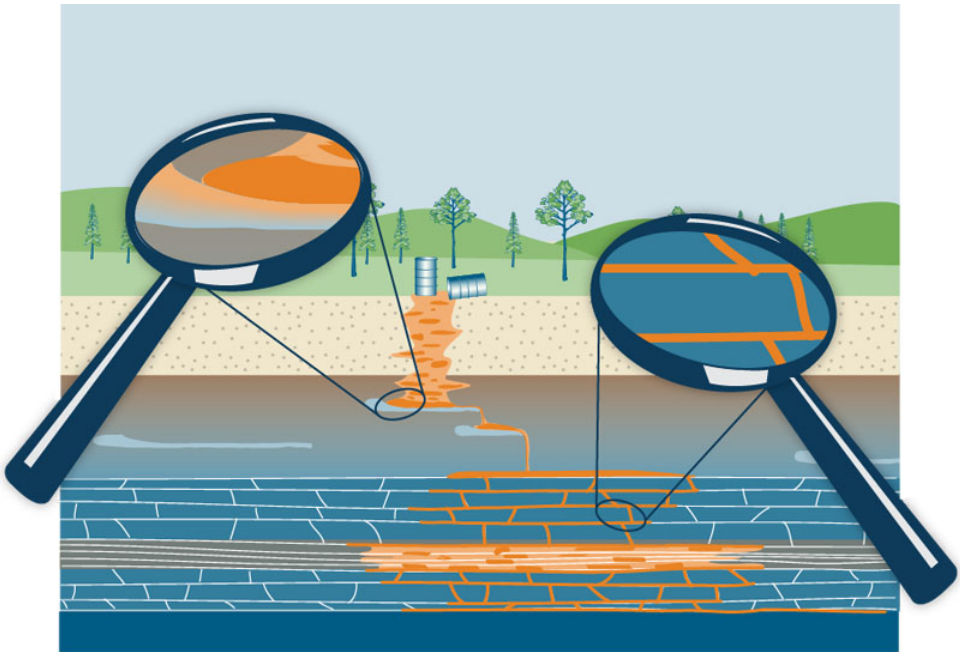
Guidance Document

Integrated DNAPL Site Characterization and Tools Selection



May 2015

Prepared by
The Interstate Technology & Regulatory Council
DNAPL Site Characterization Team

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ISC-1

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EXECUTIVE SUMMARY

Sites contaminated with dense nonaqueous phase liquids (DNAPLs) and DNAPL mixtures present significant environmental challenges. Despite the decades spent on characterizing and attempting to remediate DNAPL sites, substantial risk remains. Inadequate characterization of site geology as well as the distribution, characteristics, and behavior of contaminants—by relying on traditional monitoring well methods rather than more innovative and integrated approaches—has limited the success of many remediation efforts.

The Integrated DNAPL Site Characterization Team has synthesized the knowledge about DNAPL site characterization and remediation acquired over the past several decades, and has integrated that information into a new document that revises and replaces the 2003 ITRC technology overview document titled *An Introduction to Characterizing Sites Contaminated with DNAPLs*. Since 2003, experience and applied research have resulted in a better understanding of subsurface science and the impact of system heterogeneity on remediation efficacy. Because understanding the complexity of subsurface geologic conditions is paramount in improving DNAPL site characterization, this updated guidance document begins by reviewing current knowledge of DNAPLs and their subsurface contaminant behavior. By describing an integrated site characterization (ISC) approach, under which data of adequate resolution are collected to fully characterize a site, this new guidance recommends aligning data on contaminant distribution with site geologic heterogeneity and groundwater flow conditions at a spatial resolution appropriate to the site-specific remedial objectives. Thus, this guidance describes how, with the current understanding of subsurface contaminant behavior, both existing and new tools and techniques can be used to measure physical, chemical, and hydrologic subsurface parameters to better characterize the subsurface.

Goals

Revise the 2003 ITRC document with updated information to improve DNAPL site characterization in the following areas:

- *assessing ongoing contaminant exposures*
- *quantifying contaminant transport, storage, and attenuation patterns*
- *predicting future exposures that would occur without intervention*
- *predicting changes in future exposures that would occur in response to remedial actions*
- *selecting and designing remedial actions*

This guidance is a resource to inform regulators, responsible parties, other problem holders, consultants, community stakeholders, and other interested parties of the critical concepts related to characterization approaches and tools for collecting subsurface data at DNAPL sites.

TYPES OF DNAPLS AND DNAPL PROPERTIES

Although DNAPLs and their characteristics are addressed in peer-reviewed literature, a thorough understanding of DNAPL properties is crucial to designing an adequate characterization program.

Therefore, this guidance first addresses types of DNAPLs and the characteristics that control their distribution, fate, and transport in the subsurface.

What is a DNAPL Source Zone? A Changing Perspective…

The concept of a DNAPL site source zone has evolved in recent years. In the 1990s and early 2000s, source zones were considered to be the areas affected by DNAPL phase contamination; however, the current understanding has broadened that definition to include contaminant mass stored in low-permeability zones within the plume body.

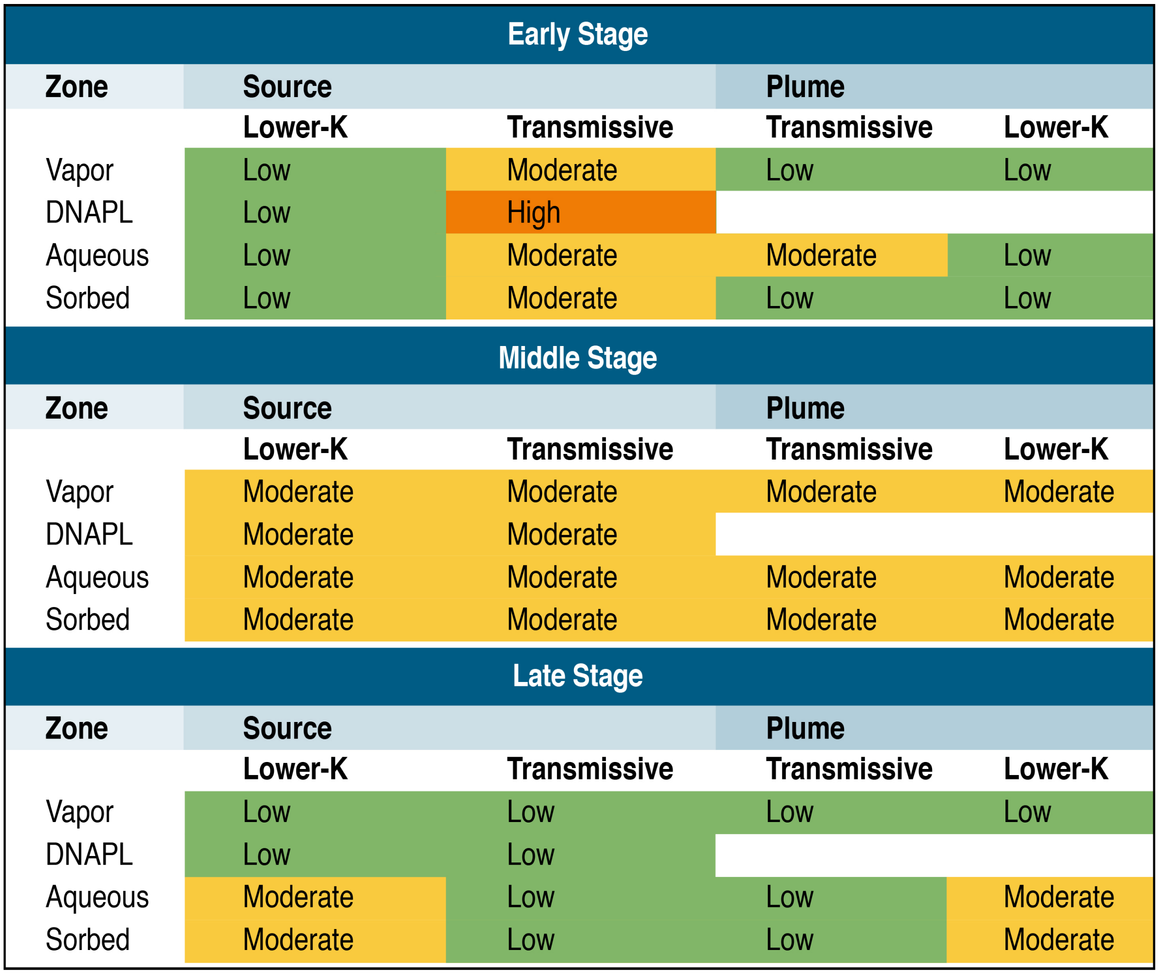
This evolution in understanding the extent of source material reflects the increasing recognition that, at many sites, DNAPL is not the primary factor in contaminant mass that sustains a plume over time. Especially at late-stage sites, the contaminant mass stored in low-permeability zones within the plume body acts as a primary source to help sustain the dissolved plume through back-diffusion processes. Thus, many of the improved characterization methods described in this document focus on delineating the geologic heterogeneity and contaminant mass distribution across different geologic units and across different contaminant chemical phases.

DNAPLs are denser than water, with limited and varying solubilities in water, and thus tend to occur in a separate nonaqueous phase in the subsurface. Common DNAPL compounds include materials that have been or are still widely used in industrial and commercial processes, such as chlorinated solvents and coal tar. Different types of DNAPLs have varying physical and chemical properties that govern their subsurface behavior. For example, chlorinated solvent DNAPLs have high solubility relative to other DNAPLs. Nevertheless, a number of primary fluid and formation properties affect all DNAPL interactions with porous media (or with other fluids) as well as their subsurface behavior. Some of these properties are inherent to the DNAPL fluid, while others involve the combined properties of the fluid and its interaction in a particular subsurface media.

The key properties at DNAPL contaminated sites include: **aqueous solubility, density, viscosity, volatility, interfacial tension, wettability, residual saturation, saturation, relative permeability, and capillary pressure**. Because the physical properties of DNAPLs affect their fate and transport in the subsurface, it is important to consider these properties at sites where DNAPL is found or existed at the site following the initial contaminant release or spill (although, as discussed below, many late-stage sites do not contain any residual DNAPL). The physical properties of pure chemical compounds that include DNAPLs are readily available in many references; however, the actual DNAPL at a site may be a mixture of chemicals with significantly different physical and chemical properties than that of fresh DNAPL or the pure-phase components.

DISTRIBUTION OF DNAPLS AND ASSOCIATED AQUEOUS, SORBED, AND VAPOR PHASES

In developing a thorough site characterization program, it is critical to determine the relative presence and distribution of DNAPL, vapor, dissolved, and sorbed chemical phases of contamination across the various geologic media and understand that the distribution of these contaminants will change over the lifecycle of the site (Figure ES-1). Furthermore, the characteristics of the subsurface control the fate and transport of DNAPL and aqueous- and vapor-phase contaminants. Therefore, both the contaminant distribution and the subsurface characteristics are vital information in developing or revising a site-specific conceptual site model (CSM).



Early Stage

Zone	Source		Plume	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	Low	Moderate	Low	Low
DNAPL	Low	High		
Aqueous	Low	Moderate	Moderate	Low
Sorbed	Low	Moderate	Low	Low

Middle Stage

Zone	Source		Plume	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	Moderate	Moderate	Moderate	Moderate
DNAPL	Moderate	Moderate		
Aqueous	Moderate	Moderate	Moderate	Moderate
Sorbed	Moderate	Moderate	Moderate	Moderate

Late Stage

Zone	Source		Plume	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	Low	Low	Low	Low
DNAPL	Low	Low		
Aqueous	Moderate	Low	Low	Moderate
Sorbed	Moderate	Low	Low	Moderate

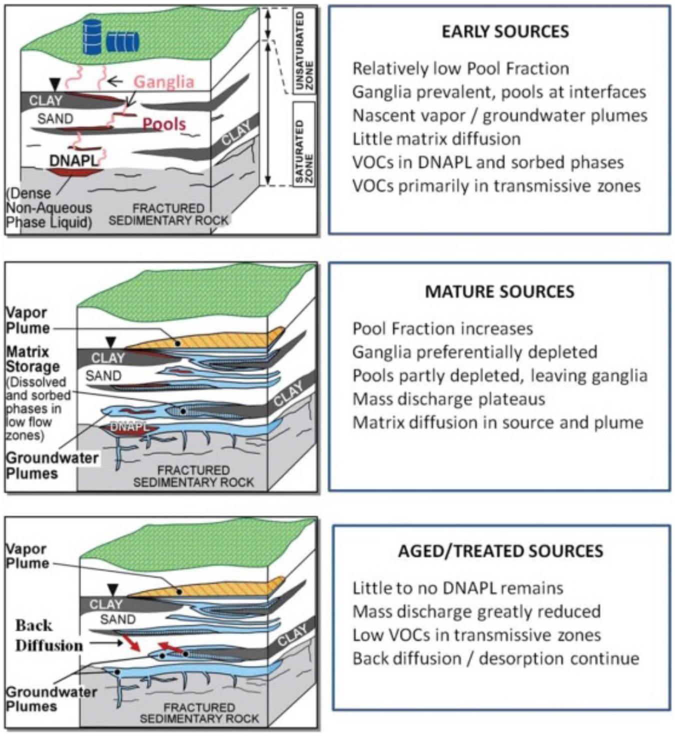
Figure ES-1. Illustration of the progression of a DNAPL-source zone and associated dissolved phase plume through time that results from mass transfers between compartments, using the 14-compartment model (Sale and Newell 2011). Groundwater flow (advection) carries contaminants from the source zone into the plume zone, and both diffusive and advective mass transfers can eventually distribute contaminants to all compartments. Over extended periods, contaminants can be diluted to lower concentrations, with stored mass in the lower-permeable zones acting as persistent sources of contamination.

The presence of DNAPL constituents represents a potentially persistent reservoir of contaminant mass that can continue to release dissolved contaminants over long periods; thus, understanding the potential presence and distribution of DNAPL in the subsurface is critical to long-term environmental site management. DNAPL migration is governed by scientific principles of multiphase flow in porous media. Downward migration of DNAPLs is largely driven by gravity. Additionally, subsurface lithologic heterogeneity leads to differences in subsurface pore structure and capillary properties. As a result, downward migration of DNAPL results in flow instability where isolated fingers of preferential DNAPL migrating along preferred pathways develop, leaving a highly variable distribution. These variations are commonly present in the subsurface matrix, even in formations that initially appear to be homogeneous. The existence of these highly variable fingers of DNAPL in the subsurface makes the detection of DNAPL challenging, driving the need for improved site characterization methods.

New Concepts for the Evaluation of Fate and Transport

- *Heterogeneity replaces homogeneity.*
- *Anisotropy replaces isotropy.*
- *Diffusion replaces dispersion.*
- *Back-diffusion is a significant source of contamination and plume growth.*
- *Non-Gaussian distribution replaces Gaussian.*
- *Transient replaces steady-state conditions.*
- *Nonlinear replaces linear sorption.*
- *Nonideal replaces ideal sorption.*

The perspective on what represents a source zone at a DNAPL site has evolved over the past few decades, and this broader understanding of the extent of source material has led to the realization that, at many sites, DNAPL may not be the primary factor in contaminant mass that sustains a plume over time. Moreover, differences in solubility significantly affect the lifecycles of DNAPLs in the subsurface. Most chlorinated solvent DNAPL sites can be described in terms of three stages of development, as discussed below and as shown in Figure ES-2 (Sale and Newell 2011).



EARLY SOURCES

Relatively low Pool Fraction
Ganglia prevalent, pools at interfaces
Nascent vapor / groundwater plumes
Little matrix diffusion
VOCs in DNAPL and sorbed phases
VOCs primarily in transmissive zones

MATURE SOURCES

Pool Fraction increases
Ganglia preferentially depleted
Pools partly depleted, leaving ganglia
Mass discharge plateaus
Matrix diffusion in source and plume

AGED/TREATED SOURCES

Little to no DNAPL remains
Mass discharge greatly reduced
Low VOCs in transmissive zones
Back diffusion / desorption continue

Figure ES-2. Evolution of a DNAPL source/plume.

In the *initial (early) stage*, DNAPL predominates and contaminants migrate downward through pore spaces of more transmissive zones of the geologic formation, leaving ganglia of residual (immobile) DNAPL held within the pores by capillary forces. In the *middle (mature source)* stage of the source zone DNAPL lifecycle, a significant portion of the contaminant mass has migrated into vapor, aqueous, and sorbed phases in both transmissive and low-permeability zones of the formation. In the *late (weathered, aged/treated sources)* stage of chlorinated solvent sites, DNAPL is often no longer detected and chlorinated solvent concentrations may persist in the aqueous phase of the transmissive zone due to desorption and back-diffusion from the contaminant mass in the low-permeability matrix into the higher-permeability matrix. A late-stage site that no longer contains DNAPL is still considered to be a “DNAPL site” because DNAPL was an important part of the historical CSM.

Including the DNAPL life cycle and matrix diffusion in a CSM has several important implications for initial site characterization and remediation-based characterization activities. For example, **low-solubility DNAPL sites** (coal tar, creosote sites) are often dominated by the early phase of the DNAPL life cycle. At these sites, the transport of the DNAPL itself is important in understanding the DNAPL properties described above. **High-solubility DNAPL sites** (chlorinated solvent sites) are more likely to be middle- and late-stage sites. At these sites, the transport of the DNAPL itself is typically not important, but a good understanding of matrix diffusion is critical. Appendix F contains a tool to help determine if a site is in the early, middle, or late stage of its life cycle.

INTEGRATED DNAPL SITE CHARACTERIZATION

ISC is a process for improving the efficiency and effectiveness of characterization efforts at DNAPL sites. ISC encourages characterization at a sufficient resolution to capture the effects of the heterogeneities that direct contaminant distribution, fate and transport, and remediation effectiveness, so that an integrated three-dimensional CSM can be developed. The specific steps in an ISC process are as follows:

- Define the problem and uncertainties in the CSM.
- Identify the data gaps and spatial resolution required in the investigation.
- Establish the data collection objectives.
- Design the data collection process.
- Select the appropriate investigative tools.
- Manage, evaluate, and interpret the data.

Is ISC only applicable to DNAPL?

Although this guidance specifically addresses characterization of DNAPLs, an ISC process can and should be used at any site with subsurface contamination. Additionally, many of the tools included in this guidance can collect data that is relevant to characterization of the subsurface contaminated by other chemicals, including petroleum hydrocarbons and metals.

This guidance provides a Tools Selection Framework for the interactive selection of over 100 tools based on geologic, hydrologic, and chemical data needs at a site. The Tool Selection Worksheet is linked to more detailed descriptions of each tool—including its applicability, data quality capability, and limitations or challenges. In addition, case studies are presented to illustrate the application of ISC principles (for example, linking characterization objectives to data needs, resolution, and tools selection) at sites with various scales of heterogeneity and investigation complexity. Finally, methods and models for managing, evaluating, and visualizing data are discussed. Evaluating the data against characterization objectives and updating the CSM will reduce uncertainty and support decision making. Data analysis is linked back to characterization objectives to identify any further data gaps and assess the value of additional site characterization.

REGULATORY PERSPECTIVES

To improve upon the characterization of subsurface geological, hydrological, and chemical conditions, new characterization tools and technologies are required; the ISC approach for developing CSMs incorporates these new tools and technologies. For regulatory agency personnel who may have limited training opportunity and have been operating under what may now be considered outdated conceptual models for subsurface contamination, there is a clear challenge to incorporate the newer views of contaminant behavior into already ongoing cleanups.

Many of the regulatory challenges regarding advanced site characterization approaches and tools result from unfamiliarity with, and a lack of understanding of, the new methods and changing knowledge base. Some of the prominent issues are as follows:

- lack of familiarity and understanding of subsurface dynamics
- objectives-based characterization
- mass discharge as a regulatory metric
- use of nontraditional characterization methods
- use of collaborative data sets to refine the CSM
- differentiating between matrix storage and DNAPL

There are great benefits to accepting advanced characterization methods and gaining familiarity with collaborative data sets (Figure ES-3). Improved characterization methods, with representative resolution, can clarify nonuniform source distribution, subsurface heterogeneities, and geochemical variations. This should produce a more refined CSM with a more efficient allocation of resources, resulting in greater accuracy in subsurface characterization. These methods will improve remedial design and monitoring and result in a shorter remedial time frame and reduced life cycle costs.

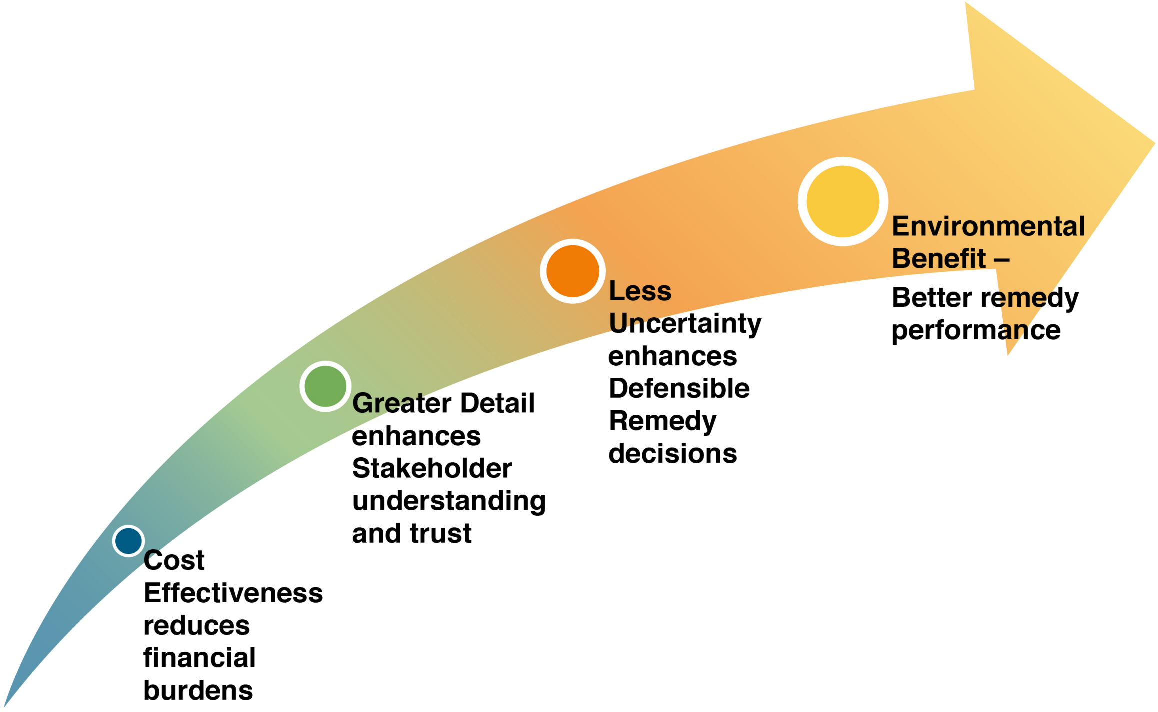


Figure ES-3. Benefits of integrated DNAPL site characterization.

There is an inherent challenge in explaining the data-dense outputs of the new characterization methods. Traditional characterization approaches, relying on relatively few soil, sediment, and groundwater samples, were often presented graphically with intense extrapolation between data points. In any outreach setting, higher resolution and attention to the development of a scientifically based CSM allows all interested parties to discuss the future of the site based on science, contaminant transport, and long-term protection of drinking water resources, human health, surface water, and the environment (Figure ES-3).

STAKEHOLDER AND TRIBAL PERSPECTIVE

The ISC approach outlined in this guidance includes a process for selecting and applying new tools and approaches to characterize sites contaminated by DNAPLs. The science supporting these technologies and approaches is based on quantifying how geology, chemistry, and hydrogeology interact to influence contaminant transport in rock, soil, sediments, and groundwater. This new ISC approach allows more detailed and representative interpretations without what has been traditionally referred to as data gaps from conventional limited data investigation techniques. It should therefore follow that regulatory performance and remedies implemented to protect human health and the environment would be greatly improved through the application of these investigative strategies and technologies. Stakeholders are likely to embrace these tools and analysis techniques because they are specifically designed to better characterize and define contaminated sites to more effectively clean them up.

SUMMARY

This guidance document contains the following two elements:

1. It acts as a resource, describing important DNAPL characteristics and the behavior of DNAPL and its various phases in the subsurface. An understanding of DNAPL characteristics and behavior are critical when developing and testing a CSM.
2. It covers the ISC process—including planning; a Tool Selection Worksheet to assist in selecting a parameter-driven suite of tools to test geologic, hydrologic, and chemical characteristics of the subsurface; and data management and interpretation. Over 100 tools are contained in the Tool Selection Worksheet, and selecting various search parameters reduces the list of applicable tools to a manageable number. The Tool Selection Worksheet is downloadable, and each tool links to additional resources that describe the applicability, advantages, and limitations of that tool.

TABLE OF CONTENTS

1.0 INTRODUCTION 1

1.1 Background of an Integrated Site Characterization Approach 1
1.2 Benefits of an Integrated Site Characterization Approach 3
1.3 Return on Investigation 4
1.4 Objective of this Guidance 7

2.0 TYPES OF DNAPLS AND DNAPL PROPERTIES 10

2.1 Types of DNAPLs 10
2.2 DNAPL Properties and Terminology 11
2.3 Effects on DNAPL Properties 16
2.4 Special Considerations for DNAPL Mixtures 22

3.0 DISTRIBUTION OF DNAPLS AND ASSOCIATED AQUEOUS, SORBED, AND VAPOR PHASE CONTAMINATION 37

3.1 DNAPL Behavior in the Subsurface 39
3.2 Changing Concept of a DNAPL Source Zone 41
3.3 DNAPL Life Cycle Conceptual Model 41
3.4 Implications of DNAPL plus Matrix Diffusion Source Model 43
3.5 Considerations in Fractured Bedrock 47
3.6 DNAPL Considerations for Clay 51

4.0 INTEGRATED DNAPL SITE CHARACTERIZATION 53

4.1 Objectives-Based Data Collection 55
4.2 Define the Problem and Assess the CSM 57
4.3 Identify Data Needs/Gaps and Resolution 61
4.4 Establish Data Collection Objectives 62
4.5 Design Data Collection and Analysis Process 64
4.6 Tools Selection 69
4.7 Perform Data Evaluation and Interpretation 72
4.8 Update Conceptual Site Model 77
4.9 Interpretative Tools 83

5.0 REGULATORY PERSPECTIVES 89

5.1 Regulatory Challenges 89
5.2 Regulatory Benefits of Integrated DNAPL Site Characterization 92
5.3 USEPA Priority Actions in Climate Adaptation 94
5.4 Public Education and Outreach 94

6.0 STAKEHOLDER AND TRIBAL PERSPECTIVES 96

6.1 Economy and Long-Term Resource Protection Concerns 96
6.2 Stakeholder Views Regarding Remedial Decisions 97
6.3 Stakeholder Acceptance 97

7.0 REFERENCES 98

APPENDIX A. APPLICATION OF INTEGRATED SITE CHARACTERIZATION USING OBJECTIVES-BASED CHARACTERIZATION TECHNIQUES 125

APPENDIX B. CASE EXAMPLES OF OBJECTIVES-BASED SITE CHARACTERIZATION 133

APPENDIX C. SPREADSHEET FOR ESTIMATING CONTAMINANT MASS IN THE 14 COMPARTMENT MODEL 175

APPENDIX D. TOOLS DESCRIPTIONS 179

APPENDIX E. DATA TYPES AND DEFINITIONS 272

APPENDIX F. SCREENING METHOD TO ESTIMATE IF A CHLORINATED SOLVENT RELEASE IS IN THE EARLY, LATE, OR MIDDLE STAGE 286

APPENDIX G. FIELD APPLICATION OF TOOLS CASE STUDIES 296

APPENDIX H. EMERGING TECHNIQUES FOR SITE CHARACTERIZATION—RECONSTRUCTING SOURCE HISTORY 321

APPENDIX I. REPRESENTATIVE VALUES FOR FOC 324

APPENDIX J. TEAM CONTACT LIST 345

APPENDIX K. ACRONYMS 351

APPENDIX L. GLOSSARY 355

LIST OF TABLES

Table 1-1. Example of ROI for source zone at Well 12A remediation 6

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. 25

Table 4-1. Examples of effective data collection objectives for DNAPL sites 64

LIST OF FIGURES

Figure 1-1. ROI: Traditional vs. ISC costs over the project life cycle. 5

Figure 1-2. Cost comparisons at Well 12A resulting from a reduced vertical interval for treatment, thereby reducing the amendment, well installation, and labor costs during the life cycle of the project. 7

Figure 2-1. Mobility characteristics of DNAPL: mobile, potentially mobile, and immobile. ... 11

Figure 2-2. Solubilities of common DNAPLs and other compounds (see Appendix K for chemical acronym definitions). 13

Figure 2-3. Representative elementary volume illustrated as a % porosity compared to increasing volumes of material. Beyond V3, the representativeness does not improve appreciably. ...14

Figure 2-4. Illustration of the wetting process as an interaction between surfaces. 15

Figure 2-5. Typical conditions found in an aquifer with water present. 19

Figure 2-6. Typical conditions in an aquifer with DNAPL present when water is the wetting fluid. 20

Figure 3-1. The 14-compartment model (Sale and Newell 2011). 37

Figure 3-2. Illustration of the progression of a DNAPL-source zone and associated dissolved phase plume through time that results from mass transfers between compartments, using the 14-compartment model. Groundwater flow (advection) carries contaminant from the source zone into the plume zone, and both diffusive and advective mass transfers can eventually distribute contaminants to all compartments. Over extended periods, contaminants can be diluted to lower concentrations, with stored mass in the lower-permeability zones acting as persistent sources of contamination. 38

Figure 3-3. Evolution of a DNAPL source/plume (Stroo et al. 2012). 42

Figure 3-4. Examples of Contaminant Concentration Profiles in Soil Cores that indicate matrix diffusion is occurring (Newell et al. 2013). At Location A, the contaminant concentration decreases uniformly with depth into the low-permeability zone, indicating constant concentrations in the transmissive zone and no back-diffusion (no matrix diffusion source); however, at Location B, the Shark Fin pattern shows that contaminant diffusion gradient is from the interior of the low-permeability zone to the transmissive zone, indicating that the low-permeability zone at Location B is serving as a matrix diffusion source (diffusion is also driving contaminants deeper in the low-permeability zone). Location C is similar to Location A, but with a weaker and more recent loading from the transmissive zone to the low-permeability zone. Appendix H discusses using the concentration gradients in low-permeability sediments that are the result of matrix diffusion to help reconstruct contaminant source loading history. . 46

Figure 3-5. Illustration of fate and transport of DNAPL in a fractured rock environment through time showing distinctly different types of contaminant transport, including DNAPL movement and dissolution, dissolved-phase advection through fractures, and diffusion into the rock matrix. (a) Initially, DNAPL migrates vertically through the fracture network until the initial driving head is dissipated and the DNAPL becomes immobile. The DNAPL begins to dissolve into the water in the fractures and diffuse into the rock matrix, and over time migrate with water flowing through the fractures. These processes together with sorption will retard contaminant migration. (b) This is a conceptualization of the effect of these processes on source zone and plume evolution. 48

Figure 3-6. Schematic of fracture orientation in sedimentary and igneous rock 50

Figure 4-1. Integrated site characterization. 56

Figure 4-2. Tool selection framework diagram. 70

Figure 4-3. CSM life cycle phases during a brownfields investigation. 78

Figure 4-4. Original plume interpretation (red points are monitoring wells). 79

Figure 4-5. Plume following additional delineation (blue wells = second delineation; red wells = initial delineation). 80

Figure 4-6. Tribromoethene flux downgradient from the source. 81

Figure 4-7. Distribution of brominated compounds in source zone from multi-level monitoring wells 82

Figure 4-8. Concentration decrease in source zone under remediation pumping conditions. ...83

Figure 4-9. Predictions of various depletion models in source zone under remediation pumping conditions. 83

Figure 5-1. Benefits of integrated DNAPL site characterization. 93

1.0 INTRODUCTION

Sites contaminated with dense nonaqueous phase liquids (DNAPLs) and DNAPL mixtures present significant environmental challenges. Despite the decades spent on attempts to characterize and remediate DNAPL sites, substantial risk remains. Inadequate characterization of site geology and the distribution, characteristics, and behavior of contaminants—by relying on traditional monitoring well methods rather than more innovative and integrated approaches— has limited the success of many remediation efforts; however, the amassed experience and applied research have resulted in a better understanding of how subsurface heterogeneity affects remediation.

This document synthesizes the knowledge of DNAPL site characterization and remediation acquired over the past several decades, and provides guidance on concurrent characterization of contaminant distributions, hydrogeology, and attenuation processes to allow for improvements in the following areas:

- assessment of ongoing contaminant exposures
- quantification of contaminant transport, storage, and attenuation patterns
- prediction of future exposures that would occur without intervention
- prediction of changes in future exposures that would occur in response to remedial actions
- selection and design of remedial actions

An integrated site characterization (ISC) approach, under which data of adequate resolution are collected to fully characterize a site, significantly reduces uncertainty and enables the development of cost-effective solutions to manage contaminated sites. By applying proven scientific principles, investigation approaches, and characterization tools, a rigorous three-dimensional conceptual site model (CSM) can be constructed to more effectively support environmental management decision making.

1.1 Background of an Integrated Site Characterization Approach

The recent innovations and advancements in site characterization allow for more effective site management, remedy selection, and remedy implementation (Stroo et al. 2012). Adequate subsurface characterization of sites where DNAPLs have been released is essential to the development of effective groundwater protection strategies. Site characterization and research conducted over the past decades, together with basic scientific concepts, demonstrate the following understanding of subsurface science:

- What were sometimes treated as disparate elements (physical, chemical, and biological), are now recognized as interrelated elements of a larger whole, with interactions between different processes.

- Contamination sources and plumes are integrated systems (ITRC 2011b; NRC 2013), and contaminant storage in lower-permeability regions outside a release area is now recognized as a primary source of persistent long-term groundwater impacts.
- Site conditions are not static, and understanding the evolution of a site is critical to understanding source and plume behavior.
- The geologic setting (in particular, the distribution of low-permeability zones) is the primary factor controlling the location, storage, and migration of DNAPL mass (ITRC 2011b; Stroo et al. 2012; Payne, Quinnan, and Potter 2008; NRC 2013).
- DNAPL migration processes are especially sensitive to lithologic heterogeneity and secondary porosity.

In understanding contaminant fate and transport in the subsurface, the complexity of subsurface geologic conditions, and especially the system heterogeneity, can cause DNAPL to persist. This remnant DNAPL may persist at the interface between strata with contrasting permeability or in interbedded zones that are difficult to flush. Diffusive interchange between higher- and lower-permeability zones slows the propagation of dissolved-phase contaminants during early stages of plume development and then sustains the dissolved-phase concentrations over extended periods. Moreover, contamination that reaches low-permeability zones can be highly resistant to treatment. Collectively, these processes fall under the term matrix diffusion. In many older sites that initially contained DNAPL, matrix diffusion processes have driven the bulk of the contaminant mass into lower-permeability zones (ITRC 2011b; Payne, Quinnan, and Potter 2008; Stroo et al. 2012; NRC 2013).

Whether a remediation effort succeeds or fails depends largely on a thorough understanding of, and a remedy implementation tailored to, site-specific geology and the specific properties of the chemical contaminants. Subsurface cleanup challenges and limitations are less related to differences in remedial technologies and more related to the difficulty of identifying and targeting treatment in the most affected geologic zones (Stroo et al. 2012).

This emerging understanding holds that site conditions are dynamic, such that the evolution of a site and the trajectory of that evolution over time are as important as the site's current state. Key to understanding source and plume behavior are the nature of the release, the composition of the contaminant, the history of the contaminant (in particular DNAPL) migration, the current contaminant distribution between chemical phases and geologic units, and the manner in which the contaminants are being redistributed. Furthermore, as this understanding has developed into a consensus, maintaining a useful CSM (the primary means of expressing the integrated site view) has emerged as a critical element of DNAPL site management (ITRC 2011b).

Historically, subsurface characterization has typically involved the use of monitoring wells screened over large vertical portions of the aquifer; however, this approach is limited in that data collected from typical long-screen (generally 5–20 feet long) monitoring wells cannot inform the detailed hydrostratigraphy that controls DNAPL behavior at the centimeter-to-millimeter scale. Reliance on monitoring well data has resulted in poorly performing remedies and unacceptably low predictions of plume behavior and exposure risks (Stroo et al. 2012; NRC 2013).

The complex processes of multiphase flow in porous media, which control DNAPL migration and distribution, are especially sensitive to subsurface lithologic heterogeneity and secondary porosity. Recent advances have demonstrated that geology and variations in permeability are important controlling factors in contaminant distribution, when DNAPL is present and when contaminant transport is sustained by back-diffusion (Sale et al. 2008). The now broad recognition of complex geologic control over DNAPL migration and groundwater transport has rendered the decades-old concept of highly dispersed plumes in homogeneous media to the category of major oversimplification.

Based on the above concepts and their strong interrelationships, environmental management of DNAPL sites requires a well-developed, comprehensive, holistic (and heuristic) CSM. This requires the use of updated concepts in site characterization, better investigation strategies, and improved characterization tools. The recent advances in subsurface characterization tools and techniques included in this guidance are key to improved site management decision making and ultimately to better remedy performance. The overriding regulatory challenge will be to familiarize regulatory project managers with the new characterization tools and CSM approaches and demonstrate their benefits and reliability.

This guidance addresses the problems expressed in the introductory paragraphs of this section by describing an effective ISC approach—one that aligns data on contaminant distribution (and other biochemistry and geochemistry issues) with site geologic heterogeneity and groundwater flow conditions, at a spatial resolution appropriate to the site-specific remedial objectives. A key element is the identification of contaminant distribution with respect to low-permeability vs. transmissive zones, as suggested by Stroo et al. (2012) and NRC (2013). In its simplest form, an ISC approach might involve overlaying well logs with existing site chemical data to correlate contaminant concentrations with geologic units at as fine a scale as data are available. In more complex applications, an ISC approach can involve real-time field screening techniques and temporary exploratory borings to provide vertical profiling of subsurface conditions.

1.2 Benefits of an Integrated Site Characterization Approach

An ISC approach can result in significantly greater effectiveness of site management and remedy decisions through improvements in characterization methods and tools. The benefits of applying an ISC approach may include the following:

- identification of contaminant distribution, with respect to low-permeability vs. transmissive zones—to differentiate zones of contaminant storage (which retain and slowly release contaminants) from zones of contaminant transport (which have relatively higher permeability)
- better-performing remedies and improved predictability of plume behavior and risks
- collection of higher quantities of screening-level data to facilitate characterization at a higher resolution that corresponds more closely to the scale of geologic heterogeneity
- increased spatial precision and accuracy of characterization data, leading to more accurate CSMs

- reduced uncertainty in risk evaluation, remedy selection, and site management decisions, leading to better reductions in risk and protection of natural resources
- more defensible knowledge of contaminant distribution
- improved selection of remedial measures to address subsurface zones that feed plumes and drive up potential exposure
- facilitated communication of site conditions and enhanced stakeholder understanding and involvement

ISC should lead to remedial decisions that are (1) protective of human health and the environment; (2) provide better and more protective remedial decisions; (3) consider the necessity of source control and proactive remediation; and (4) predict a foreseeable outcome. Thus, the ISC approach is more attractive to stakeholders who can anticipate sustained resources, cost-effective contaminant source remediation, and the preservation of regional aquifer systems.

1.3 Return on Investigation

Remediation practitioners must evaluate the benefits of investigation costs against the value of the outcome. Compared to other, more traditional characterization methods, ISC often incurs higher upfront costs; however, it may also result in a more accurate CSM and thus a more effective remedial strategy.

Understanding the heterogeneity of the subsurface, its influence on the transport of contaminants, and the fate of the dissolved and nonaqueous phase contaminants depends largely on delineating the distribution and frequency of fractures, faults, lithologic changes, mineralogy, grain size morphology and distribution, and other physical parameters of the subsurface. As well, the hydrogeology and chemical characteristics of the contaminants inform the CSM on the fluid dynamics and reactions. Historically, CSM development involved collecting and analyzing data for each individual parameter, so to keep characterization costs low and make remediation decisions early in the process, assumptions and generalizations were made about the physical characteristics of the subsurface and the chemical characteristics of the contaminants. As stated previously, this traditional approach led to poor quality remediation results and repeat treatment or to additional testing and refinement of the remediation systems. With ISC, however, a more accurate and realistic CSM can be developed and, consequently, the most effective remedial strategy can be chosen.

For example, in a heterogeneous aquifer where significant contaminant mass resides in relatively thin, low-K layers, a simplified site characterization may indicate a relatively homogeneous aquifer and fail to identify the low-K layers that act as a source of dissolved phase contamination for the higher-K (transmissive) portions of the aquifer. Thus, a chemical oxidation remedy, which does not address contaminant mass in the low-K zones, will fail regardless of how many injections of chemical oxidants are applied in the higher-K formation materials. If, on the other hand, an ISC method is used, the contaminant mass in the low-K layers may be identified and a more appropriate remedy chosen.

A well-informed remediation decision requires thorough characterization using data sets that are integrated among the geologic, hydrologic, and chemical characteristics of the subsurface. While higher-resolution data collection and interpretation leads to higher cost in the short term, the benefits of implementing ISC ultimately lead to lower costs to the overall project. As shown in Figure 1-1, use of a higher-resolution site characterization method (such as ISC) results in better decision making and more reliable performance when it comes to the remedial technology, thereby reducing the remediation cost through the end of the project. The figure illustrates that, following the Stage 1 preliminary investigation (similar costs regardless of characterization methods to be used), using ISC (dashed black line) for the Stage 2 characterization is initially more costly than using traditional characterization methods (solid blue line); however, the return-on-investigation (ROI) costs (shown as the difference between the dashed black and solid blue curves in Stage 3) are lower. Additionally, the lifetime of the project is likely shorter, thereby reducing ongoing liability for the site.

Improved CSMs and focused cleanups improve reliability and certainty of outcome while also reducing costs. For example, the costs of ISC and higher-resolution site characterization can be offset by optimizing a DNAPL source zone in situ remedy. Thus, a site characterization effort that employs the new methods and tools (such as ISC)—resulting in a more robust CSM, fewer permanent monitoring wells, and a focused remediation program—leads to reduced total life cycle costs and an improved ROI.

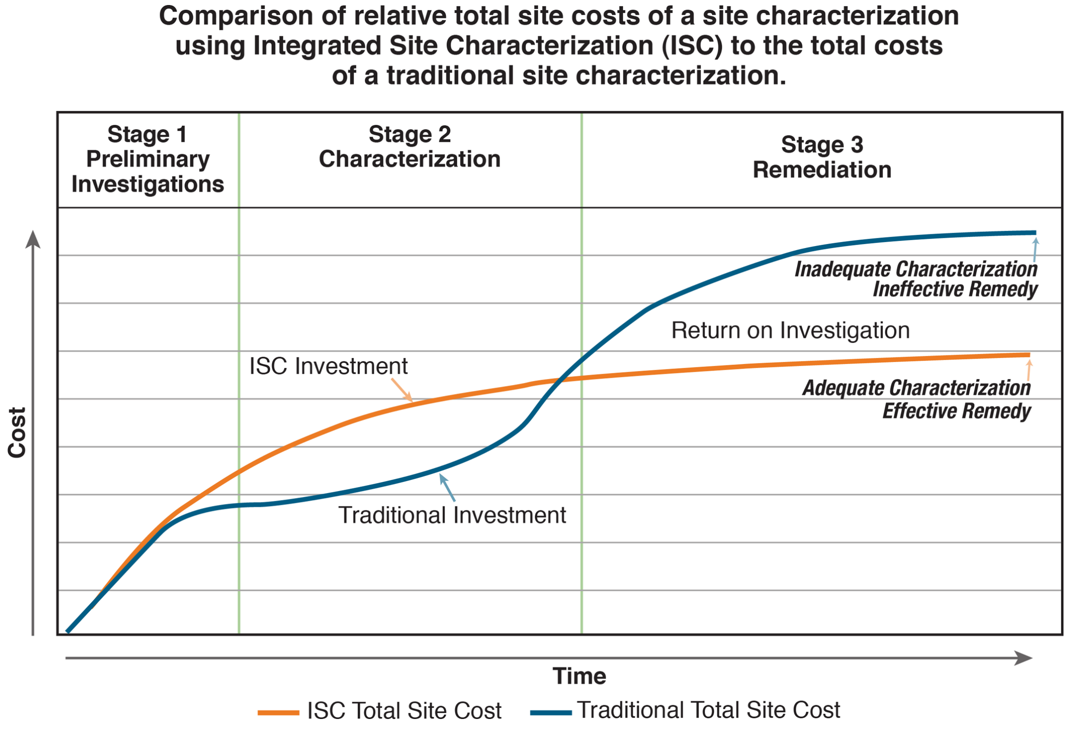


Figure 1-1. ROI: Traditional vs. ISC costs over the project life cycle.

Table 1-1 summarizes the EAB (enhanced anaerobic bioremediation) remedy cost for Well 12A, both with and without ISC. The cost without ISC was projected based on the actual cost of implementation, and adjusted over the treatment volume assuming a 50 ft treatment zone. The cost with ISC is the approximate total final costs based on a more robust CSM informed by high-resolution characterization. In this particular case, the characterization did not result in a significant change in the target treatment area, but did result in a significant change in the vertical interval for treatment. Reducing the target vertical interval for treatment from 50 ft to 12 ft (average), with a smaller portion of the site having a deeper treatment zone of 5 ft thickness, reduced the overall treatment volume by approximately 70%. This reduced the overall cost of the remediation by reducing the costs of the amendment, well installation, and labor for amendment injection for one full-scale injection event—from an estimated $4.66 million to $1.66 million. The cost of the higher-resolution characterization for the site was approximately $350,000. Even with this additional characterization cost, however, the project saved an estimated $2.65 million due to the substantial reduction in treatment volume.

Table 1-1. Example of ROI for source zone at Well 12A remediation

Characterization Costs	**Costs**		**Notes**
	Without ISC	**With ISC**	
Pre-Design Investigation	$250,000	$250,000	Phase I/II
High Resolution Source Area Investigation with Mass Discharge Estimate (Transect Method)		$350,000	
Mass Discharge Evaluation (GETS Pumping Test)	$150,000	$150,000	
Total Characterization Costs	$400,000	$750,000	
Remediation Unit Costs			
EAB-Treatment Volume	**Without ISC**	**With ISC**	
Target Area	52,000 sf	52,000 sf	No change
Target Thickness	50 ft	17 ft	Two intervals – shallow (12 feet thick) and deep (5 feet thick)
Target Volume	300,000 cy	90,000 cy	~70% reduction in treatment volume
EAB-Amendment Injection Costs	**Without ISC**	**With ISC**	
Total Amendment Cost	$1,600,000	$450,000	
Total Drilling Cost	$1,320,000	$740,000	
Total Injection Labor Cost	$1,740,000	$470,000	
Total EAB Full-Scale Remediation	**$4,660,000**	**$1,660,000**	
Overall Costs (Characterization + Remediation)	**Without ISC**	**With ISC**	
	$5,060,000	$2,410,000	

Table 1-1. Example of ROI for source zone at Well 12A remediation (continued)

Characterization Costs	Costs		Notes
	Without ISC	With ISC	
Cost Savings from ISC	**$2,650,00-0**		
Note: GETS = groundwater extraction and treatment system			

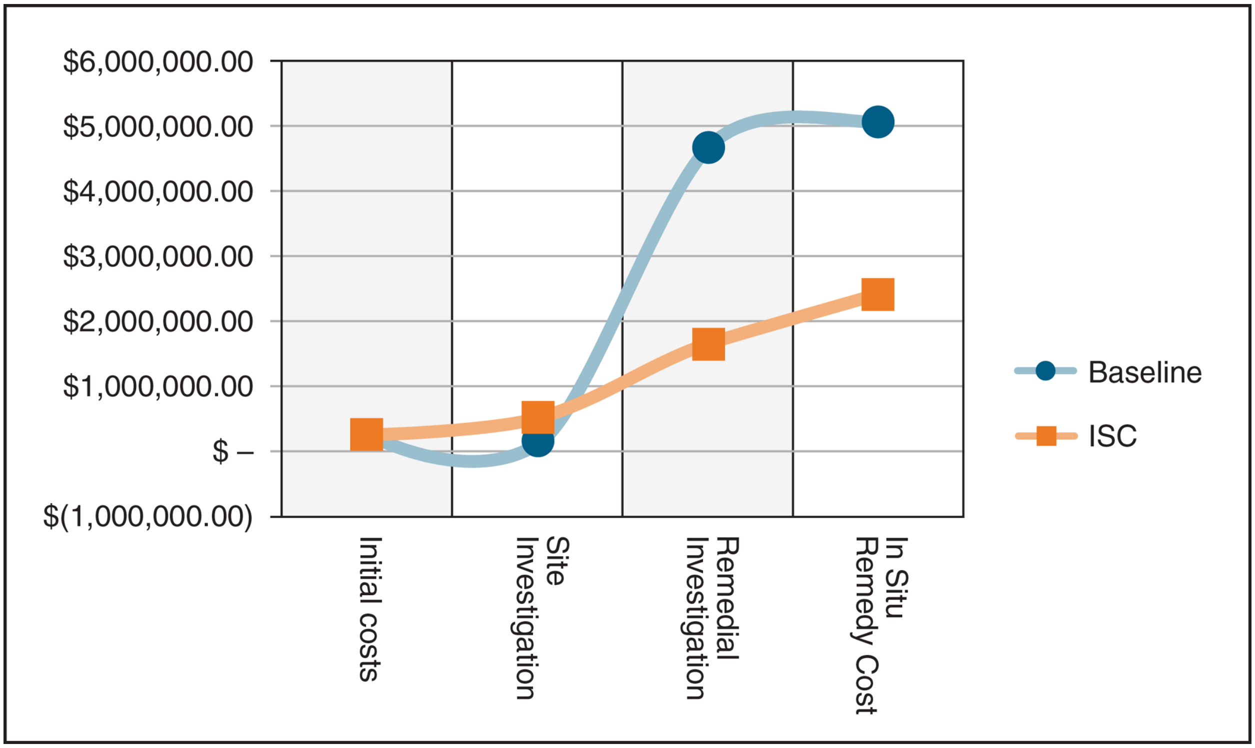


Figure 1-2. Cost comparisons at Well 12A resulting from a reduced vertical interval for treatment, thereby reducing the amendment, well installation, and labor costs during the life cycle of the project.

