | 0.13 | 0.30 | 0.39 |
| | TMB | 0.06 | 0.60 | N/A |
| | Average | 0.10 | 0.45 | 0.39 |

*Reductive Dechlorination Supported by Fuel Hydrocarbons (Type 1 Behavior)*

Fuel hydrocarbons are known to support reductive dechlorination in aquifer material (Sewell and Gibson, 1991). The equation below describes the oxidation of BTEX compounds (approximated as CH) to carbon dioxide during reduction of carbon to chlorine bonds (represented as C-Cl) to carbon to hydrogen bonds (represented as (C-H).

$$CH + 2H_2O + 2.5C\text{-}Cl \rightarrow CO_2 + 2.5H^+ + 2.5Cl^- + 2.5C\text{-}H \qquad \text{eq. (1)}$$

Based on equation (1), each 1.0 milligram (mg) of BTEX that is oxidized via reductive dechlorination requires the consumption of 6.8 mg of organic chloride and the liberation of 6.8 mg of biogenic chloride. Trichloroethene loses two C-Cl bonds while being reduced to vinyl chloride. Based on equation (1), ½ x 2.5 = 1.25 moles of TCE would have to be reduced to vinyl chloride to oxidize one mole of BTEX to carbon dioxide. Therefore, 1.0 mg of BTEX oxidized would consume 12.6 mg of TCE. If DCE were reduced to vinyl chloride, each 1.0 mg of BTEX oxidized would consume 18.6 mg of DCE. To be more conservative, these calculations should be completed assuming that TCE and DCE are reduced to ethene. However, because the amount of ethene produced is trivial compared to the amount of TCE and DCE destroyed, we have omitted this step here.

*Reductive Dechlorination Supported by Natural Organic Carbon (Type 2 Behavior)*

Wershaw *et al.*, (1994) analyzed dissolved organic material in groundwater underneath a dry well that had received TCE discharged from the overflow pipe of a degreasing unit. The dissolved organic material in groundwater exposed to the TCE was 50.57 percent carbon, 4.43 percent hydrogen, and 41.73 percent oxygen. The elemental composition of this material was used to calculate an empirical formula for the dissolved organic matter, and to estimate the number of moles of C-Cl bonds required to reduce one mole of dissolved organic carbon in this material.

$$C_{1.0}H_{1.051}O_{0.619} + 1.38H_2O + 1.91C\text{-}Cl \rightarrow CO_2 + 1.91Cl^- + 1.91C\text{-}H + 1.91H^+ \qquad \text{eq. (2)}$$

Based on equation (2), each 1.0 milligram (mg) of dissolved organic carbon that is oxidized via reductive dechlorination requires the consumption of 5.65 mg of organic chloride and the liberation of 5.65 mg of biogenic chloride. Using equation (2), ½ x 1.91 = 0.955 moles of TCE would have to be reduced to vinyl chloride to oxidize one mole of organic carbon to carbon dioxide. Therefore, 1.0 mg of organic carbon oxidized would consume 10.5 mg of TCE. If DCE were reduced to vinyl chloride, each 1.0 mg of organic carbon oxidized would consume 15.4 mg of DCE.

Table 4 compares the electron donor demand required to dechlorinate the alkenes remaining in the plume with the supply of potential electron donors. Table 3 reveals that removal of TCE and *cis*-1,2-DCE slows or ceases between points C and E. This correlates with the exhaustion of BTEX in the plume. Over this interval, the supply

of BTEX is a small fraction of the theoretical demand required for dechlorination. There are adequate supplies of native organic matter, suggesting that native organic matter may not be of sufficient nutritional quality to support reductive dechlorination in this aquifer.