1.4 Objective of this Guidance

This guidance describes how, with the current understanding of subsurface contaminant behavior, both existing and new tools and techniques can be used to measure physical, chemical, and hydrologic parameters to better characterize the subsurface. This guidance also provides a Tool Selection Worksheet that helps to screen out tools that are not applicable to specific data needs at a site. Links within the Tool Selection Worksheet navigate to descriptive information on tools and offers additional resources that, when applied properly, can improve the identification, collection, and evaluation of appropriate site characterization data. The expected result of using this guidance is a more accurate site-specific CSM, which can then be applied in the ITRC Integrated DNAPL Site Strategy (ITRC 2011b, Chapter 2).

Chapter 2 of this document reviews DNAPL types and the characteristics that control their distribution, fate, and transport in the subsurface. Although these issues are addressed in peer-reviewed literature, they are also summarized in this document because they are crucial to designing an adequate characterization program.

Chapter 3 describes the characteristics of the subsurface that control the fate and transport of DNAPL and aqueous- and vapor-phase contaminants, information that should be considered when developing or revising a site-specific CSM. Application of these site characterization techniques will increase the level of understanding related to complex site contaminant behavior, leading to more practical and effective remedy implementation and reduction in long-term costs.

Chapter 4 describes the specific steps in an ISC process, which are as follows:

- define the problem and uncertainties in the CSM
- identify the data gaps and spatial resolution required in the investigation
- establish the data collection objectives
- design the data collection process
- select the appropriate investigative tools
- manage, evaluate, and interpret the data

Chapter 4 also provides the Tool Selection Worksheet, as mentioned above, for the interactive selection of appropriate tools based on geologic, hydrologic, and chemical data needs at a site. The Tool Selection Worksheet links to more detailed descriptions of each tool—including its applicability, data quality capability, and limitations or challenges. Case study examples illustrate the application of ISC principles (for example, linking data collection objectives to data needs, resolution, and tools selection) at sites with various scales of heterogeneity and investigation complexity. Methods and models for managing, evaluating, and visualizing data are also included in Chapter 4. Evaluating the data against data collection objectives and updating the CSM will reduce uncertainty and support decision making. Data analysis is linked back to data collection objectives to identify any further data gaps and assess the value of additional site characterization.

Chapter 5 describes the regulatory challenges and benefits of applying an ISC approach to DNAPL sites.

Chapter 6 describes the perspectives of community and tribal stakeholders toward an ISC approach.

This guidance is a resource to inform regulators, responsible parties, consultants, community stakeholders, and other interested parties of the critical concepts related to characterization approaches and tools for collecting subsurface data at DNAPL sites.

This document revises and replaces the 2003 ITRC Technology Overview document: *An Introduction to Characterizing Sites Contaminated with DNAPLs*. This updated document discusses the recent understanding of subsurface DNAPL and dissolved-phase contaminant distribution, and presents integrated and real-time site characterization techniques.

2.0 TYPES OF DNAPLS AND DNAPL PROPERTIES

DNAPLs are denser than water and have limited and varying solubilities in water; thus, they tend to occur in a separate nonaqueous phase in the subsurface. In contrast, alcohols (for example, ethanol) are fully soluble in water and do not form separate nonaqueous phase liquids (NAPLs). When DNAPLs are released to the subsurface, the DNAPL phase remains separate from the other principle fluid phases, air and water, and their subsurface migration and physical behavior are governed by the physics of multiphase flow in porous or fractured media.

This chapter describes the fluid properties of DNAPLs and their direct fluid-phase interaction with porous media. Chapter 3 discusses the evolving conceptual model for distribution and transport of DNAPL-forming compounds, which has necessitated an ongoing reevaluation of DNAPL site characterization objectives and methods.

2.1 Types of DNAPLs

Common DNAPL compounds include materials that have been or are still widely used in industrial and commercial processes, such as the following:

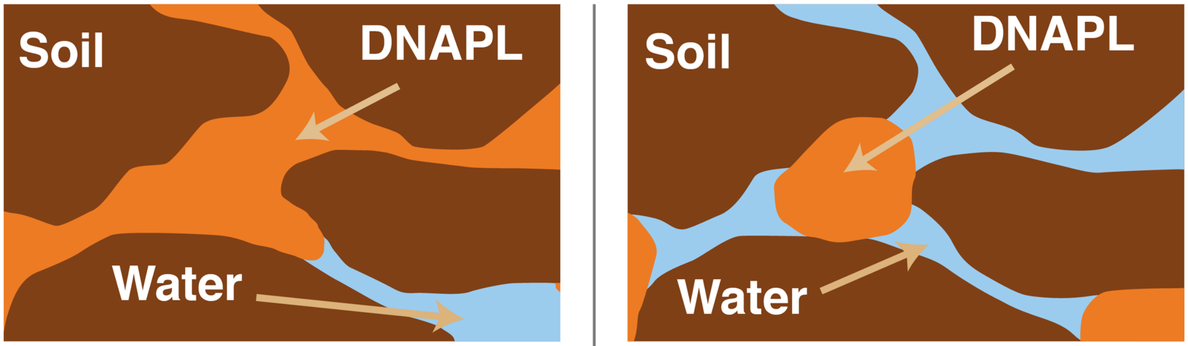
- chlorinated solvents
- coal tar
- creosote
- heavy petroleum—for example, No. 6 fuel oil products
- polychlorinated biphenyls (PCBs)
- pesticides

Possibly the most common DNAPLs are chlorinated solvents such as trichloroethylene (TCE), tetrachloroethylene (PCE), and carbon tetrachloride (CCl_4). PCE and TCE have been used as degreasers, dry cleaning fluids, and solvents in many industrial and commercial processes, and have frequently been released to the subsurface. These solvents have also been commonly used in household products such as spot removers, brake cleaner, penetrating oils, typewriter correction fluid, and finishes.

Before 1985, carbon tetrachloride was used as a grain fumigant at almost every grain storage facility across the country; thus, soil and groundwater contamination with CCl_4 and its primary degradation product chloroform is widespread across the Midwest and Plains areas of the United States (USEPA 1984). Also common is coal tar DNAPL contamination, resulting from historical spills/releases during manufactured gas plant (MGP) operations that produced coal gas for residential, commercial, and industrial uses. In portions of the country where wood treatment has been a major industry, creosote DNAPL contamination is also commonly encountered. Fuel oil products (such as No. 6 fuel oil DNAPL) may be encountered at industrial or government sites where they were used as boiler fuel, as well as at petroleum refineries and some electrical generating plants.

2.2 DNAPL Properties and Terminology

At sites where separate-phase DNAPL fluids are discovered in the subsurface, it is essential to recover and characterize fluid properties whenever possible. Each of the DNAPL fluid properties described in this section is important in helping assess the distribution and mobility of the separate-phase fluid or the partitioning/dissolution of compounds from the DNAPL to groundwater or soil vapor. Figure 2-1 describes the mobility characteristics of DNAPLs.



Mobile DNAPL
DNAPL body is continuous and its capillary pressure is high enough to exceed groundwater pore entry pressure, displace groundwater, and migrate through the subsurface.

Potentially Mobile DNAPL
DNAPL body is continuous, but its capillary pressure is not high enough to exceed groundwater pore entry pressure; under current conditions, it will not displace groundwater and migrate. If conditions change (for example, drilling through a potentially mobile DNAPL body, soil fracturing), potentially mobile DNAPL may mobilize and begin migrating.

Immobile Residual Phase DNAPL
"Droplets" of DNAPL called ganglia are present in the pore spaces but are not connected to other DNAPL ganglia. They are immobile because they cannot exceed the capillary pressure and displace groundwater in the formation.

Figure 2-1. Mobility characteristics of DNAPL: mobile, potentially mobile, and immobile.

Numerous references that provide fluid property data for neat (pure) liquids include Cohen et al. (1993), Pankow and Cherry (1996), Dwarakanath et al. (2002), and USEPA (1991); however, these data are generally not representative of DNAPL fluids after they have been released to the subsurface, and the errors that can be induced by relying on neat fluid characteristics to represent field conditions can be substantial. It is therefore important to measure site-specific DNAPL properties whenever possible rather than relying on literature-based values. DNAPL mixtures behave differently in the subsurface due to changes in the fluids' characteristics, such as solubility, viscosity, and wettability. Table 2-1 (located at the end of this chapter) provides examples of changes in fluids characteristics due to impurities and aging.

Different types of DNAPLs have varying physical and chemical properties that govern their subsurface behavior. For example, chlorinated solvent DNAPLs have high solubility relative to other DNAPLs, and moderate solubility relative to the full spectrum of groundwater contaminants (see Figure 2-2). This can result in the development of significant dissolved-phase groundwater impacts. In contrast, No. 6 fuel oil has exceedingly low solubility and often does not result in significant dissolved-phase groundwater impacts; No. 6 fuel oil is also highly viscous, which limits its DNAPL migration in the subsurface. Furthermore, coal tar and creosote have been shown, in some circumstances, to behave in porous media as wetting fluids as opposed to nonwetting fluids (see Section 2.3); this has profound implications for DNAPL migration (Hugaboom and Powers 2002). These are only a few examples of the key dissimilarities between different types of DNAPL mixtures.

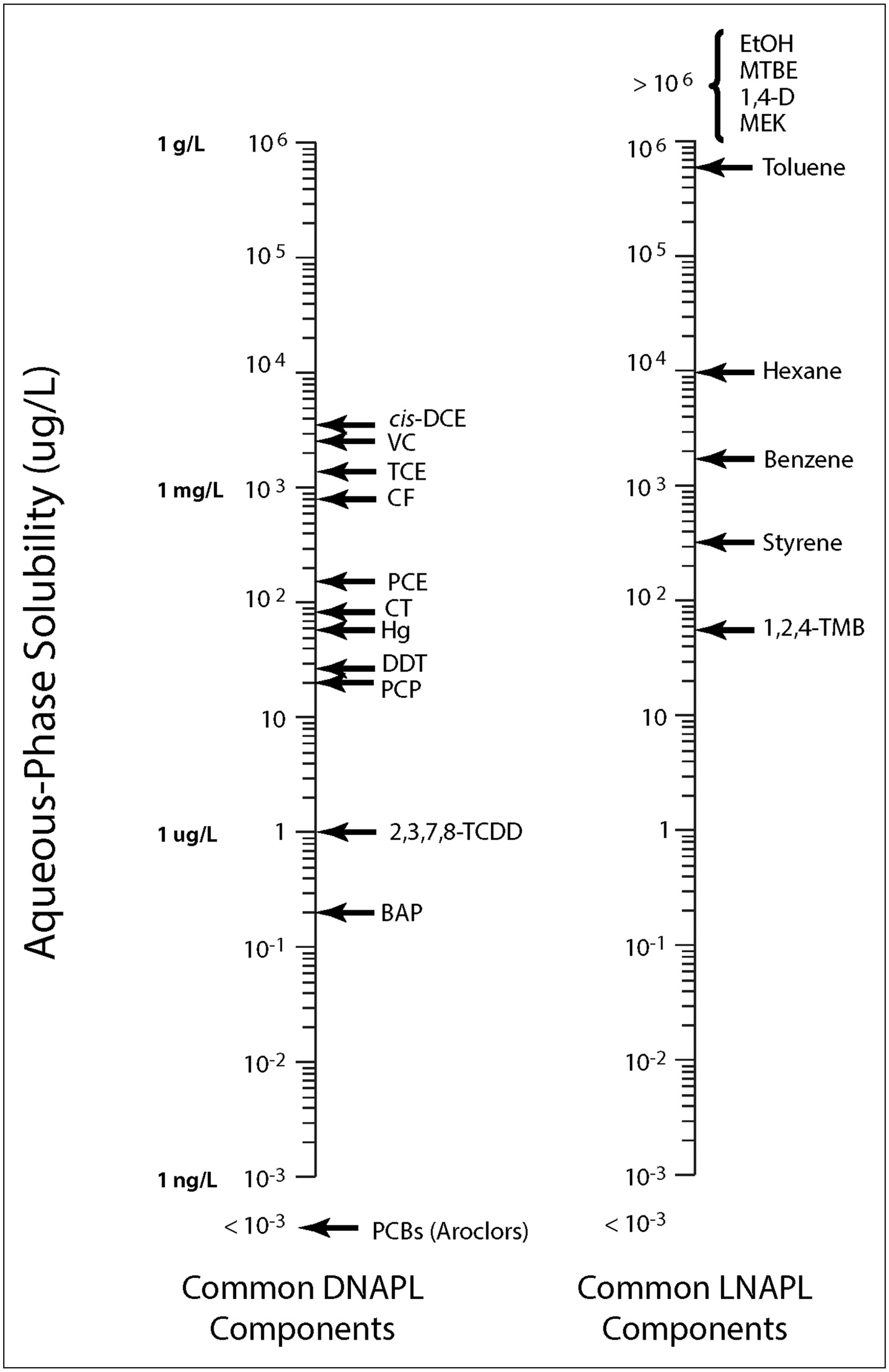


Figure 2-2. Solubilities of common DNAPLs and other compounds (see Appendix K for chemical acronym definitions).

Some of the actions that affect DNAPL in the porous media involve the combined properties of the fluid and its interaction with a particular subsurface media. As the subsurface geology creating the aquifer matrix is heterogeneous, interactions between the DNAPL and the subsurface may change over short distances with the changes in the aquifer matrix. Illustrating the combined matrix properties that represent conditions within a representative elementary volume (REV) helps to visualize the interactions between DNAPL and various portions of the aquifer matrix. Figure 2-3 illustrates that V1 and V2, both randomly selected to represent conditions of porosity of the whole mass, do not represent a REV of this site. V3, on the other hand, does appear to closely represent the REV of this site. An REV is the smallest subsurface element that can be considered to have homogeneous conditions representative of the system being evaluated.

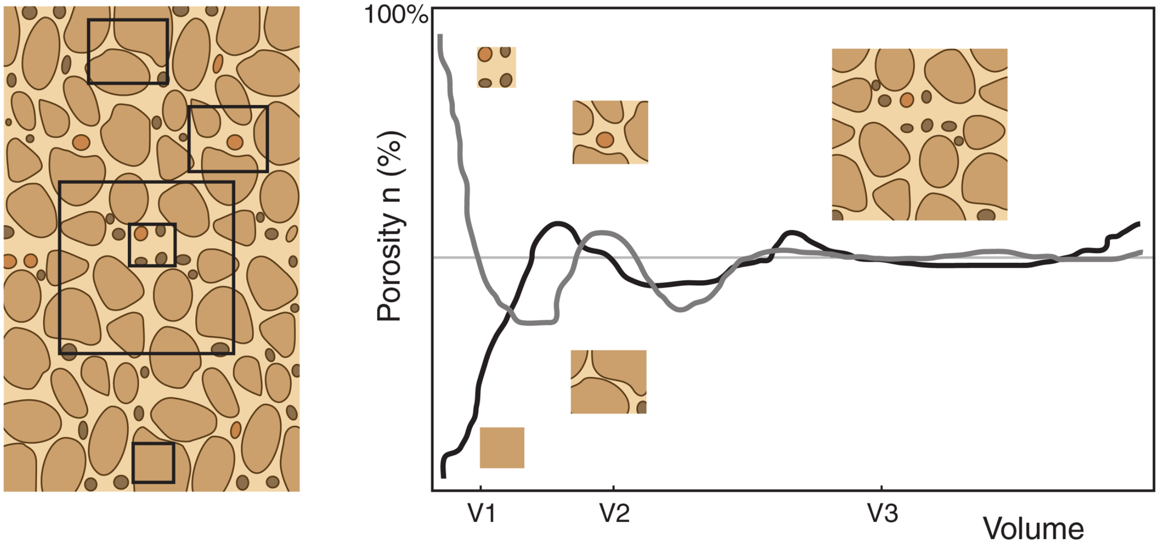


Figure 2-3. Representative elementary volume illustrated as a % porosity compared to increasing volumes of material. Beyond V3, the representativeness does not improve appreciably.

Source: Swiss Federal Institute of Technology of Lausanne 2003; modified after Bear 1979)

Key DNAPL properties that relate to the site characterization concepts and tools described later in this guidance are listed below.

Aqueous solubility is a key DNAPL property, because it controls not only the ability of the DNAPL to produce and sustain a dissolved-phase plume, but also its longevity.

Density describes the mass per unit volume of the DNAPL. It is sometimes expressed as specific gravity (SG), which is the density relative to water.

Interfacial tension represents the force parallel to the interface of one fluid with another fluid (usually air or water), which leads to the formation of a meniscus and the development of capillary forces and a pressure difference between different fluids in the subsurface.

Viscosity (dynamic) represents the *thickness* or *resistance* to shear (flow) of the fluid. For example, honey is more viscous than water, which is more viscous than air.

Volatility represents the tendency of the DNAPL chemical constituents to evaporate into the vapor phase.

Wettability represents whether a fluid is wicked into or repelled out of the subsurface media, and is defined by the contact angle of the DNAPL fluid against the matrix materials in the presence of water. Wettability is a combined property of the DNAPL and the subsurface formation materials, and can be affected by chemistry and the presence of co-contaminants. Figure 2-4 illustrates the wetting process as an interaction between surfaces. The wetting process is an interaction between surfaces. In this example, the solid surface has sufficient force to overcome the surface tension on the low-surface tension droplet on the right and the droplet is stretched out into a thin wetting layer. The solid surface energy is not high enough to overcome the high surface tension of the droplet on the left and wetting does not occur

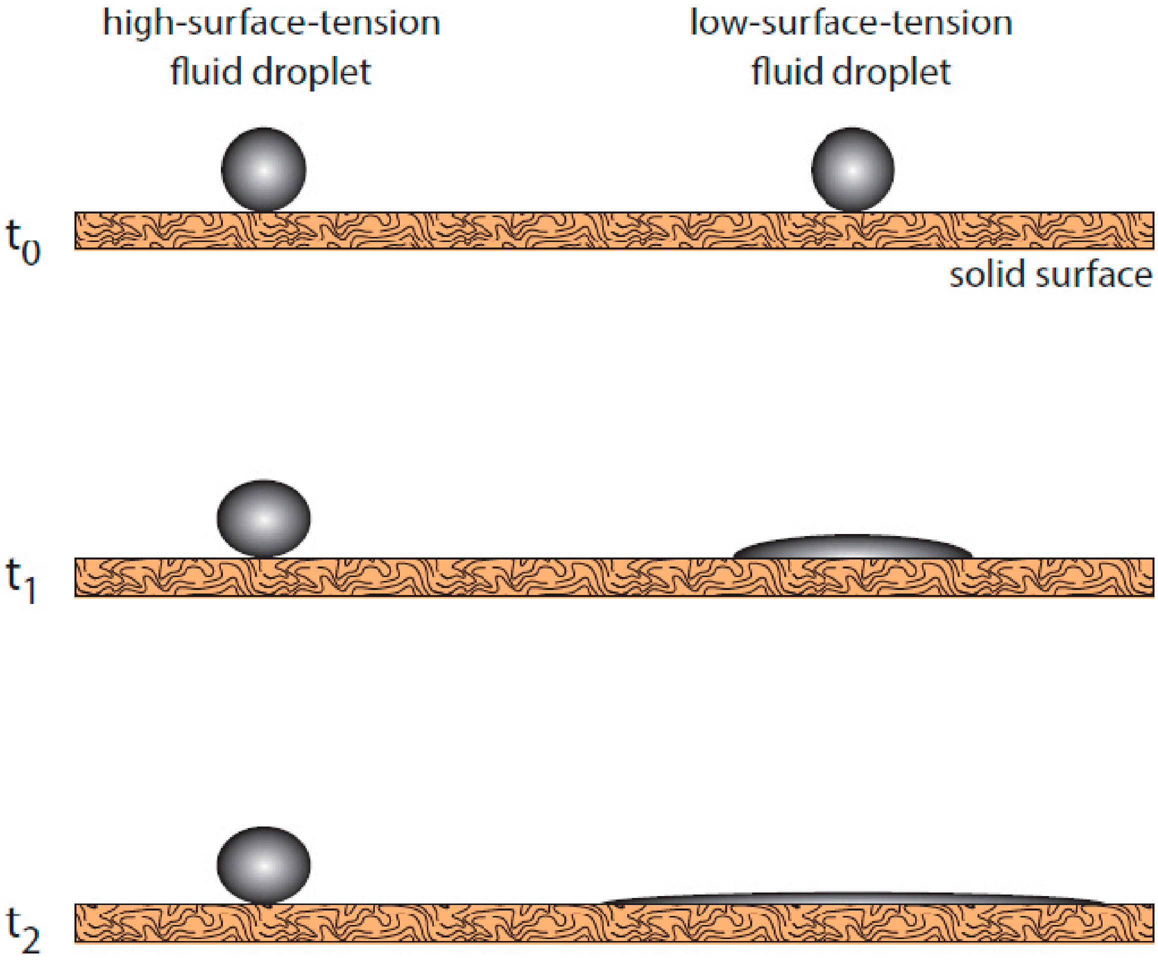


Figure 2-4. Illustration of the wetting process as an interaction between surfaces.

Saturation (S) represents the proportion of the subsurface pore space within an REV that is occupied by a fluid (either DNAPL, air, or water), ranging from 0 to 1.0. When multiple fluids are present, the sum of all fluid saturations equals 1.0. The DNAPL saturation (Sd) very rarely approaches 1.0, because the NAPL typically shares pore spaces with water or air, and most porous media are water wetting.

Residual saturation (Sr) is a combined property of the DNAPL and the subsurface formation materials. S_r is the fraction of pore space within a REV that is filled by the DNAPL at the point where it becomes disconnected from DNAPL in an adjacent REV and is no longer mobile. The value of S_r represents the fraction of DNAPL potentially remaining in zones that were previously directly exposed to DNAPL migration (Cohen et al. 1993; Pankow and Cherry 1996).

Relative permeability (kr) represents the actual or effective permeability of a fluid in a REV relative to the intrinsic water permeability of a porous medium. The value of k_r, ranges from 0 to 1.0 as a nonlinear function of saturation (S), where $k_r = 1.0$ at $S = 1.0$ and $k_r = 0$ at $S= 0$ (Parker and Lenhard 1987).

Capillary pressure (Pc) represents the pressure difference between two fluids sharing pore space within a REV. Due to interfacial tension and the formation of a meniscus, the non-wetting fluid develops a greater pressure than the wetting fluid. P_c is a nonlinear function of S, with P_c increasing at greater saturation of the nonwetting fluid (Parker and Lenhard 1987).

Capillary entry pressure (Pce) represents the capillary pressure at S_r of the non-wetting fluid. The value of P_{ce} represents the pressure that must be overcome for DNAPL (as a non-wetting fluid) to initially displace water from initially water-saturated media. The P_{ce} represents the minimum pressure required for DNAPL to be mobilized into any geologic material (Cary, McBride, and Simmons 1989; Dietrich and Dietz 2012; Schwille 1988; De Pastrovich et al. 1979; Cohen et al. 1993; Wilson et al. 1990).

2.3 Effects on DNAPL Properties

The importance and effects of the properties defined above on understanding DNAPL distribution, degradation, interactions with subsurface materials, and other behavior in the environment (as they apply to both characterizing contamination and developing remedial alternatives) are addressed in works by Cohen et al. (1993) and Pankow and Cherry (1996). Several of these key properties are summarized below; however, additional resources should be used, as needed, to assess the specific chemical and physical properties of the particular contaminant type(s) at a project site.

2.3.1 Aqueous Solubility

Aqueous solubility represents the maximum concentration of the DNAPL chemical constituents that can be dissolved in an aqueous solution (groundwater for the purpose of this document). For DNAPL mixtures, the aqueous solubility of individual components is subject to co-solvent effects. For example, under ideal conditions, the maximum concentration of a NAPL constituent (for example, PCE) is equal to the mole fraction of that constituent in the mixed NAPL multiplied by the aqueous solubility of the constituent if it were a pure NAPL (for example, PCE-DNAPL). Solubility considerations include the following:

- Low-solubility DNAPLs such as coal tar and creosote are slow to dissolve and therefore are more persistent over time, although other factors such as biodegradability are interrelated and also control longevity.
- Risk-driving compounds in groundwater are often derived from DNAPLs that have relatively high solubilities, such as the chlorinated ethene DNAPLs PCE and TCE.
- A contaminant existing in mixed DNAPLs, such as waste solvent with oil/grease content, may exhibit lower maximum concentrations in groundwater than when the contaminant exists as a pure DNAPL. For example, benzene typically represents approximately 2% of the volume of gasoline, which yields a maximum concentration in water of approximately 54 milligrams per liter (mg/L) compared to 1,780 mg/L when benzene exists as pure NAPL. Thus, at sites containing mixed NAPLs, contaminant concentrations may be much lower than would be anticipated based on the pure compound's aqueous solubility. These contaminant mixtures may persist for much longer than the equivalent mass of a single compound NAPL.
- If chlorinated DNAPLs mix with petroleum light nonaqueous phase liquid (LNAPL) products, the chlorinated DNAPLs may preferentially partition into the petroleum rather than into the groundwater. This will change the type and concentration of any dissolved-phase plume partitioning from the mixed NAPL, creating a different plume than would be expected if the chlorinated DNAPLs were present without the LNAPL.
- Coal tar, creosote, and No. 6 fuel oil DNAPL mixtures generally display extremely low bulk solubility and may result in small to negligible dissolved plumes; however, these chemical mixtures often contain soluble constituents, such as naphthalene, that dissolve into groundwater creating plumes.
- Historically, a 1% dissolved-phase concentration of chlorinated solvent DNAPLs, based on compound-specific solubility in groundwater, was thought to indicate the potential presence of DNAPL; however, this method is now viewed as unreliable (that is, either falsely positive or falsely negative). See Appendix F for methods available to evaluate the presence of DNAPL (USEPA 2009).

- The rate of dissolution of soluble DNAPL constituents is accelerated through aqueous phase treatment that reduces dissolved concentrations and drives faster dissolution rates (ITRC 2008).

2.3.2 Density/Specific Gravity

Density/SG is a critical DNAPL property, as it affects the relative buoyancy of DNAPL in the saturated zone. While, by definition, all DNAPLs have an SG greater than 1.0, some DNAPLs (such as PCE) have an SG of >1.5, while others have an SG barely greater than water. For example, No. 6 fuel oil can sometimes exist as an LNAPL with an SG of <1.0 and in other cases may exist as a DNAPL with an SG of approximately 1.05. Denser DNAPLs have a greater driving force for downward movement, while other DNAPLs may be almost neutrally buoyant.

2.3.3 DNAPL Residual Saturation

DNAPL Residual Saturation (DNAPL S_r), as described above, is a REV property and therefore represents conditions at a scale of centimeters that can vary greatly over small distances. A specific S_r at a site is a function of the DNAPL properties, including viscosity, interfacial tension, and wettability, and is particularly a function of the subsurface pore structure. *Residual saturation represents the saturation at which the DNAPL is immobilized by capillary forces as discontinuous ganglia under ambient groundwater flow conditions* (Cohen et al. 1993). Residual saturation can be affected by conditions such as temperature and groundwater chemistry, which can influence viscosity or interfacial tension. Residual saturation is also affected by groundwater gradients. Increased groundwater gradients (such as from active remediation) can mobilize residual DNAPL effectively by decreasing the residual saturation value. Similar to permeability or porosity, S_r is a REV property and can vary greatly between immediately adjacent geologic materials. The ultimate distribution of residual DNAPL is not uniform or readily predictable in the subsurface due to minute variations in pore size distributions, soil texture, soil structure, and mineralogy. DNAPL S_r typically ranges from 5% to 15%, and site-specific measurement of S_r can be potentially valuable.

2.3.4 Interfacial Tension and Wettability

Interfacial tension, viscosity, fluid density, and porous media characteristics are properties that govern DNAPL migration. In the typical scenario, water is the *wicking* or *wetting* fluid (see Figure 2-5) and DNAPL is *non-wetting*; however, for some aquifer matrices and some DNAPLs, the system may be DNAPL-wetting. Also, in a low-moisture vadose zone setting above the water table, even *non-wetting* DNAPL can be subject to capillary spreading, as DNAPL often acts as a wetting fluid relative to air. Below the water table, most but not all DNAPLs behave as non-wetting fluids. In these cases, the interfacial tension between the DNAPL and water phases act to resist DNAPL spreading (see Figure 2-6). This resistance to DNAPL movement is expressed as a pressure difference between the DNAPL and water phases, referred to as P_c. Furthermore, there are differences in the subsurface pore structure, which control the P_c that resists DNAPL movement. Therefore, subsurface geologic heterogeneity ultimately controls DNAPL migration.

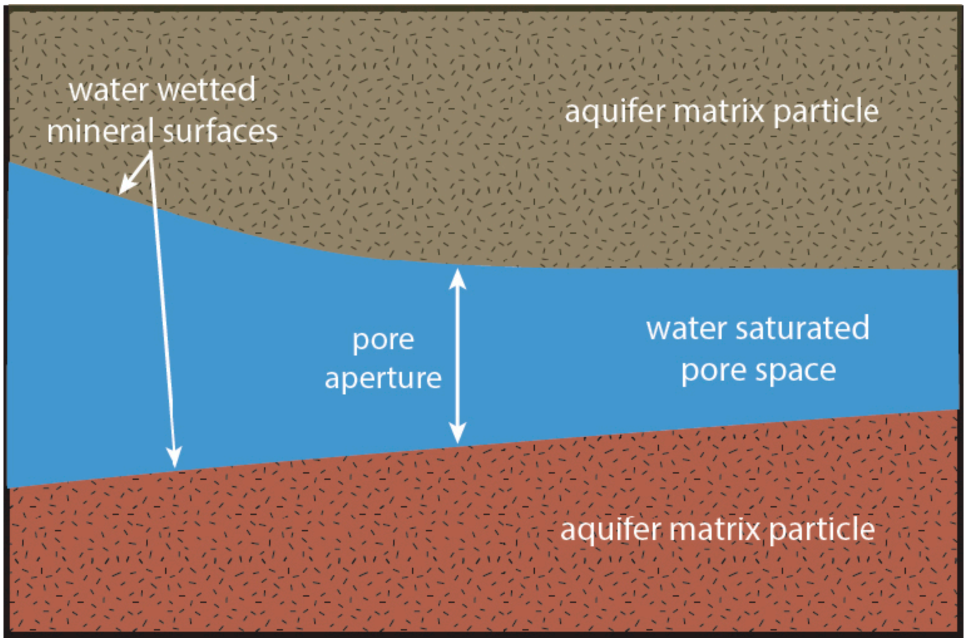


Figure 2-5. Typical conditions found in an aquifer with water present.

Figure 2-6 depicts the invasion of a NAPL into a saturated porous medium. The pore aperture is narrowing, from the left to the right. As the pore aperture narrows, the capillary pressure of the wetting fluid (water, in this case) increases, which increases the NAPL entry pressure, Pe. On the left, the NAPL pool pressure exceeds the entry pressure and the free water phase has been displaced, leaving only the wetting layer on the mineral surface. In the middle, the NAPL pool pressure matches the capillary pressure of the water, and because the two forces are in balance, the NAPL invasion has stopped. To the right, the pore aperture is smaller and the capillary pressure of the wetting fluid exceeds the NAPL pressure. As a result, the NAPL cannot invade this portion of the pore, without a change in the fluid conditions. Changes that could permit further invasion include (1) increased NAPL pool height, which increases the NAPL pressure; (2) decreasing interfacial tension, which can occur as a result of biodegradation of dissolved-phase NAPL; and (3) groundwater extraction from beneath the NAPL, which increases the effective NAPL pool pressure.

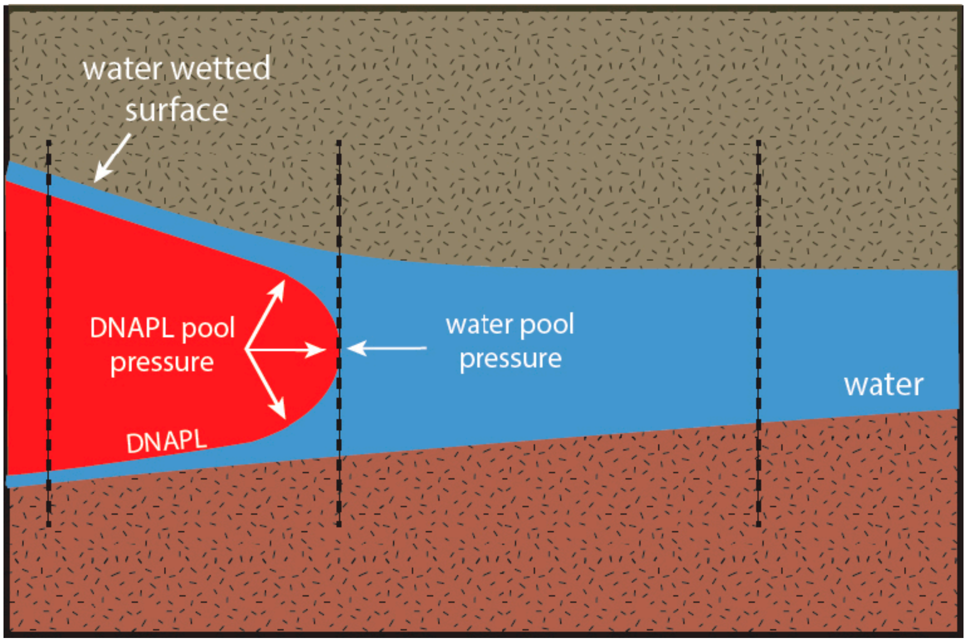


Figure 2-6. Typical conditions in an aquifer with DNAPL present when water is the wetting fluid.

2.3.5 Saturation, Relative Permeability, and Capillary Pressure

S, P_c, and k_r are interrelated and complex properties that govern fluid movement when multiple fluids are present within pore space in a REV, such as when DNAPL is present below the water table. P_c and k_r are both nonlinear functions of S, and DNAPL mobility is governed by the nonlinear S-P_c-k_r constitutive relationships. At most sites, characterization of the nonlinear constitutive relationships is not necessary unless multiphase flow modeling is undertaken; however, some related concepts are important in guiding the site characterization activities described in this document.

As described above, at S_r, DNAPL is immobile. Similarly, at very low S, approaching the value of S_r, DNAPL mobility is limited because k_r is very small. Increasing DNAPL mobility (increasing k_r) can be realized most often through changes in pressure conditions affecting P_c or by changes in chemistry that affect interfacial tension. As described above, the P_{ce} is the minimum pressure that must be overcome for DNAPL to displace water and advance its migration into new geologic materials. Subsurface geologic materials with smaller pore structure (finer grained or more densely packed) have higher P_{ce}s; therefore, DNAPL migration tends to follow the largest, most accessible pore structures. In fine-grained sediments or consolidated rock, large pore structures such as fractures or other secondary porosity pathways (such as root holes and dissolution features) may be available for migration.

2.3.6 Viscosity

DNAPL viscosity affects the rate at which DNAPL can migrate through the subsurface, but does not inherently influence whether or not DNAPL *can* migrate. DNAPL viscosity primarily comes into play if there are mobile and potentially recoverable volumes of DNAPL, as highly viscous DNAPLs such as No. 6 fuel oil, creosote, and coal tar are slow to migrate.

2.3.7 Volatility

The volatility of DNAPL constituents, as measured by vapor pressure, directly affects partitioning or transfer of these constituents into the vapor phase, either directly from a DNAPL that may be present in the vadose zone or from dissolved DNAPL constituents in groundwater. Mixed DNAPLs have reduced component vapor pressures, which can be estimated from pure compound vapor pressure data and by measuring the DNAPL solution composition.

2.3.8 Vapor Pressure

The vapor pressure is the pressure exerted by the vapor phase of a substance at equilibrium with the pure condensed (solid or liquid) phase in a closed system. For ideal gases, the vapor pressure can be converted to a concentration using the ideal gas law at a given temperature and pressure. Vapor pressure data are used in predicting the equilibrium partitioning constants between the gas phase and liquid or solid phases.

2.3.8.1 Henry's Law

$$K_H = \frac{p_A}{[A_{water}]}$$

$$K_{aw} = \frac{[A_{air}]}{[A_{water}]}$$

For dilute solutions, Henry's law is the ratio of the vapor pressure to the solubility of a substance; that is, solubility and vapor pressure are directly proportional, at a given temperature and pressure, for sparingly soluble compounds. Using the ideal gas constant and temperature, the Henry's law constant can be converted to a dimensionless form that is the ratio of concentration in air to the concentration in water at equilibrium at a given temperature and pressure. Use of the Henry's law constant assumes a linear relationship between the partial pressure of a substance and its concentration in water up to saturation, which is generally only true in dilute solutions.

Where K_H is Henry's law constant, P_A is the partial pressure, A_{water} is the concentration of a substance in water, K_{aw} is the dimensionless Henry's law constant, and A_{air} is the concentration of a substance in air.

2.3.8.2 Raoult's Law

For an ideal solution, Raoult's law states that the mole fraction of each substance in a mixture is equal to the mole fraction of the vapor pressure of that substance in a closed system at equilibrium.

$$P_i = x_i P_i^o$$

$$x_i = \overset{n_i}{\sum_j} n_j$$

Where P_i is the partial pressure of substance i, x_i is the mole fraction of substance i in the mixture, P_i^o is the vapor pressure of i, n_i is the number of moles of i, and j is the number of substances in the mixture. Raoult's law is generally used for mixtures of organic compounds, such as petroleum or solvents.

2.3.8.3 Fick's Law

Fick's first law states that flux is directly related to the concentration gradient of a chemical multiplied by a diffusion coefficient for that chemical. Diffusion can only be affected by the manipulation of one of these terms, which limits remedial alternatives where diffusion controls mass transfer.

$$Flux\left(\frac{mass}{time\text{–} area}\right) = J = -D\frac{dC}{dx}$$

2.3.8.4 Peclet Number

The Peclet number is the ratio of advective transport rate to diffusive transport rate. It is used to estimate where diffusive transport or advective transport dominate under a given set of conditions. In low Peclet number environments, Fick's first law predominates. In high Peclet number environments, the fluid velocity controls transport.

$$P_e = LU / D$$

Where P_e is the Peclet number, L is the characteristic length, U is the velocity, and D is the mass diffusion coefficient for a given chemical.

2.4 Special Considerations for DNAPL Mixtures

DNAPL mixtures such as creosote and MGP tars, which are characterized by high viscosity and low solubility, generally have a higher potential to migrate in the subsurface, and for longer periods, than other DNAPL types such as chlorinated solvents. The relatively high viscosity of these DNAPL mixtures leads to longer-term continuity of the mobile DNAPL phase, sustaining mobility and contributing to mobility within small-scale geologic features. The relatively low solubility of many of the components of these DNAPL mixtures leads to less weathering of the DNAPL mixture in the environment, maintaining the mobile DNAPL phase longer than DNAPL types that contains higher solubility components. Finally, DNAPL mixtures that contain large fractions of heavy-weight hydrocarbons have been shown to alter the solid phase wettability that can also sustain DNAPL mobility. For example, prolonged contact of MGP tar with soil can cause water-wet soil to effectively become DNAPL-wet. When a soil becomes DNAPL-wet, the residual saturation decreases, resulting in lower DNAPL retention within the soil structure, sustaining the DNAPL migration potential of DNAPL mixtures for longer periods of time as compared to pure component DNAPL releases.

The DNAPL may also have weathered over time in the subsurface since its release. Some industrial-grade DNAPLs have impurities that, while acceptable to a manufacturing process, change the properties enough to influence subsurface fate and transport in a manner different from those of the pure DNAPLs. Therefore, at any DNAPL site, analysis of site-specific NAPL acquired from the subsurface is recommended if at all possible to facilitate site assessment. In addition to the potentially significant differences between pure and aged NAPLs, properties of similar NAPLs at different sites and in different site areas can also vary.

Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, and field aged/weathered DNAPLs—including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote—are presented in Table 2-1. The published literature and the measurements contained in Table 2-1 indicate the following:

- Coal tar creosote—a multicomponent DNAPL composed of hundreds of polycyclic aromatic hydrocarbons; phenols; benzene, toluene, ethylbenzene, and xylene; and other compounds—has been detected at many wood-treating sites due to long periods of process operation, large releases from multiple areas (such as drip tracks, process area, and wastewater management ponds), chemical persistence, and ease of detection (due to its characteristic odor and dark color).
    - Coal tar creosote density and viscosity can vary substantially between and within wood-treating sites due to variation in creosote product sources and mixtures as well as sequential weathering effects that change creosote properties over time.
    - Measured physical property values from 15 wood-treating sites in the United States range from 1.06 to 1.12 grams per cubic centimeter (g/cc) density, 12 to 57 centipoise (cP) viscosity, and 19 to 28 dynes per centimeter (dynes/cm) interfacial tension.
    - Coal tar and creosote DNAPL is also encountered below ground at many former MGP and wood-treating sites where substantial releases occurred over decades. The large volume, low solubility, and high viscosity of coal tar and DNAPL released at wood-treating and former MGP sites can result in much longer periods (often decades) of DNAPL migration than typically occurs at chlorinated solvent release sites. Measured physical property values from former MGP sites in the Unites States typically range from 1.02 to 1.10 g/cc density, 20 to 100 cP viscosity, and 15 to 27 dynes/cm interfacial tension.

- Releases of unused and spent chlorinated solvent DNAPLs have occurred at thousands of contamination sites, including dry cleaner, metal works, chemical manufacturing, and waste disposal sites. Determination of chlorinated solvent DNAPL properties in samples recovered from the subsurface, however, is relatively rare because of small release volumes, limited and complex subsurface DNAPL distributions, low-resolution characterization, and solvent loss due to volatilization, dissolution, and diffusion.

- The physical properties of PCE and TCE DNAPLs extracted from wells at several contamination sites are listed in Table 2.1. As shown, measured density and viscosity values for these samples are similar to those reported for the pure compounds, particularly where solvent was released from product storage tanks or pipelines prior to use. Spent solvents are frequently mixed with oil/grease that decreases DNAPL density and increases DNAPL viscosity. The interfacial tension of chlorinated solvent DNAPLs in the subsurface is generally much lower than that of pure solvent compounds due to the admixture of surface-active agents from soil humus and other waste materials.
- DNAPLs in the subsurface at mixed chemical waste release sites (associated with chemical manufacturing, waste disposal, and waste recycling facilities) can have highly variable physical properties, as shown in Table 2-1.
- PCB DNAPL releases in the United States may have occurred at facilities where PCBs were produced (for example, Monsanto plants in Sauget and Anniston, Alabama); used as insulating and cooling fluids (for example, GE Fort Edward and Hudson Falls, New York plants and Westinghouse Bloomington, Indiana plant); used to manufacture or recycle high-temperature capacitors, transformers, hydraulic oils, and other products; and used at former solvent and waste oil reprocessing and disposal sites (for example, Smithville, Ontario). Monsanto Aroclor PCB products consisted of a series of technical mixtures in which fluid density and viscosity increased with chlorine content and decreased with increasing carrier fluid content, which typically consisted of up to 70% chlorobenzenes or mineral oil (Wischkaemper et al. 2013).
- Although site data are generally unavailable for PCB DNAPLs, based on product specifications, the density and viscosity at contaminated sites are expected to vary between 1.1 and 1.5 g/cc and 10 and 50 cP, respectively. PCB-rich LNAPLs are also encountered at some sites. Interfacial tension data for field-weathered PCB samples were not readily found in available literature. The high viscosity of PCB oils indicates that the timescale of their separate phase migration may occur over decades at some sites (Kueper et al. 2003).

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise.