Table 4

Comparison of the Estimated Electron Donor Demand to Support
Reductive Dechlorination to the Supply of BTEX and Native Organic Carbon

| Point | Chloride (mg/L) | Organic Chloride (mg/L) | BTEX Available (mg/L) | BTEX Demand (mg/L) | Total Organic Carbon Supply (mg/L) | Organic Carbon Demand (mg/L) |
|---|---|---|---|---|---|---|
| A | 63 | 58.1 | 16.8 | 8.5 | 80.4 | 10.3 |
| B | 43 | 7.72 | 4.2 | 1.13 | 31.1 | 1.37 |
| C | 57 | 8.26 | 3.9 | 1.21 | 24.3 | 1.46 |
| D | 13.6 | 1.34 | 0.09 | 0.20 | 13.8 | 0.24 |
| E | 18.4 | 0.78 | 0.04 | 0.114 | 8.2 | 0.14 |

## DISCUSSION AND CONCLUSIONS

Available geochemical data indicate that the geochemistry of groundwater in the source area and about 1,500 feet downgradient is significantly different than the groundwater found between 1,500 and 4,000 feet downgradient from the source. Near the source the plume exhibits Type 1 behavior. At about 1,500 feet downgradient from the source, the plume reverts to Type 3 behavior. Figure 6 shows the zones of differing behavior at the site.

*Type 1 Behavior*

In the area extending to approximately 1,500 feet downgradient from the former fire training pit (source area), the dissolved contaminant plume consists of commingled BTEX and TCE and is characterized by anaerobic conditions that are strongly reducing (i.e., Type 1 behavior). Dissolved oxygen concentrations are on the order of 0.1 mg/L (background = 10 mg/L), nitrate concentrations are on the order of 0.1 mg/L (background = 10 mg/L), iron (II) concentrations are on the order of 15 mg/L (background = <0.05 mg/L), sulfate concentrations are < 0.05 mg/L (background = 25 mg/L), and methane concentrations are on the order of 3.5 mg/L (background = <0.001 mg/L). Hydrogen concentrations in the source area range from 1.4 to 11 nanomolar (nM). As shown by Table 2, these hydrogen concentrations are indicative of sulfate reduction and methanogenesis, even though there is no sulfate available and relatively little methane is produced. Thus, reductive dechlorination may be competitively excluding these processes. In this area BTEX is being used as a primary substrate and TCE is being reductively dechlorinated to *cis-1,2*-DCE and vinyl chloride. This is supported by the fact that no detectable DCE or vinyl chloride was found in the LNAPL present at the site and is strong evidence that the DCE and vinyl chloride found at the site are produced by the biogenic reductive dechlorination of TCE. Furthermore, the dominant isomer of DCE found at the site is *cis*-1,2-DCE, the isomer preferentially produced during reductive dechlorination. Average calculated first-order biodegradation rate constants in this zone are as high as 1.24/year, 0.75/year, and 0.29/year for TCE, *cis-1,2*-DCE, and vinyl chloride, respectively. Figure 6 shows the approximate extent of this type of behavior. Because reductive dechlorination of vinyl chloride is slower than direct oxidation, vinyl chloride and ethene are accumulating in this area (Figure 7).

*Type 3 Behavior*

Between 1,500 and 2,000 feet downgradient from the source area, the majority of the BTEX has been biodegraded and the system begins to exhibit Type 3 behavior. Dissolved oxygen concentrations are on the order of 0.5 mg/L (background = 10 mg/L). Nitrate concentrations start increasing downgradient of where Type 3 behavior begins and are near background levels of 10 mg/L at the downgradient extent of the CAH plume. Iron (II) concentrations have significantly decreased and are on the order of 1 mg/L (background = <0.05 mg/L). Sulfate concentrations start increasing to 15 mg/L at the downgradient extent of the CAH plume. Methane concentrations are the highest in this area but could have migrated from upgradient locations. The hydrogen concentrations at points E and F are 0.8 nM and 0.25 nM, respectively, suggesting that the dominant terminal

electron-accepting process in this area is iron (III) reduction. These conditions are not optimal for reductive dechlorination and it is likely that vinyl chloride is being oxidized via iron (III) reduction or aerobic respiration. Average calculated rate constants in this zone are -0.3/year, 0.07/year, and 0.47/year for TCE, *cis-1,2*-DCE, and vinyl chloride, respectively. The biodegradation rates of TCE and DCE slow because reductive dechlorination stops when the plume runs out of primary substrate (i.e., BTEX). The rate of vinyl chloride biodegradation in this area increases, likely because vinyl chloride is being oxidized. Because biodegradation of vinyl chloride is faster under Type 3 geochemical conditions than the biodegradation of other CAH compounds, the accumulation of vinyl chloride ceases and the accumulated vinyl chloride rapidly degrades. Ethene concentrations also begin to decrease because ethene is no longer being produced from the reductive dechlorination of vinyl chloride (Figure 7).