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
Water				0.998	1.0	74.4 (air)	
Gasoline				0.71–0.77	0.5	27 (15°C)	Wang et al. 2006
Diesel fuel				0.80–0.85	1.1–3.5	27 (15°C)	Wang et al. 2006
TCE, pure			100% TCE	1.46	0.57	34.5	Pankow and Cherry 1996 Cohen et al. 1993

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
TCE-rich spent vapor degreasing solvent DNAPL at Hill Air Force Base, UT OU2	Spent degreasing solvents (mainly TCE) were disposed of in unlined trenches between 1967 and 1975.	~41,000 gallons of DNAPL have been pumped from a sand and gravel channel aquifer ~45–50 ft bgs that is underlain by clay. DNAPL sampled from recovery wells was analyzed circa 1994.	DNAPL consisted of TCE (53%–60%), TCA (5%–12%), PCE (3%–5%), and other chlorinated degreasing solvents and oil and grease (~25%).	1.38	0.78	9	Oolman et al. 1995 Jackson and Dwarakanath 1999 Meinardus et al. 2000 Dwarakanath et al. 2002 USAF 2009
TCE degreasing solvent DNAPL (unused) from a metal parts manufacturer in Connecticut (Site A)	TCE was apparently released from leaking USTs and product distribution lines between the late 1950s and the early 1970s.	DNAPL, which had accumulated at the bottom of a glacial outwash	>99.5% TCE with minor PCE, CCl_4, and TCA	1.45	0.54–0.55	21.1–23.5	Parker et al. 2003 Chapman and Parker 2005

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
PCE, pure		sand aquifer (~30 ft bgs) above a thick clay layer, was pumped from two wells and analyzed in 1996.	100% PCE	1.63	0.9	44.4	Pankow and Cherry 1996 Cohen et al. 1993
PCE DNAPL from a dry cleaning facility at Camp Lejeune, NC, Site 88	PCE dry cleaning fluid releases occurred between the 1970s and 1995 from leaking USTs, floor drains, and pipes.	DNAPL was located adjacent to and beneath the dry cleaning building in fine sand and silt at 17–20 ft bgs just above a clay layer.	The reduced density suggests that the PCE DNAPL contained a small fraction of dissolved mineral oils and grease.	1.588	0.85–1.10	10.4	Duke Engineering & Services 1999 Dwarakanath et al. 2002

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
PCE-rich vapor degreaser solvent DNAPL recovered from a well in shallow alluvium at Kelly Air Force Base, TX	Solvents, which leaked from degreasers and piping between the 1940s and 1980s, migrated to and pooled in alluvial deposits at ~40 ft bgs.	The analyzed DNAPL sample was pumped from a well in 1997. DNAPL was discovered in 1997 beneath buildings that housed metal plating and degreasing operations. Approximately 1,000 gallons of DNAPL was pumped from the alluvium in 1998.	PCE-rich DNAPL	1.60	0.9	14.6	USEPA 2000 Dwarakanath et al. 2002
PCE degreasing solvent DNAPL (unused) from a former plating shop degreaser and a PCE bulk storage tank	PCE solvent was apparently released from degreasers and USTs between 1950 and the late 1980s.	DNAPL present in fine to coarse sand	>99.9% PCE, <0.1% TCE	1.62	1.11	23.6–34.2	Parker et al. 2003

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
at the Connecticut 'B' Site		layers was pumped from two wells in 2003.					
Mixed TCE and PCE vapor-degreasing DNAPL from Site X701B at the USDOE's Portsmouth Gaseous Diffusion Plant, OH	An estimated 80,000 gallons of solvent waste from degreasing and other operations was released to a holding pond between 1953 and 1988.	DNAPL migrated into the lower sand and gravel unit of the Gallia Sand at approximately 30 ft bgs. Sample analysis was performed in 1995.	Lab analysis of a DNAPL sample indicated three times more TCE than PCE, but contaminant recoveries in the analysis were very low.	1.43	4	NR	Young et al. 1999
Mixed chemical waste DNAPLs, including chlorobenzenes, chlorophenols, and chlorotoluenes from the Love Canal chemical waste landfill in Niagara Falls, NY	An estimated 22,000 tons of chemical plant wastes was deposited in an abandoned canal and pits between 1942 and 1954.	DNAPL was sampled from eight wells completed into the buried waste cells in 1988.	Lab analyses indicate that the DNAPLs are variable complex multi-component mixtures.	1.09–1.50	<16–270	NR	Cohen et al. 1993

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
Chlorobenzene			100% chlorobenzene	1.11	0.799	37.4	Mercer and Cohen 1990
DNAPL (mixed chlorobenzene and DDT) from the Montrose Chemical Superfund Site, a former DDT manufacturing facility in Los Angeles County, CA	Mixed chlorobenzene and DDT DNAPL was released from the Central Processing Area of the Montrose facility, presumably between the 1950s and early 1980s.	DNAPL was documented in silt and sand lenses at ~70 ft– 95 ft bgs within an aquitard unit. DNAPL samples were pumped from four wells in 2003.	Mixed chlorobenzene and DDT, multicomponent DNAPL	1.24–1.25	2.5–2.8	13–15	Hargis and Associates 2004 Davis and Hayworth 2006

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
DNAPL (mixed chemicals) from the Casmalia Resources Superfund Site in Santa Barbara County, CA	An estimated 5.6 billion pounds of mixed chemical wastes were disposed of in landfills, ponds, trenches, and shallow wells between 1973 and 1989.	DNAPL samples were pumped in 2003 to 2004 from wells completed in fractured claystone at ~75–150 ft bgs.	Complex mixture of numerous VOCs and SVOCs	1.01–1.09	3.3–9.7	2.8–7.1	Casmalia Resources Site Steering Committee 2011
Mixed chlorinated solvent DNAPL (such as PCE or CCl_4) from chemical manufacturing releases the at ICI/Orica Botany Bay site, Sydney, Australia	An estimated 14 million kg of chlorinated hydrocarbons, including PCE, TCE, 1, 2-DCA, and CCl_4, were released in different site areas between 1944 and the 1990s.	DNAPL has migrated down through ~90 ft of sand to a clay layer. Samples taken from three wells in the southern plume area were analyzed in 2006.	Lab analyses indicate major components of the mixed DNAPL area: PCE (55%–60%), CCl_4 (25%–30%), and hexachloroethane (7%–9%).	1.6	0.63 – 3.8	10 - 15	Golder and Associates 2011

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
Creosote wood-preservative DNAPL				1.01–1.13	20–50	NR	Kueper et al. 2003
Creosote wood-preservative DNAPL from 17 sites				1.065–1.128	11.8–57.1	19.5–27.8	Foster 2013 Personal communication regarding physical property measurements made by Key Environmental, Inc., on DNAPL samples taken from 16 Beazer East, former Koppers, wood-treating and coal tar refining sites in the United States)

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
Weathered creosote DNAPL pumped from seven wells at the Cabot Carbon/Koppers Superfund site, FL	Creosote used to preserve utility poles and timbers between 1916 and 1992 was released in lagoon, cooling pond, and drip track areas.	Creosote DNAPL has migrated through surficial aquifer sand (~20–25 ft thick) and into the Upper Hawthorne Group clay. DNAPL samples pumped from seven wells were analyzed in 2006.	Weathered creosote DNAPL	1.02–1.10 (60°C)	4.9–25.5 (40°C)	17–23	Mercer et al. 2006
Former MGP coal tar typical range of data	~1850 to 1950	Aged releases	Aged MGP coal tar	1.02–1.1	20–100 (but can be much higher)	15–27	See data and references below
Eight former MGP sites	Various	Sampled in 1989 to 1990	Aged MGP coal tar	1.06–1.43	34–6,600 (40°C)	NR	Lee et al. 1992 EPRI 1993
Spring Gardens Former MGP, Baltimore, MD	Operated from 1955 to ~1973	Coal tar migrated	Aged MGP coal tar	1.07–1.1	56–126 (100°F)	21.1	EPRI 2000

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
NW Natural Gas Co., Former MGP, Portland, OR	Former MGP operated from 1915 to 1956; site was also used for coal tar distillation (1965 to 1973) and storage/transfer of creosote and coal tar pitch (post-1977)	through mixed fill over clay and was pumped from a well ~18 ft bgs. Analyzed samples were collected from 1988 to 1998. Samples were collected in 1998 from wells in shallow fill (22–32 ft bgs) and underlying alluvium (30–80 ft bgs).	Aged MGP coal tar	1.05–1.10	72–113	14.2–15.8	Hahn & Assoc. Inc. 2007
Former MGP coal tar, Auburn,	Operated from 1902 to 1946	Sample col-	Aged MGP coal	1.066	63.6	26.6	Kong 2004

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
NY		lected circa 2001	tar				EPRI 2004
Former MGP coal tar, Cape May, NJ	Operated from 1853 to 1937	Sample collected circa 2001	Aged MGP coal tar	1.054	51.0	22.6	Kong 2004 EPRI 2004
Former MGP coal tar, Charleston, SC	Operated from 1855 to 1957	Sample collected circa 2001	Aged MGP coal tar	1.104	425.3	20.7	Kong 2004 EPRI 2004
Former MGP coal tar, Fairfield, IA	Operated from 1878 to 1950	Sample collected circa 2001	Aged MGP coal tar	1.062	62.9	24.1	Kong 2004 EPRI 2004
Former MGP coal tar, Portland, OR	Operated from 1852 to 1965	Sample collected circa 2001	Aged MGP coal tar	1.054	34.7	NM	Kong 2004 EPRI 2004
Former MGP coal tar, Saranac, NY	Operated from 1896 to 1944	Sample collected circa 2001	Aged MGP coal tar	1.062	62.9	24.1	Kong 2004 EPRI 2004
Former MGP coal tar, Shippensburg, PA	Operated from ~1898 to 1948	Sample collected circa 2001	Aged MGP coal tar	1.076	32.0	21.9	Kong 2004 EPRI 2004
Former MGP coal tar, Stroudsburg, PA	Operated from ~1880 to 1945	Sample collected circa 1982	Aged MGP coal tar	1.017 (15.5 °C)	19 (7°C)	22	Villaume 1985
PCB DNAPLs consisting of				1.1–1.5	10–50	NR	Kueper et al. 2003

Table 2-1. Physical properties (density, viscosity, and interfacial tension) of water, select reference fluids, pure NAPLs, and field aged/weathered DNAPLs (including chlorinated solvents, mixed DNAPLs, MGP coal tar, and coal tar creosote). All values were measured at 20° to 25°C unless noted otherwise. (continued)

Liquid	Release Source and Age/Date	Sample Source and Date	NAPL Composition	Density (g/cc^{-3})	Viscosity (cP)	Interfacial Tension, Water Interface (dynes·cm^{-1})	References
variable mixtures of congeners and carrier fluids (for example, chlorobenzenes and mineral oil)							
Creosote 1		Aged release	Aged release	1.111	74.8	38.9	
Creosote 2		Aged release	Aged release	1.046	95.5	35.5	
# 6 fuel oil		Aged release	Aged release	1.05	2,300	~40	
Mixed DNAPL		17% chlorinated VOCs	17% chlorinated VOCs	1.05	10.4	11.6	
Weathered mixed DNAPL		<0.1 % chlorinated VOCs	<0.1 % chlorinated VOCs	1.04	51.7	14.3	
NAPL collected at a MGP		MGP tar mix	MGP tar mix	1.03	1,389	83.75	

°C = degrees Celsius
°F = degrees Fahrenheit
bgs = below ground surface
DCA = dichloroethane
ft = feet
g = grams
kg = kilograms

NM = not measured
NR = not recorded
s = seconds
SVOC = semivolatile organic compound
TCA = trichloroethane
USDOE = U.S. Department of Energy
UST = underground storage tank
VOC = volatile organic compound

3.0 DISTRIBUTION OF DNAPLS AND ASSOCIATED AQUEOUS, SORBED, AND VAPOR PHASE CONTAMINATION

In developing a thorough site characterization program, it is critical to determine the presence and distribution of DNAPL, vapor, dissolved, and sorbed chemical phases of contamination across the various geologic media. The relative distribution of contaminants between different chemical phases and across geologic media within the primary source zone as well as the more distal plume are important in developing a holistic CSM. Understanding the direction and rate of mass transfer within the system indicates the current *trajectory* of the source/plume evolution over time, which is a key element of a comprehensive CSM.

A CSM should address the following basic questions:

- Where does the contamination mostly reside?
- Where is it being transported?
- Is adsorbed or residual mass in low-permeability zones dissolving and diffusing into more permeable zones that form an expanding or persistent plume?

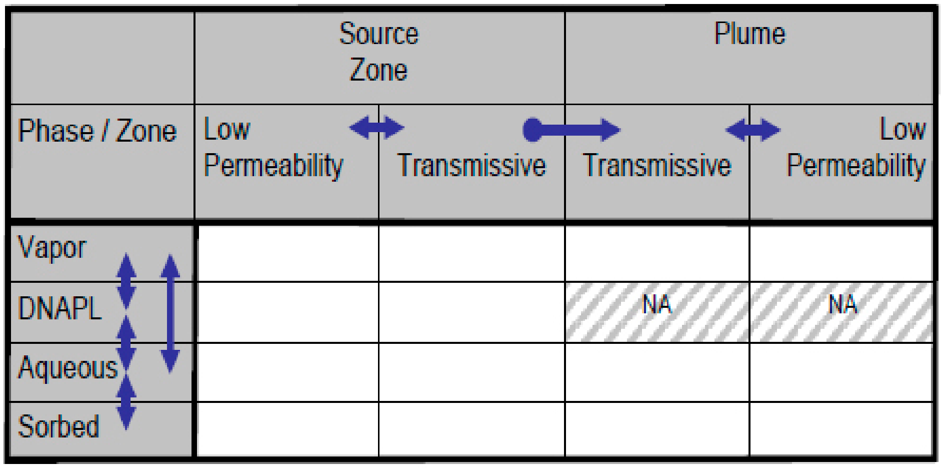
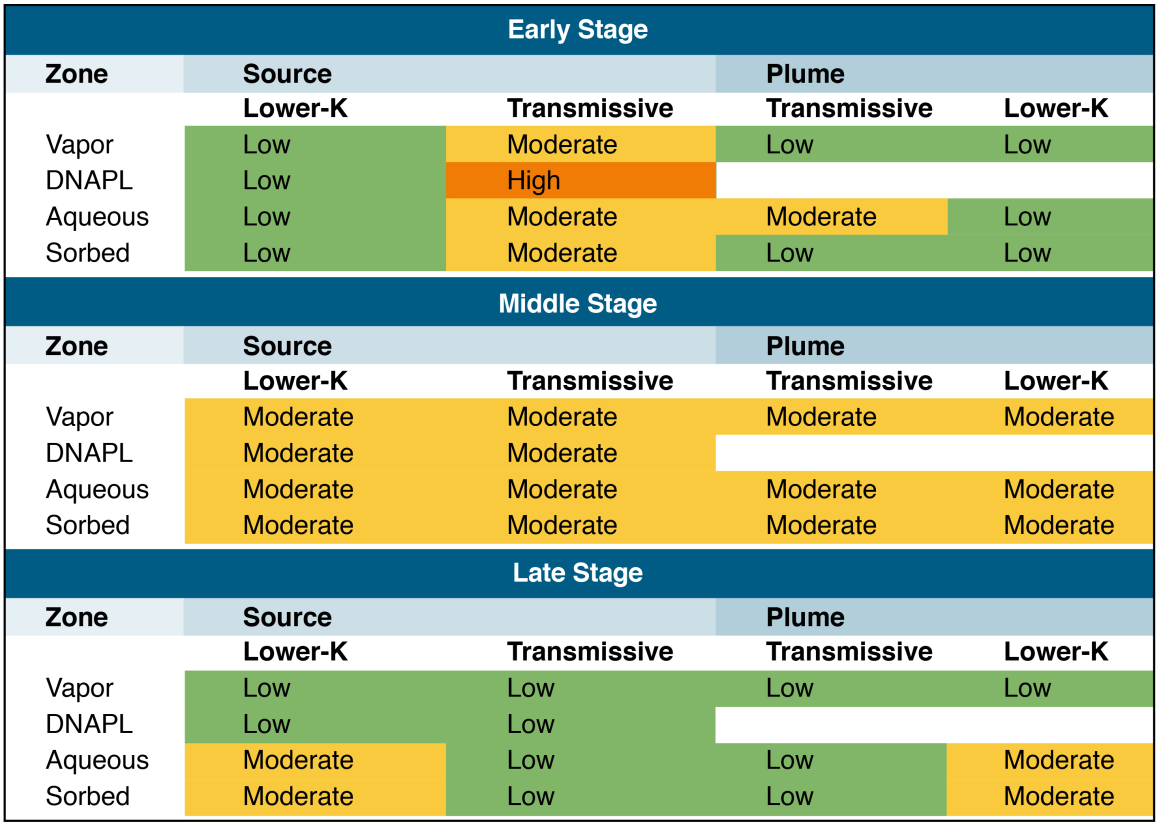


Figure 3-1. The 14-compartment model (Sale and Newell 2011).

The 14-compartment model (Sale and Newell 2011) is a useful tool for visualizing the distribution and movement of contaminants between the chemical phases that may be present at DNAPL sites (Figure 3-1). The 14-compartment model can help describe the relative locations of contaminants within various subsurface compartments, highlighting the direction in which diffusive mass transfer may be occurring (ITRC 2011b, Section 2.5 and Section 2.6). The 14-compartment model guides the selection of a remedy by showing how contaminants may distribute throughout various compartments, the potential mass transfer (fluxes) among them, and how remediation may or may not equally affect each compartment within the source or plume. The 14-compartment model raises questions about the inclusion of various compartments in the CSM, which in turn influences the data collection objectives and data needs. Thus, it is a powerful tool for site characterization planning and CSM development.

Figure 3-2 illustrates how the 14-compartment model can be used as a characterization planning tool (ITRC 2011b, Table 2-3), showing the early-, middle-, and late-stage plumes described below in Section 3.3. The transmissive zones of early-stage plumes contain the highest volatile organic compound (VOC) concentrations in their sources, particularly near the DNAPL phase.



Early Stage

Zone	Source		Plume	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	Low	Moderate	Low	Low
DNAPL	Low	High		
Aqueous	Low	Moderate	Moderate	Low
Sorbed	Low	Moderate	Low	Low

Middle Stage

Zone	Source		Plume	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	Moderate	Moderate	Moderate	Moderate
DNAPL	Moderate	Moderate		
Aqueous	Moderate	Moderate	Moderate	Moderate
Sorbed	Moderate	Moderate	Moderate	Moderate

Late Stage

Zone	Source		Plume	
	Lower-K	Transmissive	Transmissive	Lower-K
Vapor	Low	Low	Low	Low
DNAPL	Low	Low		
Aqueous	Moderate	Low	Low	Moderate
Sorbed	Moderate	Low	Low	Moderate

Figure 3-2. Illustration of the progression of a DNAPL-source zone and associated dissolved phase plume through time that results from mass transfers between compartments, using the 14-compartment model. Groundwater flow (advection) carries contaminant from the source zone into the plume zone, and both diffusive and advective mass transfers can eventually distribute contaminants to all compartments. Over extended periods, contaminants can be diluted to lower concentrations, with stored mass in the lower-permeability zones acting as persistent sources of contamination.

Source: ITRC 2011b

Over time, the early-stage DNAPL phase, based on aqueous-phase equivalent concentration, is diminished—by advection, biotic and abiotic degradation, and mass transfer into lower-permeability regions through matrix diffusion and other chemical phases within the source and plume. In the middle stage, the aqueous-phase equivalent concentrations across affected phases and zones are relatively equal. In late-stage plumes, contaminant concentrations have attenuated in the more permeable (transmissive) zones and the larger remaining concentrations reside in the lower-permeability zones within both the source and the plume (Section 3.4) where the mass transfer reverses from the lower-permeability zones into the higher-permeability zones (back-diffusion).

These concepts are a useful part of site-specific CSM development because plume maturity has a major effect on the response to treatment of a source and plume, and therefore on the potential efficacy of possible remediation efforts. Understanding the age of a site and the compartments that require investigation (and to what degree and resolution) is critical in identifying data needs, developing effective data collection objectives, and selecting appropriate site investigation/data management tools. Appendix F presents a screening method for estimating whether a chlorinated solvent release is in its early, middle, or late stage.

3.1 DNAPL Behavior in the Subsurface

DNAPL behavior in the subsurface includes processes related to its transport; interphase chemical mass transfer into aqueous, sorbed, and vapor phases; and degradation reactions. Barring any remedial measures, natural degradation reactions generally occur slowly. Chlorinated solvent, coal tar, and other DNAPL aqueous solubilities are relatively low, and DNAPL mass transfer to the aqueous phase is typically limited by diffusive processes, either at the pore scale or at the scale of stratigraphic (for example, sand and silty sand interbeds) or bedrock (sandstone to siltstone interbeds, layered volcanics, fractured metamorphic rock) heterogeneities. As a result, DNAPLs may persist in the subsurface for long periods (several decades or more), depending on their site-specific solubility, type, mass, and distribution, as well as geologic conditions.

The presence of DNAPL constituents represents a potentially persistent reservoir of contaminant mass that can continue to release dissolved contaminants over long periods; thus, understanding the potential presence and distribution of DNAPL in the subsurface is critical to long-term environmental site management. Characterizing sites contaminated with DNAPLs must take into account the subsurface behaviors of DNAPL and subsequent phases, including the physics of DNAPL migration that control three-dimensional distribution and dissolved-phase contaminants.

With its primary goal of extracting oil (that is, NAPL) from the subsurface, the petroleum industry has conducted exhaustive research on the dynamics of immiscible fluids and the importance of subsurface permeability architecture (stratigraphic or in fractured media). In the 1980s and 1990s, the wealth of understanding originating from the field of petroleum reservoir geology began to be applied to environmental releases of DNAPLs. As it relates to DNAPL transport and behavior in porous media and multiphase flow, this information is summarized below.

DNAPL migration is governed by scientific principles of multiphase flow in porous media. The study of the simultaneous flow of multiple immiscible fluids originated from the fields of soil irrigation science (Richards 1928) and petroleum engineering (Muskat 1937), and there is nearly a century of scientific literature and understanding in this area. The application of multiphase flow concepts to water resources and the DNAPL problem was pioneered by Schwille (1988), and early reviews of the relevant immiscible fluid concepts were provided by Corey (1986), Mercer and Cohen (1990), Cohen and Mercer (1993), and Pankow and Cherry (1996).

Downward migration of DNAPLs is largely driven by gravity (that is, downward density flow); however, if a continuous body of DNAPL develops, pressure head can be transmitted from overlying DNAPL. For nonwetting DNAPLs below the water table, capillary forces within the subsurface media are the primary resisting force to migration. The key capillary properties influencing DNAPL migration are interfacial tension with groundwater, wettability, and P_{ce}.

Capillary entry pressure is the key property governing DNAPL penetration into a given subsurface media. It is significantly influenced by the subsurface matrix (including pore throat size and heterogeneity) and the interfacial tension between the groundwater and the specific DNAPL constituents. Because DNAPLs are generally nonwetting and hydrophobic, greater pressures are required to displace groundwater and enter lower-permeability (smaller-pore-sized) media. Therefore, DNAPLs migrate generally downward until they encounter materials with pore sizes too small to penetrate, at which point they spread laterally and potentially accumulate until enough pressure is created to allow the DNAPLs to displace the groundwater and penetrate the pore throat. Cohen and Mercer (1993), Pankow and Cherry (1996), and Payne et al. (2008) provide more discussion on DNAPL migration into or through low-permeability layers.

Subsurface lithologic heterogeneity leads to differences in subsurface pore structure and capillary properties. As a result, downward migration of DNAPL results in flow instability where isolated fingers of preferential DNAPL migrating along preferred pathways develop, leaving a highly variable distribution. These variations are commonly present in the subsurface matrix, even in formations that initially appear to be homogeneous. The existence of highly variable fingers of DNAPL in the subsurface is a key factor, making detection of DNAPL challenging, and leading to the need for improved site characterization methods.

After cessation of the release, as a DNAPL migrates through the subsurface, it leaves a residual *trail*, which is essentially immobile unless subsurface pore pressures change due to disturbance of the matrix or other activities. There may also be higher-than-residual-saturation zones of DNAPL that are not actively migrating—for example, where thin lenses of DNAPL are perched above low-permeability zones. While these zones are potentially mobile if disturbed, they are isolated; they do not have the ability to enter the smaller pore spaces as separate phase liquids and will remain in place unless subsurface conditions change. Although residual DNAPL is considered immobile under normal subsurface conditions, it can act as a long-term source of dissolved-phase groundwater contamination. As groundwater moves through the subsurface and contacts isolated DNAPL ganglia and pools, the DNAPL slowly dissolves into the groundwater based on its effective solubility. Residual DNAPL in the vadose zone also acts as an ongoing source for soil gas contamination, vapor migration, and potential vapor intrusion.

3.2 Changing Concept of a DNAPL Source Zone

The perspective of what represents a source zone at a DNAPL site has evolved in recent years. In the 1990s and early 2000s, source zones were considered to be the areas affected by DNAPL phase contamination; however, the current recognition that contaminant mass (sorbed or dissolved phase) can be stored in lower-permeability zones within the plume body has broadened that definition.

This evolution in understanding the extent of source material reflects the increasing recognition that, at many sites, DNAPL is not the primary factor in contaminant mass that sustains a plume over time. Especially at late-stage sites, the contaminant mass stored in low-permeability zones within the plume body acts as a primary source to help sustain the dissolved plume through back-diffusion processes. Thus, many of the improved characterization methods described in this document focus on delineating the geologic heterogeneity and contaminant mass distribution across different geologic units and across different contaminant chemical phases.

3.3 DNAPL Life Cycle Conceptual Model

As discussed in Section 2.2 and Section 2.3, some DNAPLs such as chlorinated solvents have relatively higher solubilities than others such as coal tar and creosote. This section briefly discusses how the differences in solubility significantly affect the life cycles of DNAPLs in the subsurface, including the persistence of DNAPLs and their ability to create dissolved-phase contaminant plumes in groundwater.

3.3.1 Chlorinated Solvent and other High-Solubility DNAPL Sites

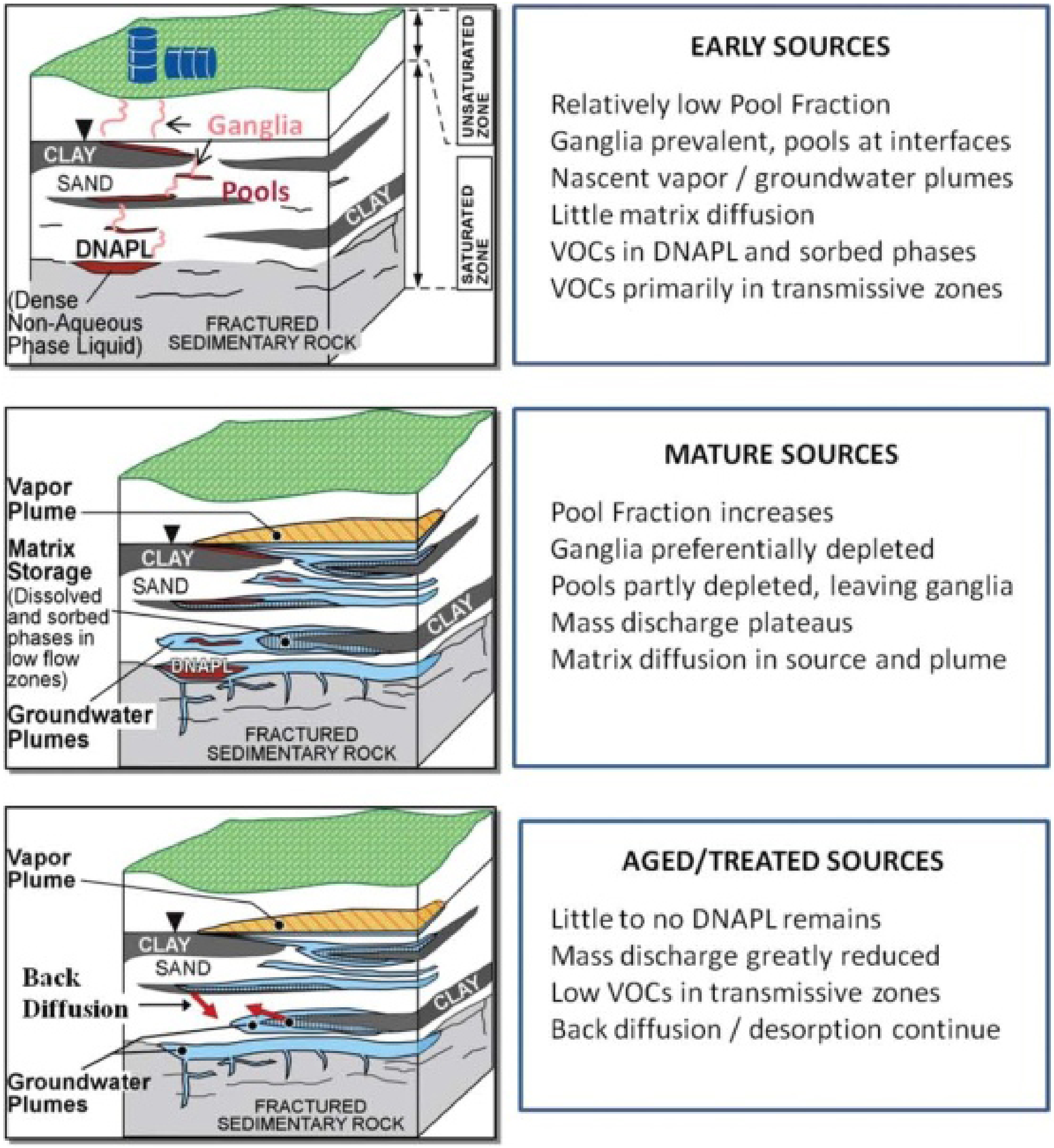
Most chlorinated solvent DNAPL sites can be described in terms of three stages of development (Sale et al. 2008; Sale and Newell 2010; Stroo et al. 2012, ITRC 2011b), as discussed below.

In the initial (early) stage, DNAPL predominates and contaminants migrate downward through pore spaces of more transmissive zones of the geologic formation, leaving ganglia of residual (immobile) DNAPL held within the pores by capillary forces. If an initial release is large enough, DNAPL may pool on top of low-permeability zones. Contaminants also begin to partition into soil gas and groundwater, forming dissolved-phase and potentially vapor plumes. Contaminants also sorb to soil and sediment surfaces. This process occurs more readily in the more transmissive zones of a formation, but mass also begins to transfer to less permeable zones.

In the middle (mature source) stage of the source zone DNAPL life cycle, a significant portion of the contaminant mass has migrated into vapor, aqueous, and sorbed phases in both transmissive and lowest permeability zones of the formation. The DNAPL phase may not enter the lowest permeability zones of the formation; instead, dissolved-phase contaminant molecules diffuse into the groundwater in the lower permeability matrix (Chapman and Parker 2005; Parker, Chapman, and Guilbeault 2008).

In the late (weathered, aged/treated sources) stage of chlorinated solvent sites, DNAPL is often no longer detected and chlorinated solvent concentrations may persist in the aqueous phase of the transmissive zone due to desorption and back-diffusion from the contaminant mass in the low-permeability matrix into the higher-permeability matrix. The maturation process is influenced by a number of factors, including the amount of initial release, solubility of the contaminant in water, groundwater flow velocity, and architecture of the transmissive and low-permeability zones of the formation (Sale et al. 2008).

These three stages are illustrated in Figure 3-3. Appendix F presents a newly developed screening method for estimating whether a chlorinated solvent site is in its early, middle, or late stage.



EARLY SOURCES

Relatively low Pool Fraction
Ganglia prevalent, pools at interfaces
Nascent vapor / groundwater plumes
Little matrix diffusion
VOCs in DNAPL and sorbed phases
VOCs primarily in transmissive zones

MATURE SOURCES

Pool Fraction increases
Ganglia preferentially depleted
Pools partly depleted, leaving ganglia
Mass discharge plateaus
Matrix diffusion in source and plume

AGED/TREATED SOURCES

Little to no DNAPL remains
Mass discharge greatly reduced
Low VOCs in transmissive zones
Back diffusion / desorption continue

Figure 3-3. Evolution of a DNAPL source/plume (Stroo et al. 2012).

Figures 11 and 12 in Sale and Newel's work (2011, pp 28-29) illustrate the evolution of chlorinated solvent plumes using the 14-compartment model.

3.3.2 Coal Tar, Creosote, and Other Low-Solubility DNAPL Sites

DNAPL life cycles at coal tar and creosote vs. chlorinated solvent sites can be similar, but can also be significantly different due to varying chemical and physical properties. Because coal tar and creosote DNAPLs may have significantly lower solubility and higher viscosities than chlorinated solvents, the early phase of the DNAPL life cycle often dominates at coal tar and creosote sites.

Historically, it was common for very large amounts of coal tar and creosote DNAPLs to be disposed of or released over time in industrial areas. These contaminants often saturated the subsurface and either fully or partially displaced groundwater; thus, it is not uncommon to find several feet of coal tar or creosote DNAPL in monitoring wells and DNAPL-saturated portions of the subsurface. Depending on the NAPL saturation, these DNAPLs may be mobile or immobile. At sites where the release is old and no longer occurring, although DNAPL saturations may be high enough to be mobile, the gradients no longer exist that could drive migration unless site conditions are disturbed. The DNAPL-saturated portions of the subsurface also prevent or significantly limit groundwater flow through a site because of decreases in relative permeability due to the presence of dissimilar fluids. The limited groundwater flow and low solubility of these fluids may limit the amount of dissolved-phase contamination and lengthen the occurrence of DNAPL.

Coal tar DNAPL released at any site can also have significant physical and chemical differences over time. MGPs originally used coal to manufacture gas for distribution. Later, many MGPs switched to fuel oil for this purpose. The resulting *coal tar* wastes may have different characteristics, complicating an assessment of a DNAPL site. (The chemical and physical properties of the oil- or grease-saturated DNAPL released at many chlorinated sites can also be significantly different from pure, unused product). Coal tar LNAPLs and neutrally buoyant NAPL emulsions may also be present at some of these sites.

3.4 Implications of DNAPL plus Matrix Diffusion Source Model

Including the DNAPL life cycle and matrix diffusion in a CSM has several important implications for initial site characterization and remediation-based characterization activities. Several key differences between a DNAPL-centric and DNAPL-plus-matrix-diffusion site characterization programs are discussed in following sections.

3.4.1 High-Solubility DNAPL Sites

While low-solubility DNAPLs such as coal tar and creosote may remain as separate phase compounds in the subsurface for decades, dissolution may largely remove the separate phase compounds of chlorinated solvent DNAPLs from the subsurface; however, when matrix diffusion is considered, indirect measurements of DNAPL may actually be *false positives*. In such cases, DNAPL may no longer be a key part of the CSM, and continued attempts to locate DNAPL by indirect measurements may be addressing the wrong source material (Parker, Gillham, and Cherry 1994; Parker, Chapman, and Guilbeault 2008).

A modeling study (Seyedabbasi et al. 2012) showed site characterization results (50-year-old, 675-kilogram release of TCE) consistent with late-stage sources. In late-stage sites, the contaminant mass in low-permeability matrices serves as the primary source material, resulting in elevated dissolved-phase concentrations for a longer period than the DNAPL itself. The simulated TCE source in the model, DNAPL ganglia in a series of small pools, persisted for about 40 years, whereas back-diffusion from low-permeability zones maintained the average plume concentration above drinking water standards for at least an additional 83 years.

This modeling effort supports the DNAPL source zone life cycle model, illustrating a hypothetical site at which actual DNAPL persisted for only a few decades before being dissolved away. Dissolved-phase mass stored in lower-permeability zones supplanted DNAPL as the source through the action of matrix diffusion, and was able to maintain a dissolved contaminant plume above drinking water standards for an even longer period after all DNAPL was removed from the system.

A modified form of Fick's Law is typically used to describe diffusion in unconsolidated deposits and porous bedrock (Parker et al. 2003).

$$J_D = -\eta D^* \frac{dC}{dx}$$

Where J_D is the diffusive flux (grams/[cm^2-sec]), η is the porosity (dimensionless), D* is the effective diffusion coefficient (in centimeters per second [cm/s]) and dC/dx is the concentration gradient (in g/cc). D* is usually less than the free solution diffusion coefficient (D_o), which ranges from 10^{-5} to 10^{-6} cm/s for most chemicals, because of the tortuosity of the porous media. This modified form of Fick's Law indicates that the porosity of the low-permeable media is an important factor in evaluating diffusive flux. The concentration gradient, the driving force for diffusion can vary by orders of magnitude; however, the surface area over which the diffusive flux occurs can be an even more important factor in contaminant mass transfer and plume behavior. For example, in fractured porous media such as fractured sedimentary rock and fractured clayey deposits, the contaminant mass in fractures is exposed to a large surface area of rock such that diffusion-driven mass transfer of the contaminant mass into the matrix may be large.

At sites where high-solubility DNAPLs have been released, the contaminant mass may have been transferred to lower-permeability media, which is now generating a dissolved-phase contaminant plume without actual DNAPL remaining in the source zone. For such sites, determining the contaminant distribution, identifying the geologic media with the greatest contaminant mass, and measuring the physical properties of this media (contaminant concentration, media porosity, and permeability) can be more useful than trying to confirm or refute the presence or absence of DNAPL in the subsurface; however, DNAPL that remains at many sites across North America is a continuing source of contamination, creating and sustaining dissolved plumes and vapor plumes. In summary, if DNAPL has not been identified at a site, it may not exist; however, when it is found at a site, it must be included in the CSM.

3.4.2 Determining Matrix Diffusion Sources

While it may be difficult to prove that DNAPL is present, there are proven techniques for evaluating the presence of matrix diffusion sources. A scoping approach and a detailed site characterization approach are described below.

A *scoping approach* relies on source history, hydrogeology, and contaminant type to indicate if significant matrix diffusion sources could be present. Sale et al. (2008) identify the following general conditions driving matrix storage effects:

- geologic settings that are heterogeneous and clay rich with transmissive zones that are a small fraction of the aquifer's total volume
- contaminants that are present at high concentrations
- contaminants that are stable in their physical setting (for example, TCE in an aerobic aquifer)
- systems with relatively slow groundwater flow rates
- sediments with high fractions of organic carbon
- sites where large amounts of contaminant were released
- older sites where there has been a sufficient amount of time for contaminants to move into low-permeability zones

While these factors can be used in a qualitative sense, other tools can be used to determine semi-quantitative effects of matrix diffusion. For example, the Matrix Diffusion Toolkit is a public domain software tool that can help site personnel estimate what effects matrix diffusion will have at their site. The software contains two different matrix diffusion models, both relying on a simple two-layer conceptualization (a low-permeability layer and a transmissive layer), and a two-phase timing structure: (1) a loading period (when contaminants diffuse from the transmissive zone into the low-permeability zones); and (2) a back-diffusion period (when the low-permeability zone acts as a source to the transmissive zone). The software was developed to assist site personnel in updating or creating a more accurate CSM, which will enable them to determine whether matrix diffusion processes are significant enough to cause *rebounding* groundwater concentrations in a downgradient plume at concentrations above remediation goals after plume remediation or isolation is complete.

A field-oriented approach, on the other hand, relies on detailed site characterization techniques such as those described by Chapman and Parker (2005). These techniques have the following key elements:

- detailed hydrostratigraphic analysis to determine the presence of transmissive, low-permeability interfaces in the subsurface, using tools such as the cone penetrometer, hydraulic profiling tools, or the Waterloo Profiler®
- continuous coring (for example, at intervals of a few centimeters) the low-permeability zones to determine the permeability architecture (for example, bedding thickness and sediment composition), and the presence and vertical distribution of contaminants that have diffused into

low-permeability zones

- membrane interface probe (MIP) or membrane interface probe-hydraulic profiling tool (MiHpt) logging of unconsolidated formations to observe the distribution of low-permeability layers within transmissive zones, and also the contaminant distribution within and across these materials (Case Study 1, Appendix G)

The field-oriented approach can provide strong evidence of the mass of contaminants in low-permeability zones, and more importantly can link the location of the contaminant plume to diffusion from the low-permeability zones. For example, matrix diffusion sources are indicated if the low-permeability zone has a *shark-fin* type vertical contaminant distribution. Present-day *soil concentration vs. penetration depth* profiles can provide insight into expected diffusion patterns as well as the style of the past concentration history. For example, a shark-fin pattern indicates diffusion gradients from the interior of low-permeability zone to the interface (see Location B in Figure 3-4).

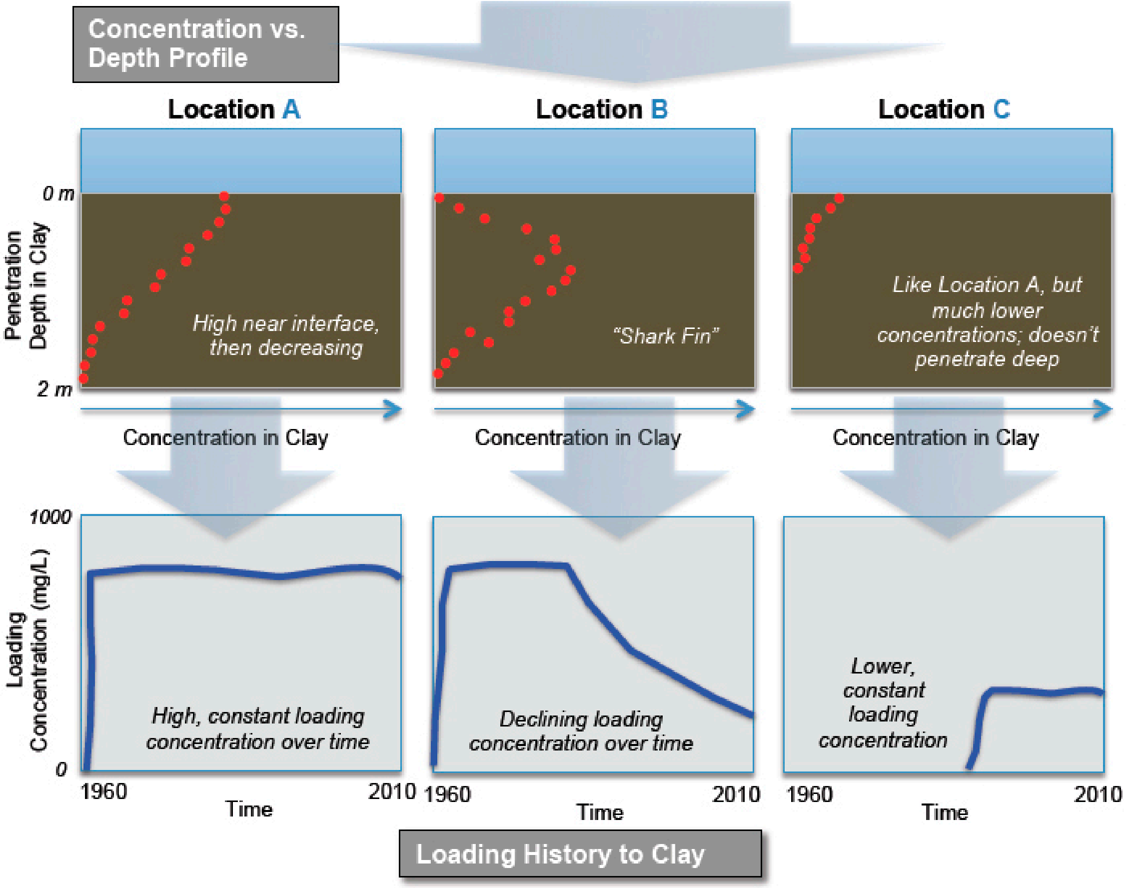


Figure 3-4. Examples of Contaminant Concentration Profiles in Soil Cores that indicate matrix diffusion is occurring (Newell et al. 2013). At Location A, the contaminant concentration decreases uniformly with depth into the low-permeability zone, indicating constant concentrations in the transmissive zone and no back-diffusion (no matrix diffusion source);

however, at Location B, the *Shark Fin* pattern shows that contaminant diffusion gradient is from the interior of the low-permeability zone to the transmissive zone, indicating that the low-permeability zone at Location B is serving as a matrix diffusion source (diffusion is also driving contaminants deeper in the low-permeability zone). Location C is similar to Location A, but with a weaker and more recent loading from the transmissive zone to the low-permeability zone. Appendix H discusses using the concentration gradients in low-permeability sediments that are the result of matrix diffusion to help reconstruct contaminant source loading history.

3.4.3 Low-Solubility DNAPLs

As described in Section 3.2, DNAPLs at coal tar and other sites may be readily identifiable and present in large amounts. Characterization at these sites must include an assessment of the distribution of immobile, potentially mobile, low-saturation DNAPLs, as well as the transmissivity of the geologic matrix to NAPL migration. New tools and methods are available that can identify residual phase and thin lenses of DNAPL at relatively low cost.

3.5 Considerations in Fractured Bedrock

Initially, DNAPL penetrates into bedrock and migrates generally downward through fracture networks (Figure 3-5). The DNAPL continues to migrate until the driving head in the DNAPL has been dissipated and it essentially becomes immobile. The DNAPL gradually dissolves into the groundwater within fractures as well as within the rock matrix porosity in contact with the DNAPL. The dissolved-phase constituents in the groundwater diffuse into the rock matrix porosity. The relative permeability within fractures increases as DNAPL saturation decreases, and water saturation increases as more and more of the DNAPL is dissolved. The dissolved-phase material migrates with the water flowing through the fractures, forming a plume downgradient of the release area. As this plume migrates, molecular diffusion occurs from the plume within the fractures to the matrix porosity.

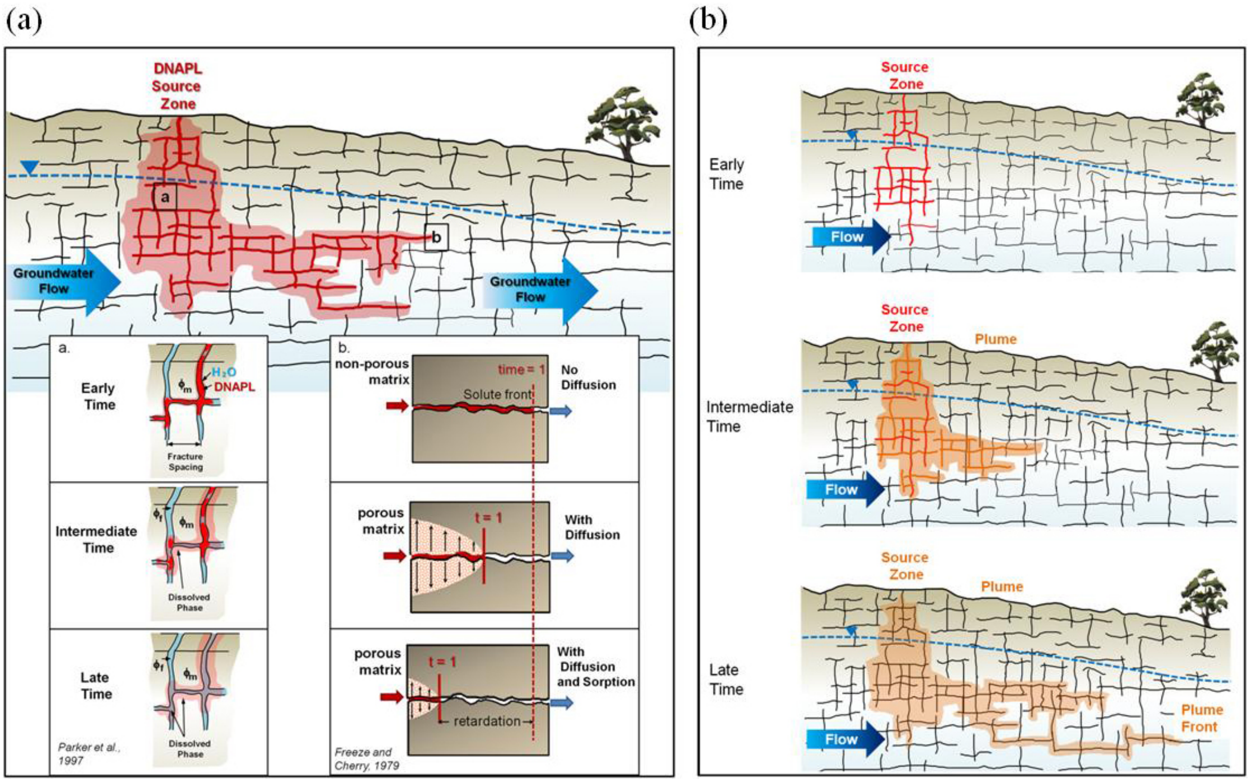


Figure 3-5. Illustration of fate and transport of DNAPL in a fractured rock environment through time showing distinctly different types of contaminant transport, including DNAPL movement and dissolution, dissolved-phase advection through fractures, and diffusion into the rock matrix. (a) Initially, DNAPL migrates vertically through the fracture network until the initial driving head is dissipated and the DNAPL becomes immobile. The DNAPL begins to dissolve into the water in the fractures and diffuse into the rock matrix, and over time migrate with water flowing through the fractures. These processes together with sorption will retard contaminant migration. (b) This is a conceptualization of the effect of these processes on source zone and plume evolution.

Source: Parker et al. 2012.

If significant matrix porosity is present within the bedrock, DNAPL dissolution is relatively enhanced and, in later stage releases, the DNAPL may dissipate near the release area such that there is no distinction between the dissolved-phase plume areas and the former release area. The dissolved-phase contaminants that have diffused into the matrix porosity may then back-diffuse from the rock matrix porosity into groundwater within the fractures. This may sustain elevated concentrations in the zone formerly containing DNAPL as well as the dissolved-phase plume within the fractures where dissolved contaminants have diffused into the matrix.

Sedimentary rock typically has significantly larger primary porosity than igneous or metamorphic rock, with a notable exception of a variety of volcanic rock. Therefore, DNAPL usually dissipates sooner in sedimentary rock because of its larger matrix storage capacity. The matrix storage capacity can be enhanced significantly due to contaminant sorption, particularly in higher fraction of organic carbon (f_{oc}) rock types (mainly siltstones and shales, but all sedimentary rocks can have high f_{oc}).

Figure 3-6 illustrates characteristic fracturing for sedimentary and igneous rock types. In sedimentary rock, the fractures are predominantly horizontal along bedding planes, which typically occur at a larger frequency than vertical fractures that intersect at generally right angles. Igneous rock fractures tend to be more chaotic in orientation because of the lack of bedding planes. Igneous rock typically has lower rock matrix porosity than sedimentary rock.

The fracturing and porosity characteristics of crystalline rock present a lower potential for matrix diffusion; however, fault zones or shear zones within igneous or metamorphic rocks can provide laterally extensive two-dimensional features of high permeability and porosity that can behave as rapid migration pathways.

As stated above, Figure 3-5 illustrates the fate and transport of DNAPL over time in sedimentary bedrock. DNAPL initially observed in fractures may dissipate through the combined mechanisms of matrix diffusion and dissolution into groundwater within fractures. In the resulting later stage, the source area may then exhibit back-diffusion from the rock matrix porosity into groundwater within the fractures, but DNAPL would not be observed. In contrast with sedimentary bedrock, DNAPL that migrates into fractures of igneous rock with its characteristic chaotic fracturing and limited rock matrix porosity is more likely to be present as actual DNAPL at older sites (Parker, Gillham, and Cherry 1994).

Due to the nature of consolidated media environments (for example, bedrock), drilling of individual borings may require higher-capacity equipment and thus involve higher cost; however, characterization is still practical. Additionally, in contrast to the approach applied to unconsolidated media, fewer core holes may be drilled in consolidated media, with greater reliance on higher-resolution borehole tools to characterize the geology, hydrogeology, and contaminant distribution within and between holes. Given the complexities associated with tool selection, Chapter 4 is dedicated to this topic and discusses tools applicable to both unconsolidated and consolidated media.