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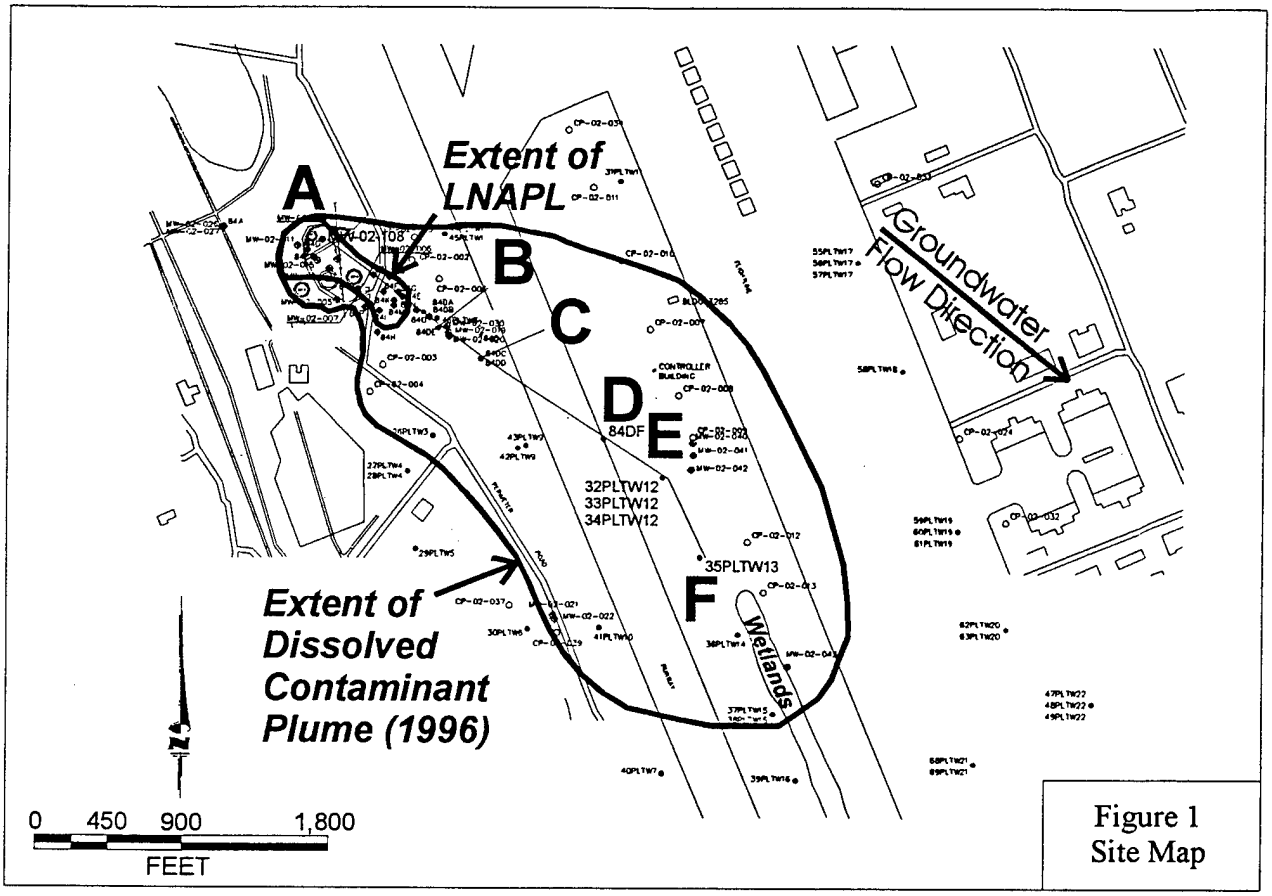



Figure 1
Site Map

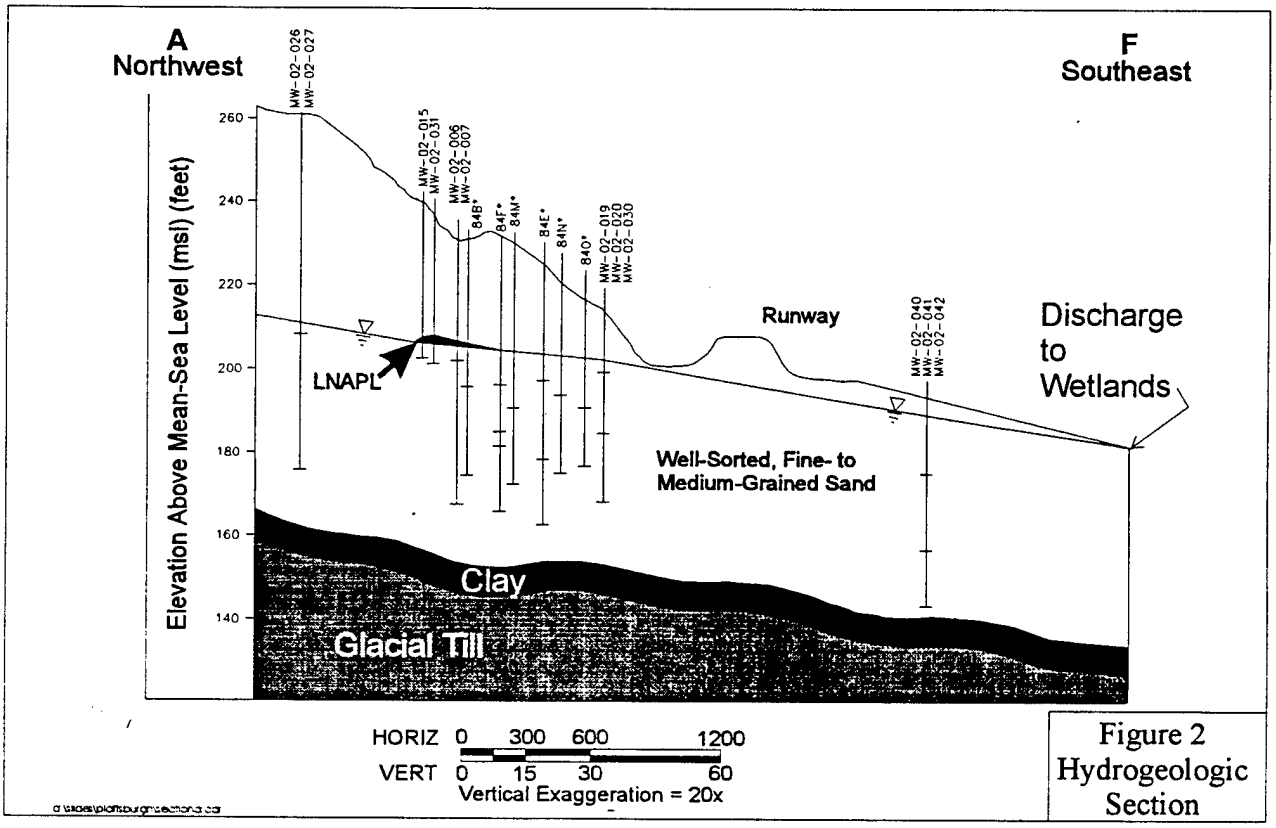



Figure 2
Hydrogeologic Section