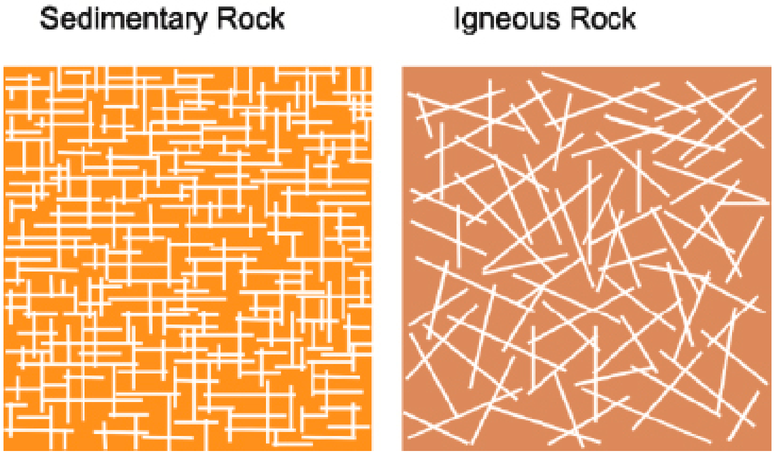


Figure 3-6. Schematic of fracture orientation in sedimentary and igneous rock

Source: Figure courtesy of Patryk Quinn.

It is necessary to define the types, size, orientation, frequency, and distribution of fractures when characterizing contaminant distribution and flow in fractured bedrock, as they create the primary contaminant advective flow paths. A variety of tools are available to help characterize bedrock fractures. Not all fractures are hydraulically connected; during characterization, it is therefore important to evaluate fracture connectivity using tools that allow methods such as cross-hole testing to gain an understanding of the potential flow paths for groundwater movement and to obtain information for gradient calculations. If a fracture or set of fractures are not directly connected to the contaminant transporting fractures, these fractures are less significant from a contaminant migration perspective.

Some fractures that may connect to contaminant-bearing fractures may dead end and not contribute significantly to the advective transport of the dissolved-phase contamination. Such *dead end* fractures can, however, provide significant surface area and be important sinks for matrix diffusion.

The primary challenge when characterizing fracture networks is determining their role in contaminant transport (that is, advection or diffusion). For this evaluation, it may be useful to test discrete portions of a borehole or single fracture opening, and to monitor in depth-discrete portions of nearby holes and within other portions of the hole being tested. Information gained by connectivity tests on entire boreholes may not provide the discrete fracture transport pathway information required to adequately characterize the contaminant plume. Multiple tests and development of a collaborative data set will also be required to provide the data necessary to understand contaminant flow and distribution. Fracture transmissivity, orientation, and hydraulic interconnectivity data are critical for developing rigorous CSMs in fractured rock environments.

Naturally occurring organic carbon (measured as f_{oc}) may be found lining fractures (secondary porosity) or may occur within the rock matrix itself (that is, within the matrix or primary porosity). The occurrence of organic carbon within the fractures, or matrix of a particular fractured bedrock, can play a significant role with regard to fate and transport and ultimately the remediation of DNAPL, for the following reasons:

- Residual and pooled DNAPL diffuses into the matrix of the rock (matrix diffusion). The occurrence of organic carbon increases DNAPL sorption in the rock matrix. The occurrence of organic carbon in the rock matrix and lining the fractures is a significant factor in this matrix diffusion/retardation.
- The rate of dissolved-phase contaminant migration is significantly less than the groundwater velocity.
- Over time, the mass of contaminant in the rock matrix can be greater than that found in open fractures. The occurrence of organic carbon in the rock matrix can augment this effect.
- The time required to attain functional and absolute remediation objective(s) may be governed by back desorption from organic carbon and back-diffusion of the dissolved-phase con-

> taminant that originally diffused from DNAPL into the rock matrix. Higher f_{oc} in the rock matrix prolongs the time frame for achieving these objectives.

Consistent with site characterization objectives, f_{oc} should be analyzed for fractured bedrock, although not all fractured bedrock is equally likely to exhibit organic carbon. The occurrence of organic carbon is possible at sites underlain by sedimentary, igneous, or metamorphic rock; however, it is more likely to occur in sedimentary rock, which is more likely to exhibit matrix porosity. Where the site characterization objectives include gaining an understanding of the fate and transport and providing a basis for ultimately remediating the site, and where DNAPL and dissolved contamination occurs within fractured sedimentary rock, analysis of f_{oc} should always be performed. Similarly, analysis of f_{oc} should be performed for sites where DNAPL or dissolved contamination occurs within fractured igneous or metamorphic rock that additionally exhibits primary porosity due either to the rock type (for example, slate, phyllite, schist, and gneiss, for which foliation is common) or the use of other site characterization tools that indicate the occurrence of primary porosity. For metamorphic rock in particular, foliation, microfractures, and the degree of crystallization can result in primary porosity, and such rocks should be evaluated for f_{oc}.

3.6 DNAPL Considerations for Clay

As discussed in this document, it is clear that low-permeability materials in the subsurface, such as fine silts and clays, may impede vertical DNAPL migration. In some cases, however, the presence of a clay layer may not fully protect groundwater below. Many clay deposits in the subsurface are not pure clay and do not resemble fully plastic modeling clay. Variations in grain size and composition and depositional environments create the same heterogeneities that affect DNAPL migration and groundwater flow in coarser materials.

There may also be significant secondary porosity. Clays are commonly fractured, especially in the unsaturated zone. Fractures in the clay create preferential pathways for advection of DNAPL and dissolved-phase contamination, and create new surfaces for matrix diffusion to occur. Plants may create significant preferential pathways as they grow and their roots advance through the subsurface. Depending on the depositional history, a clay deposit may be small with minimal lateral extension. Past erosional events may have also removed portions of the clay, creating direct pathways through it. The act of investigating a site may also create pathways through clays when boreholes are not fully sealed or when sealed with a material that is incompatible with the site-specific DNAPL (McCaulou and Huling 1999).

When DNAPL and bentonite or other material are used to grout a borehole, some DNAPLs such as TCE or creosote can desiccate bentonite clay, facilitating the creation of cracks that significantly increase hydraulic conductivity (McCaulou and Huling 1999). If this occurs where DNAPL is resting on a low-conductivity clay layer, any cracks that form due to desiccation of the clay by the DNAPL may act as preferential pathways for DNAPL migration through the clay.

Additionally, according to the SERDP-ESTCP ER-1737 Fact Sheet (Abdul et al. 1990):

> Low permeability zones in the subsurface contain clay and previous research with landfill liners suggests that contact between nonchlorinated organic liquids can cause the clay structure to compress, creating macropores in the clay and resulting in an increase in hydraulic conductivity of up to five orders of magnitude. If such a process occurs with chlorinated DNAPLs in the subsurface, then diffusion into the low-permeability regions may be enhanced, and advection, which is usually considered negligible, may also be important. Furthermore, waste DNAPLs contain surfactants. If these surfactants diffuse into the low-permeability materials and sorb to the mineral surfaces, the materials may become organic-wet, resulting in active imbibition of the DNAPL.

Considering clay intervals as impermeable to DNAPL and associated aqueous compounds can often result in erroneous predictions and underestimation of fate and transport. Careful characterization of the clay content and mineralogy of these lower fine-grained layers helps to account for physical disturbance and chemical reactions that may provide avenues for DNAPL transport.

4.0 INTEGRATED DNAPL SITE CHARACTERIZATION

Integrated site characterization is a process for improving the efficiency and effectiveness of characterization efforts at DNAPL sites. It encourages characterization at a *sufficient resolution* to capture the effects of the heterogeneities that direct contaminant distribution, fate, and transport, and remediation effectiveness, so that an integrated three-dimensional CSM can be developed and refined. The CSM should distinguish among transport and storage zones and identify relevant mass.

The goal of DNAPL ISC is iterative development of a CSM with sufficient depth and clarity to evaluate risks and develop appropriate remediation strategies.

DNAPL sites have too often been characterized at a resolution insufficient for this understanding, and it is therefore reasonable to equate ISC with high(er) resolution site characterization; however, ISC should focus on whatever resolution is needed to adequately determine contaminant distribution, fate, and transport, and thereby define and effectively remediate (if necessary) any site risk.

ISC supports *iterative refinement of the CSM* over the *project life cycle* with information obtained during site investigation, remedy design, and remedy optimization. Similar to the USEPA's data quality objectives (DQOs), it relies on a systematic *objectives-based site characterization* process that includes defining the uncertainties and CSM deficiencies; determining the data needs and resolution appropriate for site conditions; establishing clear, effective data collection objectives; and designing a data collection and analysis plan (Figure 4.1 and Section 4.1). Through ISC, the most appropriate and up-to-date site characterization tools are selected to effectively characterize site stratigraphy, permeability, and contaminant distribution. Once the data are collected, the process includes evaluating and interpreting the data and updating the CSM.

New Concepts for the Evaluation of Fate and Transport

- *Heterogeneity replaces homogeneity.*
- *Anisotropy replaces isotropy.*
- *Diffusion replaces dispersion.*
- *Back-diffusion is a significant source of contamination and plume growth.*
- *Non-Gaussian distribution replaces Gaussian.*
- *Transient replaces steady-state conditions.*
- *Nonlinear replaces linear sorption.*
- *Nonideal replaces ideal sorption.*

ISC is the most effective way to develop CSMs that address groundwater contamination in general and DNAPL in particular. ISC involves eight new concepts based on the current understanding of DNAPL and aqueous-phase plume behavior and the controlling effects of hydrogeologic heterogeneities and matrix diffusion. These new concepts—which represent a substantial reconsideration of the data necessary to develop effective CSMs for DNAPL sites in both unconsolidated and consolidated hydrogeologic settings—are discussed below.

1. **Heterogeneity replaces homogeneity.** The assumption of subsurface homogeneity has led to successful modeling and problem solving in the water supply field. In many cases, however, this assumption does not promote an understanding of groundwater contaminant fate and transport. Furthermore, understanding the scale of the controlling heterogeneities is crucial, as both micro- and macro-scale geologic heterogeneities play a controlling role in the fate and transport of both DNAPL and dissolved-phase contamination.
2. **Anisotropy replaces isotropy.** In many cases, the assumption of an isotropic (uniform in all directions) subsurface has not provided an adequate understanding of groundwater contaminant fate and transport. As with heterogeneity, geologic anisotropy (directional dependence) plays a controlling role in the fate and transport of both DNAPL and dissolved-phase contamination.
3. **Diffusion replaces dispersion.** Based on the above two concepts, it is now known that matrix diffusion largely controls lateral (y-dimension) and vertical (z-dimension) contaminant distribution in many subsurface systems (Hadley and Newell 2013).
4. **Back-diffusion is a significant source.** When contaminant concentrations are greater in higher-permeability media, they diffuse into lower-permeability media. Once this matrix diffusion has occurred and contaminant concentrations have decreased in the higher-permeability media (due to remediation or natural attenuation), contaminants then back-diffuse into the higher-permeability zones. Back-diffusion is based on this reversed concentration gradient and can act as a long-term source of dissolved-phase contamination to higher-permeability unit(s). At late-stage sites, plumes are sustained primarily by back-diffusion rather than by DNAPL dissolution.
5. **Non-Gaussian distribution replaces Gaussian.** Geologic deposits are not typically distributed in a Gaussian (normal) fashion. Therefore, statistical methods that assume a normal distribution are often ineffective for understanding, characterizing, and predicting contaminant fate and transport. The actual distribution of permeability within geologic deposits can often be represented by a lognormal distribution rather than a Gaussian distribution or, less commonly, a nonparametric distribution where the cumulative distribution function is estimated from observed data.
6. **Transient-state replaces steady-state.** While conditions at a site may appear to be in a steady state over portions of its life cycle, equilibrium is dynamic. It changes as the plume migrates, ages, and degrades; as source materials are depleted or migrate; and as new geologic features are encountered by migrating contamination.
7. **Nonlinear sorption replaces linear sorption.** Many mathematical models (for example, BIOSCREEN) used for predicting DNAPL contaminant fate and transport in subsurface systems assume linear sorption of reactive solutes. Nonlinear sorption processes can dramatically alter contaminant transport, delaying the appearance and sharpening the plume front, and result in prolonged plume tailing. The latter effect can be confused with or misinterpreted as either rate-limited mass transfer between mobile-immobile water (physical non-equilibrium) or rate-limited sorption-desorption (chemical non-equilibrium).

8. **Nonideal sorption replaces ideal sorption.** Nearly all groundwater transport models assume that dissolved solutes exhibit ideal sorption behavior in equilibrium. Ideal sorption behavior indicates that the adsorption (forward reaction) and desorption (reverse reaction) processes are reversible, yielding identical isotherms at equilibrium; however, aging or prolonged soil-contaminant exposures may result in nonideal behavior, where it is difficult to remove the contaminant from the solid phase, even with aggressive extraction procedures. This can result in persistent release of the contaminant from impacted aquifer solids and, as above, can be confused with either nonlinear desorption or rate-limited mass transfer.

4.1 Objectives-Based Data Collection

ISC relies on objectives-based data collection, which provides a scientifically defensible foundation for characterization activities and helps define data needs and manage project uncertainty. ISC is a systematic, stepwise process similar to the USEPA's DQOs, which employ the Triad approach: (1) systematic project planning; (2) dynamic work strategies; and (3) real-time measurement technologies.

ISC can be applied at any stage—development of the preliminary CSM, baseline characterization, CSM characterization, CSM design, CSM remediation/mitigation, or post-remedy (USEPA 2011a) —or when troubleshooting a nonperforming remedy.

Although not intended as a rigid sequence, Figure 4-1 illustrates the main elements of ISC. Appendix A provides case examples that illustrate the first five steps of ISC. Particular attention is focused on how data collection objectives were established for specific reasons, and in some cases modified, as the CSM was refined with additional data.

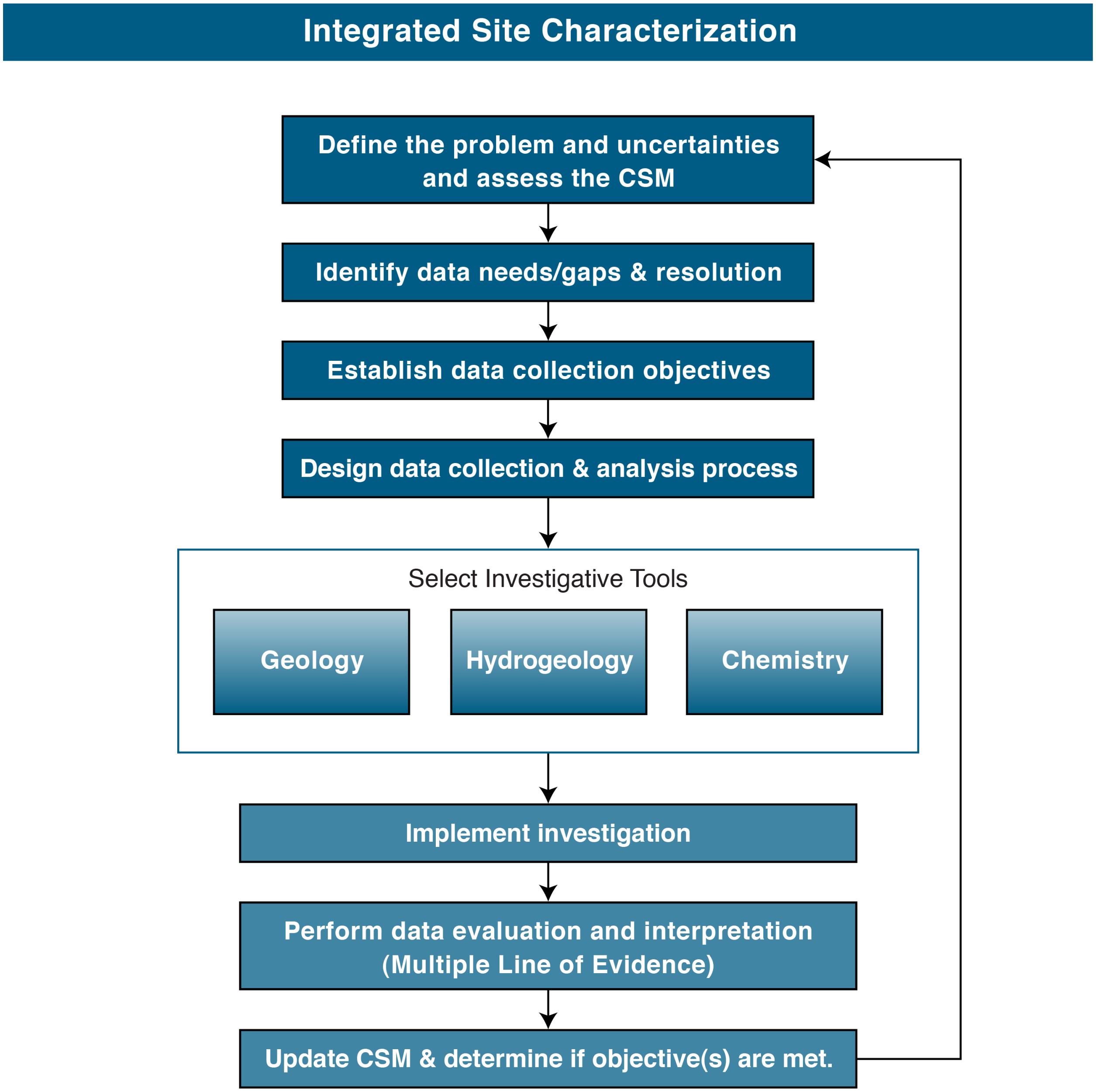


Figure 4-1. Integrated site characterization.

The following reference materials provide additional information about systematic project planning and the USEPA's Triad approach:

- *Technical and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management* (ITRC 2003)
- *Best Management Practices: Use of Systematic Project Planning Under a Triad Approach for Site Assessment* (USEPA 2010)
- *Improving Decision Quality: Making the Case for Adopting Next Generation Site Characterization Practices* (Crumbling, D. M., J. Griffith, and D. M. Powell 2003)

4.2 Define the Problem and Assess the CSM

The goal of DNAPL ISC is to develop a CSM with sufficient depth and clarity to accurately assess risks and develop appropriate remediation strategies. The first step of the ISC approach is to review the current CSM and determine its adequacy against that goal. If a problem becomes apparent, it should be defined in terms of uncertainties/deficiencies with the CSM so that data needs/gaps and resolution can be identified and characterization objective(s) established. An advantage of defining the problem in terms of uncertainties is that it can help determine the cost benefit, or sustainable ROI, of collecting additional data.

The baseline for ISC is any existing site information that helps develop an accurate, representative CSM. Existing data generated using traditional investigation approaches are valuable in formulating a CSM from which to identify initial data needs and gaps; however, the quality of that existing data and the sophistication of that CSM may be less than optimal. Conventional soil and groundwater characterization involved the use of soil borings and monitoring wells to collect relatively coarse subsurface interval sampling (for example, soil samples every 5 feet and groundwater samples from 10 ft screened monitoring wells). At some sites, soil samples were only collected from the unsaturated zone because it was assumed that anything below the groundwater table was best characterized by groundwater samples from monitoring wells. As a result, conventional CSMs were often founded in precise data, yet provided an inaccurate representation of contaminant distribution.

Following are some important considerations when reviewing existing site information and evaluating its usefulness:

4.2.1 Understand the Available Data and Implications for Lithologic or Structural Heterogeneity

This initial review phase should focus on determining what is known about DNAPL use and releases at a site; depending on the available surface and subsurface data, it should describe the heterogeneity due to lateral and vertical lithologic changes, depict the hydrostratigraphic framework from the paleoenvironmental characteristics or the structural features controlling flow, and explain how resolution of existing data affects the reliability and usability of any existing CSM. An initial draft CSM should be created if none exists.

The case study (Appendix B.3) describing Reese Air Force Base in Lubbock, Texas, illustrates a complex pattern of mass flux laterally and vertically downgradient from the source. The aquifer is composed of a very heterogeneous system of interbedded sediments varying from gravels to clays, deposited by alluvial fans and braided streams. The existing monitoring well network was effective at quantifying groundwater concentrations and identifying potential risks, but the long well screens provided limited information on detailed plume structure. The initial phase of the project required reassessment of groundwater concentrations using all available data. This included a sitewide synoptic data set collected using all of the investigation wells (>500 wells) and remediation wells

(~50), as well as grab samples from over 100 private irrigation and supply wells within and adjacent to the plume. The revised plume map revealed two significant findings:

1. The contaminant distribution and its movement are highly structured.
2. A significant volume of the aquifer previously identified as contaminated was clean.

4.2.2 Recognize Limitations of Historical Data

Historically, data sets often were smaller and of lower-resolution spatially than those more commonly collected within the past decade. In addition, historical data sets were often limited by higher detection limits than are available today or did not acknowledge the potential for temporal variation in contaminant concentrations. For example, many large sites are monitored on a continuous, rolling basis over periods of months to years, yet interpretations are made from data sets spanning months to years. Further, hydraulic data sets may be based on slug tests that interrogated a relatively small volume of the subsurface. Historical data sets often include higher detection limits that do not adequately characterize the vapor intrusion pathway and are not adequate for decision making during later stages of a project life cycle.

Therefore, historical data may or may not be usable when evaluating a CSM. Comparing the results of historical data with new data requires knowledge of historical data collection and analysis methods. The project team must understand the historical data collection methods, analytical procedures and sampling plans that influence the historical data set, and the usability of those data. Often, historical data sets can be integrated with new, often higher-resolution, data sets when the limitations of the historical data set are acknowledged and incorporated into the updated CSM.

Another case study (Appendix B.2) illustrates the effect of incomplete site characterization on the final CSM. Three dry cleaner sites in Indiana were in the process of remedial action, but uncertainty in the CSMs for each site led to the need for further characterization. The decision to conduct further characterization was based on concerns over vapor intrusion. The three sites are reasonably close together and were assumed to have identical CSMs. Fairly high-density vertical and horizontal soil sampling was conducted at one of the sites, and the results were applied to the sampling plans for the other two sites. When PCE concentration in soil gas could not be explained by the CSM, a dynamic work plan was developed to define the subsurface lithology controlling the aqueous and vapor transport of PCE. Direct-push sampling was conducted, and an on-site lab analyzed the soil gas and groundwater samples. At all three sites, soil PCE source areas, aqueous-phase distribution of PCE, and soil gas (vapor intrusion) pathways were delineated.

4.2.3 Review Existing Release Data

The following data should be reviewed: the types of contaminants that were used on site, where they were stored, how they were transported, the waste disposal methods used, and where they may have been unintentionally or intentionally been released to the environment. These data should be used to determine potential releases, release period (dates), release sites, and possible contaminant source zones on site.

4.2.4 Review Existing Lithologic Data and Vertical Resolution Data

Existing data are often ignored or misinterpreted. When existing data are inadequate to determine the vertical lithologic variability, the following questions should be asked:

- Are there continuous lithologic data in the form of high-quality continuous core descriptions? Logs of such cores may contain valuable information, including bedding thickness, degree of interbedding of fine- and coarse-grained lithology, indications of clay types and content, and descriptions of sedimentary or tectonic structures.
- Are there MIP, hydraulic conductivity profiling tool (HPT), or cone penetrometer (CPT) data, or only 18 inch samples every 5 feet with Unified Soil Classification System classification?
- Can MIP, HPT, or CPT data be calibrated against lithologic descriptions or analytical data, and therefore serve as a proxy for lithologic data or contaminant distribution? Once the data are understood, they can be ranked according to reliability and resolution.

In Case Example 1 (Appendix B.1), it was established that thermal treatment would be effective on a coal tar DNAPL site if the spatial distribution of the DNAPL were clearly defined within differing geologic units. Required data included the volumes of discrete lithologic logs, porosity, saturation, and properties of the DNAPL. Evaluating the subsurface involved an adaptive management approach with a number of physical and chemical investigative tools and visual methods.

4.2.5 Review Existing Contaminant Data

The following data should be reviewed: the types of contaminants that were used on site, where they were stored, how they were transported, the waste disposal methods used, and where they may have been unintentionally or intentionally released to the environment. These data should be used to determine potential releases, release period (dates), release sites, and possible contaminant source zones on site.

My site has been characterized using conventional techniques. Do I need to redo this work using the higher resolution methods?

If you think your existing site conceptual model is sound and the site management strategy has been successful, an extensive supplemental site characterization program is not needed.

However, if questions remain about key components of the site conceptual model—e.g., hydrogeology; contaminant distribution, fate, and transport properties; and risk—additional characterization using high-resolution techniques can be both beneficial and cost-effective. Some sites may not have been precisely delineated by conventional characterization methods (e.g., soil borings and monitoring wells); in such cases, high-resolution techniques can provide clarity on how to move forward in the site remediation/ management process

4.2.6 Evaluate Groundwater Chemical Signature Data

While groundwater quality data presented on figures are commonly in call-out boxes or shown as isoconcentration contour maps for the primary contaminant(s) of concern (COCs), this approach often results in incomplete interpretation of groundwater quality data. One way to enhance the interpretation of groundwater quality data is to prepare pie charts depicting the chemical signature at each sampling point. A chemical signature is the relative abundance of COCs. When preparing these pie charts, color schemes should take into account the relationship between various compounds. For example, at sites affected by chlorinated solvents, the chlorinated ethenes can be shown using red for PCE, orange for TCE, bright yellow for cis- and trans-1,2-dichloroethene, and pale yellow for vinyl chloride. Similar related color schemes can be assigned to any series of related compounds to enable rapid visual interpretation of chemical signature data on plan-view maps or cross-sectional diagrams.

This approach is critical, as interpretation of chemical concentration data alone is often misleading; groundwater chemistry data collected from monitoring wells represent flow-weighted averages of aquifer conditions in the well vicinity. It is common to find monitoring wells installed along the periphery of a historical source. In such cases, the concentrations of contaminants detected are typically orders of magnitude lower than those present within a short distance of the well screen; however, the chemical signature of those contaminants is typically consistent with a source area or plume core signature (that is, enriched in parent compounds), whereas the chemical signature detected outside of a source area or plume core is often relatively enriched in degradation products. Thus, the use of chemical signature data can enable interpretation of source areas and plume cores that are easily missed when relying on chemical concentration data alone.

4.2.7 Review Existing Fracture Data

In cases where fracture porosity dominates fluid flow and contaminant transport, sufficient data must be acquired to characterize the fractures in terms of spatial orientation, distribution, interconnectivity, and potential for transport or storage of contaminants. Once the strengths and weaknesses and vertical and lateral resolution of the existing site data are understood, hydrogeologic and chemistry data can be integrated to produce an initial CSM and identify data needs/gaps.

4.3 Identify Data Needs/Gaps and Resolution

Once the uncertainties in the CSM are recognized, specific data needs (for example, type, location, amount, and quality) as well as data resolution (spacing or density) can be described. Spatial resolution should be assessed laterally and vertically. The goal is to achieve a data resolution related to the scale of subsurface heterogeneity that is effectively controlling contaminant transport and distribution. Data resolution should be commensurate with that scale to ensure that the distribution of contaminants is sufficiently delineated and that an effective remedial strategy, if necessary, can be developed.

The necessary resolution may be different for different areas of the site or phases of the project, and depends on the depositional environment (see Appendix A). Collecting system design information may require higher resolution sampling, while determining potential for risk and necessity of remedial action may necessitate a lower vertical resolution to make that determination. One way to cost-effectively achieve the appropriate resolution is to collect collaborative data (see Section 4.7) by taking advantage of the speed and coverage of real-time reconnaissance tools like MIP and laser induced fluorescence (LIF) to target areas of contamination for higher vertical resolution (USEPA 2010). At appropriate locations, the slower, more costly techniques of higher-resolution geology/stratigraphy and quantitative contaminant evaluations are used, which helps to limit high-resolution vertical sampling in areas where real-time tools do not indicate contamination.

Determining the correct resolution of data to collect can be difficult. The locations (plan view) and frequency (vertical) of samples are based on the initial understanding of the site prior to deployment. The density of data varies depending on site-specific data collection objectives for each of the data types (geology, hydrogeology, and chemical). For example, if a site has highly varying stratigraphy, more geologic and hydrogeologic data will be required than at a site with less stratigraphic variability.

An effective approach for determining the correct density of data required is to use on-site, real-time analysis coupled with efficient drilling techniques (see Case Example 2, Appendix B.2). Cost-effective tools are available for real-time collection of geology, hydrogeology, and contaminant distribution data; often, direct-push and sonic drilling tools are used. These tools are discussed in detail in Tool Selection Worksheet.

With real-time results, project managers are able to identify subsequent sampling locations based on the evolving CSM (see Section 4.1). If on-site, real-time data are not used, there is a risk of oversampling (involving increased and unnecessary costs) or undersampling (resulting in an inaccurate final CSM, which then requires redeployment and additional sampling). The real-time data approach allows for efficient allocation of available resources to collect the required density of data to produce a final CSM. The final CSM should meet project characterization objectives and contain an acceptable amount of uncertainty in the understanding of the geology, hydrogeology, and contaminant distribution.

It is important to recognize and elucidate the shortcomings of the existing CSM to develop an efficient path forward. A solid understanding of the data collected and work performed at the site to date, coupled with a hydrostratigraphic framework founded on the concepts of facies and depositional environments, provides a clear picture of what is known about the subsurface and a road map for identifying data gaps and developing data collection objectives. This process could involve the following tasks:

- Identify data *outliers* and, if they are artifacts of data resolution, formulate hypotheses to explain why.
- Understand any remedial actions past and present, as well as off-site conditions that affect the CSM (for example, contaminants entering the site, groundwater pumping). Classify the scale of variability of the stratigraphy and contaminant distribution in the subsurface. This requires careful definition of DQOs to ensure correct tool selection; the tools should provide sufficient resolution and accuracy to map the stratigraphy and classify the behavior and distribution of contaminants. Often, site-specific calibration and verification are required to determine the limits of applicability and utility of selected tools to meet screening and quantitative objectives before full-scale characterization efforts are undertaken.

4.4 Establish Data Collection Objectives

Once the data needs (including type and resolution) are identified, specific objectives can be established. Often data collection objectives are vague statements that do not fully describe the intentions and needs of a sampling program—for example, an objective might be to *define the lateral and vertical contaminant distribution*, and without further specificity, it would be difficult to demonstrate that this objective was met. In this example, the characterization objective should be developed in a way that considers (1) the type of data needed (for example, chemical concentrations); (2) the data density and spatial resolution (for example, lateral and vertical spacing and depth); and (3) the specific concentration endpoints for each contaminant.

The lack of specificity also makes selection of appropriate data collection/investigation tools challenging and could easily lead to misapplication or a recharacterization effort later on. To avoid this, objectives should be continually parsed into increasingly specific sub-objectives, until they are sufficiently succinct and the specific data needs become clear (see Appendix B for examples).

A characterization effort is not a disparate assembly of site data, nor is it an intent, for example, to collect mass discharge data across a site. Assumptions and known conditions about a contaminated site can lead to the selection of specific treatment technologies, both of which have discrete treatment capabilities and costs. To optimize their application, a focused effort to characterize specific parameters of the site may be required. At Well 12A (Appendix B.4), a multicomponent treatment approach was required based on previous characterization data, earlier treatment results, and multiple performance reviews. To do so, a detailed characterization effort was implemented with the following objectives:

- evaluate contaminant mass extents across the source area
- map different remediation technologies across the site
- develop SMART (specific, measureable, achievable, relevant, and time-bound) objectives for individual remediation technologies (ITRC 2011b)
- evaluate methods for measuring contaminant mass discharge and select one to use for the remedial action objective compliance metric (ITRC 2010)

The specific data collection objectives included the following:

- describe the major stratigraphic units of the upper aquifer containing contaminant mass
- quantify hydraulic properties of the stratigraphic units within the contaminant zone
- map the contaminant distribution of contaminants within the stratigraphic units, including NAPL and soil and groundwater contaminant levels
- estimate contaminant volume and mass
- estimate contaminant mass discharge within stratigraphic units
- map contaminant mass discharge delivered to extraction wells of the groundwater extraction and treatment system

A three-dimensional model was used to define the source and plume boundaries and to evaluate uncertainty.

ITRC champions the use of SMART remediation objectives for DNAPL sites. Although data collection objectives are not bound to meet all SMART attributes, they should be as specific as possible given what is and is not known about the site. This helps to ensure that characterization activities are driven by clear, focused, specific objectives.

Following are examples of the types of questions that can lead to development of effective data collection objectives depending on site conditions and geologic environment:

- What problem is being investigated?
- What decisions should be made?
- What are the uncertainties and project risks?
- What is the scale of the controlling heterogeneities at the site?
- Is matrix diffusion occurring at the site and what role does it play?
- Are fractures possibly transporting contaminants and what role do they play?
- What quantity of data is required and at what resolution?
- What quality of data is needed?
- What are the cost-benefits of collecting more data?
- How quickly is the information needed?

Table 4-1 provides examples of effective data collection objectives for DNAPL sites.

Table 4-1. Examples of effective data collection objectives for DNAPL sites

- Delineate the geologic heterogeneities and contaminant mass distribution in all phases in all geologic units.
- determine whether contaminant back-diffusion from low-permeability zones is or will be a significant source.
- Assess if DNAPL is present, and if so delineate its distribution.
- Evaluate whether there is a vapor intrusion threat.
- Determine baseline mass flux and mass discharge from the source zone and the leading edge of the dissolved-phase plume.
- Delineate the lateral and vertical extent of the dissolved-phase plume, and ascertain whether it is stable, contracting, expanding, or detached. Determine the rate of attenuation or expansion and migration.
- Determine the type, size, orientation, frequency, and distribution of fractures, and the fracture connectivity.
- Determine the hydrostratigraphy at a scale that is controlling the source and plume distribution and behavior.
- Determine the age of the release.
- Assess aquifer assimilative capacity.
- Develop a quantitative linkage between hydrostratigraphy and permeability to map and distinguish among transport and storage zones and identify relevant mass.

4.5 Design Data Collection and Analysis Process

Data collection and analysis is simply the implementation of the chosen data measurement system and the subsequent organization of the collected data. Three types of data—quantitative, semi-quantitative, and qualitative—are generally collected. All may be collected and analyzed differently. Effective data collection objectives determine the type of data collection required, which tools to use, and how the data will be analyzed. The Tool Selection Worksheet will aid in selecting the most appropriate tool.

The Tool Selection Worksheet describes conventional and new sampling and logging techniques for collecting direct measurements, as well as sensor-based technologies. Because of the complex nature of DNAPL sites, which can involve mass distribution in the NAPL, soil, groundwater, and vapor phases, it is important to start with an approach that is designed to resolve the scale of heterogeneity of contaminant phase(s), concentration, and composition in the unsaturated and saturated zones. By collecting stratigraphic and permeability data at the same time, it is possible to discern the controlling influence that subsurface architecture (permeability and structure) has on mass distribution and interphase mass transfer. The key is to collect data at sufficient frequency, in both the vertical and horizontal directions, to ensure that the mass transport behavior of the system can be classified at a minimum, and characterized explicitly when possible in simpler geological settings, early in the characterization process. Tool selection typically depends on geologic conditions, logistical considerations, and DQOs. For example, at a site contaminated by chlorinated solvents and underlain by stratified sand and silt deposits, one of the following approaches could be used:

- A number of different tools could be used to collect data of adequate resolution. An MIP could be used to collect vertical semi-quantitative contaminant distribution data at the desired depth increment (for example, 30 cm, 50 cm, or 100 cm intervals). If coupled with a CPT, HPT, or electrical conductivity (EC) dipole array, high-density, vertical, semi-quantitative geologic information could be collected.
- Continuous soil cores could be collected using a variety of drilling methods, sub-sampled at intervals ranging from inch to foot scale, and field screened or analyzed using a field or fixed laboratory.

Both approaches could produce data sets with resolutions adequate for generating rigorous CSMs; however, the first approach would likely be faster and cheaper than the second approach, although the data would be less quantitative. If the same release occurred at a site underlain by glacial till deposits, the tool selection would likely change. Due to their compact nature and the common presence of cobbles and boulders in glacial tills, use of the MIP might be infeasible, while continuous soil sampling using sonic drilling techniques would remain practical. Depending on the target investigation depths and nature of the till, continuous soil sampling using direct-push drilling techniques might also be feasible, and on-site field contaminant analysis (using a mobile laboratory) of continuous core samples at the desired resolution can provide data sets that produce a rigorous CSM.

Logistical considerations also affect tool selection. Small-scale direct-push drill rigs can be used to access most site settings (for example, inside buildings, in wetlands using temporary roads, in alleyways), whereas larger-scale track-mounted CPT or sonic drill rigs cannot fit in some target investigation areas. Full-scale truck-mounted drill rigs, direct-push rigs, CPT rigs, and sonic drill rigs are further restricted by their size; however, these larger rigs possess greater power and can typically drill to greater depths through more difficult geologic conditions than can the smaller rigs. As the cost of drilling increases (due to more difficult geology and greater depths), the importance of real-time data for cost-effective drilling increases as well. Having a flexible work plan and an on-site laboratory to allow contaminant information to be plotted on maps and cross sections during the investigation helps allow the choice of effective sampling locations and can significantly reduce the overall project drilling budget while ensuring that enough usable data are collected to create a robust CSM.

Data quality objectives also affect tool selection. Using the examples presented above (chlorinated solvent release at a site underlain by stratified sand and silt deposits), if the target detection limit is 1 microgram per liter for PCE, the MIP would not be a viable tool due to sensitivity limitations. In that case, the Waterloo^{APS} or the HPT-groundwater sampler could be used to collect high-density hydrostratigraphic data and discrete-interval groundwater samples for analysis using a mobile or fixed laboratory. This would result in a decrease in the vertical resolution of the contaminant distribution data and would likely prohibit collection of groundwater samples from low-permeability zones, but the contaminant data would meet the DQOs that require contaminant speciation and low-level concentration data. The low-permeability zones could be investigated using soil sampling and analysis for selected locations and depths where determination of the stored dissolved-phase contaminant is an important project DQO. This approach would generate a data set that could be used to develop a rigorous CSM and achieve the project objectives.

4.5.1 Data Limitations

Data limitations should be taken into consideration before tool selection to ensure that the site characterization goals are met with an acceptable level of uncertainty. For example, collecting and evaluating qualitative data prior to quantitative data incorporates the limitations of qualitative data into the data analysis and interpretation process. Consider the following performance characteristics when selecting the tools that best meet the project needs:

- specificity
- sensitivity
- accuracy
- precision
- turnaround time
- training requirements
- cost

By recognizing limits in the selectivity, sensitivity, accuracy, and precision of qualitative data, yet capitalizing on rapid turnaround times and lower training limits, the project team can quickly and cost-effectively develop a CSM to direct focused qualitative site characterization efforts.

4.5.2 Data Management Challenges

When characterizing a site, a substantial volume of data are generated. Many of the tools described in this document generate electronic data that must be managed and interpreted, and this large volume of electronic data provides both opportunities and challenges. The importance of managing data is noted by USEPA (2011a) as: "…the ability to efficiently access and interpret data is essential to guiding project teams through the entire cleanup process, from project planning to site completion."

Plan for Data Management

It is just as critical to plan how the data will be managed as it is to select the appropriate tools.

A significant challenge in using tools such as the MIP or LIF is that the data they collect are considered qualitative or semi-quantitative and must be integrated, managed, and interpreted along with the quantitative data (for example, contaminant concentrations, hydraulic conductivity). Qualitative and semi-quantitative data frequently have unique quality assurance/quality control measures; they typically are not validated or assigned *flags*, as may be done for laboratory analytical data. In addition, data from profiling-type tools can represent many individual data points, because they measure parameters at high density (cm to inch scale) with depth and time. All of the above factors can make these data more difficult to manage than data collected solely from point measurements; however, the profiling and logging tools often provide information about contaminant distribution and hydrogeologic architecture that could not be accomplished with conventional point sampling techniques and lab analyses due to budget limitations.

Data from the tools described in this document are typically provided to the consultant or site owner after the end of the field mobilization. In some cases, data can be interpreted in real time to support the field decision-making process. The data format may be digital images or logs, field notes, spreadsheets, or plots of parameters versus depth for logging tools. The data should be archived and transferred into whatever data management tool has been selected for the project. Ideally, the data management tool is capable of handling all of the types of data to be generated as part of the characterization effort. Thus, the data management needs of the project should be considered during tool selection/evaluation. Data management options can range from commercial off-the-shelf database programs to complex three-dimensional visualization software.

When the appropriate data management and visualization tools are used, it is possible to efficiently store, interpret, and present large volumes of electronic data. Higher-end data management tools (for example, visualization software) can provide capabilities for data analysis and communication/presentation. Therefore, just as it is critical to consider the strengths and limitations of each characterization tool in the selection process, it is also important to consider how the data from those tools will be managed and integrated with other data from the site (see Appendix D).

4.5.3 Data Analysis Process

Data collection is generally an expensive process; therefore, it is imperative to glean as much information as possible from the data. As previously stated, three types of data are generally collected: quantitative, semi-quantitative, and qualitative. During DNAPL site characterization, the appropriate data types are collected and the appropriate tools are used to answer questions posed by the following data collection objectives:

- **Screening method.** Qualitative tools may be used to further refine the understanding of site conditions or direct further data collection and analysis. Once existing data and qualitative data are assembled into a collaborative data sets (see USEPA [2010] Triad Resource Center), such data can be interpreted to improve a CSM and direct quantitative data collection.
- **Fill in the gaps.** If not included in the existing CSM, develop a quantitative linkage between the stratigraphy and permeability of the aquifer so that transport zones can be distinguished from storage zones and mapped across the investigation area. In essence, this phase of characterization is focused on selecting and using tools that can map the mass flux in the aquifer. This is where higher-resolution data collection is recommended to ensure adequate horizontal and vertical resolution for understanding contaminant transport at the site. Historically, it was assumed that a plume could be accurately mapped from the inside out, by stepping out at large distances from the source to map the spatial extents, without understanding how mass flux is distributed at the site; however, different quantitative tools (and combinations of tools) are now available, and required to accurately detect and map the occurrence of DNAPL and high-concentration source zones, compared to moderate or maximum contaminant level concentrations in the distal portions of the plume. Different tools may be required to provide quantitative measurements of dissolved-phase contaminants in permeable transport zones compared to less permeable storage zones. Further specialization of characterization tools is required when contamination is deep, or when it occurs in different types of bedrock.

Monitoring Wells and Bias

Monitoring wells, as traditionally constructed and used, are not recommended as primary characterization tools in unconsolidated aquifers because of vertical and volumetric averaging of contaminant concentrations associated with this type of sampling. Bias is also introduced in how wells are sampled, because the volume and intensity of sampling further affects the vertical and volumetric averaging, making conclusions based on monitoring wells unreliable.

- **Map the extent of the contamination to enable definition of the source zone(s) and the distal dissolved-phase plume(s).** In this step, the site CSM is used to define DQOs for specific zones, potentially subdivided further based on hydrostratigraphy for large plumes within complex geologic settings. Guided by the knowledge of the behavior in the transport zones and storage zones, it is possible to begin to optimize the application of tools and adapt the frequency and location of quantitative sampling necessary to delineate the source and dissolved-phase plumes. Practitioners are advised to focus on tools that enable remedy decision making and risk assessment early in the process to avoid having to repeat quantitative sampling at field-screening locations, especially when it is impractical to correlate quantitative results with field screen measurements.

Use of multilevel devices (for example, packer and port systems or discrete interval direct-push samplers) with hydrologic characterization methods (for example, HPT and EC or CPT logging, multilevel slug tests, hydraulic tomography) and chemical sampling provide an integrated and adequate level of resolution to the characterization process. This level of characterization translates into a more informed selection of the remedy (Einarson 2006; McCall et al. 2006; Dietrich et al. 2008; Kober et al. 2009; Dietrich and Dietz 2012). In addition, packers in the wells avoid concentration averaging and migration of contaminants to new or less-contaminated zones.

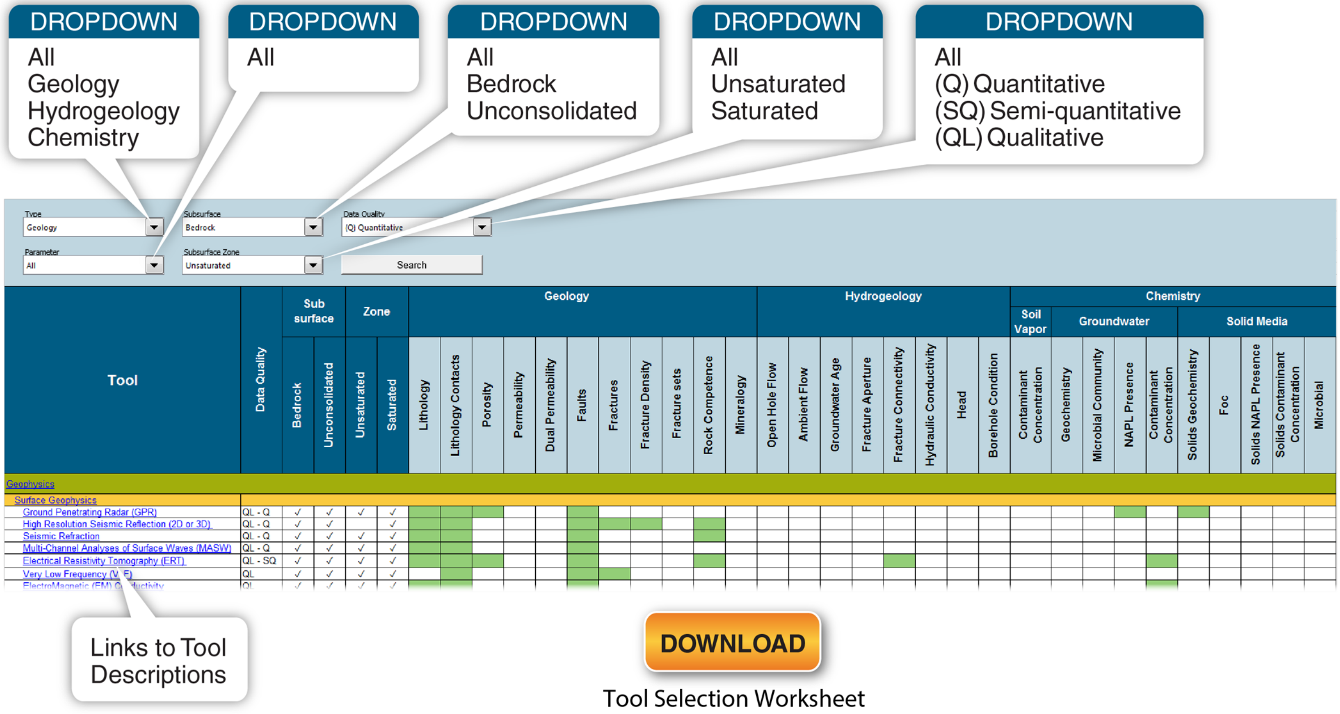
4.6 Tools Selection

This guidance provides an interactive Tool Selection Worksheet that is useful in selecting tools to characterize contaminated sites. The Tool Selection Worksheet offers a rapid method of identifying the appropriate tools and information for collecting geologic, hydrologic, and chemical data. Specific tools and techniques are listed in the following categories within the left column of the Tool Selection Worksheet:

- geophysics
    - surface geophysics
    - downhole testing
- hydraulic testing
    - single well tests
    - cross borehole testing
    - flow metering
- vapor and soil gas sampling
- solid media sampling and analysis methods
    - solid media sampling methods
    - solid media evaluation and testing methods
- direct-push logging (in situ)
- discrete groundwater sampling
    - multilevel sampling
- DNAPL presence
- chemical screening
- environmental molecular diagnostics
    - microbial diagnostics
    - stable isotope and environmental tracers tests
- on-site analytical techniques

In each type of subsurface terrain, there are physical features that may control the behavior of DNAPL or soluble or gaseous phases of DNAPL contaminants (Chapter 3). Each geologic parameter in the Tool Selection Worksheet helps in understanding the macroscopic and microscopic characteristics of the subsurface that affect the transport of all phases of contaminants (NAPL, dissolved, sorbed, and gaseous). Each geologic parameter informs the physical framework of the CSM that controls the hydrologic characteristics of the subsurface. Analyzing the physical framework of the subsurface against the measured hydrologic properties of flow in the subsurface helps in understanding contaminant migration and distribution and in further refining and verifying the CSM. The geology, hydrology, and chemistry should be evaluated simultaneously and interpreted collectively.

Figure 4-2 describes the options offered in the downloadable Tool Selection Worksheet from which you can select a suite of characterization tools. Figure 4-2 displays examples on mousing over each box.