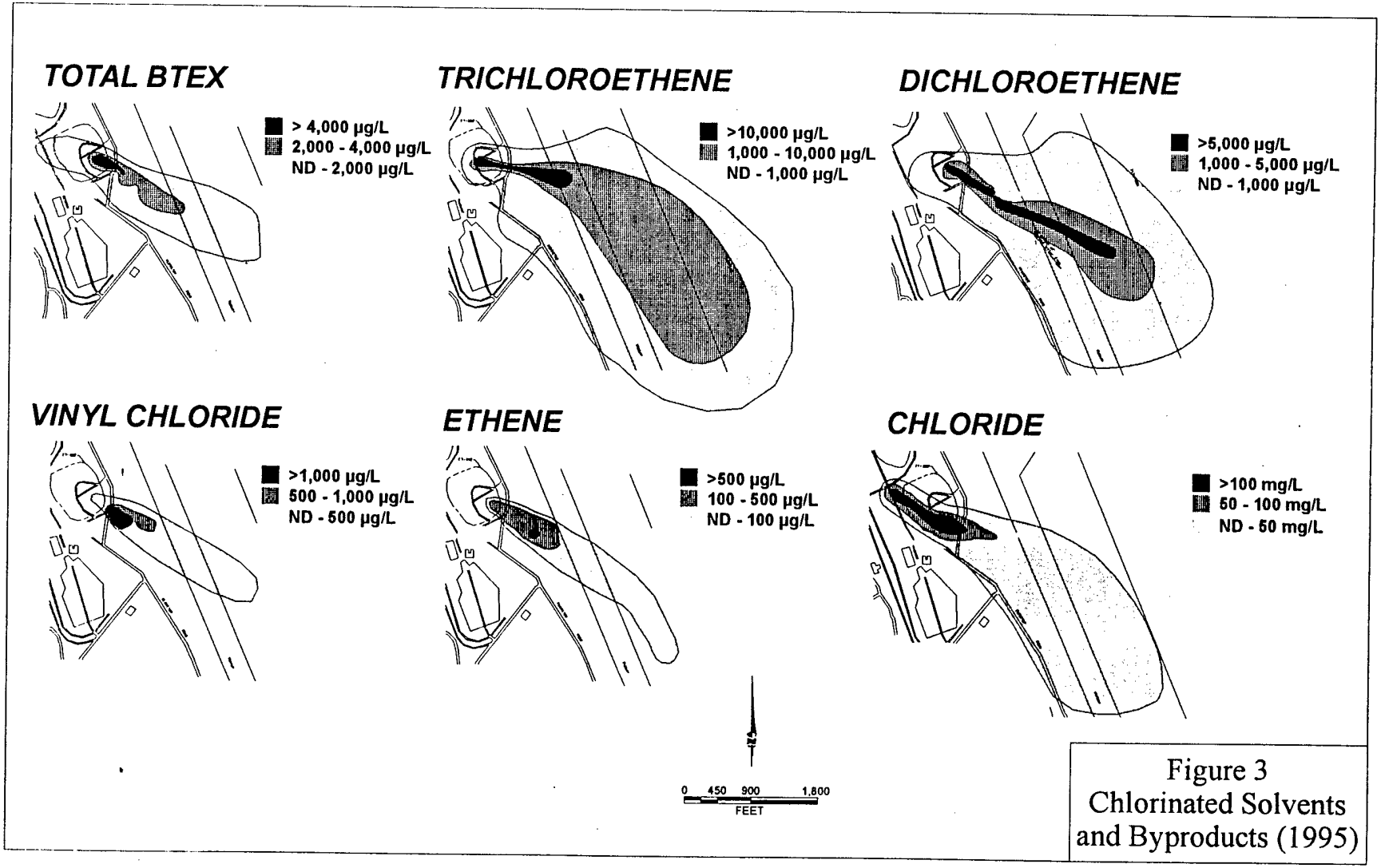



Figure 3
Chlorinated Solvents
and Byproducts (1995)