Type: Geology
Subsurface: Bedrock
Data Quality: (Q) Quantitative
Parameter: All
Subsurface Zone: Unsaturated

Tool	Data Quality	Sub surface		Zone		Geology											Hydrogeology								Chemistry									
																									Soil Vapor	Groundwater				Solid Media				
		Bedrock	Unconsolidated	Unsaturated	Saturated	Lithology	Lithology Contacts	Porosity	Permeability	Dual Permeability	Faults	Fractures	Fracture Density	Fracture sets	Rock Competence	Mineralogy	Open Hole Flow	Ambient Flow	Groundwater Age	Fracture Aperture	Fracture Connectivity	Hydraulic Conductivity	Head	Borehole Condition	Contaminant Concentration	Geochemistry	Microbial Community	NAPL Presence	Contaminant Concentration	Solids Geochemistry	Foc	Solids NAPL Presence	Solids Contaminant Concentration	Microbial
Geophysics																																		
Surface Geophysics																																		
Ground Penetrating Radar (GPR)	QL - Q	✓	✓	✓	✓	🟩	🟩	🟩			🟩																	🟩		🟩				
High Resolution Seismic Reflection (2D or 3D)	QL - Q	✓	✓		✓	🟩	🟩				🟩	🟩	🟩		🟩																			
Seismic Refraction	QL - Q	✓	✓	✓	✓	🟩	🟩				🟩				🟩																			
Multi-Channel Analyses of Surface Waves (MASW)	QL - Q	✓	✓	✓	✓	🟩	🟩				🟩																							
Electrical Resistivity Tomography (ERT)	QL - SQ	✓	✓	✓	✓	🟩	🟩	🟩			🟩				🟩						🟩								🟩					
Very Low Frequency (V F)	QL	✓	✓	✓	✓		🟩				🟩	🟩																						
ElectroMagnetic (EM) C ductivity	QL	✓	✓	✓	✓	🟩	🟩				🟩																		🟩					

Figure 4-2. Tool selection framework diagram.

Figure 4-2 contains an image of the header rows of the Tool Selection Worksheet. Within the downloadable Tool Selection Worksheet, dropdown boxes allow you to choose variables in each of four categories: (1) **type** of investigation; (2) **subsurface** terrain; (3) **parameter** or data required; and (4) **data quality**. Once the selections are completed, a **search** will populate another sheet with tools capable of collecting the type of data described by the first set of selections. If additional date types are required, another set of variable can be selected and an **additional search** can be completed and added to the sheet containing the first search. The search variables for both searches are listed at the top center.

Clicking on a specific parameter, for instance **lithology**, links to a description of the parameter and why it should be collected during characterization of the geology in a CSM. These descriptions are available for all parameters.

In the Tool Selection Worksheet, each tool name links to more information on the tool. Descriptions of the tool, applicability of the tool, its advantages and limitation, its data quality capability, and difficulties that may be encountered when using the tool are included. Additional information is contained in the references provided at the end of each technology description table. These are linked to the full reference information.

Many of the tools are capable of collecting data in all subsurface conditions; however, some are more limited. For example, some tools cannot be used in screened or cased holes or in unsaturated conditions, and others may be able to penetrate relatively shallow depths in unconsolidated material but cannot penetrate bedrock subsurfaces without a borehole.

The downloadable Tool Selection Worksheet illustrates the applicability of each tool by shading the cell that corresponds to the tool (leftmost column) with the parameter (uppermost columns). For example, ground penetrating radar (GPR) can be used to identify lithology, lithologic contacts, and faults. The data obtained by a GPR survey can be qualitative, semi-quantitative or quantitative depending on the care taken in calibrating the tool responses to specific geologic conditions. The Tool Selection Worksheet contains 97 tools and techniques that can be used to collect and analyze site parameters.

Having established the data needs of the DNAPL site investigation, the shaded cells of applicable tools help in selecting a suite of tools capable of collecting data to assess the site parameters in the data collection objectives. For instance, Appendix B, Case Example 1 assumes that thermal treatment is a preferred approach in remediating a DNAPL source; however, proper design requires a thorough understanding of the three-dimensional variability of porosity, saturation, NAPL properties, and distribution. Some tools selected include LIF to delineate the three-dimensional distribution of coal tar NAPL accompanied by a CPT friction log to assess the variability within the vertical stratigraphy. Physical core recovery and logging is used to estimate the ranges of porosity within discrete geologic facies. This initial suite of tools is only capable of collecting the applicable data without considering data quality, availability, cost, deployment challenges, limitations, and access, among other parameters.

The links to the Tools Descriptions (Appendix D) must be reviewed to assess the best tools for a particular site situation. References make research of specific tools easier and much quicker as a number of the tools, originally classified as applicable, can be eliminated due to site conditions, access, cost, availability, deployment challenges, or DQOs. As discussed earlier, this Tool Selection Worksheet does not select individual tools, but it does allow for the elimination of many tools depending on the data needs and investigation plan.

Data Quality

Quantitative = Q, *tool that provides compound-specific values in units of concentration based on traceable standards (such as µg/L, ppm, or ppbv)*

Semi-quantitative = SQ, *tool that provides compound-specific quantitative measurements based on traceable standards but in units other than concentrations (such as ng or µg) or provides measurements within a range*

Qualitative = QL, *tool that provides an indirect measurement (for example, LIF and PID measurements provide a relative measure of absence or presence, but are not suitable as stand-alone tools for making remedy decisions)*

The data quality determination is not tool specific. Many tools can collect semi-quantitative data as well as quantitative data if care is taken to calibrate the tools with the subsurface and collect and analyze the data carefully. Many of the downhole geophysical tools have the capability to collect qualitative as well as quantitative data depending on the requirements of the investigation. Depending on the DQO, availability, accessibility, and cost, the final selection of tools may not be appropriate and alternative tools must be considered. Regardless, an adequate investigation requires that the characterization objective be met. There is no need to collect less or more data than necessary; however, the data collected must fill the data gap in the CSM.

4.7 Perform Data Evaluation and Interpretation

The objective of evaluation and interpretation of site characterization data is to gain a clear understanding of past, present, and potential future environmental conditions at a site. Through the context of the CSM, data evaluation and interpretation can facilitate more informed remedial decisions for the site. Thus, only through data analysis and interpretation can the project team make decisions (for example, characterization efforts answer a stated characterization objective, or an assumption about the conditions of the subsurface are not supported by the data, and the original assumptions must be revisited). Specifically, the data should reduce the levels of uncertainty in the CSM, with respect to the data collection objectives at the site, to an acceptable level. Through integration of all of the data types (geologic, hydrologic, and chemical), collaborative data sets (USEPA 2010) can be generated. This multiple-lines-of-evidence approach enables the CSM to provide a clearer description of contaminant transport, storage, and attenuation.

4.7.1 Geologic Conditions

Typical approaches to evaluating geologic data include preparation of cross sections, fence diagrams, or three-dimensional representations across a site. Contour maps of relevant geologic surface elevations (isopach maps) are also helpful for many sites. When evaluating the geology, consider answering the following questions:

- Is the subsurface an unconsolidated environment (sedimentary) or a consolidated environment (bedrock, fractured rock, karst)?
- What is the horizontal and vertical extent and continuity of lower-permeability facies that can act as diffusive sources under present or future conditions?
- What is the vertical heterogeneity of strata? This question is important for identifying potential facies changes and permeability contrasts that can act as either of the following:
    - vertical migration barriers for DNAPL that may represent areas where pools and lateral spreading are more likely to be present in the vicinity of a source zone (even small contrasts in permeability between facies are important)
    - impediments to in situ remediation approaches since groundwater flux rates through permeable sediment facies with large contrasts in permeability can limit the effectiveness of remedial (for example, injection or extraction) technologies
- Are there preferential pathways in the subsurface for DNAPL flow?
- Is fracturing a significant source of permeability, and are there dual permeabilities?
- What is the extent of boundary conditions (for example, faults, lithologic contacts, fracturing, facies changes) that influence horizontal and vertical groundwater flow downgradient of a NAPL source zone?
- What are the geologic features that influence vapor transport in the unsaturated zone?

Special considerations in the evaluation and interpretation of the geologic data are as follows:

- **Boring logs.** Boring logs are fundamental to most subsurface investigations; however, they can be tedious and prone to errors and inconsistent judgments. Logging should be completed from the collar, or top of the boring, through the completion depth of the boring. Throughout the length of the boring, depths should be recorded for any recognizable contacts, changes in grain size, sorting, modality, cementation, rock type, mineral content and percentage, fracturing and attitude when possible, competence, lithology, crystalinity, alterations, color, porosity, moisture content, and any other relevant and noticeable change in facies. These logs not only provide direct information for interpretation of the paleoenvironment and tectonic environment of the subsurface, they are also used to index other downhole testing and data collection instruments (for example, CPT, HPT, EC, MIP, natural gamma, GPR, and resistivity – see additional examples in the Tool Selection Worksheet). Appendix A contains examples of how to use boring logs to define the depositional environment of the vertical section, and then to identify data gaps and develop future data collection objectives.

4.7.2 Hydrogeologic Conditions

Hydrogeologic data support calculation of average linear groundwater velocity, groundwater volumetric flow, chemical travel time, mass flux, and mass discharge. These site-specific determinations must fit into the regional geologic setting to validate the hydraulic conditions against the physical factors in the subsurface. Examples of hydrogeologic characteristics relevant to a DNAPL site investigation include the following:

- horizontal and vertical hydraulic conductivity of hydrostratigraphic units relevant to the transmission of groundwater, vapor, or DNAPL flow
- spatial and temporal (for example, seasonal, production well pumping intervals) variations in the hydraulic gradients, flow rate, and direction
- minimum and maximum water table elevations
- groundwater/surface water interface and springs
- capillary zone thickness
- vertical water saturation profile in the unsaturated zone (which influences the amount of pore space available for vapor transport)
- surface cover (soils) conditions (relevant to vapor transport)

Special considerations in the evaluation and interpretation of the hydrogeologic data are as follows:

- **Well construction logs.** Wells constructed for monitoring may provide very little reliable data for characterization. This may be because the screen length was intentionally installed to obtain average groundwater chemical concentrations over the entire length of the screened interval; often, the screened interval is far longer than the thickness of the discrete stratigraphy or facies changes being investigated in the subsurface. The depth of the well, and in particular the screened interval, must coincide with the segment of the vertical profile being investigated. Well construction logs define these parameters prior to sample collection. Well construction logs should also document the size of the borehole, amendments used in completing the drilling and construction, composition and internal diameter of any casing or screen used, and depths of changes in the material or size of casing used to develop the well.
- **Evaluation of groundwater elevation data.** Groundwater elevation data are often used to estimate groundwater flow direction and groundwater flow velocities

Groundwater elevation gradients may not be a reliable indicator of flow direction- The groundwater elevation gradient for an aquifer expresses the gravitational driving force supporting groundwater flow, but it is not the only determinant of groundwater flow direction. The hydraulic conductivity structures of heterogeneous, anisotropic aquifers are often not aligned with the fall line of the groundwater elevation gradient. In these cases, relatively small hydraulic conductivity contrasts can direct groundwater flow and contaminants in directions significantly off the elevation fall line" (Payne et al. 2008).

(when coupled with geologic properties and hydraulic conductivity data). The use of groundwater elevation data alone, however, without incorporation of geologic structure and the spatial distribution of hydraulic conductivity, does not reliably predict groundwater flow direction, especially at small-length scales that are increasingly relevant to DNAPL remediation activities. Groundwater elevations typically vary seasonally; therefore, it may not be possible to predict long-term groundwater flow patterns based on only a few monitoring events.

Groundwater elevations also vary in response to significant precipitation or drought events, local and regional pumping, as a result of remedial activities, or changes in site conditions such as the extent of paved surfaces. The CSM should consider variations in groundwater elevation over time and the potential for these variations to influence the mass fluxes into and out of the groundwater system. Estimates of the apparent groundwater flow velocity from groundwater elevation and estimates of hydraulic conductivity are prone to error due to the inherent inaccuracy of hydraulic conductivity estimates (+/-50%) and variations in the ratio of the effective to total porosity (+/-50%) spatially within and between stratigraphic units.

- **Groundwater flow and contaminant transport.** An acceptable understanding of groundwater flow and DNAPL and aqueous phase contaminant transport cannot be based accurately on groundwater elevation alone. An understanding of the subsurface stratigraphy or facies changes, primary and secondary porosity, permeability, and structural feature (faults, fractures, and contacts), coupled with the groundwater elevation and climatic data, is necessary to define groundwater flow and contaminant transport. Wells exhibiting similar groundwater elevation data may be drilled into different geologic units that are not hydraulically connected. There may be seasonally perched groundwater that inhibits contaminant transport, apparent confining layers may leak, and unidentified facies changes may influence flow paths and velocity, all of which may result in unexpected transport into what were assumed to be clean geologic units.

4.7.3 Chemistry

A variety of analyses may be conducted using chemical data collected during investigation of a DNAPL site:

- Whenever possible, the composition of DNAPL source zone(s), including the types of constituents and relative mass or mole fractions of each constituent in the NAPL, should be identified, to facilitate an understanding of the effective solubility of each constituent in the NAPL mixture. This understanding will then help in evaluating the applicable technologies and remediation time frame. The dominant constituents in a source are often focused upon without sufficient consideration of constituents with lower values of effective solubility. This may influence the time required for remediation or selection of remedial technologies.
- Dissolution of a multicomponent NAPL may be evident in historical concentration vs. time. Compound(s) with higher effective solubility show a decline in concentration where concentrations of compounds with lower effective solubility may increase or remain stable in

concentration. These trends may help in evaluating the degree of DNAPL depletion that has occurred as a result of natural dissolution.
- Potential and confirmed NAPL source zones can be determined using the lines-of-evidence approach and NAPL indicators (USEPA 2009).
- The source strength (that is, mass discharge) downgradient of a source zone, and how this source strength has changed over time, can be evaluated. ITRC (2010) provides more information on the uses and methods for estimating mass discharge and mass flux.
- The 14-compartment model (ITRC 2011b) can be used to evaluate mass distribution in various phases and locations in the subsurface, including the following:
  - delineation of diffusive sources in lower-permeability units based on an interpretation of soil and groundwater data
  - delineation of groundwater plumes downgradient of NAPL or diffusive source zones
  - evaluation of vapor transport as a result of one or more sources in the unsaturated zone or saturated zone
- The distribution of physical characteristics such as primary and secondary porosity, fraction of organic carbon (f_{oc}, used for soil partitioning and retardation calculations) and DNAPL properties (for example, density, interfacial tension, viscosity) can be evaluated. See Appendix I for examples of f_{oc} in various geologic media.
- Biogeochemical conditions can be characterized and the biodegradability and other potential attenuation mechanisms for COCs can be evaluated (ITRC 2008). For example, dissolved methane in groundwater is an important parameter for mapping and finding evidence of natural attenuation, and specifically reduction and attenuation of DNAPL zones in plumes. This is another parameter that tends to be overlooked and not used as an early warning with respect to plume migration and source areas of highly concentrated chlorinated solvents.

Special considerations in the evaluation and interpretation of the chemical data are discussed below.

It is uncommon to conduct tracer tests at sites, unless they are in karst terrains; however, due to the historical use of multiple chemicals at different times and in different portions of sites, *trace* contaminants present can often be used to interpret the locations of distinct source areas and plumes. When evaluating trace contaminants, it is important to include both parent and daughter products. A simple approach for identifying potential trace contaminants is to arrange chemicals in data tables with respect to their parent-daughter relationships. Related compounds in certain wells are easily observed. Once trace contaminants have been identified, the sum of related compounds (that is, parent and associated daughter compounds) can be plotted on plan-view maps or cross-sectional diagrams. It is possible to use tracer data to differentiate among the footprints of multiple distinct plumes that are dominated by a single primary contaminant (for example, TCE).

For example, mapping geochemical parameters such as total dissolved solids and chloride can serve as chemical tracers. Reductive dechlorination could produce an increase in chloride concentration relative to background, which can be detectable in advance of the migrating dissolved-phase plume. Because the chloride increase does not represent a drinking water criterion exceedance, it has often not been considered relevant and thus not used as a means to further investigate an aquifer; however, it can be an early sign of the presence of DNAPL, and can point toward the location of an early plume migration at depth. If vertical aquifer sampling data show increases in chloride at select depth zones, this may well indicate a pooled source of DNAPL upgradient. Therefore, chloride increases should be considered when mapping in three dimensions, and as a part of the CSM. At the very least, increased chloride concentrations can identify the preferential contaminant flow paths that are important to the CSM even if the source is a site-specific activity that released chloride not associated with dechlorination. Further geochemical analyses may help delineate the two sources.

Deuterium, oxygen-18, and carbon-13 isotopes provide qualitative information on the origin of water and can be used to infer age. Radioactive isotopes can infer age by determining the rate of decay of a radioactive isotope. Common isotopes include hydrogen, (tritium) carbon-14, and chlorine. These may be useful in indirectly estimating bimodality in water sources, and could be an indication of dual permeability and fracture connectivity (Harte 2013b; Cook and Böhlke 2000; Coplen, Herczeg, and Barnes 2000).

The age of the groundwater can indicate whether it is from an ancient, potentially subsurface source or whether the aquifer is being replenished with modern water from the surface. If an aquifer is being replenished with modern water, the aquifer water is vulnerable to contamination encountered while infiltrating from above. With careful testing, the flow regime can be clarified according to the chemical age of the water. Examined along a flow path, for instance, if the age increases rapidly from one sampling point to another, movement between the two sampling locations is slow.

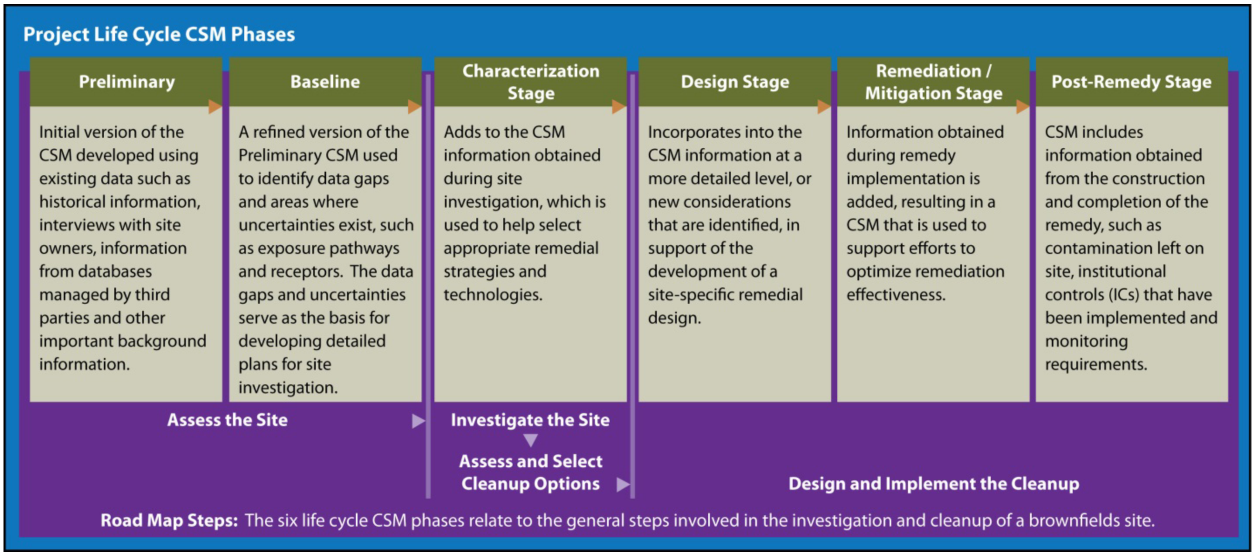
4.8 Update Conceptual Site Model

The overall goal of an ISC is to collect the data necessary to provide an updated, site-specific, three-dimensional CSM, sufficiently detailed at the relevant scale, to effectively and efficiently guide site environmental management. The process of developing and updating the CSM includes compiling and synthesizing existing information, identifying data gaps and uncertainties, and determining subsequent data needs. As described in Chapter 1, oversimplified characterization of subsurface conditions has led to the concept of engineering around geology; however, remedy performance track records have shown that concept to often be flawed.

The focus of a CSM may shift from characterization toward remedial technology evaluation and selection, and later, remedy optimization. Throughout the extent of a project, decisions, data needs, and personnel shift to meet the needs of particular project stages and the associated technical requirements. Continuing to refine the CSM as the project progresses requires the ongoing collection of an adequate amount of qualitative data. In the latter stages of a CSM, additional data collection is often driven by the goal of answering specific questions or reducing uncertainty of highly specific components. At all points in the CSM life cycle, the CSM is simply a hypothesis of site conditions and processes, and therefore additional quantitative data collection should continue to test the hypothesis at the appropriate levels.

For example, a CSM may indicate that most of the contaminant mass migration is occurring in one of many laterally extensive sand stringers within a large low-permeability silt and clay layer. The characterization objective for additional work would then be to measure the contaminant flux through the sand stringers, and this could be accomplished through a number of the tools presented in the Tool Selection Worksheet. In this simple example, the result is essentially binary, asking the question: “is the migration through a single stringer? The CSM may require updating based on the results and additional investigation/evaluation undertaken as needed.

A CSM is rarely composed of individual elements with weak reliance on each other. The examination of how additional quantitative information can have a material effect on the CSM as a whole, and on other individual elements, should be central to the updating process. The integration of new data into old concepts requires experienced practitioners, particularly as detailed site investigations in the middle stages of the CSM life cycle can often have far-reaching effects not readily apparent simply from the gathered data.



Project Life Cycle CSM Phases

Preliminary	Baseline	Characterization Stage	Design Stage	Remediation / Mitigation Stage	Post-Remedy Stage
Initial version of the CSM developed using existing data such as historical information, interviews with site owners, information from databases managed by third parties and other important background information.	A refined version of the Preliminary CSM used to identify data gaps and areas where uncertainties exist, such as exposure pathways and receptors. The data gaps and uncertainties serve as the basis for developing detailed plans for site investigation.	Adds to the CSM information obtained during site investigation, which is used to help select appropriate remedial strategies and technologies.	Incorporates into the CSM information at a more detailed level, or new considerations that are identified, in support of the development of a site-specific remedial design.	Information obtained during remedy implementation is added, resulting in a CSM that is used to support efforts to optimize remediation effectiveness.	CSM includes information obtained from the construction and completion of the remedy, such as contamination left on site, institutional controls (ICs) that have been implemented and monitoring requirements.

Road Map Steps: The six life cycle CSM phases relate to the general steps involved in the investigation and cleanup of a brownfields site.

Figure 4-3. CSM life cycle phases during a brownfields investigation.

Source: *USEPA 2015*

4.8.1 Example 1 – Simple Site Characterization

Scenario. Tetrabromoethane (PBA) has been released from a mineral processing facility into layered silt/sand/gravel stratigraphy. The initial characterization-stage CSM indicated that the plume was contained within the property limits and that groundwater velocities were very low (Figure 4-4).

Uncertainties. Monitoring wells were originally installed with long-screened intervals (~ 10 meters). This screen length was not likely to identify geologic controls on the plume. As a result, surface water receptors could have continued to be at risk.

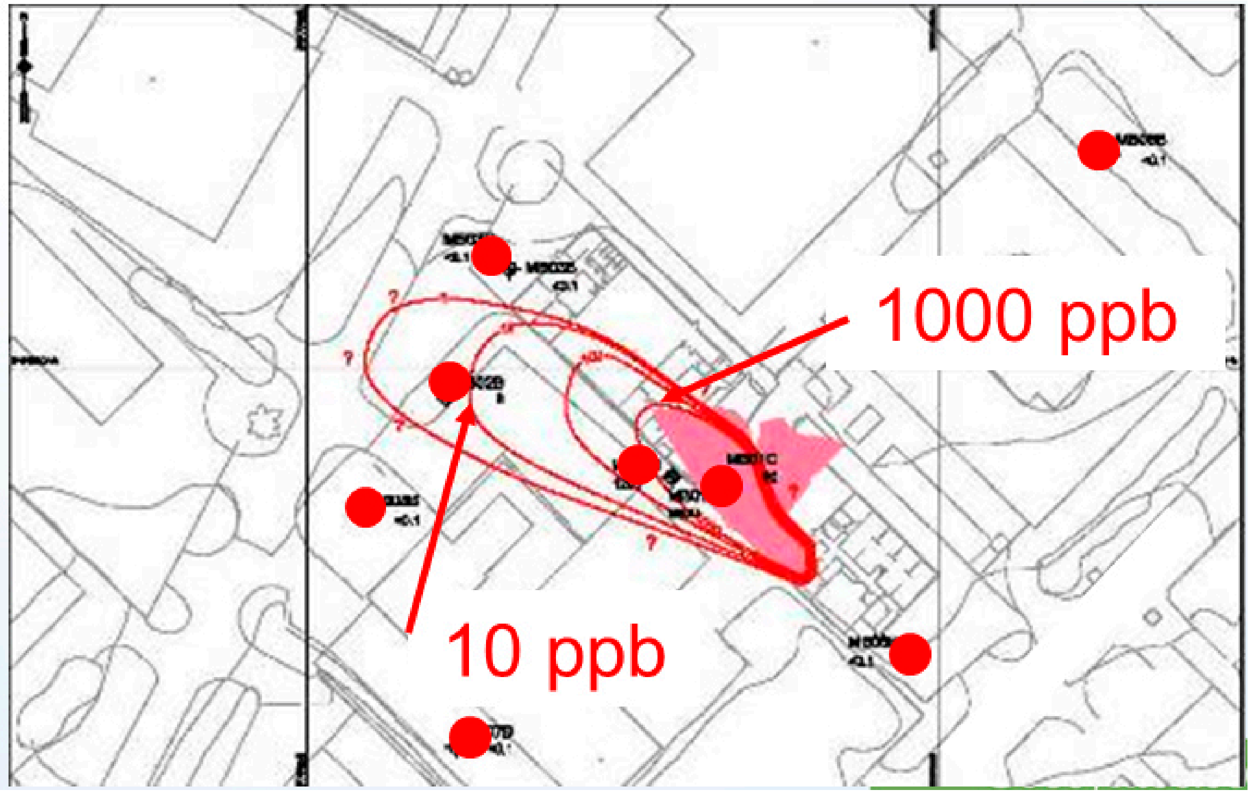


Figure 4-4. Original plume interpretation (red points are monitoring wells).

New data. An extensive drilling and sampling event was undertaken using sonic technologies and detailed core analysis followed by MIP for high precision placement of 1 meter well screens. Surface water sampling was also implemented.

Effects on the CSM. Additional sampling and new data identified a larger plume than recognized from historical data. The plume is now expected to reach a surface water receptor (Figure 4-5). There is a need to understand the discharge dynamics between groundwater and surface water as contaminants are not seen in surface water at levels predicted by a mixing model.

4.8.2 Example 2 – Source Zone Refinement for Remedy Design

Scenario. PBA has been released from a mineral processing facility into layered silt/sand/gravel stratigraphy (same site as in previous example). The plume is primarily contained in two high-permeability sand/gravel layers within silty formation. No detectable concentrations were found below a lower clay aquitard, and DNAPL is suspected to be present in sand layers and in preferential pathways through silty layers.

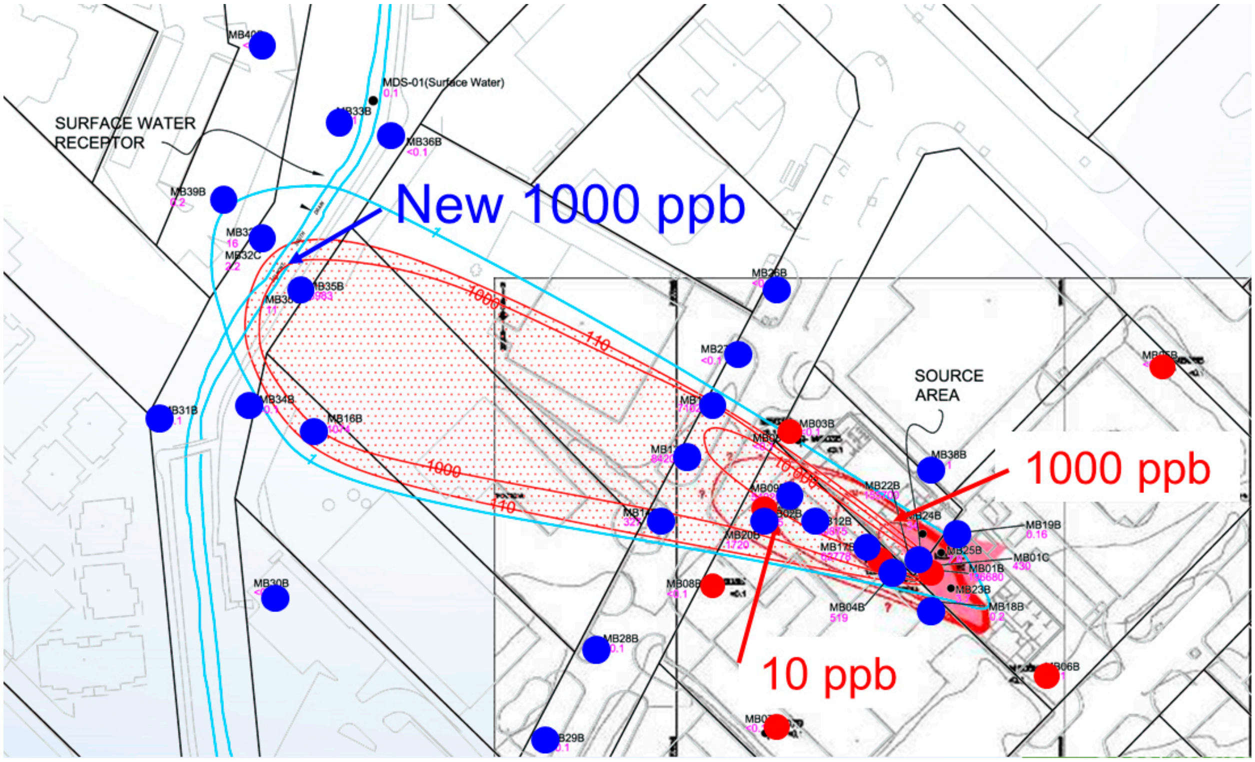


Figure 4-5. Plume following additional delineation (blue wells = second delineation; red wells = initial delineation).

Uncertainties. Neither the location of most of the DNAPL mass nor the amount of total DNAPL mass in the subsurface are known. DNAPL PBA is very dense (SG = 2.97) and is thought to have minimal lateral migration following release. The highest dissolved concentrations are in the sand/-gravel layer immediately above the clay aquitard, and it is not known if DNAPL has pooled there.

New Data. Passive flux meters were deployed in a downgradient transect. The source zone is located inside a very low overhead building, and it is determined that CPT-based tools are not viable. A mini-sonic rig is used to install very-high-resolution monitoring wells (4 inch screens). A partitioning interwell tracer test (PITT) is also conducted.

Effects on the CSM. Most of the contaminant flux is through upper sand and silt layers. In addition, most groundwater flux is through a lower sand layer (Figure 4-6). The implication is that there is little DNAPL in the lower sand layer in the original source area. Figure 4-7 indicates that most of the DNAPL is present in upper regions; PBA naturally breaks down to tribromoethene quickly. The distribution of PBA in the source zone and the contaminant mass in the lower sand are the result of the plume diving to the highest-permeability layer.

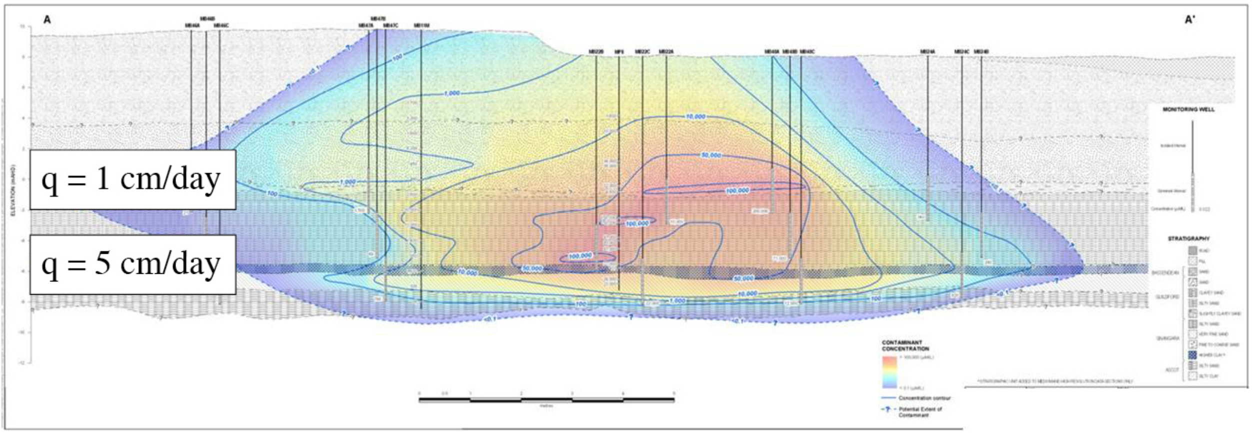


Figure 4-6. Tribromoethene flux downgradient from the source.

Source: *Johnston et al. 2013.*

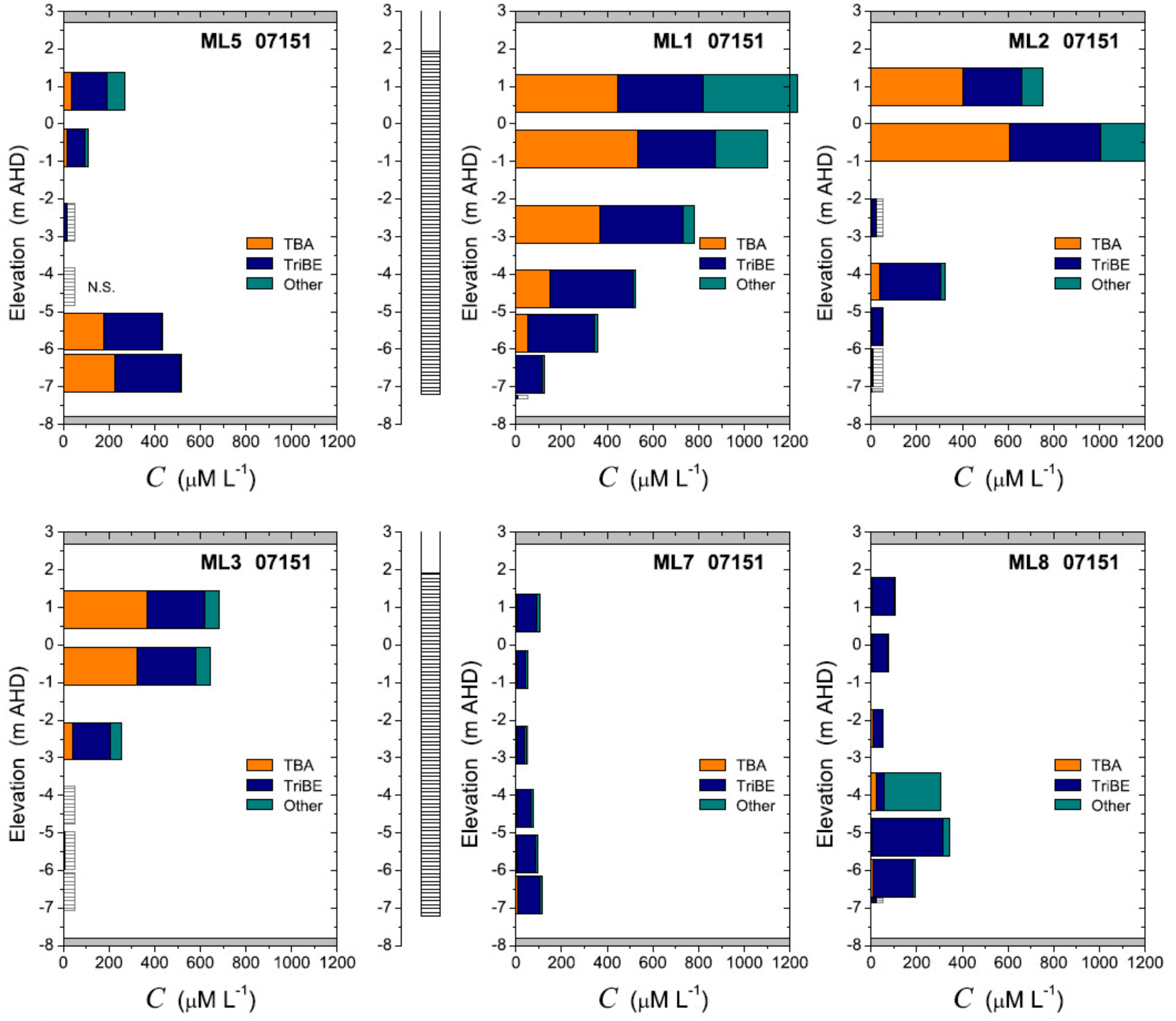


Figure 4-7. Distribution of brominated compounds in source zone from multi-level monitoring wells

Source: Johnston et al. 2013.

4.8.3 Example 3 – Optimizing an Existing Remedial Technology

Scenario. PBA has been released from a mineral processing facility into a layered silt/sand/gravel stratigraphy (same site as in previous examples). Most of the DNAPL mass is present in the upper regions of the source zone. Low DNAPL mass estimates (from PITT – not discussed) pointed to slow source zone pumping as the remedial approach (Figure 4-8).

Uncertainties. The mass estimate was arrived at through a number of different lines of evidence; however, uncertainty resulted in an estimated lifespan for source zone DNAPL of 3–20 years.

New Data. Detailed monitoring during pilot pumping (from multilevel wells as in the previous example, and from a single centralized extraction well) was used to calibrate source depletion models (Figure 4-9).

Effects on the CSM. It was determined that flow channeling may lead to extended remediation times under a pure pumping approach. The DNAPL mass estimate was increased from 220 kg to 258–295 kg.

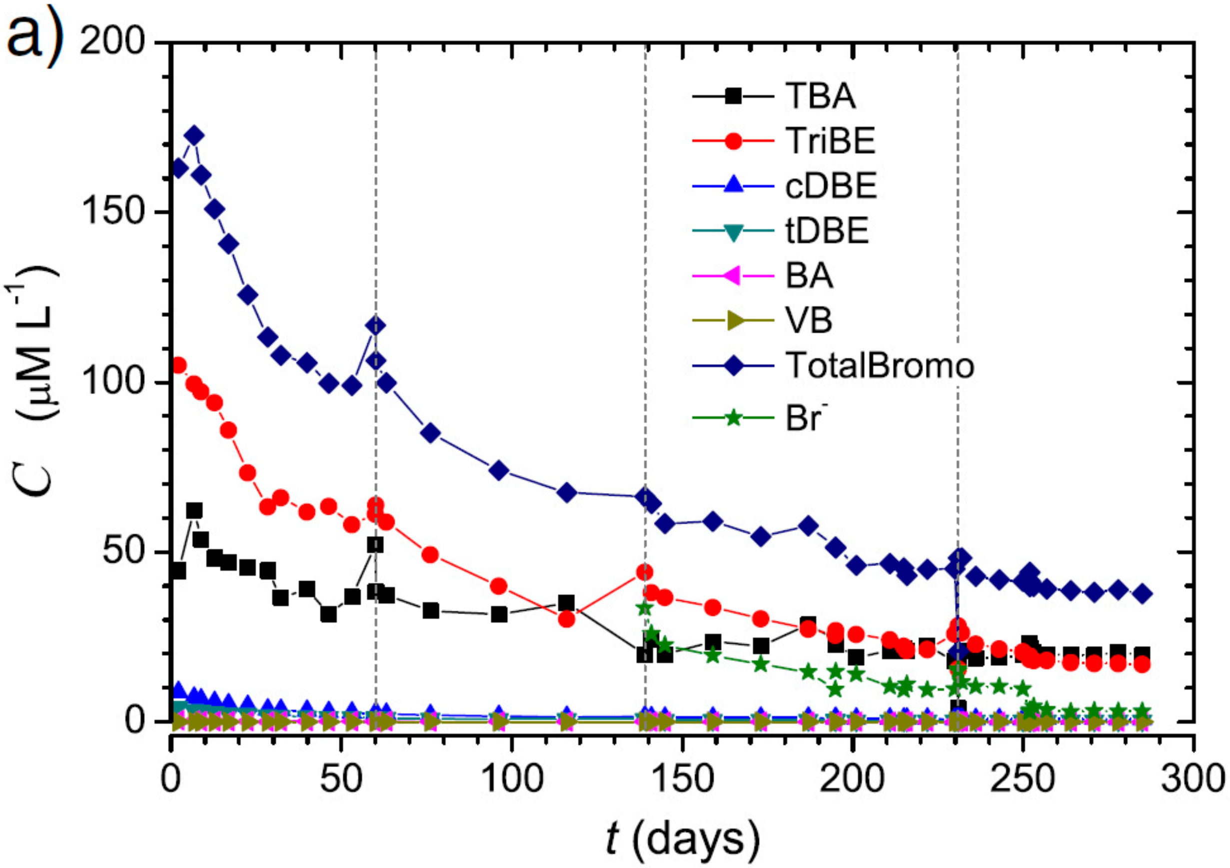


Figure 4-8. Concentration decrease in source zone under remediation pumping conditions.

Source: *Johnston et al. 2013*.

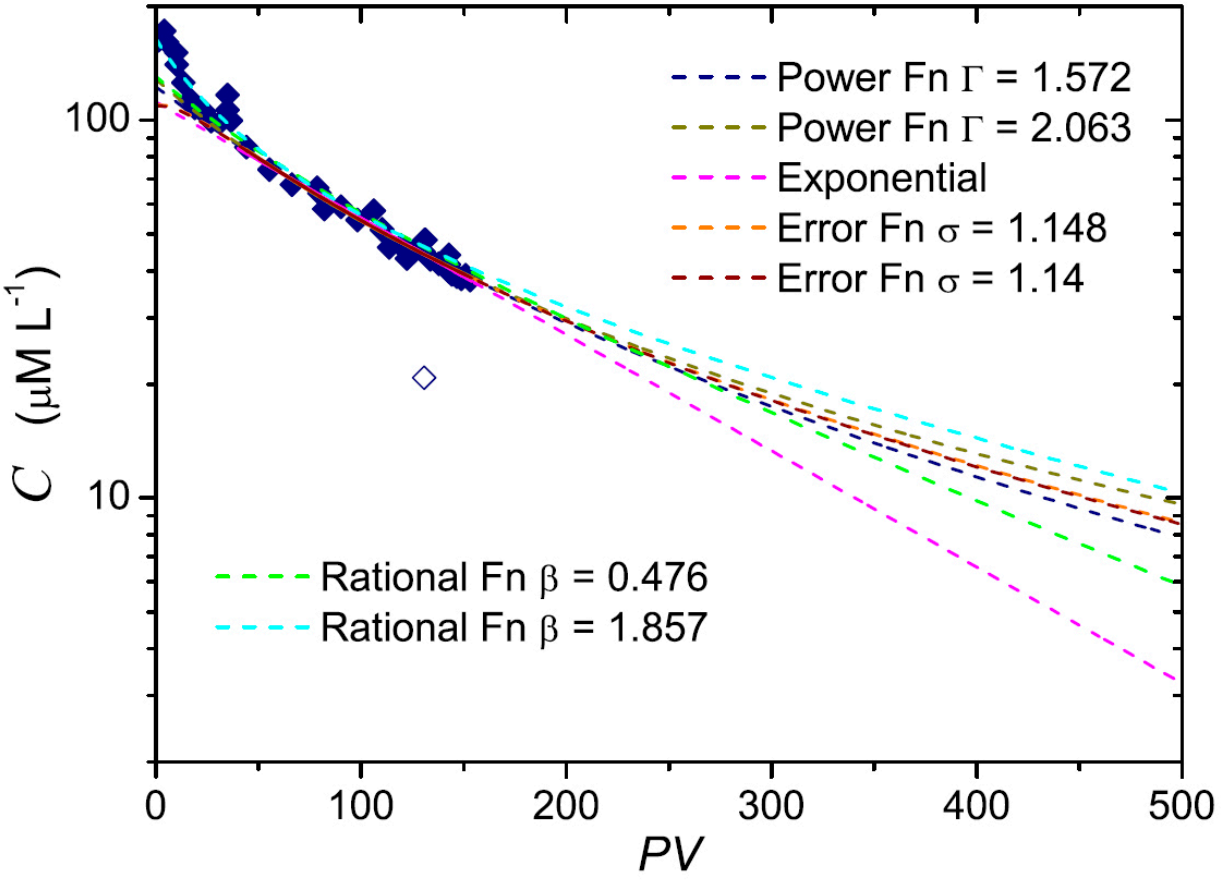


Figure 4-9. Predictions of various depletion models in source zone under remediation pumping conditions.

Source: *Johnston et al. 2013*.

4.9 Interpretative Tools

Characterization data are commonly interpreted through the use of visual representations and analytical and numerical models. Visual representations may be two- or three-dimensional representations, usually combining one or more types of characterization data to provide an increased understanding of contaminant distribution and behavior. Whichever interpretive tool is used, the results are only as accurate as the data used to prepare them and the skill of the modeler.

4.9.1 Visual Representations

Visual representations integrate different types of characterization data in a meaningful way, which can facilitate communication of complex geologic, hydrologic, and chemical concepts to both technical and nontechnical audiences (see USEPA training, “Use of Geostatistical 3-D Data

Visualization/Analysis in Superfund Remedial Action investigations”). These visual representations range from simple two-dimensional cross section with lithologic layers and groundwater elevations models to web-based dynamic geospatial-based three-dimensional models incorporating hydrological conditions and contaminant mass flux information (see example of an environmental visualization of DNAPL migration into a regional aquifer from a drum disposal area).

Although many public domain/freeware packages are available, they may be limited in types of data that can be analyzed, extent of visualization, quality of graphics, graphic output format options, and breadth of statistical analyses. Commercial packages vary widely in price, features, and technical support services. Data interpolation algorithms also vary considerably, and the same data set could be rendered differently by different software packages.

Visualization software may include some or all of the following features:

- time series
- contouring
- contouring with time series
- two- and three-dimensional playback loops of specified time frames for the following parameters:
    - groundwater flow direction
    - constituent concentration
    - groundwater velocity
    - mass flux and discharge
    - atmospheric pressure
    - transect slices
    - statistical controls
- importation and integration of data with geo-referenced maps

The evaluation of high-resolution data sets and the integration of newly developed data with lower-resolution legacy site data is particulary challenging. The use of statistical data evaluation tools to interpret data requires a high-resolution data set in both the vertical and horizontal dimensions. Many tools develop high-resolution vertical data sets, but it is not always cost effective to generate high-resolution horizontal data sets. Plumes are rarely characterized using a grid approach; more commonly, a transect approach is used. When using transects to characterize sites, it is possible to accurately interpret data within a single transect, but often it is not possible to interpolate data between transects with a high degree of accuracy.

The use of statistical data evaluation tools to interpret data may be considered a relatively objective means of interpreting site data; however, it is possible to adjust the manner in which the data are interpreted and presented. To do so in a defensible fashion requires some knowledge of geostatistics. Alternatively, a statistical tool can be used to develop a visually appealing rendering of site data that may not be statistically justified, but that is consistent with a subjective interpretation of a collaborative data set from the site.

Collaborative data sets are generated when multiple tools are used at a single site. This is commonly the case when both historical and newly generated data are used to develop a rigorous CSM. Collaborative data sets are also developed at sites where a variety of tools are used (for example, a combination of qualitative screening tools and quantitative confirmation tools). In such cases, it may not be possible to use statistical data evaluation tools to support data interpretation or visualization, and it may be necessary to subjectively interpret the various types of data and present them in plan or cross-sectional views using traditional data presentation tools (for example, CAD or GIS).

4.9.2 Tools and Models

Various analytical and numerical models are available to help interpret data (past and present) to refine a CSM. Analytical models can range from simple equations to more complex equations that are evaluated using spreadsheet tools, and they can be used by a wide range of practitioners. Numerical models are typically used by practitioners with a more specialized background and generally involve more sophisticated input data sets.

Analytical and numerical models provide a simplified representation of complex conditions that occur in the field. While uncertainty is involved with applications of these models, tangible benefits can be gained by using these tools, such as an enhanced understanding of physical and chemical conditions in the subsurface, range of remediation time frames that can be expected, and range of behaviors to expect during or after implementation of a remediation system.

Analytical or numerical models can be used to estimate the following areas of analysis:

- NAPL source zone delineation
- distribution of mass contained in a NAPL or a diffusive (low-permeability) source zone
- current source strength (that is, mass discharge leaving a source zone) over time, and the past and potential future rates of decline in source strength
- attenuation rates downgradient of a NAPL source zone
- rate of enhanced NAPL source strength depletion associated with remediation
- time-varying ratios of solute concentrations adjacent to a source zone for multicomponent NAPLs as a result of natural or enhanced dissolution
- number of orders of magnitude reduction in source strength expected to occur for a given in situ remediation technology
- time frame for partial or more complete NAPL remediation
- time frame for back-diffusion to cease causing exceedances of groundwater cleanup criteria
- plume behavior in response to a reduction in source strength

4.9.2.1 SourceDK

SourceDK is a planning-level screening model for estimating groundwater remediation time frames and the uncertainties associated with the estimated time frame (Farhat et al. 2012). In this document, *remediation time frame* is the time required for the high-concentration source zones at a site to reach a certain target concentration. It is public-domain software developed for the Air Force Center for Engineering and the Environment by GSI Environmental, Inc. (GSI). SourceDK consists of three tiers, as discussed below.

- **Tier 1** – Extrapolation. Source zones that have extended records of DNAPL site characterization data vs. time can be analyzed using the Tier 1 extrapolation tool. With this tool, log concentration vs. time is plotted and then extrapolated to estimate how long it will take to achieve a cleanup goal, assuming the current trend continues. This tool also provides the 90% and 95% confidence level in the estimate of the time to achieve the cleanup goal.
- **Tier 2** – Box Model. In this tier, the simple box model developed for the BIOSCREEN model has been enhanced to include source mass estimation software and other features. The box model estimates source attenuation from a source mass estimate, mass flux of constituents leaving the source zone, and biodegradation processes in the source zone. The uncertainty in the source lifetime estimate is also provided.
- **Tier 3** – Process Models. This tier employs more detailed fundamental process-based equations to determine the time and amount of naturally flowing groundwater required to flush out dissolved-phase and NAPL-dominated constituents from the source zone.

4.9.2.2 REMChlor and PREMChlor

REMChlor (Remediation Evaluation Model for Chlorinated Solvents) is a contaminant source model based on a power function relationship between source mass and source discharge, and it can consider partial source remediation at any time after the initial release. The source model serves as a time-dependent mass flux boundary condition to the analytical plume model, where flow is assumed to be one-dimensional. The plume model simulates first-order sequential decay and production of several species. The decay rates and parent-daughter yield coefficients are variable functions of time and distance. This approach allows for flexible simulation of enhanced plume degradation that may be temporary in time and limited in space, and which may have different effects on different contaminant species in the decay chain. Cancer risks posed by carcinogenic species in the plume are calculated assuming that the contaminated water is used in a house for drinking, bathing, and other household uses.

PREMChlor is a probabilistic version of the REMChlor model. DNAPL site characterization data can be used to develop a potential *glide path* for either monitored natural attenuation or for remediation projects that can be compared against future DNAPL site characterization data. Sites where the future data compare well against the glide path have adequate CSMs, while sites where the future data deviate against the glide path may need review and adjustment of the current CSM.

4.9.2.3 BIOBALANCE

The BIOBALANCE Toolkit is a mass-balance-based modeling/data analysis system that allows the user to perform the following tasks:

- assess the stability of plumes originating from both vadose and submerged source zones
- evaluate plume stability (time and size) using an iterative approach that solves equations in BIOCHLOR and documents the relative contributions of various attenuation mechanisms
- examine the sustainability of anaerobic degradation processes based on an approximate balance of electron acceptor and electron donor
- provide an overarching accounting of mass balance results from the various modules in the form of a summary report

BIOBALANCE can help DNAPL site managers better interpret and understand their DNAPL site characterization data using one or more of the following modules: Source Module, Competition Module, Donor Module, and Plume Module.

4.9.2.4 Monitoring and Remediation Optimization System

The Monitoring and Remediation Optimization System (MAROS) methodology allows users to apply statistical techniques to existing site characterization data to suggest if and where improvements to current monitoring system are needed. These improvements include changes to the monitoring frequency, parameters evaluated, and the number and location of groundwater monitoring wells. The software uses both statistical plume analyses (parametric and nonparametric trend analysis) developed by GSI, and allows users to enter external plume information (empirical or modeling results) for the site. These analyses allow recommendations on future sampling frequency, location, and density to optimize the current site monitoring network while maintaining adequate delineation of the plume as well as knowledge of the plume state over time to meet future site-specific compliance monitoring goals.

4.9.2.5 Mass Flux Toolkit

Recently, there has been increased emphasis on the use of mass flux and mass discharge concepts for DNAPL site characterization (ITRC 2010, ITRC 2011b). The Mass Flux Toolkit is an easy-to-use, free software tool that compares different mass flux/mass discharge approaches, calculates mass discharge from transect data, and applies mass discharge to manage groundwater plumes. The Mass Flux Toolkit allows users to calculate the mass discharge across one or more transects of a plume and plot mass discharge versus distance to show the effect of remediation and effect of natural attenuation processes. Three types of uncertainty analysis are included: uncertainty range due to interpolation; uncertainty due to the variability in the input data using a Monte Carlo-like analysis; and an uncertainty analysis that shows the dependency of the mass discharge estimate on data from each monitoring point.

4.9.2.6 Matrix Diffusion Toolkit

The Matrix Diffusion Toolkit is an easy-to-use, comprehensive, free software tool that can assist in effectively and efficiently estimating the effects of matrix diffusion at a site and then transferring the results to stakeholders. The software can also assist project managers in determining if remediation goals are achievable in the short term. It can be applied to most sites with heterogeneity in the subsurface, with DNAPL, and where persistent groundwater contaminant concentrations have been observed after source-zone remediation.

The Matrix Diffusion Toolkit is a valuable resource for the development of CSMs, supporting site characterization efforts, planning remedial designs, and determining if matrix diffusion will affect remediation goals for contaminated groundwater sites. The software can assist site personnel in updating or creating a more accurate CSM, which will enable them to determine whether matrix diffusion processes are significant enough to cause rebounding groundwater concentrations of downgradient plume concentrations above remediation goals after plume remediation or isolation is complete. Having this information available before a remedy is implemented can assist site decision makers in selecting more appropriate remedies and effectively and efficiently addressing the potential issues of matrix diffusion with regulators. Furthermore, addressing extended remediation time frames caused by matrix diffusion leads to project cost savings.

5.0 REGULATORY PERSPECTIVES

Although many regulators are receptive to the advanced site characterization information provided by the ISC approach and newer characterization tools, some regulators may not be comfortable with the departure from standard site characterization practices. For regulatory agency personnel who have been operating under what may now be considered outdated conceptual models for subsurface contamination, there is a clear challenge to incorporate the newer views of contaminant behavior into ongoing cleanups. A key area of potential conflict for regulators is the use of potentially less accurate but less expensive characterization and analytical techniques. In many circumstances a high-resolution, high-density data set composed of slightly less accurate data (such as colorimetric test kit data or vapor-phase sampling) can reveal more about a site than a much more limited amount of extremely high-quality data (such as Contract Laboratory Program [CLP] data); however, some activities require more precise data (for example, compliance/site closure).

This chapter discusses some of the potential regulatory acceptance issues associated with the advanced DNAPL site characterization methods—including the new tools and technologies used to develop a more detailed CSM; the types of analyses, decisions, and responses associated with the various types of data collection (which vary depending on site and project circumstances); and reconciling the advancements in site characterization with current regulatory expectations and requirements.

5.1 Regulatory Challenges

As discussed above, many of the regulatory challenges regarding advanced site characterization approaches and tools result from unfamiliarity with, and a lack of understanding of, the new methods and changing knowledge base. Some of the prominent issues are discussed below.

5.1.1 Lack of Familiarity and Understanding of Subsurface Dynamics

The advanced understanding of subsurface contaminant behavior (Chapter 3) has yet to be promulgated on a scale sufficient to allow most regulators, as well as investigation/remediation practitioners, to benefit from the new methods and technologies. The improved understanding of subsurface dynamics—provided in the Key Elements (Chapter 4) of *Integrated DNAPL Site Characterization Strategies*—should be made readily available to regulators. This web-based guidance and the ITRC's free internet-based training (IBT) is a major step in providing the understanding necessary to put the ISC approach and the use of advanced characterization tools into broad practice.

5.1.2 Objectives-Based Characterization

Many regulators have been accustomed to using qualitative, general site characterization objectives in developing CSMs. Chapter 4 describes the development of specific data collection objectives based on understanding a site's uncertainty and the spatial resolution (scale) necessary to adequately develop and refine a CSM. Using this approach, characterization activities can be appropriately driven by the objectives, and the objectives can be made as clear, focused, and specific as possible. ITRC champions the use of SMART objectives for remediation of chlorinated solvent-contaminated sites, with or without DNAPL (ITRC 2011b). Although characterization attributes are not necessarily required to meet all SMART objectives, they should be as specific as possible (given what is and is not known about the site) so that a more accurate CSM can be developed. Although objectives-based characterization can be challenging for regulators who are unaccustomed to the newer approach, their concerns can be alleviated by learning how to develop site-specific objectives (ITRC 2011b).

5.1.3 Mass Discharge as a Regulatory Metric

An additional challenge for regulators involves the need to link metrics to each cleanup objective. Regulations rely on the use of concentration-based standards; however, concentration data alone may not provide a sound basis for defining the point at which a cleanup objective is attained. Thus, estimating mass discharge may provide more meaningful supportive data, even though the role of mass flux and mass discharge information in the regulatory decision framework is not clear or consistent. Because mass discharge as a regulatory metric is a fairly new concept (ITRC 2010), many regulators are unclear about how it might relate to concentration-based standards as well as how to use such mass discharge estimates in decision making.

Chapter 3 of ITRC (ITRC 2010) and the associated IBT discuss the benefits and challenges of mass flux and mass discharge data; ITRC (2011b) also discusses the application of mass flux and mass discharge data into DNAPL remediation projects. For example, mass flux and mass discharge data can be used to measure the effectiveness of source remediation; however, defining the role of these values in remedial decision making and performance monitoring remains a challenge, at least in part because the regulatory benefits are not always clear and their role as a potential regulatory metric is not yet consistently accepted. Because of their potential usefulness, site data collection objectives and data gathering activities should consider mass flux and mass discharge data as a more central part of site investigations than they were in the past.

5.1.4 Use of Nontraditional Characterization Methods

Many regulators are accustomed to traditional investigative methods such as using groundwater monitoring wells to collect water samples and borings to collect soil and soil gas samples. In addition, traditional methods are sometimes incorporated into state regulations or reimbursement criteria for liability trust fund. As discussed above, improved understanding of subsurface dynamics requires newer, less traditional characterization methods to define site-specific dynamics; however, the resulting data sets from multiple characterization tools must be integrated with traditional data, such as groundwater monitoring data. Furthermore, as discussed in Chapter 4, monitoring wells are not recommended as primary characterization tools in unconsolidated aquifers because of vertical and volumetric averaging of contaminant concentrations in the boreholes. In many cases, apparent regulatory impediments to the use of newer characterization tools may be addressed through the use of collaborative data sets as well as discretionary use of alternative methods that would result in improved site characterization.

Chapter 4 also discussed another recent characterization method that has been increasingly applied over the past decade: the iterative investigative approach. The iterative approach is presented in the ITRC Triad document (ITRC 2003). While developing this guidance, the iterative approach (involving systematic planning using real-time data and dynamic work plans) has gained much wider acceptance and has been used extensively in the area of emergency response. Use of the iterative approach during characterization of DNAPL sites can determine the cost-effectiveness of the investigation.

As the Triad guidance and IBT training are further promulgated and iterative investigations become more commonplace, these methods will become more widely accepted. In particular, there is a need for more examples of iterative investigations, successful site characterization, and remediation using these newer methods.

A third area of nontraditional characterization is the use of potentially less accurate but also less expensive characterization and analytical techniques (many of which are described in this document). The use of such tools is an important component of ISC, allowing real-time or near real-time data to guide the site investigation. Another considerable advantage of using these newer methods is that, in many cases, a higher-resolution, higher-density data set composed of slightly less accurate data (such as colorimetric test kit data or vapor-phase sampling of groundwater samples) can reveal much more about a site than can a more limited amount of extremely high-quality data (such as CLP-type analytical data). As discussed in the next section, the results of these methods can be used collaboratively with more traditional laboratory data, and they do not preclude the use of traditional laboratory data for compliance/site closure activities.

5.1.5 Use of Collaborative Data Sets to Refine the CSM

Guidance documents historically have not discussed the use of collaborative data sets (Section 4.3) for developing CSMs, and the reliance on such incomplete guidance has not allowed for the development of effective site-specific CSMs. For example, some states may require the use of SW-846 in the collection and analysis of samples from investigations of contaminated sites; however, several of the characterization methods discussed earlier might not meet all of the requirements found in SW-846. Some data, although obtained in a manner not included in SW-846, could provide useful information for site characterization; thus, CSM development would be less efficient if such data were not accepted by regulators. Through integration of all data types, collaborative data sets can be generated and used to enhance the completeness of the CSM.

Data sets that might not be effective in project decision making when considered solely could, when considered together, manage all relevant relational, sampling, and analytical uncertainties to the degree necessary to support defensible decision making. Typically, less expensive analytical methods are used to generate an effective sampling density and real-time turnaround so that an accurate CSM can be constructed and sampling uncertainties managed. Any analytical uncertainty remaining from the data set is then managed by analyzing selected samples (sample representativeness are established via field-based methods) with more rigorous analytical methods to obtain lower quantification limits and analyte-specific results. Collaborative data sets often are not directly comparable, and, if not, should not be mathematically combined. This may be considered a type of weight-of-evidence approach for CSM development. Collaborative data sets are also used to develop field-to-laboratory correlations and field-based decision criteria. This multiple-lines-of-evidence approach enables the CSM to provide a better picture of contaminant transport, storage, and attenuation.

Once again, it appears that this can be addressed by demonstrating to the regulators the effectiveness of using collaborative data sets. This guidance and the ITRC Triad guidance provide documentation on the usefulness of this approach and are provided, along with IBT, to help foster a more informed regulatory community.

5.1.6 Differentiating Between Matrix Storage and DNAPL

In choosing an effective source remedy, it is necessary to differentiate between the residual DNAPL area and the aqueous phase contamination associated with matrix storage. Treatment of DNAPL in a transmissive zone is much different than treatment of back-diffusion aqueous phase contamination from low-transmission zones. If the objective is to treat residual DNAPL, the areal extent of the DNAPL must be understood, and a technology that will destroy, degrade, or mobilize the residual is needed. Where matrix storage contributes some or all of the contamination through back-diffusion, other technologies are required to treat the aqueous phase contamination in the transmissive zone or the stored contamination in the low-permeability zone. The Tool Selection Worksheet offers information on tools that can collect geology, hydrogeology, and chemistry data to make these distinctions; Appendix G provides case examples that can help site managers determine whether their site is dominated by matrix diffusion. Providing the regulators with information and case studies describing the advantages and limitations of the tools that provide the data needed to differentiate between matrix storage of contaminants and DNAPL will help in gaining their acceptance.

5.2 Regulatory Benefits of Integrated DNAPL Site Characterization

As much as they are a challenge, there are great benefits to accepting advanced characterization methods and gaining familiarity with collaborative data sets. Current groundwater regulatory policies generally focus on (1) controlling contaminant sources and migration; and (2) protecting/restoring beneficial uses. Early remediation efforts for DNAPL sites demonstrated that pump and treat (groundwater extraction) for contaminant mass removal is inefficient, particularly for depleting contaminant sources where NAPL is present. Furthermore, conventional long-screened monitoring wells yield sample results that are flow-weighted averages (USEPA 2004) and thus miss important spatial variability, presenting regulators with an inaccurate CSM.

The benefits of ISC are described in Section 1.3. For regulators, the most valuable is the environmental benefit of *greater performing remedies*. Other important benefits to regulators are as follows:

- cost-effectiveness and reduction of financial burdens for responsible parties
- higher resolution in the CSM, enhancing stakeholder understanding
- less uncertainty, resulting in more defensible remedy decisions
- greater environmental benefit resulting from better performing remedies

Improved characterization methods, with representative resolution, can clarify non-uniform source distribution, subsurface heterogeneities, and geochemical variations. This should produce a more refined CSM with a more efficient allocation of resources, resulting in greater accuracy in subsurface characterization. These methods will improve remedial design and monitoring and result in a shorter remedial time frame and reduced life cycle costs.

As illustrated in Figure 5-1, a more accurate picture of the subsurface, developed using an ISC approach, gives regulators a higher level of confidence upon which to make remedy decisions.

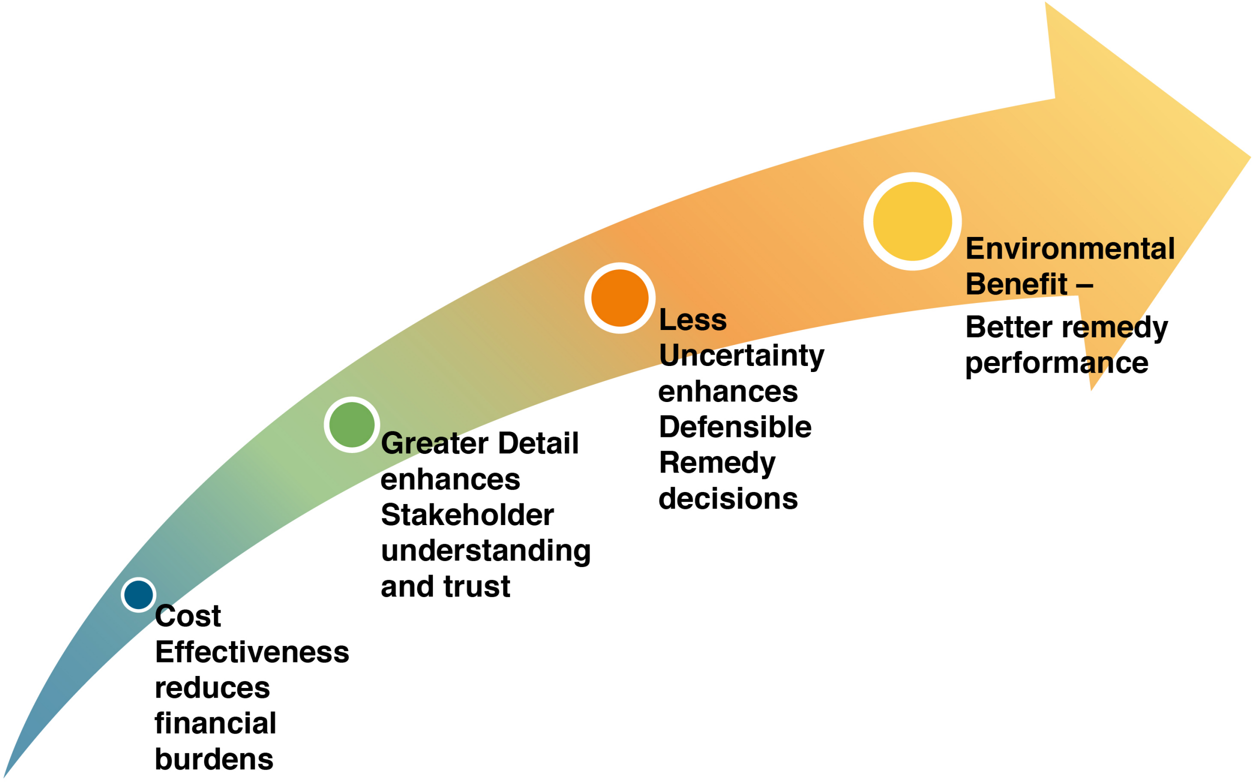


Figure 5-1. Benefits of integrated DNAPL site characterization.

5.3 USEPA Priority Actions in Climate Adaptation

The USEPA has released a draft *Climate Change Adaptation Implementation Plan* (USEPA 2014b). As the USEPA moves forward in identifying priority actions to address potential vulnerabilities to climate change, some of the action areas being discussed include (1) increasing engineering controls for contaminant migration at sites where a remedy is constructed; and (2) evaluating remedy effectiveness. These two areas score *high vulnerability* when exposed to a greater incidence of flooding, hurricanes, drought, wildfires, or other consequences of climate change. The use of ISC may provide states and tribes with an increased understanding of specific vulnerabilities for sites in drought areas, which could affect fractured subsurface clays, or changes to in situ treatment technologies if prolonged flooding occurs.

5.4 Public Education and Outreach

There is an inherent challenge in explaining the data-dense outputs of the new characterization methods. Traditional characterization approaches, relying on relatively few soil, sediment, and groundwater samples, were often presented graphically with intense extrapolation between data points. In any outreach setting, higher resolution and attention to the development of scientifically based CSM allows all interested parties to discuss the future of a site based on science; contaminant transport; and long-term protection of drinking water resources, human health, surface water, and the environment.

This challenge can be met by the new ISC approach, which relies on measurements that present an accurate, scientifically based characterization of contaminants' current effect on the environment as well as insight into how they may behave in the future. Developing remedial goals based on reliable characterization and science-based remedial decision making will generate acceptable outcomes for all interested parties; however, the process must adhere to resource protection, human health and the environment, and the regulatory principles of state and federal programs.

Presentation of the data to the public can be challenging; however, because subsurface cross sections are now developed with frequent data collection points, providing proper representation of preferential flow paths, the public can have greater confidence in the contaminant representations. Where conventional tools and illustrations fell short, the newer three-dimensional representations and fence diagrams that accurately represent the density of data as well as all data collection points present a much more precise CSM. The accuracy and visual aspect of the presentation of data will allow interested parties to easily see what is happening at the site and to trust in the decision making and remedial approach.

Presentation techniques should include the real-time data collected in the field, the science supporting the technology, and the defensible science-based conclusions that can be drawn from the data. Statistical representation of the confidence attributes associated with analytical and data density should be a part of any presentation that supports a CSM. Explanations of the technology, which data it collects, and how it contributes to the CSM should be presented in a format that is easily understood by the public. Public acceptance and understanding of the difficulties with the site will be enhanced if the data, CSM, and interpretation are presented with transparency and in a format that sequentially lays out the decision making processes.

6.0 STAKEHOLDER AND TRIBAL PERSPECTIVES

The ISC approach outlined in this guidance includes a process for selecting and applying new tools and approaches to characterize sites contaminated by DNAPLs. The science supporting these technologies and approaches is based on quantifying how geology, chemistry, and hydrogeology interact to influence contaminant transport in rock, soil, sediments, and groundwater. These data are collected at a resolution adequate to reduce the uncertainty of contaminant fate and transport to an acceptable level for all parties involved in the characterization of a site. This new ISC approach allows more detailed and representative interpretations without what has been traditionally referred to as data gaps from conventional limited data investigation techniques. It should therefore follow that regulatory performance and remedies implemented to protect human health and the environment would be greatly improved through the application of these investigative strategies and technologies. Stakeholders are likely to embrace these tools and analysis techniques because they are specifically designed to better characterize and define contaminated sites to more effectively clean them up.

The ISC approach allows administrative agencies to compel more protective and cost-effective remedies that do not involve loss of public groundwater resources. It also helps to reduce the danger from direct contact, ingestion, and indoor inhalation pathways. With the new fate and transport concepts and characterization methods/tools, stakeholders can expect to sustain resources, cost-effectively remediate sources, and prevent the loss of regional aquifer systems due to failed remedies. The ISC approach aids in sustainability to balance environmental, economic, and social stakeholder concerns (ITRC *Green and Sustainable Remediation*, 2011, Table 3-2).

6.1 Economy and Long-Term Resource Protection Concerns

Poor remedial decisions, based on limited data, have put tremendous long-term economic burdens on communities due to loss of property values, lower development potential, institutional restrictions on aquifers, and long-term subsurface contamination. Quite often, the aesthetic quality of an aquifer is diminished on a long-term basis downgradient of contaminated sites, which essentially makes the aquifer unusable for domestic water supplies and much more expensive to treat for municipal water supplies. These treatment costs are often passed on to the individual property owner and the community.

The ISC approach promotes targeted remediation and reduction of source mass, which will immediately reduce risk and the long-term remediation costs incurred by remedies that proceed with little or no source control. The stakeholders desire this approach as it will minimize the loss of groundwater through failed remedies and institutional controls, and it will reduce the economic loss of development potential of large tracts of land.

Improved site subsurface characterization will lead to more appropriate remedial decisions and reduce the damage to precious groundwater resources. Thus, the proper use and application of the approaches and technologies presented in this document will lead to greater protection of human health and the environment by ensuring that groundwater and other natural resources critical to health, commerce, economic vitality, and quality of life continue to be available for future generations.

6.2 Stakeholder Views Regarding Remedial Decisions

The proper use and application of this approach, as viewed by stakeholders, should promote more protective and proactive remedies at many sites that require periodic assessment of their protection of human health and the environment according to state and federal law and regulation. Stakeholders openly embrace this approach when it is objectively presented and tied to remedial actions objectives that restore aquifers, protect future groundwater resources, and reduce human health and environmental risk.

The ISC approach is clearly capable of providing information that can help determine whether an existing remedy is protective of human health and the environment, whether financial resources are being wasted in the long term on non-cost-effective remedies, and if source control or a multitude of other cost-saving actions can be implemented.

Both public- and private-sector monetary resources should focus on returning resources to a useful and economically productive status. The current regulatory model of restricting the use of and access to resources (that is, institutional controls) can be a long-term stigma to the community, and may even prevent the return of the community to economic prosperity. Protection of human health and the environment go hand-in-hand with economic viability and community prosperity. There is no need to sacrifice either of these goals to achieve a cost-effective and successful remedy.

6.3 Stakeholder Acceptance

The public trust has been shaken by inadequate site characterizations and extensive use of risk-based decision making to justify large-scale, long-term natural attenuation remedies for aquifers. In many cases, the traditional approach to characterization and decision making at DNAPL sites has led to non-effective remedies, allowing for the long-term destruction of groundwater resources, and the implementation of institutional controls that restrict the use of regional and local groundwater resources. Aquifers have been taken from current and future generations unnecessarily in many instances. In short, the public has been waiting for a more proactive approach to cleaning up contaminated sites.

Source control and proactive remediation is a foreseeable outcome of the proper use of ISC. The ISC approach should lead to remedial decisions that are protective of human health and the environment, including natural resources, and that gain the trust and support of all stakeholders.

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APPENDIX A. APPLICATION OF INTEGRATED SITE CHARACTERIZATION USING OBJECTIVES-BASED CHARACTERIZATION TECHNIQUES

Historically, characterization efforts were based largely on soil borings for soil sampling and monitoring wells for ground and nonaqueous phase liquid sampling. The bias of collecting soil samples from the unsaturated zone limited the ability to understand contaminant mass distribution, especially in finer-grained soils where groundwater sampling is impractical due to low yields.

Conventional soil and groundwater methods typically used a linear strategy of relatively coarse subsurface interval sampling—for example, one sample every 5 feet for soils or a 10-foot well screen for monitoring wells. This historical convention involved subjecting all samples to rigorous quality control to ensure precision and accuracy. This method was costly and it reinforced the paradigm of collecting relatively few (but very high-quality) samples. The primary drawback, however, was that the sampling frequency was not based on the scale of variability or the process controlling the distribution of contaminants in the subsurface—that is, hydrostratigraphy. Thus, conceptual site models (CSMs) developed from conventional characterization methods, while often founded in precise data, provided an inaccurate understanding of the nature and distribution of contaminant mass.

The newer direct-sensing tools (for example, membrane interface probes, and optical screening tools) provide practitioners with mapping capability at resolutions that were previously unattainable. Integrated site characterization takes advantage of new tools to characterize the site stratigraphy and contaminant distribution at high-resolution (up to centimeter scale) in a nearly real-time manner; however, real-time, high-resolution sampling is only part of the integrated site characterization approach. The key is applying the methods in the context of a dense nonaqueous phase liquid (DNAPL) CSM that evolves as several lines of inquiry are combined and iteratively refined during the project life cycle—through site investigation, remedy design, and remedy optimization.

A.1 Step 1 - Evaluate existing DNAPL CSMs using modern DNAPL concepts and depositional models

Over the past several decades, data have been collected and some form of CSM has been developed for many complex groundwater sites. The quality of the collected data, level of interpretation, and sophistication of the resulting CSMs for these sites has varied considerably. When scrutiny of these sites increases due to regulatory or commercial interest, financial prudence dictates that the existing site data and CSM be evaluated in light of modern concepts of DNAPL behavior to maximize the efficiency of any additional required data collection. This process includes the phased approach identified in Chapter 4, with examples provided below.

A.1.1 Phase I - Understand available database and implications for lithologic, structural, or anthropogenic heterogeneity

This review phase is focused on establishing what is known about the scales of lithologic heterogeneity laterally and vertically, understanding the hydrostratigraphic framework and how it was constructed, and determining the impact of existing data resolution on the reliability and usability of the existing CSM. The steps to take, and associated questions to ask, are outlined below.

Existing lithologic data vintages should be reviewed and vertical resolution determined. Otherwise stated, are there continuous lithologic data in the form of high-quality continuous core descriptions? Logs of such cores may contain valuable information, including bedding thickness, degree of interbedding of fine- and coarse-grained lithology, indications of clay types and content, and descriptions of sedimentary structures. Do vintage cone penetrometer data exist, or only 18 inch samples every 5 feet with United Soil Classification System (USCS) classification? Can cone penetrometer data be calibrated against lithologic descriptions or analytical data, and thus serve as a proxy for lithologic data?

In cases where fracture porosity dominates fluid flow and contaminant transport, have sufficient data been acquired to characterize the fractures in terms of spatial orientation, distribution, and potential to transport or store contaminants?

Once there is an understanding of the different vintages of data collected, the data can be ranked according to reliability and resolution so that continuous (high-resolution) data, as well as logs with good sedimentologic/stratigraphic detail, can be given greater weight in the analysis of the existing CSM.

A.1.2 Phase II - Critically review the existing CSM in the context of modern DNAPL concepts, depositional models, and site data limitations

Once the strengths and weaknesses and vertical and lateral resolution of the existing lithology data set are understood, hydrogeologic and chemistry data can be accurately viewed and the existing CSM can be assessed. Critical to the CSM review is determining whether the depositional environment has been sufficiently considered and whether the architecture depicted by the CSM is consistent with depositional models corresponding to that environment. An integrated, geologically defensible CSM incorporates depositional models and provides a powerful roadmap for evaluating any additional data and identifying the correct amount and type of data required to answer the questions and advance the site status. While the importance of adhering to classical geologic methods and principles has been discussed in the groundwater remediation industry for many years, few have applied it in practice. A brief discussion of depositional environments and some practical guidance on how they can be applied to groundwater remediation data sets and CSMs is provided below. If an existing CSM shows major diversion from geologic processes and is therefore geologically infeasible, or if the CSM fails to provide an explanation for observed phenomena (that is, it contains many outlier data), a revised CSM should be developed.

The impact of depositional environment on permeability heterogeneity has long been studied in the context of hydrocarbon production. Figure A-1 shows hydrocarbon recovery plotted according to depositional environment. While this plot sparked considerable controversy, the idea that different depositional environments have inherent differences in connectivity is represented by recovery efficiency. In relation to DNAPL contamination, this can be equated to potential for matrix diffusion processes to dominate. In other words, if a DNAPL is released into a deltaic depositional system, it is expected to be more contained than in a barrier island complex, but may be more likely to become incorporated into the matrix and thus provide a long-term contaminant source. This is due to a greater degree of heterogeneity and channelization in deltaic deposits, as well as an increased percentage of fines.

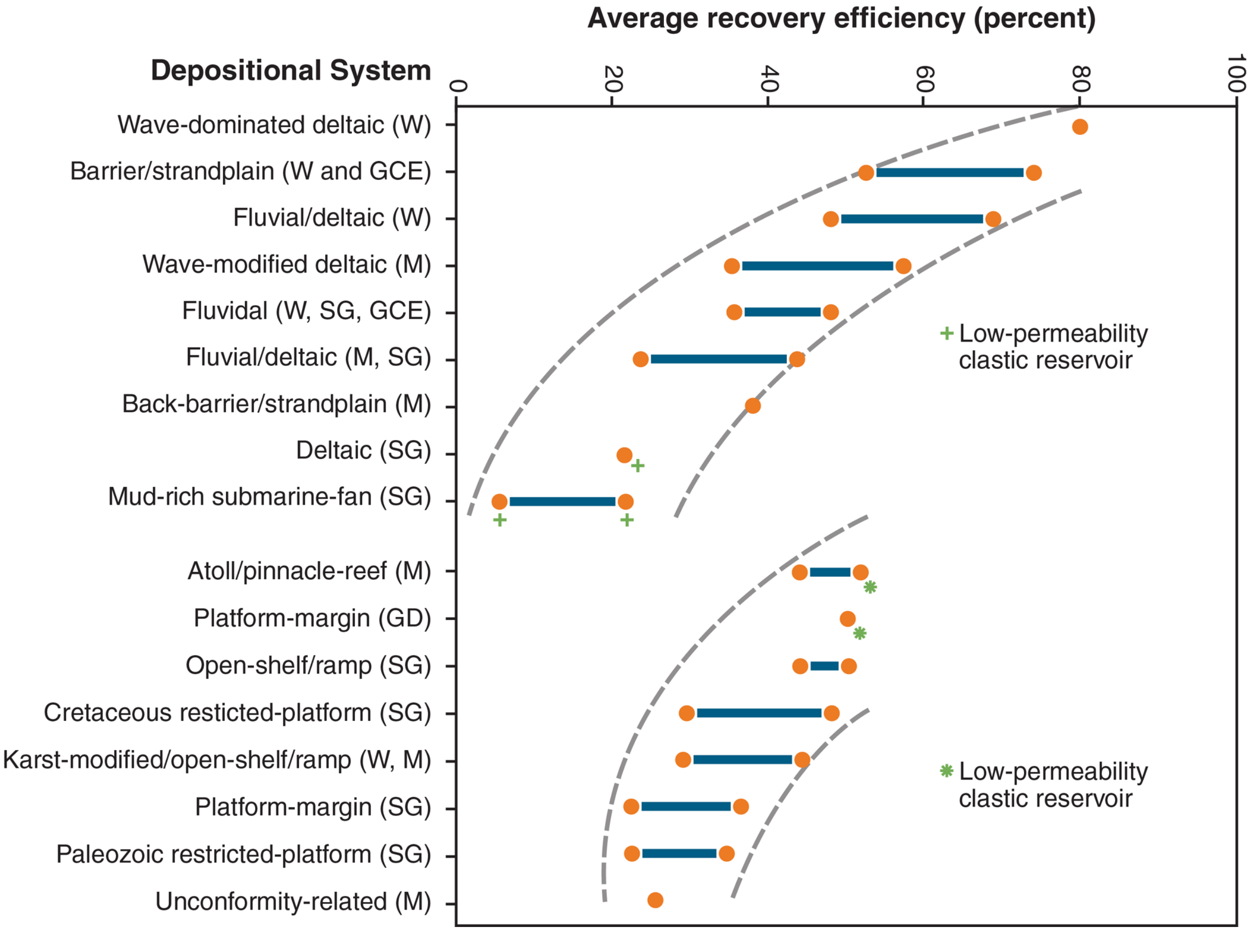
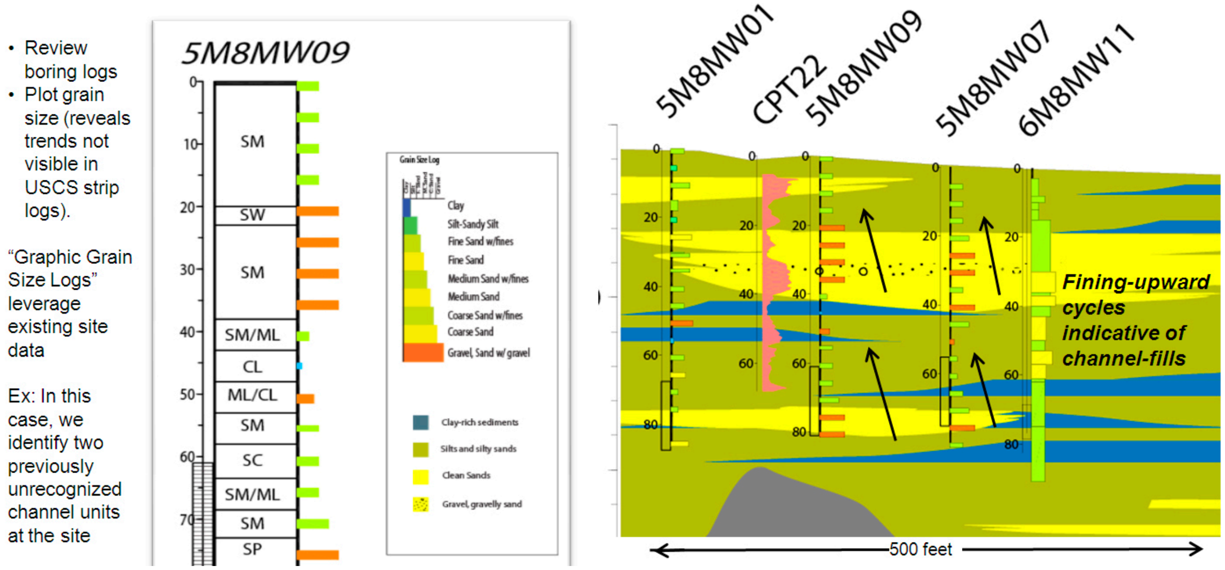


Figure A-1. Cross-plot of recovery-efficiency range versus depositional system and drive mechanism for major sandstone and carbonate reservoirs in Texas showing decreasing recovery efficiency with increasing reservoir complexity. Drive mechanisms: W - water; GCE - gas cap expansion; GD - gravity drainage; SG - solution gas; M - mixed (combination of W, GCE, and SG).

Source: Courtesy of Mike Shultz; modified from Tyler et al. (1984).

In many cases, important details recorded in vintage boring logs can be used to extract valuable stratigraphic information that can be used to develop or refine a CSM. Figure A-2 illustrates this concept.



- Review boring logs
- Plot grain size (reveals trends not visible in USCS strip logs).

"Graphic Grain Size Logs" leverage existing site data

Ex: In this case, we identify two previously unrecognized channel units at the site

Figure A-2. Grain size log.

Source: Courtesy of Mike Shultz.

At the complex site illustrated in Figure A-2, as is typical of many sites, the USCS codes were posted on well bores and used to correlate the subsurface materials, resulting in a view of the hydrostratigraphy that precluded mapping of the subsurface permeability architecture; however, when boring logs from the site were reviewed to address data outliers, it became clear that the geologist who logged the borings for monitoring well installation recorded information beyond the USCS classification. In this case, samples were taken at 5 ft intervals, and the maximum grain size identified in each sample in the boring log was posted on the cross section as deflection from the vertical axis. Two fining-upward trends were recognized, and these sequences were consistent from boring to boring. These fining-upward cycles represent two episodes of channel erosion and deposition stacked vertically, consistent with depositional models for fluvial deposits. In addition, the fluvial models predict high permeability at the bases of the channels. While not all sites have adequate data to perform such work, when possible, this frees the geologist from the limitations of the USCS classification system, and provides a means to "normalize" lithology data collected by disparate field data collection techniques over many years and by different field geologists. In this case, great value was extracted from vintage data (that were acquired at significant cost), providing a framework for any future data collection. In addition, identification of these channels led to a prediction: all channels have margins, and channel margins are finer-grained and represent likely areas for contaminant storage. When the depositional environment corresponding to a site is determined (either from regional work or site data such as the grain size trends outlined above), a host of predictions that bear directly on DNAPL site CSMs can be made. These predictions are important when planning or analyzing any high-resolution data sets (see chart below).

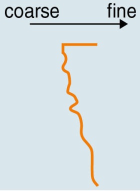
Depositional environment and typical grain size profile	Major aquifer elements and their common dimensions	Major aquitard elements and their common dimensions	Effect on CSM	Required data resolution
Alluvial Fan 	Proximal fan channels, mid-fan sheet sands, distal fringe sands X: 10^2 m–10^3 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10's m	Playa lake deposits commonly vertically separate fans X: 10^2 m–10^3 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10's m	Laterally extensive playa lake deposits can easily be missed by traditional sampling methods due to their thinness, but can vertically compartmentalize aquifers with dramatically different contaminant concentrations. Playa deposits dip basinward, at 2 to 6 degrees, leading to the potential for erroneous correlations.	High in vertical sense, medium to low in horizontal sense
Meandering Fluvial 	Channel axial fill, point bar, crevasse splays X: 1 m–10's m Y: 10^2 m–10^3 m Z: 10^{-1} m–10 m	Floodplain deposits, levee deposits, clay drapes on lateral accretion surfaces, plugs filling abandoned channels X: 10^2 m–10^3 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10's m	Due to well-sorted sand and gravel at bases of channels, permeability can be orders of magnitude higher in this zone. High risk of off-site contaminant transport due to groundwater flow controlled by channel orientation and not groundwater gradient. Local groundwater flow up to 270 degrees from regional gradient. Channel-fills highly asymmetric with cutbank characterized by sharp erosional edge and point bar characterized by interfingering with floodplain fines impacting potential for contaminant mass storage. Lateral accretion drapes can separate point bar deposits that would appear to be connected laterally.	High if site size is greater than channel widths
Braided Fluvial 	Channel axial fill, bar forms X: 1 m–10's m Y: 10 m–10^2 m Z: 10^{-1} m–1's m	Floodplain deposits, silt and clay plugs filling abandoned channels X: 10^2 m–10^3 m Y: 10's m–10^2 m Z: 10^{-1} m–1's m	Streaky" groundwater flow with isolated high-permeability zones. Overall high permeability and porosity with amalgamated channel deposits. Local groundwater flow up to 90 degrees from gradient, but typically within 45 degrees of gradient.	High, but depends on degree of amalgamation of channels determined by fines content (greater fines content results in less channel connectivity)
offshore 	Offshore bar, transgressive sand X: 10's m–10^2 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10 m	High-frequency transgressive flooding shales X: 10's m–10^2 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10 m	Laterally extensive, sand-rich deposits. Interbedded storm deposits (coarser grained) with fair-weather deposits (finer-grained) lead to high degrees of vertical heterogeneity, and low to very low Kv/Kh ratio.	Low in lateral sense, high in vertical
Near-shore, deltaic 	Shoreface (beach), in upper part, shelf in lower parts X: 10's m–10^2 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10 m	High-frequency transgressive flooding shales X: 10's m–10^2 m Y: 10^2 m–10^3 m Z: 10^{-1} m–10 m	Laterally extensive, sand-rich near-shore units in upper parts of sequences. High degree of interbedding of coarse and fine-grained units in lower parts. Silt and clay beds capping sequences dip basinward, may lead to erroneous correlations at distances of hundreds of meters to kilometers.	Low in lateral sense, high in vertical

Figure A-3. Illustration of grain size profile of depositional environments and the potential effect that grain size distribution may have on CSMs.

Source: Courtesy of Mike Shultz.

Well screens and relationships to stratigraphy should be reviewed and hydrogeologic data (for example, pump tests) should be integrated to determine whether permeability can be directly correlated with lithology and chemistry data. In addition to validating the association of hydrostratigraphic units, this will also determine the potential for fine-grained units to be long-term contributors to a dissolved-phase plume. If the lithology and geology are simple, 10 ft well screens may be adequate; if the geology is complex, higher-resolution data may be required. For example, a well screened entirely in a coarse-grained unit may show different concentration data historically as the site evolves—that is, as contaminants become progressively incorporated into fine-grained lithologies and coarse-grained lithologies become flushed. Are lithologic data of sufficient resolution to illustrate the likely proportion of fine-grained material intersected by the screen, so that the contribution of the fine-grained intervals to any ongoing matrix diffusion sources can be determined? Accurate representation of data resolution on cross sections and maps, such as the example on Figure A-2, allows for analysis of screened intervals relative to hydrostratigraphy and identification of the degree of uncertainty not previously possible at the site.

A.1.3 Phase III - Recognize and explicitly state the shortcomings of the existing CSM to develop an efficient path forward

What interpretive liberties were taken that impact its uncertainties? Are alternative correlations possible? How would these impact the CSM?

A solid understanding of data collected and work performed at the site to date, coupled with a hydrostratigraphic framework founded on the concepts of facies and depositional environments, provides a clear picture of what is known about the subsurface and a road map for identifying data gaps and developing data collection objectives.

Data *outliers* should be identified and, if they are artifacts of data resolution, hypotheses for this should be developed.

All remedial actions, past and present, as well as any off-site conditions that impact the CSM (for example, contaminants entering the site, groundwater pumping) should be reviewed. The scale of fluctuation of the stratigraphy and contaminant distribution in the subsurface should be classified. This process requires careful definition of the data quality objectives so the proper tools can be selected to provide sufficient resolution and accuracy for classifying the behavior and distribution of contaminants and stratigraphy. Often, site-specific calibration and verification are required to determine the limits of applicability and utility of selected tools to meet screening and quantitative objectives before full-scale characterization efforts are undertaken.

In complex geologic settings, or where DNAPL is encountered, it is not possible to explicitly characterize and map the individual centimeter-scale beds comprising an interbedded facies or DNAPL ganglia in space; however, it is practical to use classical geological methods to interpret and map the stratigraphy in terms of hydrofacies (which might include mapping an interbedded zone that controls the distribution of the DNAPL ganglia in the aquifer) and to then classify and map the composite zone (which contains DNAPL). Identification of depositional environments is often possible from regional information or site information, and depositional models should be applied throughout the process.

A.2 Step 2 - Fill in the gaps

If not available in the existing CSM, the model should be refined by quantitatively linking the stratigraphy and permeability of the aquifer so that transport zones can be distinguished from storage zones and mapped across the investigation area. In essence, this phase of characterization focuses on selecting and using tools that can map the mass flux in the aquifer. This is where the application of data collection transects is required. High-resolution data collection may be necessary to ensure adequate horizontal and vertical resolution to understand transport at the site. The major historical flaw was assuming that a plume could be accurately mapped from the outside in, by stepping out at large distances from the source to map the spatial extents, without understanding how mass flux is controlled. It is important to recognize that different tools or combinations of tools are required to accurately detect and map the occurrence of DNAPL and high-concentration source zones, compared to moderate- or MCL-level concentrations in the distal portions of the plume in the subsurface. Further, different tools are required to provide quantitative measurements of dissolved-phase contaminants in permeable transport zones compared to less permeable storage zones. It should also be recognized that further specialization of characterization is required when contamination is deep, or when it occurs in different types of bedrock.

A.3 Step 3 - Map the extent of the contamination to enable definition of the source zone(s) and the distal dissolved-phase plume(s)

At this stage, the key is to use the DNAPL CSM to define data quality objectives for each zone, potentially subdivided further based on hydrostratigraphy for large plumes with complex geologic settings. Guided by the knowledge of the behavior in the transport zones and storage zones, it is possible to begin optimizing the application of tools and adapt the frequency and location of quantitative sampling necessary to delineate the source and dissolved-phase plumes. Practitioners should focus on tools that enable remedy decision making and risk assessment early in the process to avoid having to repeat quantitative sampling at field-screening locations, especially when it is impractical to correlate quantitative results with field screen measurements.

Monitoring wells as traditionally constructed and used are not recommended as primary characterization tools because of vertical and volumetric averaging of contaminant concentrations associated with this type of sampling. Bias is also introduced in how wells are sampled, because the volume and intensity of sampling further impacts the vertical and volumetric averaging, making conclusions based on monitoring wells subjective; however, the use of multilevel devices—packer and port systems allowing high-resolution characterization with traditional or emerging hydrologic characterization methods (for example, multilevel slug tests, hydraulic tomography), chemical sampling, and pumping or injection for remediation (alone or together)—allows for high-resolution characterization and remediation in wells constructed or adapted for multilevel sampling (Einarson 2006). Packers in the wells avoid concentration averaging or the migration of contaminants to new or less contaminated zones. For wells with sand packs in the annular space outside the screen, placement of bentonite rings at appropriate length intervals in the sand packs can disrupt vertical migration through this artificial high-permeability zone. In addition, wells (with or without screens and annular space and fill) and in-well equipment may be the best alternative in contaminated fractured rock aquifers and other aquifers where direct-push methods cannot be used. Regardless, upon completion of the delineation phase, it is appropriate to use monitoring wells to evaluate temporal trends and to begin answering specific questions about plume stability and attenuation. Therefore, it is important to develop well-specific monitoring objectives and tailor the design of the wells and sampling program accordingly.