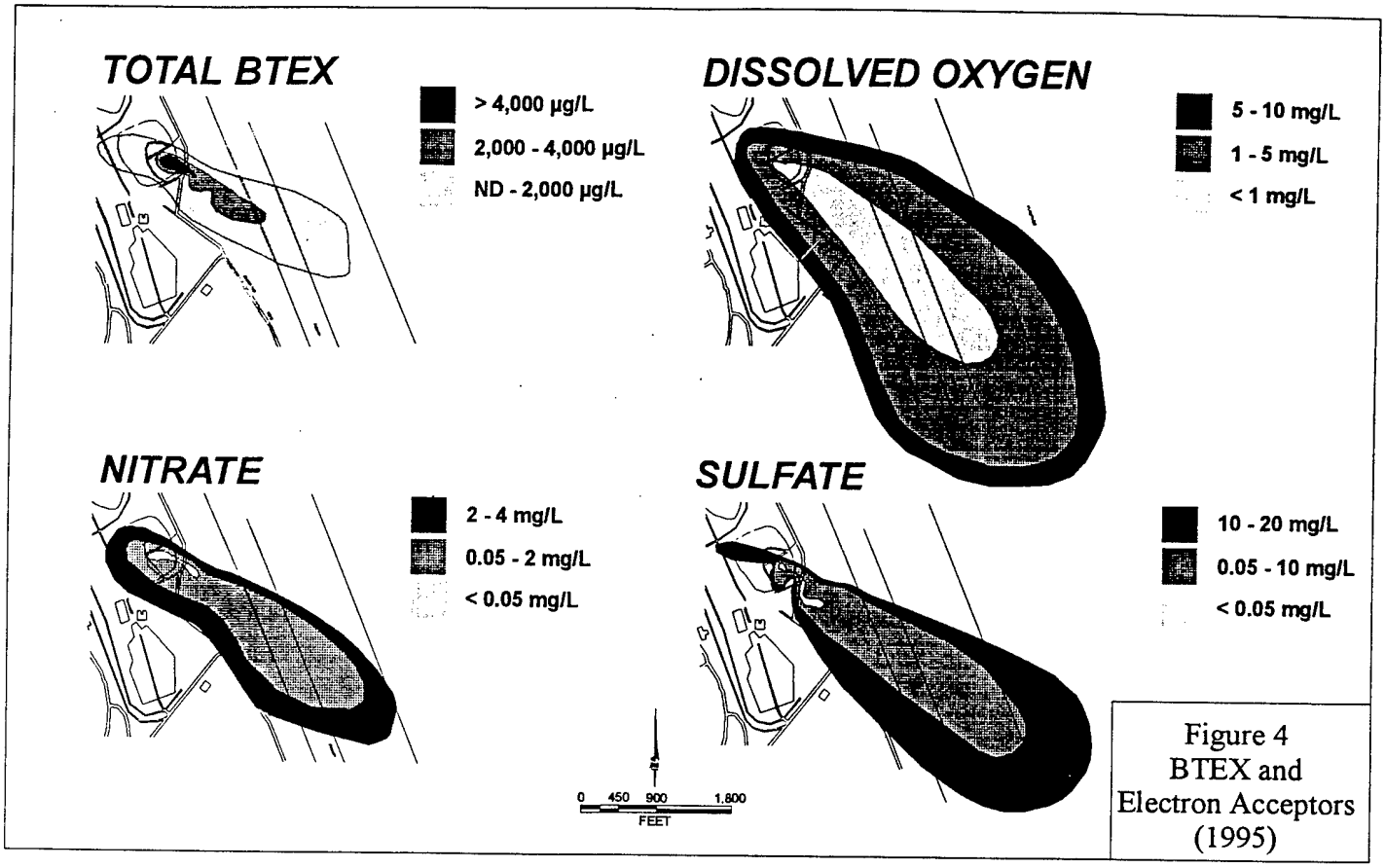



Figure 4
BTEX and
Electron Acceptors
(1995)