A.4 Step 4 - Stakeholders must understand that site characterization is not simply the initial phase of the remediation project life cycle

The decision to perform additional characterization phases when developing remedy designs or optimizing performance should be weighed by the return-on-investigation (see Section 1.3) in terms of the potential to reduce total life cycle costs or improve the risk profile at each site. Many DNAPL sites have not been successfully remediated—not because remediation technologies are flawed, but because understanding of the DNAPL CSM has been limited by the linear nature of the historical investigate-then-remediate philosophy that is ingrained in the technical and regulatory process, especially at sites with large plumes in complex hydrogeologic settings. Historically, the specific elements and objectives of the remedy have been dictated before adequate information is available to test the DNAPL CSM through initial remedy implementation. Stakeholder acceptance of the newer site characterization techniques will enable more flexibility in remediation and more robust CSMs based on the collection of higher quality data.

APPENDIX B. CASE EXAMPLES OF OBJECTIVES-BASED SITE CHARACTERIZATION

This section contains case examples to show how the integrated site characterization (ISC) process can be implemented at various stages of a dense nonaqueous phase liquid (DNAPL) project. The ISC process includes developing objectives, establishing data needs from those objectives, and linking data needs to the selection of characterization tools.

B.1 Example 1 – Coal Tar Site in Newark, New Jersey

Current and emerging site characterization tools were selected for a remedial investigation at a former coal tar manufacturing facility in Newark, New Jersey (the site). The purpose of the investigation was to reduce the footprint of an in situ thermal remediation (ISTR) treatment for coal tar DNAPL.

The areas surrounding the site were once flood plains and tidal mudflats along the Passaic River. In the late 1800s, the site and surrounding areas were covered with fill material (historical fill) to allow for development. From approximately that time until May 1983, the site housed various industrial operations involving the production of road tars, phenols, and methyl phenols (cresol and cresylic acid). The site remained vacant from 1986 until approximately 2002, when it was leased as a shipping container storage yard. The site was vacated in early 2012 to allow access for contaminant delineation and to prepare for remediation activities.

Identified contaminants of concern (COCs) from the historical site operations include volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons, phenols, and petroleum hydrocarbons. Contaminants related to the historical fill include semivolatile organic compounds (SVOCs) and metals such as arsenic and lead.

B.1.1 Problem Statement

Uncertainties in the historical conceptual site model (CSM) required a more detailed characterization of the site—in particular, delineating the spatial distribution and estimating the volume and mass of the coal tar DNAPL—to aid in modifying the design of the ISTR.

B.1.2 Uncertainties/Deficiencies with the CSM

The historical CSM for the spatial distribution of DNAPL was based mainly on identifying the areas of the site that were formerly occupied by coal tar production operations. The spatial distribution of DNAPL was unknown within the differing lithological units, but was assumed to be primarily within the historical fill.

B.1.3 Data Collection Objectives and Their Basis

The data collection objectives for the site included the following:

- a detailed lithologic description for the design of the thermal treatment system (vertical)
- a contaminant distribution to design the aerial distribution of thermal treatment (three-dimensional [3D])
- a contaminant mass estimate to design the thermal treatment and duration within each lithology

B.1.4 Data Needs and Gaps

The following data were required to meet the data collection objectives for the thermal treatment remedy:

- the volumes of discrete lithologic units affected by coal tar DNAPL
- the characteristics that differentiate each lithological unit (porosity)
- the DNAPL saturation distribution within each lithological unit
- the properties of the nonaqueous phase liquid (NAPL)
- a contaminant mass estimate to design the thermal treatment and duration within each lithology

B.1.5 Data Resolution

The density of the data collected and the interpolation routine for estimating the extent of the DNAPL distribution were used to select the locations for the thermal treatment wells. The wells were placed on approximately 10 ft centers for the shallow treatment and 20 ft centers for the deep treatment. The density of the data collection varied depending on the historical production practices of each given area (for example, administrative area, lagoon area).

B.1.6 Investigative Tools and Data Collection

A site investigation “toolbox” was used to significantly enhance the ability to characterize the spatial architecture of DNAPL source zones. This toolbox approach provided multiple scales of measurement and data quality, within two main categories of technologies: (1) dense spatial data, often with higher detection limits, and producing qualitative information used to guide the sampling strategy; and (2) compound-specific, generating quantitative, precise data with low detection limits. These two categories of measurement technologies used in tandem produce a more complete and accurate data set, which can further inform the quantification and uncertainty assessment of DNAPL mass. The following site characterization tools were used as part of the remedial investigation:

- cone penetrometer (CPT) friction log on laser induced fluorescence (LIF) tool
- LIF profiles providing semiquantitative response to concentration of coal tar
- sonic percussion coring, core recovery, and logging
- shallow test pit logging
- real-time adaptive site management tools (Sharepoint)

- core subsampling and analysis of VOCs, SVOCs, and extractable petroleum hydrocarbons
- qualitative field methods (visual and enhanced visual)
- physiochemical testing for NAPL density and viscosity (R104)

B.1.7 Data Evaluation and Interpretation

With the site investigation toolbox, an adaptive site characterization can be developed by combining both qualitative and quantitative data sets and incorporating real-time updates. The high-qualitative 3D spatial density of the LIF tool was validated by a limited number of detailed sonic cores, analytical samples, and test pits, and the results of the qualitative and quantitative data correlations were compared. The data from the high-density LIF sampling were communicated to the interpretation team, allowing for real-time revisions to the investigation grid where necessary.

The results of the investigation verified that the DNAPL distribution was localized in the historical site production areas; however, the delineation of the DNAPL indicated a need for thermal treatment of DNAPL at depth, which was not part of the historical CSM. The resulting soil volume requiring treatment, as defined in the updated CSM, was three times lower than the initial estimate.

Table B-1. Objectives-based site characterization – Example 1

Goal or problem	The distribution of coal tar DNAPL had to be quantified so a thermal remedy could be designed.
Uncertainties/Deficiencies with CSM	The spatial distribution of DNAPL was unknown within differing lithological units.
Data Collection Objectives	• Describe the lithology. • Map the contaminant distribution. • Estimate the contaminant volume and mass.
Data Needs/Gaps	• Determine volumes of given lithologies. • Determine porosity range within each lithology. • Determine DNAPL saturation range within each lithology. • Determine NAPL properties.
Resolution Required	Data density and interpolation routine adequate to locate 20 ft-center thermal wells was required.
Investigation Tools	• CPT friction log on LIF tool • Sonic percussion coring, core recovery, and logging • Test pit logging (shallow only) • Subsampling from cores for laboratory analysis of total porosity • Soil concentration from laboratory analysis of VOCs and SVOCs • LIF profiles (providing semiquantitative response to concentration of coal tar) • Qualitative field methods (visual and enhanced visual) • Physicochemical testing (density, viscosity) from recovered NAPL
Data Evaluation and Interpretation	N/A
Comments	Adaptive site characterization was required to respond to findings in real time, communicate data to the interpretation team, and revise the investigation grid (where necessary).

B.2 Example 2 – Dry Cleaner Sites in Indiana

Three former dry cleaner sites located in northern Indiana were investigated using adaptive site management tools that collected real-time data to develop a high-resolution site characterization. Dry cleaner operations began at two of the sites in the 1950s and the third in 1981. All three of the sites were operated as dry cleaners into the 2000s, two as recently as 2008. Between 2004 and 2008, each site was characterized with traditional sampling and off-site analysis. Each site had also been subject to in situ chemical oxidation (ISCO) remediation using a single-event direct injection followed by a later nutrient injection to enhance bioremediation.

B.2.1 Problem Statement

The effectiveness of prior remedial actions at the sites had not been assessed. Although reasonably high-density soil sampling (both horizontal and vertical) had been performed at one of the three sites prior to this investigation, the potential threat to adjacent properties had not been assessed, especially the vapor intrusion pathway. Because the three dry cleaner sites were located within a 5-mile radius of each other, the investigation of the sites was coordinated to allow the sampling and on-site laboratory resources be used most efficiently.

B.2.2 Uncertainties/Deficiencies with the CSM

Post-remediation assessment had been performed at only one of the three sites. The amount and spatial distribution of both separate-phase tetrachloroethylene (PCE) and dissolved-phase PCE and daughter products at each site was unknown. All three dry cleaners were located adjacent to both commercial and residential properties that were at risk from potential vapor intrusion.

B.2.3 Data Collection Objectives and Their Basis

- Describe the lithology at each site to identify storage zones and transport zones for the DNAPL and dissolved-phase plume.
- Map the contaminant distribution in the soil source area, dissolved-phase plume, and vapor phase at adjacent commercial and residential building to assess risk.

B.2.4 Data Needs and Gaps

A site lithology assessment was required to better understand the transport and storage of PCE and daughter products in both the source area and associated plume. The density of soil concentration data in the source areas of two of the three sites were needed to determine whether there was a remaining source to groundwater or soil vapor. The groundwater plumes at all three sites were poorly defined in both the horizontal and vertical dimensions. Potential vapor intrusion from the contamination due to off-site groundwater plume and vapor transport had not been assessed at any of the three sites.

B.2.5 Data Resolution

High-resolution data collection was determined to be necessary to address the uncertainty in the distribution of potential PCE source post-remediation, determine the vertical and aerial extent of the associated groundwater plume, and assess the potential vapor intrusion at adjacent commercial and residential properties. Real-time data collection was selected as the best approach to manage placement of sampling locations and vertical resolutions for each phase investigated. Using real-time data to support selection of sampling locations increases the efficiency of resource allocation, significantly reducing the uncertainty of the resulting CSM due to subsurface heterogeneity.

B.2.6 Investigative Tools and Data Collection

To maximize efficiencies, the United States Environmental Protection Agency's (USEPA) Triad approach was used with a dynamic work plan and on-site real-time analysis for PCE and daughter products at all three sites in one deployment. The project required direct-push technology (DPT) sampling using two rigs for soil, groundwater, and soil vapor. Field analysis was performed at the on-site mobile laboratory, with direct sampling ion trap mass spectrometry using USEPA Method 8265. A limited number of samples for all matrices was collected for off-site laboratory analysis to inform risked-based remedial decision making.

The project involved 15 days of fieldwork—including sampling at the three sites in all three phases (soil, groundwater, and soil vapor) and on-site analysis. Contamination of the soil, groundwater, and soil vapor was assessed by collecting and performing on-site analysis of 640 discrete samples from 172 plan view locations, averaging 64 analyses per day (see Table B-2 below). The actual field execution was completed in 10 days, covering characterization in the soil source areas, associated groundwater plumes, and potential vapor intrusion pathways.

Table B-2. On-site analysis of soil, groundwater, and soil vapor sampling

	Soil		Groundwater		Soil Vapor	
Dry Cleaner Sites	**Number of Samples**	**Plan View Locations**	**Number of Samples**	**Plan View Locations**	**Samples**	**Plan View Locations**
Site 1	153	30	110	36	35	17
Site 2	11	1	89	24	33	18
Site 3	108	13	84	23	17	10
10-Day Totals	**272**	**44**	**283**	**83**	**85**	**45**

B.2.7 Data Evaluation and Interpretation

When collecting high-resolution data sets, it is important to manage them in real time so the extracted information can support on-site decision making and the data can be communicated effectively to off-site stakeholders and decision makers. A high-resolution site characterization project requires development of a data management and communication plan.

Before any on-site field activities were conducted, the initial CSM for each of the three sites was constructed based on all data available from the previous investigations. All previous contaminant, geologic, and hydrogeologic data were organized into tables and maps. During field execution, the project manager received the data in real time to further direct field operations. This was accomplished with various communications approaches, depending on the location of the project manager (on site or at the office). Hard-copy data of analytical results were provided, often plan view location by plan view location, when the project manager was present on site. When the project manager was not present, the data were transmitted by email. The project manager provided two-dimensional maps to the field crews, often with multiple revisions each day, to assist in the location of future sampling locations. Thus, the project manager was able to determine where data gaps relative to project data quality objectives still existed and to direct resources to fill those gaps.

Final data presentation was in the form of maps, tables, and verbal interpretation in a site characterization report submitted to the Indiana Department of Environmental Management, as required by regulation. The report included all field data, as well as a limited number of off-site fixed laboratory analyses for soil, groundwater, and soil vapor from samples collected concurrently with the samples collected for on-site analysis.

The high level of interaction of the project manager with the field staff is a primary reason the project was able to be executed within significantly less time than allotted. In addition, the project was completed significantly faster than planned because the project team—including the drilling crew, on-site laboratory, and consulting project staff—had executed similar dry cleaner site characterizations using the same approach.

Table B-3. Objectives-based site characterization – Example 2

Goal or problem	The distribution of PCE and daughter products as potential remaining source, dissolved phase, and vapor phase had to be defined at three former dry cleaner sites, all within a 5 mile radius of each other, in a single deployment. Each site had been subject to source remediation using ISCO three to four years before the current investigation.
Uncertainties/Deficiencies with CSM	• The spatial distribution of potential DNAPL in sources areas was unknown after ISCO remediation at each site. • Associated groundwater plumes were either uncharacterized or poorly characterized. • Potential vapor intrusion into adjacent commercial and residential buildings was uncharacterized.
Data Collection Objectives	• Describe the lithology at each site to identify storage zones and transport zones for DNAPL and dissolved-phase plume. • Map the contaminant distribution in the soil source area, dissolved-phase plume, and vapor phase at adjacent commercial and residential building to assess risk.
Data Needs/Gaps	• 3D characterization of lithologies at each site to identify storage zones and transport zones for DNAPL and dissolved phase • PCE and daughter product soil concentration at high resolution in and adjacent to source remediation area • PCE and daughter product concentration at high resolution in groundwater to map plume

Table B-3. Objectives-based site characterization – Example 2 (continued)

	• PCE and daughter product concentration in shallow soil gas to identify potential vapor intrusion into adjacent properties
Resolution Required	Data density (plan view and vertical) adequate to achieve the following: • Evaluate the effectiveness of previous source remediation. • Identify any residual source areas. • Map dissolved-phase plumes to determine potential impacts, including from vapor intrusion. • Investigate potential vapor intrusion impacts to adjacent buildings.
Investigation Tools	• DPT soil sampling with continuous coring and geologist logging soils • Subsampling from DPT soil cores for laboratory analysis using USEPA Method 5035 and on-site analysis using USEPA Method 8265; real-time decision making using contaminant data to refine sampling locations • DPT groundwater sampling of the saturated zone and on-site analysis using USEPA Method 8265; real-time decision making using contaminant data to refine sampling locations • DPT vapor sampling at two depth intervals at each plan view location, with the deepest interval immediately above the groundwater surface; real-time decision making using contaminant data to refine sampling locations
Data Evaluation and Interpretation	• Samples were analyzed on site in real time. The data were provided to the project manager on a location-by-location basis to allow for real-time decision making on allocating resources to meet project objectives. • The CSM for each of the three sites was revised as data became available, and decisions were made in real time to ensure that project objects were met.
Comments	• Adaptive site characterization was required to respond to findings in real time, communicate data to the interpretation team, and revise the investigation grid (where necessary). • Objectives were met at all three sites using high-resolution site characterization. • Significant time and cost saving were realized because sampling operations could be rapidly relocated from Site 1 to Site 2 or 3 while utility clearance was obtained to expand the area of investigation at Site 1. The mobile laboratory remained in one location throughout the field deployment. • The project was completed using only two-thirds of the resources estimated to be required to achieve project objectives.

B.3 Example 3 – Reese Air Force Base

Beneath the former Reese Air Force Base (AFB) in north Texas is a typical, large, diffuse trichloroethylene (TCE) plume that illustrates the investigative and remedial challenges of achieving USEPA Maximum Contaminant Levels (MCLs). From 1941 to 1997, the site served as a training facility for pilots, and the operations included aircraft maintenance to clean engine parts using TCE. Spent TCE from these operations leaked from an industrial waste line into the underlying groundwater, forming at its maximum extent a 3 mile by ½ mile diffuse plume in the Ogallala Aquifer. This aquifer is the sole source of water for agriculture and potable use for the surrounding community. Vertically, the hydrostratigraphy consists of three major depositional sequences, 20 ft–

30 ft of silt, 30 ft–50 ft of caliche, and 100 ft–130 ft of aquifer material. Generally, the groundwater plume extends from the water table 130 ft below ground surface (bgs) over the full saturated aquifer thickness of 50 ft. The aquifer is composed of a very heterogeneous system of interbedded sediments varying from gravels to clays, deposited by alluvial fans and braided streams.

The TCE remediation goal at Reese AFB was to achieve the MCL of 5 micrograms per liter (µg/L). The performance period during development of the original remedy was estimated to be greater than 30 years. Remediation was initiated in 1997 with groundwater extraction and treatment via air stripping and granular activated carbon, with all treated water injected back into the aquifer. The system gradually expanded as the plume was revealed through investigation and sampling of private wells; by 2004, there were 50 extraction and injection wells, using more than 17 miles of piping to transport and treat over 650 gpm.

During the first 8 years of operation (1997 through 2004), more than 1.6 billion gallons of groundwater was treated and reinjected at the site; however, the TCE plume showed only limited retreat. In 2004, the site was transitioned to a Performance Based Contract, requiring all monitoring, agricultural, and potable wells affected by the TCE plume to achieve MCLs within 10 years and to maintain those levels for at least 3 years post-treatment monitoring. Figure B-1 shows the TCE plume status at the time of transition to the Performance Based Contract.

The remedy improvements under the Performance Based Contract accelerated the pace of the remediation, reducing the period of performance by at least 22 years. Figure B-2 shows the TCE plume status in February 2010. Focused groundwater pumping along the core of the plume, combined with strategically directed reinjection of treated groundwater, caused the TCE footprint to contract to a sand-and-gravel channel extending along the axis of the plume. The pace-of-remediation diagram (Figure B-3) shows that the plume footprint has contracted steadily at approximately 3 acres per week. As of 2012, all groundwater concentrations were below the MCL. The total life cycle cost savings achieved through shortening the period of performance is estimated to be greater than $20 M.

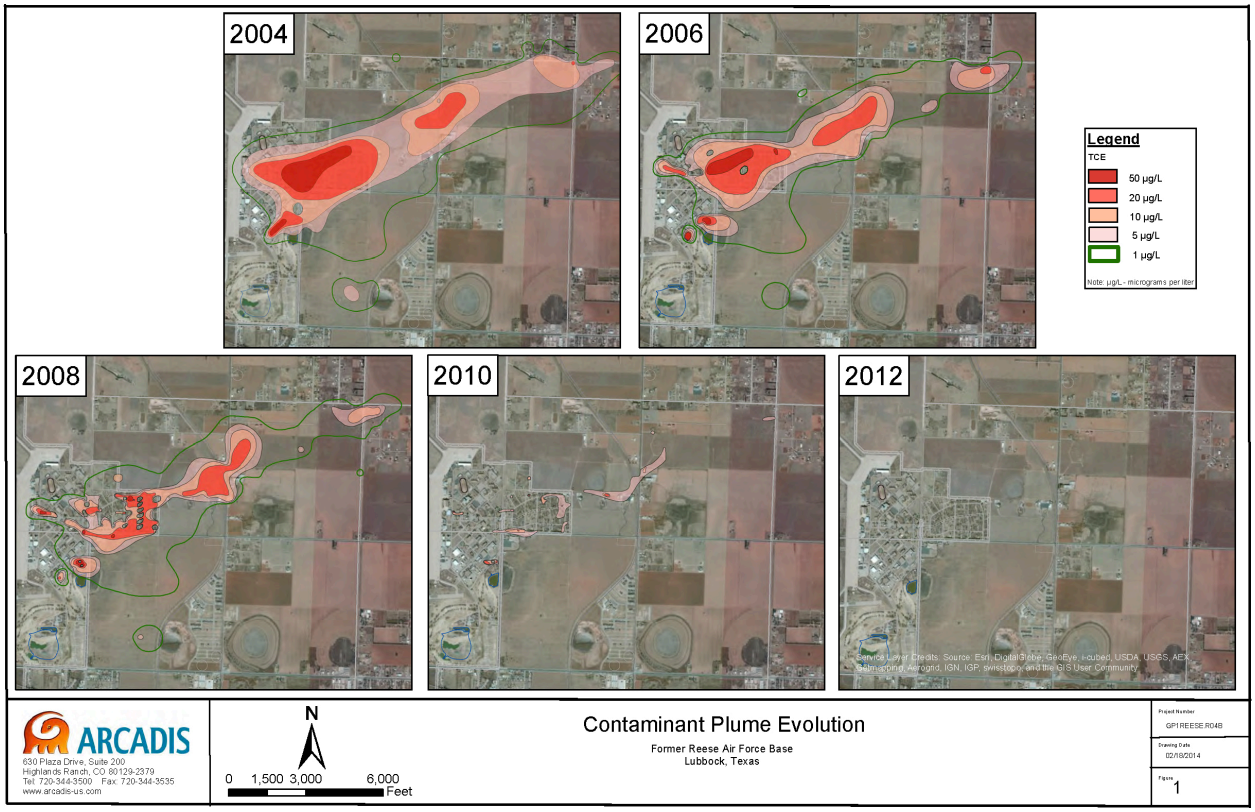


Figure B-1. Contaminant plume evolution, Reese Air Force Base, Lubbock, Texas.

Source: Courtesy of Fred Payne, Arcadis.

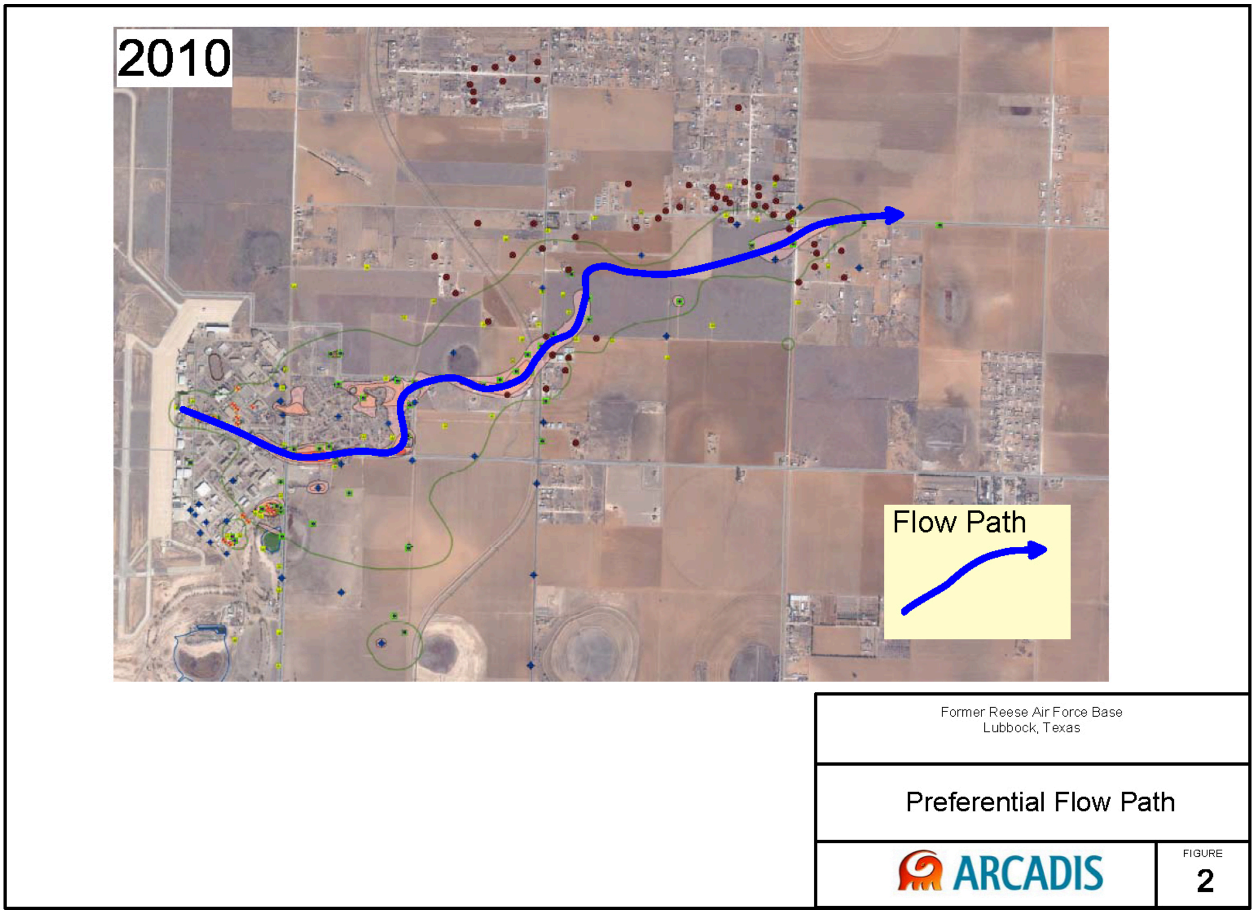


Figure B-2. The plume's preferential flow path as of February 2010, Reese Air Force Base, Lubbock, Texas.

Source: Courtesy of Fred Payne, Arcadis.

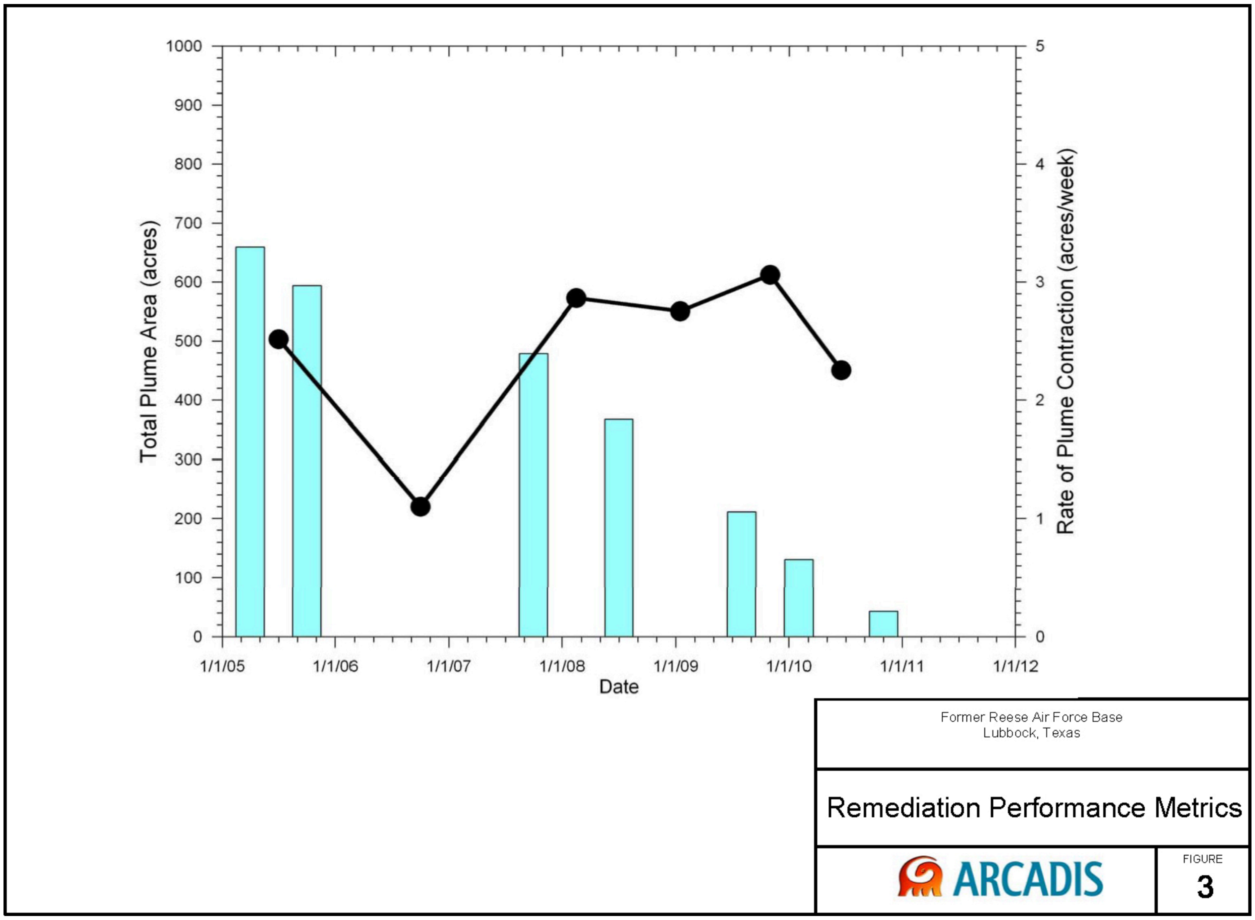


Figure B-3. Pace of remediation, Reese Air Force Base, Lubbock, Texas. The pace of remediation progressed at approximately 3 acres per week.

Source: Courtesy of Fred Payne, Arcadis.

B.3.1 Problem Statement

The problem involved identifying a more effective remedy to shorten the period of performance to less than 10 years and to comply with the pump-and-treat remediation stipulated in the existing Record of Decision (ROD). To achieve site closure within 10 years, the period of active remediation had to be completed within 7 years (allowing for 3 years of post-remediation sampling to confirm remedy completion). The remedial goal was to restore the aquifer to unrestricted potable use by reducing groundwater concentrations for all COCs to less than the MCLs.

The site hydrogeology significantly hindered the remediation effort, with the aquifer structure creating a complex pattern of mass discharge downgradient from the source zone. Thus, the strategy was revised to emphasize the influence of aquifer structure on plume movement, the benefits of pumping and injecting water in targeted locations where remedial performance had slowed, and the use of in situ biological treatment in former source areas to degrade TCE.

B.3.2 Uncertainties and Deficiencies with the CSM

The aquifer structure results in a very complex pattern of mass flux laterally and vertically downgradient from the source. The existing monitoring well network was effective at quantifying groundwater concentrations and identifying potential risks; however, the long well screens provided limited information on detailed plume structure. The initial phase of the project required reassessment of groundwater concentrations using all available data. This included a site-wide synoptic data set collected from all of the investigation wells (>500 wells) and remediation wells (~50 wells), as well as grab samples from more than 100 private irrigation and supply wells within and adjacent to the plume. The revised plume map revealed the following significant findings:

- The contaminant distribution and its movement were highly structured.
- A significant volume of the aquifer previously identified as contaminated was clean.

A review of the CSM and revised plume assessment identified the following inconsistencies:

- Large-scale depositional changes could be identified along the length of the plume.
- Aquifer anisotropy caused a 30-degree deviation between contaminant transport (plume axis) and hydraulic gradient.
- The plume had not invaded the full saturated aquifer thickness in all areas along the plume axis.
- There was no consistent pattern to the plume structure along the plume length—that is, the plume was moving like a ribbon with peak concentrations varying between the bottom, middle, and top of the aquifer, without a discernable pattern.

B.3.3 Data Collection Objectives and Their Basis

The primary data collection objectives were to determine the mass flux along the axis of the plume to better focus remediation efforts. The strategy for optimized site remediation was built around the premise that restoration would accelerate and life cycle costs would decrease if remedy elements were always targeted on the highest mass flux.

B.3.4 Data Needs and Gaps

The strategy required detailed information on the plume and aquifer structure, including the hydrostratigraphy, hydraulic conductivity, groundwater concentrations, hydraulic gradients, and mass flux along and perpendicular to the plume axis.

B.3.5 Data Resolution

Balancing the intermediate scale of depositional features in the aquifer (5 ft–15 ft sequences of sediments), the scale of the remediation (3 miles), and costs to collect data and install remedial systems ($20,000 to $40,000 per soil boring), quality data collected over 10 ft intervals were considered high-resolution information for this site.

B.3.6 Investigative Tools and Data Collection

Soil borings were collected using Rotosonic methods. Grab groundwater and soil samples were collected for each soil boring. Both short- and long-duration aquifer testing were performed to assess aquifer behavior by extracting and injecting water.

B.3.7 Data Evaluation and Interpretation

The CSM was updated based on the groundwater flow and dissolved contaminant transport being focused in the most conductive pathways. This enabled reinterpretation of the composite data from long-screened monitoring wells. Higher groundwater concentrations downgradient of source areas could be used to identify preferred pathways of groundwater and contaminants—that is, the zones with the highest mass flux. The site-wide CSM was subdivided into five smaller units based on variability in groundwater concentrations, age of the plume, accessibility, geology, and local performance metrics. The remedial strategy was recast to match the CSM in each separate sub-unit. This simple strategy, combined with nearly continuous remedy optimization using real-time performance monitoring data, was used to develop remedy enhancements and achieve remedial goals.

Table B-4. Objectives-based site characterization – Example 3

Goal or problem	The problem involved identifying a more effective remedy to shorten the period of performance to less than 10 years and comply with the stipulated remedy (pump and treat) in the existing ROD.
Uncertainties/Deficiencies with CSM	Assumptions on groundwater flow velocities had been used to develop inefficient pump-and-treat systems. The preliminary CSM overestimated the size of the plume and was not refined enough to discern the areas of higher hydraulic conductivity.
Data Collection Objectives	The primary data collection objectives were to determine the mass flux along the axis of the plume to better focus remediation efforts.
Data Needs/Gaps	The strategy required detailed information on the plume and aquifer structure – including the hydrostratigraphy, hydraulic conductivity, groundwater concentrations, hydraulic gradients, and mass flux along and perpendicular to the plume axis.
Resolution Required	Balancing the intermediate scale of depositional features in the aquifer (5- to 15 ft sequences of sediments), the scale of the remediation (3 miles), and costs to collect data and install remedial systems ($20,000 to $40,000 per soil boring), quality data collected over 10 ft intervals were considered high-resolution information for this site.
Investigation Tools	Soil borings were collected using Rotosonic methods; grab groundwater and soil samples were collected for each soil boring; and both short- and long-duration aquifer testing was performed to assess aquifer behavior by extracting and injecting water.
Data Evaluation and Interpretation	The site-wide CSM was subdivided into five smaller units based on variability in groundwater concentrations, age of the plume, accessibility, geology, and local performance metrics.
Comments	N/A

B.4 Example 4 – Well 12A Superfund Site in Tacoma

The Well 12A site has been designated as Operable Unit 1 (OU1) of the Commencement Bay – South Tacoma Channel Superfund site in Tacoma, Washington (Figure B-4). In 1981, chlorinated solvent, specifically TCE, was detected in groundwater extracted from Well 12A, a municipal water supply well owned and operated by the City of Tacoma Water Department. A ROD-specified air-stripping treatment system developed for Well 12A began operation in July 1983 (USEPA 1983), and based on the findings of a USEPA site investigation, the site was added to the National Priorities List on September 8, 1983.

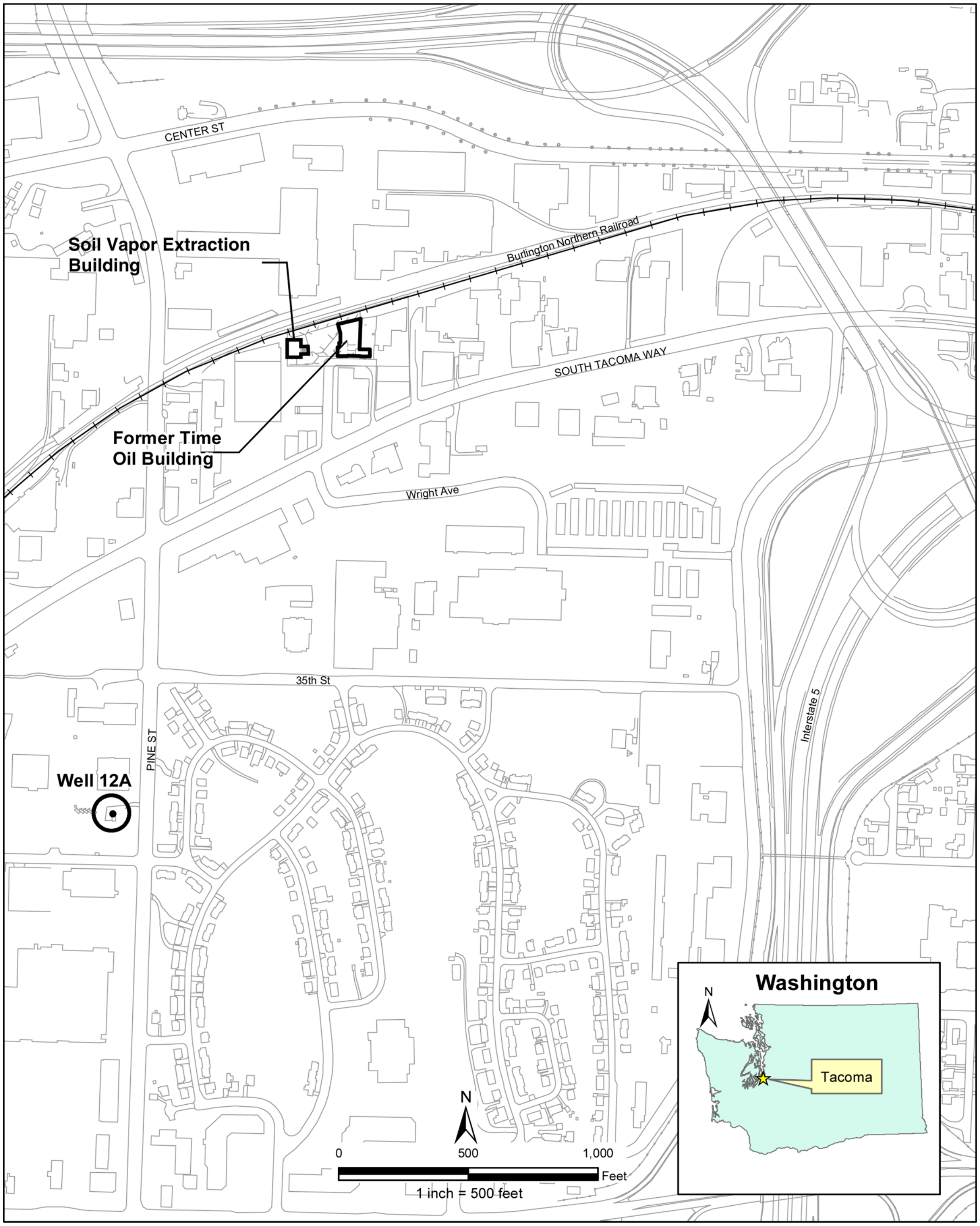


Figure B-4. Well 12A site location map.

Source: Courtesy of CDM Smith.

In early November 1983, Well 12A ceased continuous operations when it was no longer needed for that season. Since then, Well 12A and the treatment system has continued to be used to meet peak summer demand; however, due to the cost of operating the treatment system, use of the well has gradually declined over the years. Well 12A is now typically pumped only during the summer or early fall. However, due to its projected water use, the City seeks restoration of the groundwater to allow for unlimited use of Well 12A.

Further investigation of the TCE contaminant plume identified the primary source of contamination to be the Time Oil Company site. In 1923 or 1924, a paint and lacquer thinner manufacturing facility and an oil recycling facility began operating at the site. The paint and lacquer thinner manufacturing process involved the use of many solvents that were stored on site in barrels, some of which may have leaked. In addition, the process resulted in the formation of a tar-like sludge that was disposed of or stored in various piles on the site. Some of this sludge was also used for fill around the site. These operations continued until 1964 when Time Oil acquired the majority of the property and concentrated on reprocessing waste oil; the waste oil reprocessing continued intermittently until 1976. Following a fire at the facility that destroyed the waste oil processing apparatus in 1976, Time Oil limited operations to the canning of oil, which continued until 1990. Contaminants of concern in groundwater include 1,1,2,2,-tetrachloroethane (PCA), PCE, TCE, cis-dichloroethene (DCE), trans-DCE, and vinyl chloride (VC).

As part of the first ROD Amendment (ROD Amendment #1) (USEPA 1985), 1,200 cy of contaminated soil along a rail spur north of the former Time Oil building was excavated. In addition to the excavation in the railroad spur, contaminated soil was excavated from a narrow strip of land just west of the current soil vapor extraction (SVE) building (Figure B-4). In addition, a groundwater extraction and treatment system (GETS) was constructed and began operation in November 1988 to pump and treat contaminated groundwater near the Time Oil source area. The initial system consisted of a single groundwater extraction well (EW-1); however, in 1995, four additional extraction wells (EW-2 through EW-5), screened at approximately 50 ft–70 ft bgs, were added to the system to improve hydraulic capture and remove more significant quantities of contaminants. Between 1988 and December 2011, the GETS treated over 860 million gallons of groundwater, removing approximately 18,625 pounds of VOCs. In August 1993, an SVE system began operation in the area west of the former Time Oil building where drum storage and disposal operations had previously occurred (also specified in ROD Amendment #1). During construction of the SVE, approximately 5,000 cy of a waste sludge (filter cake) from the oil recycling operations was excavated. Between 1994 and May 1997 (when it was taken out of operation), the SVE removed approximately 54,100 pounds of VOCs. Approximately 25% of the VOCs were chlorinated and the remainder consisted of light-end hydrocarbons.

In 2004 and 2005, USEPA collected soil and groundwater samples from the Well 12A site to assess the effectiveness of the aging GETS. Oily product was identified in some soil samples. In general, groundwater contaminant concentrations had decreased compared to previous samples, but elevated concentrations of chlorinated VOCs were still present.

In September 2008, the third Five-Year Review was completed for the Well 12A site. The report concluded that the existing remedy was not protective, and corrective actions were initiated. In response, USEPA conducted a final Focused Feasibility Study (FFS) to analyze potential remedial alternatives to address ongoing contamination (CDM Smith 2009), and a second ROD

Amendment (ROD Amendment #2) was completed in 2009 (USEPA 2009) to address the deficiencies identified in the third Five-Year Review. ROD Amendment #2 updated the remedial action objectives (RAOs) and cleanup goals for the Well 12A site. The amended remedy added excavation and disposal of filter cake and contaminated soils, ISTR, and enhanced anaerobic bioremediation (EAB) as remedial actions for source area treatment. The goals of these additional remediation actions are to (1) address risks from exposure to contaminated soil and groundwater; (2) reduce or eliminate sources of groundwater contamination; (3) reduce the contaminant mass discharge from the source area to the downgradient plume; and (4) prevent further degradation of groundwater quality. The amended remedy included operation of the GETS, as necessary. Between September 2011 and March 2012, a shallow soil excavation was conducted beneath the former east tank farm on the east side of the former Time Oil building. A 14,280-gallon underground storage tank was removed, along with the 6,775 gallons of contaminated liquid and approximately 35 tons of pea gravel from inside the tank. Much of the excavated soil was highly contaminated and required on-site treatment via chemical oxidation prior to off-site disposal. A total of 2,131 tons of contaminated soil was removed during this work.

Implementing the multi-component source treatment required a detailed characterization effort to develop a robust CSM that would support remedial decision making. This effort involved the following:

- Evaluate contaminant mass extents across the source area.
- Map different remediation technologies across the site.
- Develop SMART objectives for individual remediation technologies.
- Evaluate methods for measuring contaminant mass discharge and select one to use for the RAO compliance metric.

The specific activities included (1) performing high-resolution vertical profiling to delineate the vertical and lateral extent of the contaminant source and plume; (2) identifying specific stratigraphic units contributing the highest mass loading (flux) to the downgradient plume; and (3) evaluating methods to measure mass discharge. A 3D visualization model (Mining Visualization Software [MVS™]) was used to define the source and plume boundaries and to evaluate uncertainty.

B.4.1 Problem Statement

Three primary remedial decisions required additional information:

1. Develop and map treatment volumes for ISTR and EAB design within the Time Oil source area.
2. Determine technology-specific SMART objectives.
3. Select the measurement method for evaluating the compliance goal for source treatment, reducing the contaminant mass discharge from the source area to the dissolved plume.

This case study focuses on the data collected in support of decision 1, above, to evaluate the extent of the residual source area, including NAPL extent. The remedial design investigation was designed to meet the following specific primary objectives:

- Collect the data necessary to delineate the horizontal and vertical extent of the soil contamination, including NAPL, beneath and in the vicinity of the former Time Oil building to support delineation of treatment zones for the multi-component remedy.
- Collect the data necessary to evaluate contaminant mass discharge within different areas of the site to evaluate performance of the treatment technologies.

B.4.2 Uncertainties/Deficiencies with the Conceptual Site Model

The investigation activities were also intended to meet the following technology-specific secondary objectives:

- Delineate the distribution of contaminant mass from the Time Oil source area, including areas containing NAPL.
- Delineate the distribution of mass from the Time Oil source area, including areas where secondary sources such as diffused contaminant mass in low-conductivity zones was prevalent.
- Assess vertical variability in specific discharge and mass flux, with the intent to identify vertical depths where the source is contributing the highest mass loading (flux) to the downgradient plume.
- Evaluate if contaminant mass is contained mostly within transmissive zones or mostly within low-permeability zones by comparing the mass flux distribution to the distribution of specific discharge and/or lithology along the transect.
- Determine hydraulic conductivity for stratigraphic units within the VOC plume.

In addition, the following data gaps required additional information to evaluate the mass discharge metrics:

- Determine the hydraulic characteristics of the aquifer.
- Evaluate capture of the source area to evaluate discharge with the GETS extraction system.

B.4.3 Characterization Objectives and Their Basis

The characterization objectives included the following:

- Describe the major stratigraphic units of the upper aquifer containing contaminant mass.
- Quantify the hydraulic properties of the stratigraphic units within the contaminant zone.
- Map the contaminant distribution within the stratigraphic units, including NAPL and soil and groundwater contaminant levels.
- Estimate the contaminant volume and mass.

- Estimate the contaminant mass discharge within stratigraphic units.
- Map the contaminant mass discharge delivered to the GETS extraction wells.

B.4.4 Data Needs and Gaps

The following data needs were identified to achieve the characterization objectives for the source remedy at Well 12A:

- Stratigraphy: Evaluate vertical intervals (elevations) of primary stratigraphic units within contaminant zone at points throughout the Well 12A source area.
- Geologic Properties: Evaluate properties important to design and implementation of treatment technologies and necessary to evaluate contaminant distribution and transport in the subsurface—such as grain size distribution, porosity, and hydraulic conductivity—for each relevant stratigraphic unit within the contaminant zone.
- NAPL Characterization: Delineate the extent of NAPL within each stratigraphic unit.
- Contaminant Extent: Evaluate contaminant levels and extents in soil and groundwater within the Well 12A source area. Evaluate the presence of secondary sources, such as isolated hotspots and/or prevalence of matrix diffusional secondary sources.
- Contaminant Mass Flux and Discharge: Evaluate mass flux and mass discharge at transects near the boundary of the Well 12A source area with sampling for hydraulic conductivity, contaminant concentration, and gradients within stratigraphic layers.
- Source Area Contaminant Mass Discharge: Evaluate capture and contaminant mass discharge of the Well 12A source area using the GETS extraction wells. Evaluate areas where significant mass discharge is occurring (relative to contaminant extents observed in soils and groundwater) to determine the locations for aggressive treatment.

B.4.5 Data Resolution

At Well 12A, 34 soil borings and 12 vertical profile borings were advanced across the source area (Figure B-5). Soil borings were logged continuously using Rotosonic continuous cores. Soil samples were collected based on high-resolution screening with a minimum interval of one sample every 5 ft to 60 ft–95 ft bgs based on results.