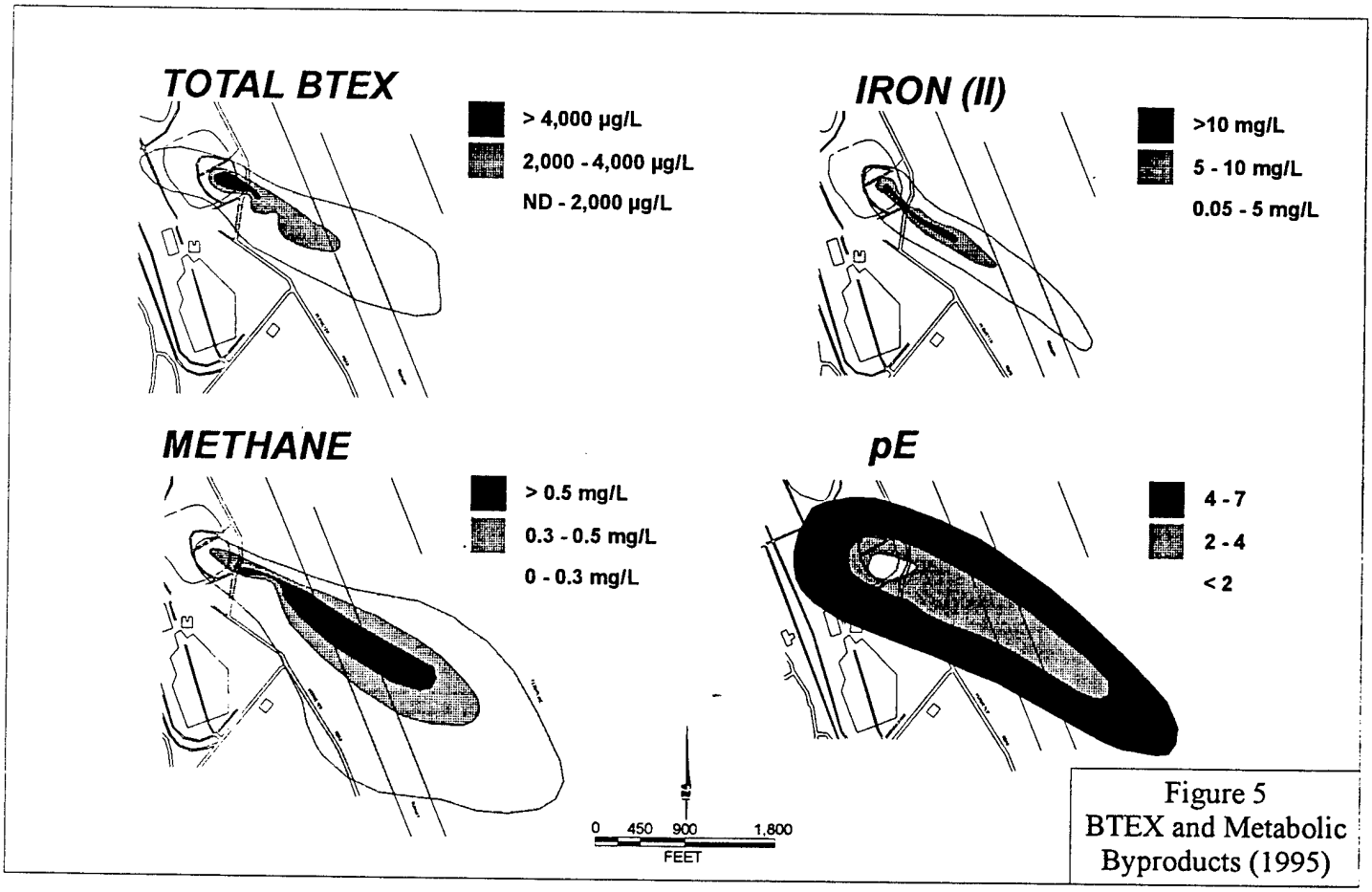



Figure 5
BTEX and Metabolic
Byproducts (1995)

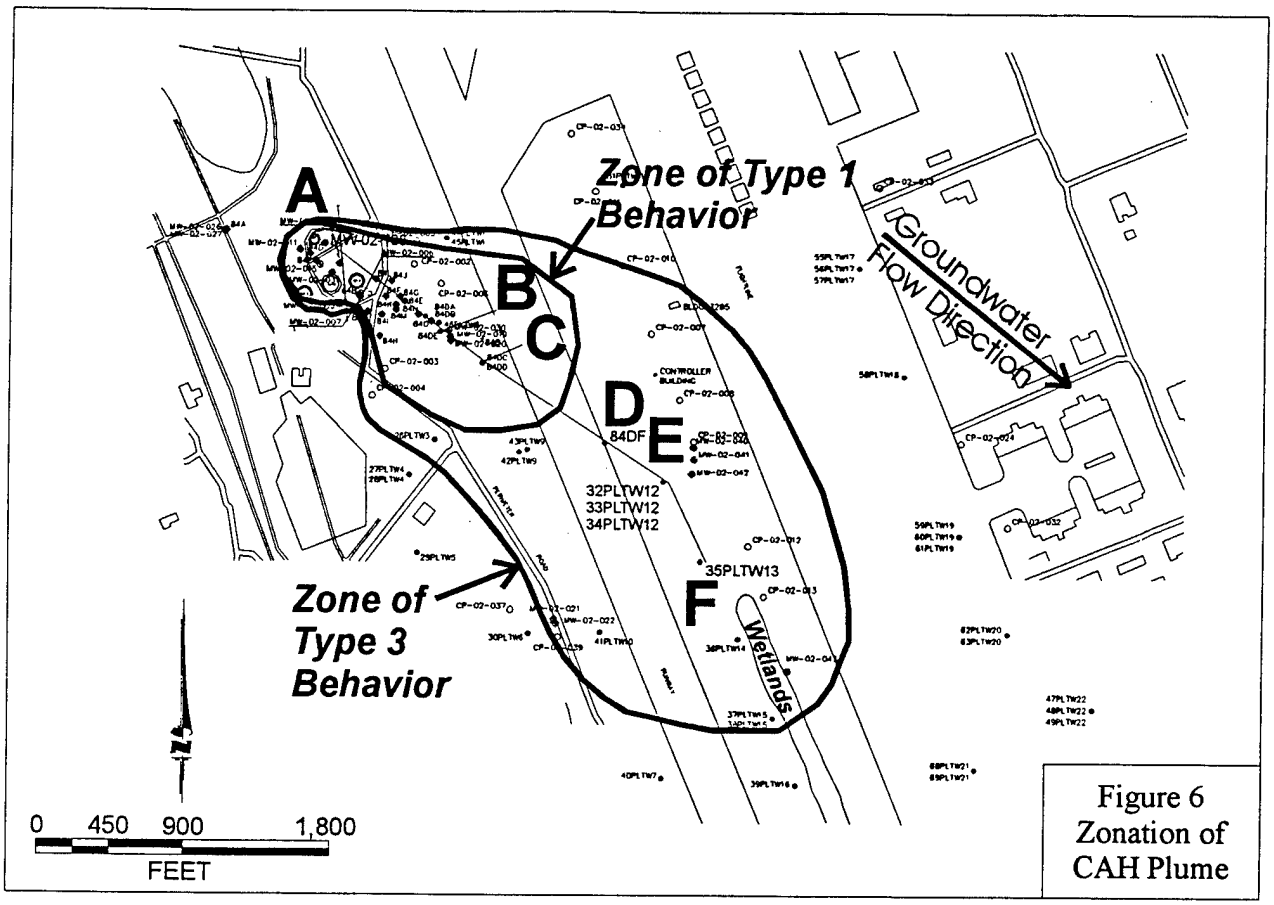



Figure 6
Zonation of CAH Plume

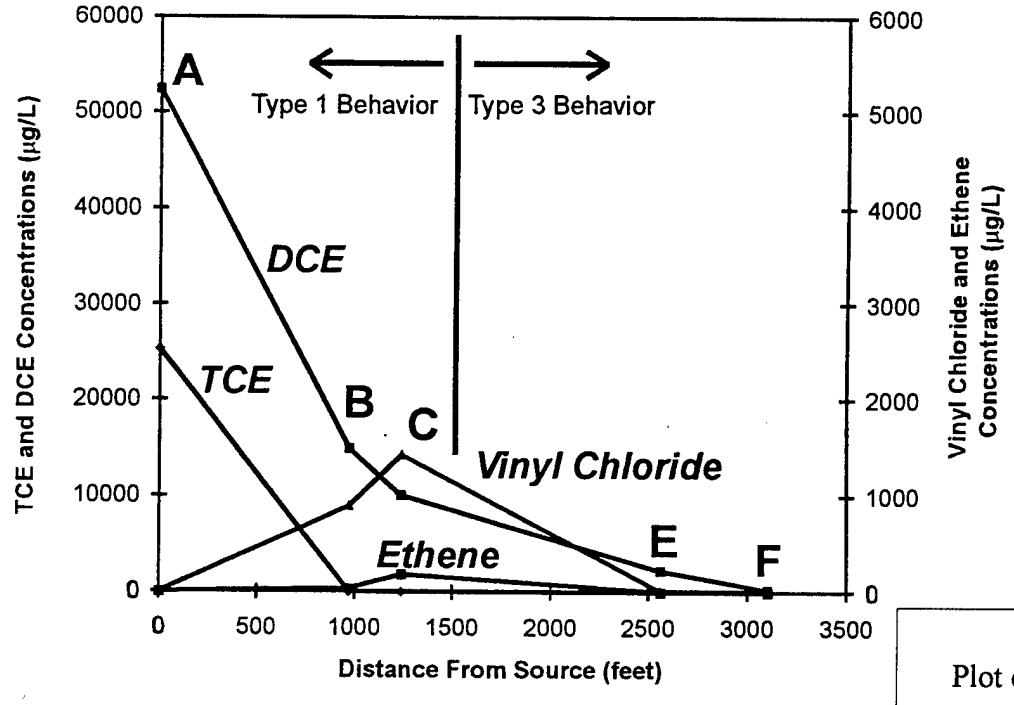



Figure 7
Plot of TCE, DCE, and Ethene vs Distance Downgradient