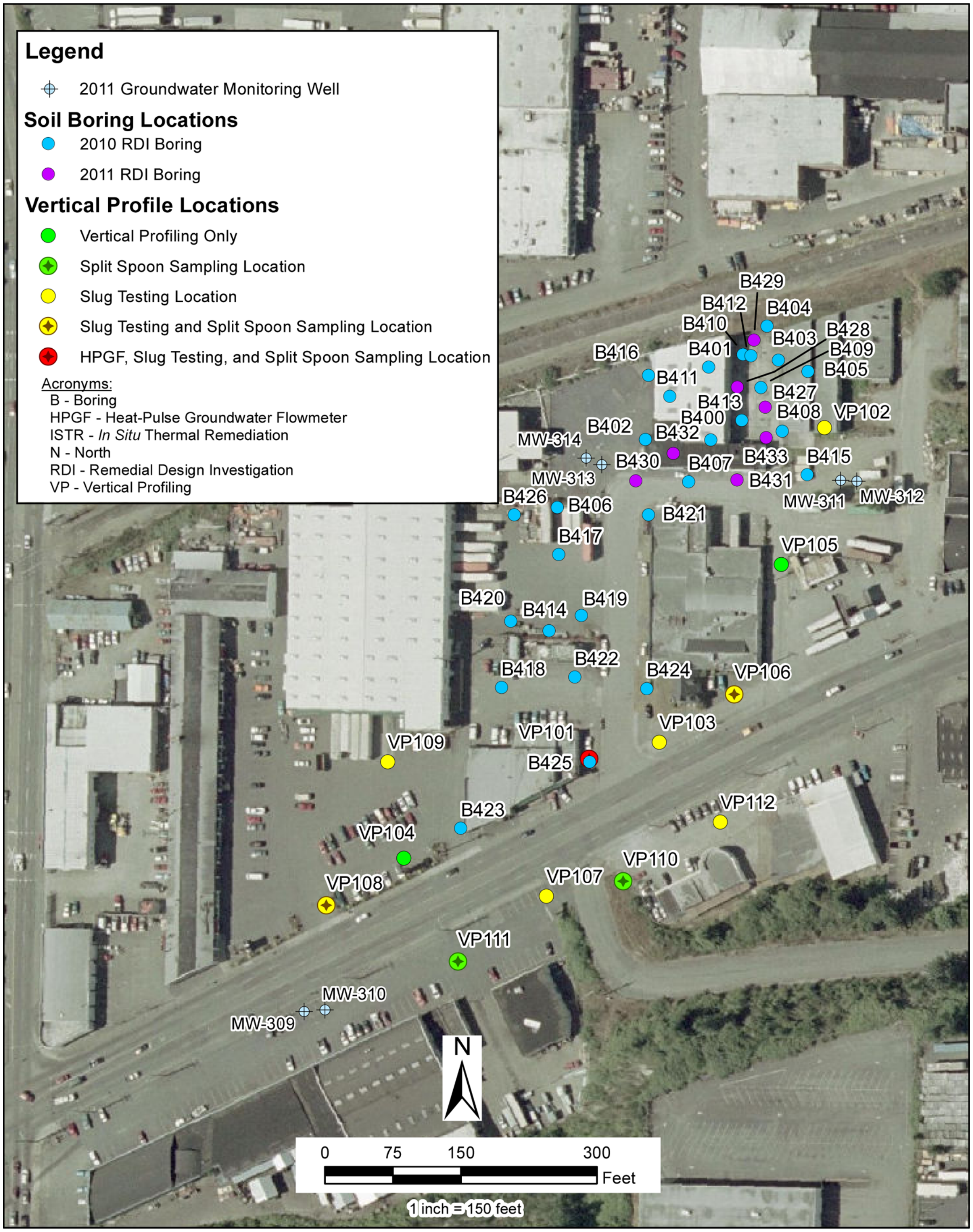


Figure B-5. Remedial design investigation and vertical proofing boring locations.

Source: Courtesy of CDM Smith.

Twelve vertical profile borings were advanced every 100 ft along the suspected boundary of the source area. Temporary well screens were initially emplaced every 5 ft from groundwater surface to 95 ft bgs and sampled for contaminant concentrations and slug tested. Sample intervals were reduced to target one sample in each of the five primary stratigraphic units identified. A total of 28 slug tests at eight borings (VP101, VP102, VP103, VP106, VP107, VP108, VP109, and VP112 – see Figure B-5) were performed at various depths to estimate the hydraulic conductivity in the five identified stratigraphic layers (Qva, Qpfc, Qpf, Qpog, and Qpogc). Synoptic groundwater elevations, to assess the horizontal and vertical gradients, were measured at wells screened at discrete depths corresponding to upper (Qva, Qpf, upper Qpfc), medium (Qpfc), and lower (Qpogc) hydrostratigraphic layers of the upper aquifer. The hydraulic conductivity data were used in conjunction with the groundwater sample results and horizontal and vertical hydraulic gradients to calculate the mass flux within each stratigraphic layer.

The GETS pumping tests were conducted by measuring flow rates at the GETS extraction well (EW-1, EW-2, EW-3, EW-5 – see Figure B-6), and at the influent to the treatment system. Pumping tests were conducted at variable pumping rates to evaluate drawdown at monitoring wells; samples were collected for contaminant levels at the extraction wells and/or at the influent to the treatment system, on a daily to biweekly basis until equilibrium was achieved. Flow rates at the extraction well effluents were set at target flow rates for the pumping test, which were as follows:

- EW-1: 80 gpm
- EW-2: 20 gpm
- EW-3: 12 gpm
- EW-5: 7 gpm

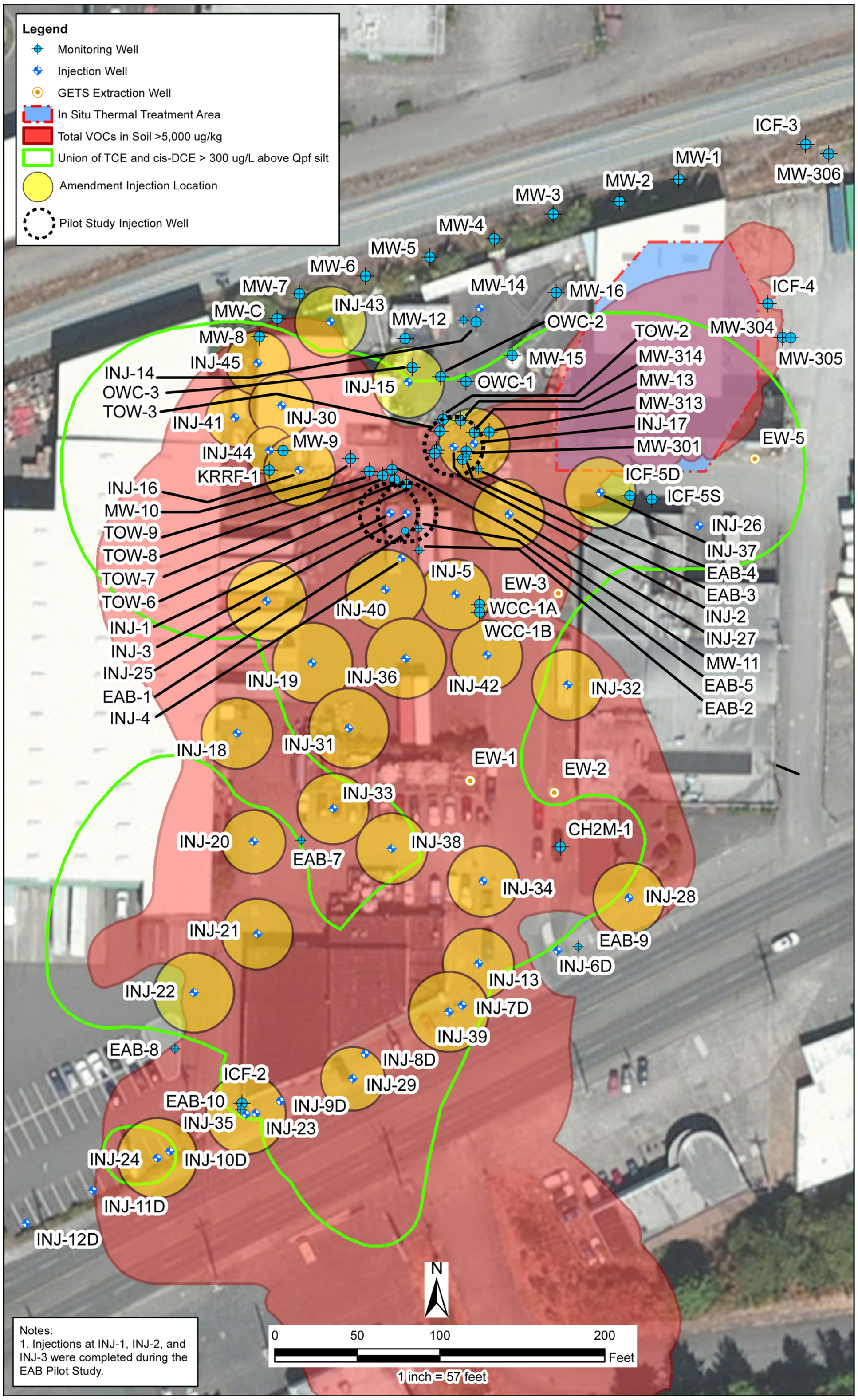


Figure B-6. High contamination zone monitoring wells.

For the mass discharge measurement, the target flow rates were chosen to represent a maximum achievable flow rate that sampled the Target Capture Zone–that is, the Well 12A source area. Using particle tracking, it was estimated that, at these flow rates, VOCs concentrations should be representative of the system in approximately 3 months (based on longest travel times from the edge of the Target Capture Zone to the extraction wells). Therefore, the GETS extraction rates determine both the capture zone and the duration of system operation required to obtain integrated measurements of VOC concentrations. To evaluate mass discharge, the integrated VOC concentration measurement from each extraction well or from the treatment system influent was multiplied by the corresponding extraction well or total system discharge, respectively.

B.4.6 Investigative Tools

A total of 34 soil borings were advanced within the known NAPL hotspot and across the downgradient plume based on the results of the screening (Figure B-5). The borings were subject to initial field screening and lithologic logging. Soil cores were field screened for the following:

- ultraviolet (UV) fluorescence – using a Koehler LSI HS-UV-365 lamp
- headspace concentration – using a photoionization detector (PID)
- NAPL – using Cheiron Resources Limited’s (Cheiron) OilScreenSoil field test
- sheen – using visual photologging

Soil samples for laboratory analyses were then collected from the intervals with the highest level of contamination based on the field screening results.

A Geoprobe 8140 track-mounted Rotosonic drill rig and Gus Pech RS 400 truck-mounted Rotosonic drill rig were used to advance 12 soil borings for vertical profiling (Figure B-5). The drill rig advanced a 3.5 inch inner-diameter core barrel ahead of a 4.5 inch outer-diameter casing to collect soil cores. A 6 inch diameter core barrel and 8 inch diameter casing were used to drill to the water table in difficult or gravelly soils. Soil cores were extruded into 5 ft-long plastic bags. The soil cores were logged and screened as described above. The stratigraphic contacts were included in the field logs and used to guide soil sampling and construction of temporary wells for groundwater sampling and slug testing.

After the soil cores were retrieved, a two-jacket drive point screen or Johnson Screen was attached to the core barrel and installed in the boring to create a temporary well for the collection of groundwater samples and slug testing. A Grundfos Rediflo2 2 inch submersible pump was installed into the medium of the drive point screen for groundwater sampling.

In general, one falling head and one rising head slug test were conducted at each location. The slug test data were downloaded from the logger and sent with test information—borehole, screen interval, lithology, water level, and slug dimensions—to a licensed hydrogeologist for data review and analysis. Slug test data were reduced and analyzed following the procedure outlined by Butler (1998) for wells screened below the water table in an unconfined formation.

B.4.7 Data Evaluation and Interpretation

A 3D visualization model was developed using C Tech's MVS™, which incorporates geostatistics. The MVS™ incorporated the site geologic, hydrogeologic and contaminant data into the model. MVS™ provides data interpolation, geostatistical analysis, and 3D visualization tools in a single software system. The following MVS™ integrated geostatistics functions were used for this project:

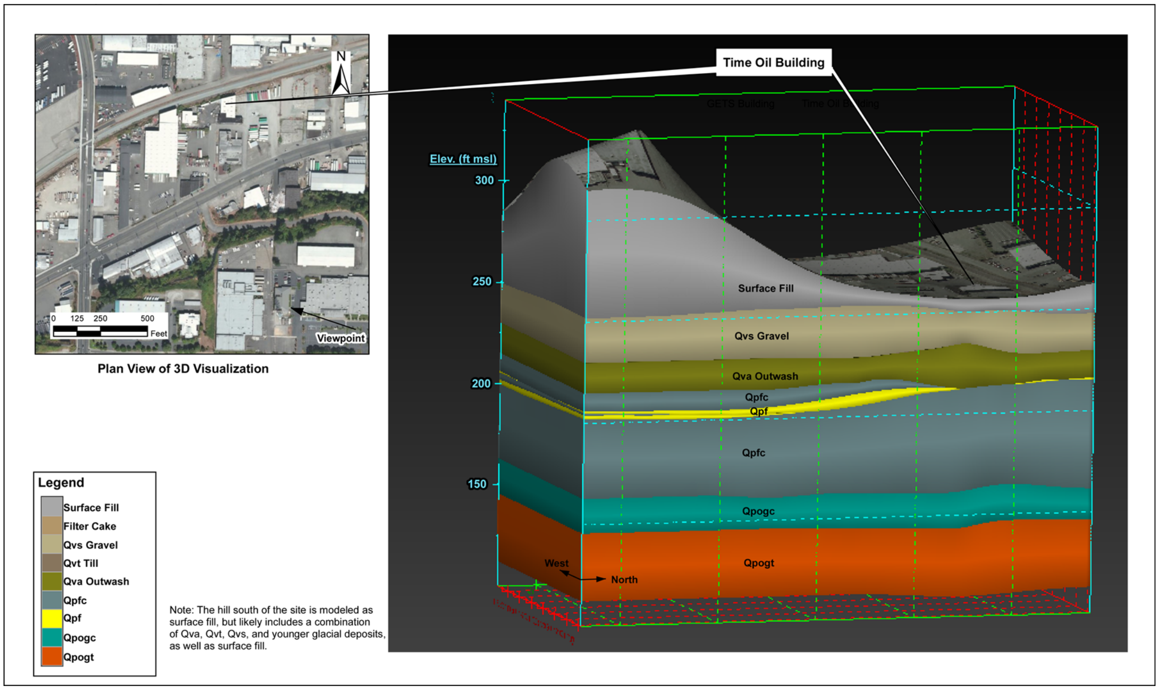
- Site Evaluation: The MVS™ “Min-Max Plume” technology quantifies the statistical variation in the volume and mass estimates resulting from the current level of characterization. This was used to determine the spatial extent of contamination in soil and groundwater.
- Geology/Stratigraphy: A 3D model of the site geology was created to determine the relationship between the geology and the contaminant plumes. The stratigraphy was updated with the lithologic information contained in the boring logs.
- Analytical Kriging: Interpolation methods were used to accurately determine the minimum and maximum possible plume extents.
- Confidence and Uncertainty Outputs: Areas requiring additional characterization were identified.
- Synoptic Water Levels: Potentiometric contour maps were generated with water level data collected during two synoptic water level measuring events.
- Communication: Visual presentation of the site geology and contamination was critical for effective communication, including the ability to integrate geologic information, environmental contamination data, site buildings, roads, and aerial photographs into a model.

B.4.7.1 Geology

The Well 12A site is located within the Clover/Chambers Creek Watershed. Stratigraphic interpretation is based on the Draft Geologic Map of the South Tacoma 7.5-minute Quadrangle (Troost 2011). Lithologies of continuous core soil samples collected during investigations were compared to stratigraphic descriptions in the geologic map, and stratigraphic information and interpretation contained within the geologic map were used to refine understanding of the lithostratigraphic units beneath the Well 12A site. The interpreted stratigraphic units include the following (from shallowest to deepest):

- filter cake and artificial fill
- Steilacoom gravel (Qvs), vadose zone
- Vashon till (Qvt), vadose zone
- Vashon advanced outwash deposits (Qva), saturated zone
- coarse-grained deposits of pre-Fraser glaciation age (Qpfc), saturated zone
- sedimentary deposits of pre-Fraser glaciation age, undifferentiated (Qpf), saturated zone
- coarse grained glacial deposits of pre-Olympia age (Qpogc), saturated zone
- till of pre-Olympia age (Qpogt), aquitard

Figure B-7 illustrates the MVS™-modeled geologic kriging and extents of each of these units across the site. Where present, fill material, including filter cake-like material, is generally encountered from ground surface to approximately 1.5 ft–5 ft bgs. The geologic map shows the Well 12A site vicinity as mantled by Qvs. Soils encountered in the uppermost portion of each boring, excluding fill and filter cake material, are consistent with the description of the Qvs unit, consisting primarily of gravelly sand and sandy gravel with varying silt content. The bottom contact with the underlying Qva unit is generally encountered at depths of 25 ft–32 ft bgs.



Note: The hill south of the site is modeled as surface fill, but likely includes a combination of Qva, Qvt, Qvs, and younger glacial deposits, as well as surface fill.

Figure B-7. 3D visualization of stratigraphic units.

Source: Courtesy of CDM Smith.

Soil characterized as Qva is first encountered at depths of 23 ft–33 ft bgs. The bottom of the Qva unit is at 35 ft–52 ft bgs. Soil characterized as Qva is generally distinctive and consists primarily of poorly graded, medium-grained sand with varying amounts of rounded gravel and lesser amounts of silt. Groundwater is typically encountered within the Qva unit.

A fine-grained silt or clayey silt layer characterized as the Qpf unit is in select areas of the Well 12A site. Where present, it is encountered at depths of 47 ft–52.5 ft bgs and observed to be 1 ft–13 ft thick. There are two noncontiguous occurrences of this unit at slightly different elevations.

The upper occurrence of this unit is generally at elevations greater than 200 ft above mean sea level (amsl), and the second occurrence is found generally below 200 ft amsl. In at least one location (VP109), both occurrences of the silt layer were observed separated by approximately 5 ft of sandy gravel. This suggests that the two separate layers of fine-grained sediment were deposited at different times and are not laterally contiguous across the Well 12A site.

In several of the borings, small wood fragments resembling bamboo shoots and grass were observed within the Qpf unit. The limited aerial extent and lateral discontinuity of the unit across the Well 12A site, combined with the presence of vegetation observed within the sediment, suggests that the origin of deposition is thin wetland deposits. The relatively small wetland deposits appear to have existed in local topographic depressions before the deposition of the Vashon advance outwash.

Soils underlying the distinctive Qva and Qpf units are characterized as Qpfc. The Qpfc unit is typically first encountered at depths of 35 ft–52 ft bgs. The soil consists of coarse grained sand and gravel with varying amounts of silt and intermittent layers of saturated silty gravel. Discontinuous layers of gravel 1 ft–8 ft thick are present within the formation. Silt content varies with depth and is generally observed to increase with depth. The sediments within this unit appear to have been deposited by both glacial and fluvial processes. The bottom of the Qpfc unit was generally observed at approximately 90 ft bgs. The GETS extraction wells are screened within the Qpfc.

The soil underlying the Qpfc unit is characterized as Qpogc. The Qpogc is similar to the overlying Qpfc unit, but is generally identified by a color change from brown to gray, occurring at approximately 90 ft bgs. The appearance of slightly clayey fines was also used to define the contact between the Qpfc and Qpogc. Moisture content decreases significantly in some parts of this unit, indicating a transitional zone above the principal aquitard.

B.4.7.2 Site Hydrogeology

Groundwater occurs in an unconfined aquifer underlying the Well 12A site. The water table is generally encountered in the Qva unit at approximately 30 ft–35 ft bgs. As described previously, a semiconfining unit, referred to as the principal aquitard, exists at elevations of 110 ft–150 ft amsl in the vicinity of the Time Oil source area, and appears to be continuous beneath the property and to a distance of at least 500 ft from the former Time Oil building in the direction of Well 12A. The water-bearing unit above the principal aquitard is referred to as the upper aquifer, and the water-bearing unit below the principal aquitard is referred to as the lower aquifer. Contaminated groundwater associated with the Well 12A site occurs primarily in the upper aquifer.

The upper aquifer comprises a heterogeneous mixture of high-permeability sand and gravel, associated with Qva glacial outwash and Qpfc fluvial deposits, underlain by lower-permeability glacial deposits of the Qpogc, which transitions to glacial till (Qpogt), marking the top of the principal aquitard. The Qpf silt, a semicontinuous layer of silt of limited thickness, is present within the coarse-grained deposits of the Qpfc. Considering the discontinuous nature of the Qpf silt and significant levels of contaminants in the deeper reaches of the upper aquifer, the Qpf silt layer does not appear to be an effective confining layer for preventing the vertical migration of contaminants in the upper aquifer.

Groundwater elevation varies seasonally and in response to aquifer pumping conditions. Typically, the water table occurs at 219 ft–224 ft amsl (30 ft–35 ft bgs near the Time Oil source area). Regional groundwater flow in the upper aquifer is generally toward the east with a relatively flat gradient. With the GETS operating, a capture zone is created and gradients in the immediate vicinity of the Time Oil property and south near South Tacoma Way are toward the GETS extraction wells (Figure B-8). Sustained operation of Well 12A and/or other nearby municipal supply wells depresses the potentiometric surface and changes the normal ambient groundwater flow direction in the vicinity of the Well 12A site. Water level measurements indicate a relatively strong downward vertical gradient, both within the upper aquifer and between the upper and lower aquifers. Vertical hydraulic gradients calculated for well clusters— including wells in the shallow, medium, and base portions of the upper aquifer and wells in the lower aquifer—indicate that the magnitude of the vertical gradient generally increases with depth. Using data from synoptic water level measurement events under natural conditions with both Well 12A and the GETS off, a moderate vertical gradient (average of 0.108) was observed through the contaminated aquifer. Despite the downward gradient, limited contamination in the lower aquifer suggests that the semiconfining Qpf unit prohibits the majority of contamination from migrating to depth beneath the site.

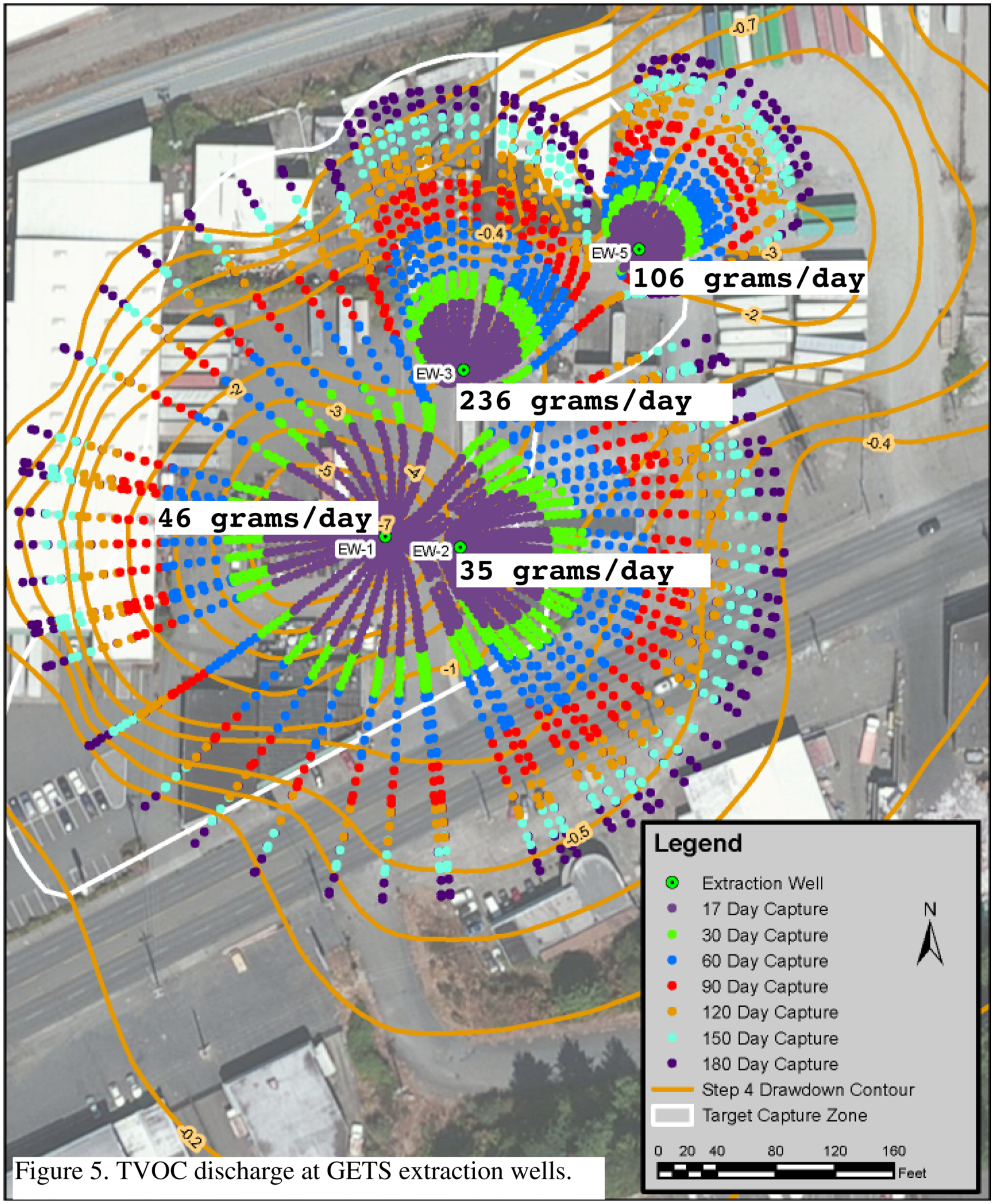


Figure B-8.TVOC discharge at GETS extraction wells.

B.4.7.3 Hydraulic Conductivity Evaluation – Stratigraphic Units

Slug testing immediately followed groundwater sample collection within temporary wells used during the vertical profiling. Results of the hydraulic conductivity profiling are provided in Table B-5 and the MVS™-modeled stratigraphic units are shown in Figure B-7. These values were assigned to different vertical intervals in the mass flux transect to calculate contaminant mass flux and mass discharge.

Table B-5. Averaged hydraulic conductivity and porosity values for mass flux

Stratigraphic Unit	Range of Horizontal K (ft/day)	Horizontal K (ft/day)	Vertical K (ft/day)	Effective Porosity[b]
	Average K per Stratigraphic Unit Used in MVS			
Qva	7-56 (n=3)[a]	21	5.18	21
Qpf	0.12-0.5 (n=2)	0.3	NA	21
Qpfc	1-3555 (n=15)	293	0.79	21
Qpogc	0.6-2 (n=7)	1	0.30	15
Qpogt	0.5 (n=1)	0.5	0.03	12.3
	Average K per Depth Measured in Qpfc			
	Depth Interval (ft bgs)	**Number Samples**	**Horizontal K (ft/day)**	
Qpfc1	50-60	5	35	
Qpfc2	70-75	5	782	
Qpfc3	80-85	2	2	

Notes:
[a] number of slug tests performed within stratigraphic unit
[b] values averaged from measured points
[c] values estimated based on lithology of the unit
K = hydraulic connectivity

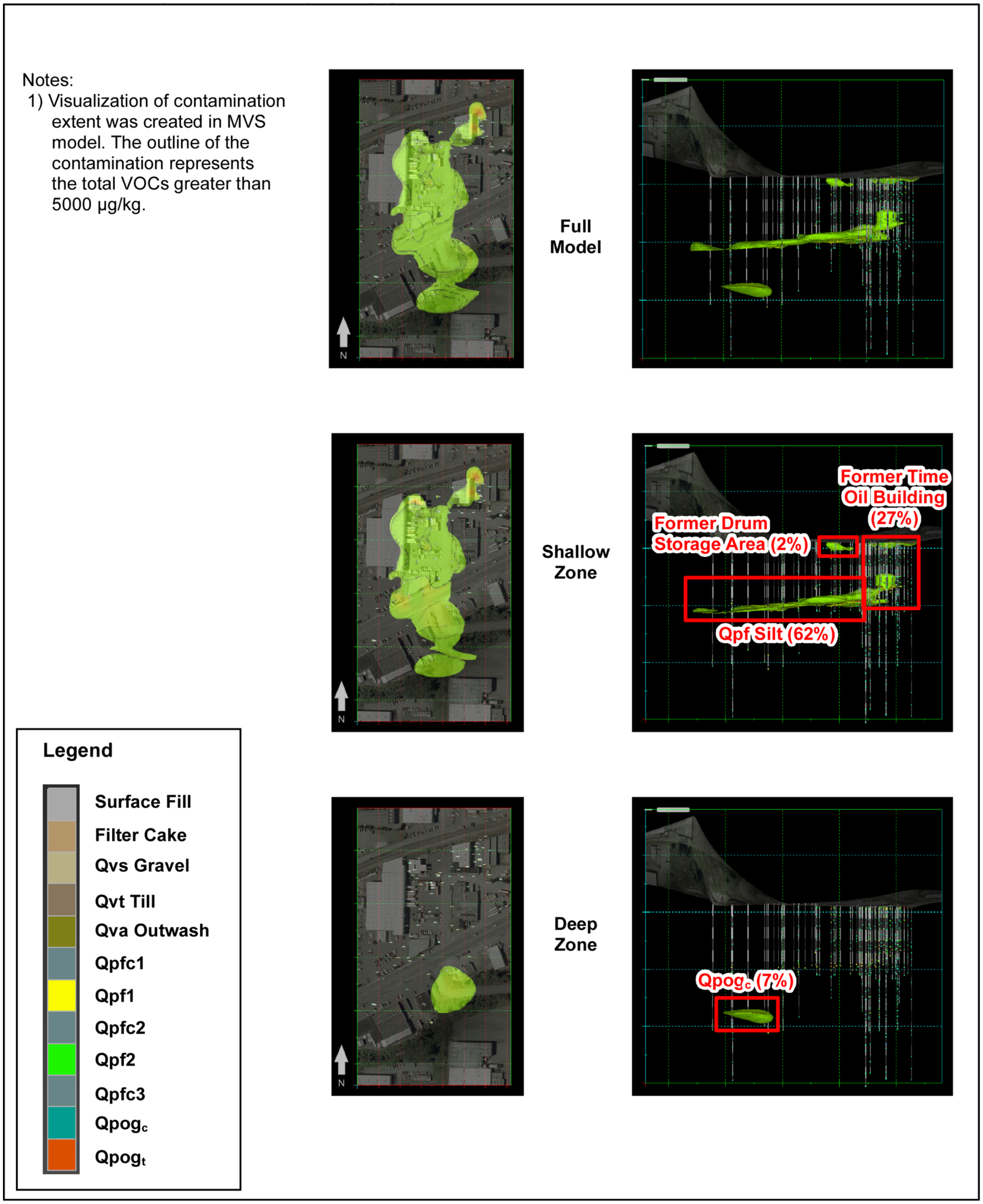
B.4.7.4 Nature and Extent of Contamination – Soil

Soil analytical data for the six primary COCs (PCA, PCE, TCE, cis-DCE, trans-DCE, and VC) were input into a 3D MVS™ model. The MVS™ model was used to visualize the distribution of contaminant mass and assist with the delineation of treatment zones for ISTR and EAB. The model domain was created using the MVS™ convex hull option to include all soil samples bounded by the extent of the geologic stratigraphic files. Thus, the soil contaminant extents could be bounded to the geologic layers of the site and allow for the visualization of soil contamination within individual stratigraphic units.

Figure B-9 shows the modeled extent of soil contamination (sum of six primary COCs) exceeding 5,000 micrograms per kilogram (µg/kg) with the stratigraphy. Overall, the majority of the contaminant mass in the Well 12A source area was found to be located in two distinct zones.

- Time Oil building area: Filter cake and shallow soils impacted by mobile and residual NAPLs was observed underneath and adjacent to the Time Oil building. The NAPL was a mixture of petroleum hydrocarbon and chlorinated solvents that included both light non-aqueous phase liquid (LNAPL) and DNAPL. Mobile NAPL was inferred by the presence of measurable NAPL in Well EW-4.

- The treatment zone slated for ISTR is beneath and adjacent to the former Time Oil building, between approximately 0 ft–10 ft bgs and 35 ft–55 ft bgs. Collectively, these areas contain an estimated 27% of the soil contaminant mass.
- Qpf silt secondary source: A second zone of high contamination was observed southwest and west of the former Time Oil building within the Qpf silt unit encountered at depths of approximately 42.5 ft–60 ft bgs and 1 ft–13 ft thick. The estimated total COC mass in the Qpf unit accounts for approximately 62% of the estimated soil mass. Residual NAPL has also been observed in discrete hotspots associated with areas underneath the soil vapor extraction area and in the former drum storage area.
- The majority of the remaining mass outside of those two zones is located within the Qpogc unit at the base of the upper aquifer (~7%) and in shallow soil southwest of the former Time Oil building near a suspected former drum storage area (~2%).



Notes:
1) Visualization of contamination extent was created in MVS model. The outline of the contamination represents the total VOCs greater than 5000 µg/kg.

Figure B-9. 3D Visualization of the extent of soil contamination.

Source: Courtesy of CDM Smith.

Table B-6 provides the MVS™-modeled estimates of the contaminated volumes within different stratigraphic units and within different volumes across the Well 12A source area.

Table B-6. MVS™-modeled contaminant mass distribution for COCs

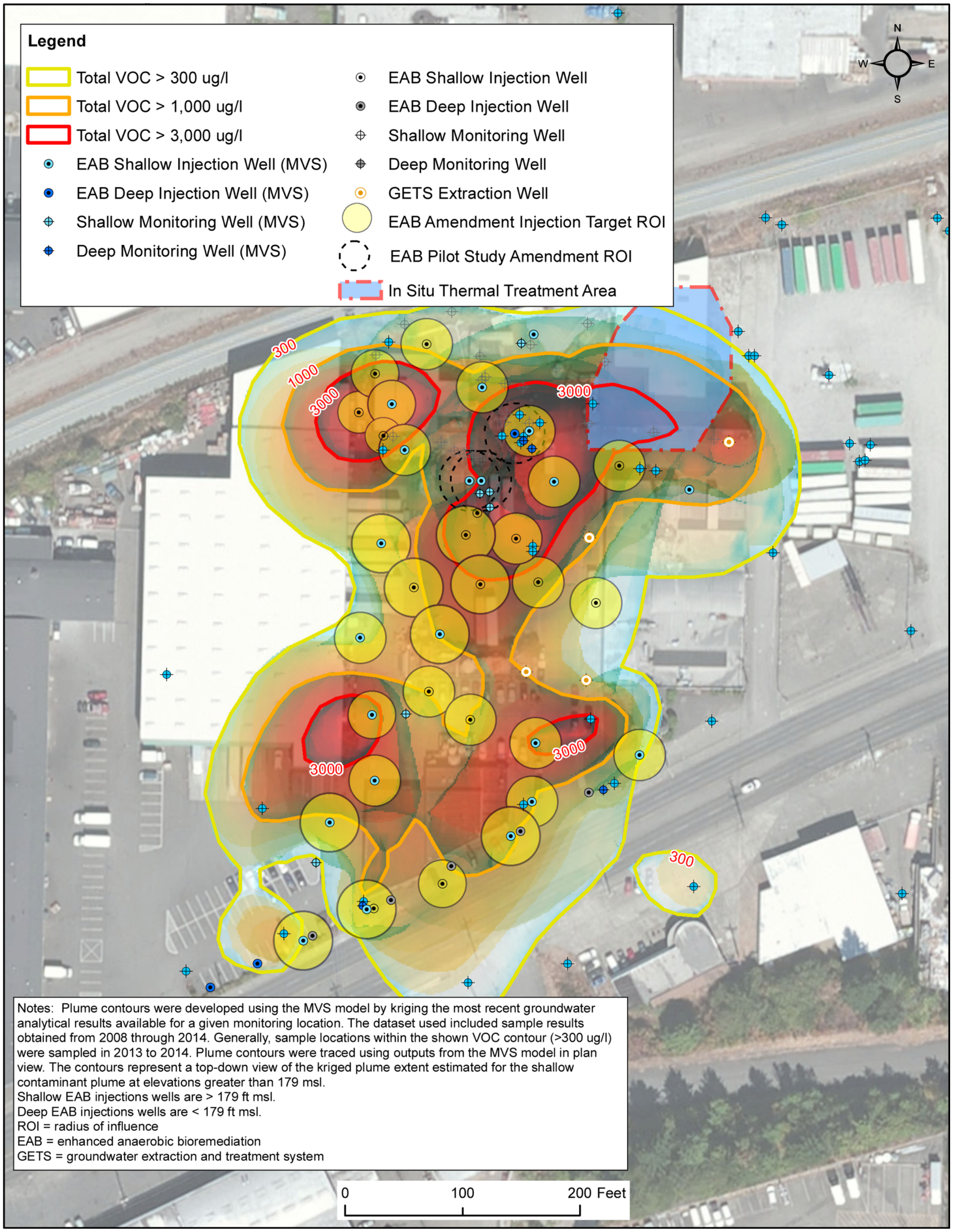
Area Description	Total COC Concentration (mg/kg)	Soil Volume (cy)	Total COC Mass in Soil (kg)	% of Total COC Mass in Soil
Time Oil building saturated zone	> 5,000	26,000	270	27%
Qpf secondary source zone	> 5,000	90,000	631	63%
Other deep and shallow	> 5,000	761	100	10%

Notes:
1. Total COCs are the sum of the six primary VOC COCs (1,1,2,2-tetrachloroethane, cis-1,2-dichloroethene, trans-1,2-dichloroethene, trichloroethene, tetrachloroethene, and vinyl chloride).
2. Field screening and analytical results from intervals where soil samples were collected above and below the Qpf unit (VP101) indicate that high concentrations of COCs in soil were largely confined to this unit. However, because the MVS™ model uses kriging (a method by which estimated concentrations are based on integrating values between two known points), the model predicted soil contamination extending significantly above and beyond the Qpf unit. Therefore, only the estimated soil COC concentrations within the Qpf unit estimated by MVS™ are used, and estimates within the Qpfc unit are excluded.

B.4.7.5 Nature and Extent of Contamination – Groundwater

Groundwater analytical data for the six primary COCs (PCA, PCE, TCE, cis-1,2-DCE, trans-1,2-DCE, and VC) were input into the existing 3D model. In general, the model includes the most recent groundwater VOC data for each well location from 2008 to the present. The model was used to visualize the contaminant plume distribution so the extent and mass of the COCs in groundwater could be evaluated. The groundwater plume domain was created using the rectilinear option, to size the domain to include all of the Time Oil source area wells and also nearby bounding wells (e.g., CBW-10 and CH2M-2). The groundwater domain was bounded on the bottom by the aquitard (Qpogt).

Figure B-10 shows the modeled extent of groundwater contamination where either TCE or cis-DCE exceeds 300 μg/L, 1,000 μg/L, and 3,000 μg/L. The 300 μg/L isopleth was used to illustrate the plume extent because it contains the known Time Oil source area and the majority of contaminant mass in groundwater. Therefore, it is referred to as the high concentration groundwater plume. Overall, the majority of the contaminant mass is distributed within the Qva, Qpfc, and Qpf units in the vicinity of the former Time Oil building with a deeper plume in the Qpogc unit extending across South Tacoma Way southwest of the Well 12A site. The high concentration groundwater plume is generally colocated with zones of elevated soil concentrations (sum of six primary COCs exceeding 5,000 μg/kg) generally associated with either the Qpf silt unit near the former Time Oil building or with the deeper Qpogc to the south of South Tacoma Way.



Notes: Plume contours were developed using the MVS model by kriging the most recent groundwater analytical results available for a given monitoring location. The dataset used included sample results obtained from 2008 through 2014. Generally, sample locations within the shown VOC contour (>300 ug/l) were sampled in 2013 to 2014. Plume contours were traced using outputs from the MVS model in plan view. The contours represent a top-down view of the kriged plume extent estimated for the shallow contaminant plume at elevations greater than 179 msl.
Shallow EAB injections wells are > 179 ft msl.
Deep EAB injections wells are < 179 ft msl.
ROI = radius of influence
EAB = enhanced anaerobic bioremediation
GETS = groundwater extraction and treatment system

Figure B-10.Total VOCs in shallow groundwater (<179 ft) from 3D model 2014 upgrade.

Source: Courtesy of CDM Smith.

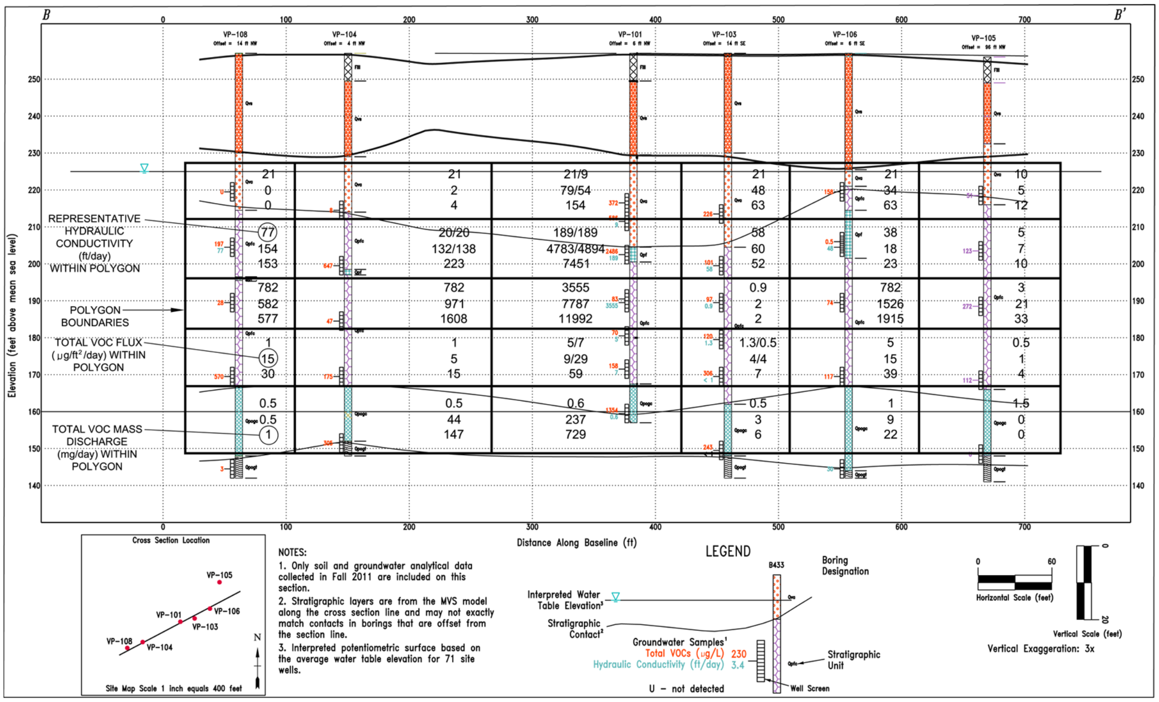
B.4.7.6 Mass Flux Transect

An evaluation of mass flux and mass discharge was conducted using a Theissen polygon method (ITRC 2010). This evaluation used groundwater samples collected from temporary monitoring points along a transect of the contaminant plume approximately perpendicular to groundwater flow. The vertical cross-sectional transect was divided into multiple discrete sub-areas of assumed uniform concentration and groundwater flow discharge (Nichols and Roth 2004). Mass discharge of groundwater was measured along the transect by combining the concentration and flow data (that is, Darcy velocity) to yield mass data in units of mass flowing normal to the control plane per unit of time. To characterize the Darcy velocity (q) across a plume transect, representative measurements are required for both the hydraulic flow gradient (i) and the hydraulic conductivity (K) of the flow system (where q = K * i).

For the mass flux calculations, the transect was divided into rectangles (polygons) that included depth intervals as follows:

- Vertical Interval 1: 40 ft–55 ft bgs for the Qva
- Vertical Interval 2: 55 ft–65 ft bgs for Qpfc1/Qpf, used when the Qpf unit is not present (the hydraulic conductivity of the Qpfc unit was used because it comprised a much greater percentage of the vertical area)
- Vertical Interval 3: 65 ft–75 ft bgs for Qpfc2
- Vertical Interval 4: 75 ft–95 ft bgs for Qpfc3
- Vertical Interval 5: 95 ft–115 ft bgs for Qpogc

Figure B-11 shows the results of the mass flux and discharge assessment for transect 1. Table B-7 presents the mass discharge measured for each stratigraphic unit for transect 1.



NOTES:
1. Only soil and groundwater analytical data collected in Fall 2011 are included on this section.
2. Stratigraphic layers are from the MVS model along the cross section line and may not exactly match contacts in borings that are offset from the section line.
3. Interpreted potentiometric surface based on the average water table elevation for 71 site wells.

Figure B-11. Mass discharge-Transect 1.

Source: Courtesy of CDM Smith.

Table B-7. Mass discharge by stratigraphic unit

	Total VOC Mass Discharge (mg/day)	% of Total Mass Discharge	TCE Mass Discharge (mg/day)	DCE Mass Discharge (mg/day)
Transect 1				
Qva	138	1%	92	32
Qpfc1/Qpf	7,912	32%	2,609	3,760
Qpfc2	16,125	66%	9,025	5,872
Qpfc3	154	1%	95	26
Qpogc	148	1%	92	52
Total	24,478		11,914	9,742
% of Total			49%	40%

Results of the mass flux transect evaluation reveal that 96% of the total VOC mass discharge from Transect 1 came from intervals Qpfc1/Qpf and Qpfc2 (approximately 55 ft–70 ft bgs). In contrast, the Qva unit comprised only 1% of the measured discharge. In deeper intervals, the mass discharge declined with 1% accounted for in the Qpfc3 interval (75 ft–95 ft bgs) and 1% in the Qpogc interval (95 ft–115 ft bgs). In addition, nearly 78% of the mass discharge was associated with the central portion of the transect represented by VP101 (Figure B-10). A substantial proportion of the discharge consisted of degradation products cis- and trans-1,2-DCE, which totaled 40% of the mass discharge compared to 49% for TCE.

B.4.7.7 Mass Discharge Using GETS

Before the Well 12A source treatment technologies ISTR and EAB were implemented, the project team evaluated multiple methods for measuring contaminant mass discharge and selected one to assess compliance with the interim groundwater RAO (CDM Smith 2011, CDM Smith 2012b, CDM Smith 2013). Contaminant mass discharge measured with a pumping test using the GETS was selected as the compliance metric for the Well 12A site interim remedy. Subsequently, the baseline mass discharge using the GETS pumping test was 403 gallons per day (gpd) total VOC (TVOC) as the sum of PCA, PCE, TCE, DCE, trans-DCE, and VC and agreed to by the project team (CDM Smith 2013). The mass discharge baseline measurement of 403 gpd TVOC was calculated as the mean of three consecutive mass discharge measurements conducted approximately two weeks apart that met the following criteria:

- Extraction well rates were within 10% of target flow rates (defined as rates demonstrated to capture the target capture zone) during the mass discharge evaluation period.
- The TVOC concentrations (629, 613, and 592 µg/L) measured in samples collected from the influent sample port (SP)-1 of the treatment system) during each of the three mass discharge measurements had a relative percent difference of less than 18.5%, the practical

analytical/sampling/operational variability for TVOC achievable based on historical SP-1 data (CDM Smith 2013).

The GETS pumping test will be used to assess if at least a 90% reduction in contaminant mass discharge is achieved following ISTR and EAB treatment within the Well 12A source area.

The mass discharge was measured using four extraction wells designed to capture and treat the contaminant plume from the source area. Figure B-9 shows the mass discharge measured at each of the extraction wells and the capture zone of each well using particle tracking modeling. The relative percentage of mass discharge from each of the extraction wells was also used to evaluate the strength of the source areas across the Well 12A source area to aid in selecting technologies, and to evaluate how treatment within different areas would affect contaminant mass discharge measured with the GETS.

B.4.7.8 Mapping Technologies - ISTR and EAB

The contaminant mass and extents, contaminated areas and volumes, and contaminant mass flux and discharge data were used to map treatment technologies (particularly ISTR and EAB) across the site to most efficiently address the contaminant mass and achieve the mass discharge reduction goal. Mapping technologies was focused on the following:

- maximizing the mass of contaminant removed and addressing mobile NAPL within the Time Oil building area
- maximizing the reduction of contaminant mass discharge while minimizing the footprint of aggressive/expensive technologies
- identifying the extent of the secondary source area where significant contaminant mass discharge is occurring outside the Time Oil building
- mapping EAB to areas that further contaminant mass discharge reduction, thereby achieving the reduction goal while minimizing the necessary treatment volume (in particular, the vertical extent)

To achieve these objectives, the following were evaluated: various treatment volumes, associated contaminant mass within the treatment volumes, and estimated contaminant mass discharge from the treatment volumes. Table B-8 summarizes the outcome of this volumetric contaminant mass and the volume estimates for the designated excavation, ISTR, and EAB treatment zones. The treatment technologies were mapped based on maximizing contaminant mass removal from the Time Oil building NAPL zone with aggressive technologies (excavation and ISTR) to address a significant proportion of the mass and a more significant proportion of the total contaminants discharged to the GETS.

Table B-8. Summary of treatment zones for well 12A technologies

Zone	Treatment Zone Surface Area (sf)	Approximately Treatment Depth (ft bgs)	Treatment Zone Volume (cy)	TVOC Mass within Treatment Volume (kg)	TVOC Discharge to GETS[a]
Excavation zone	3,800	0–10	1,400	510	-
In situ thermal remediation	13,000	5–55	26,000	~270	224 gpd[b] (53%)
Enhanced anaerobic bioremediation	162,000	48–60, smaller area with 85–90	90,000	~631	199 gpd[c] (47%)

Notes:
[a] TVOC = sum of 1,1,2,2-PCA, PCE, TCE, cis-1,2-DCE, trans-1,2-DCE, and VC
[b] Discharge estimated as TVOC discharge = EW-5 + ½ discharge to EW-3.
[c] Discharge estimated as TVOC discharge = EW-1 +EW-2+ ½ discharge to EW-3.

ROD Amendment #2 identified ISTR as the selected remedy for the highly impacted portions of the deep vadose zone and upper saturated zone near the former Time Oil Building. The ISTR treatment zone presented in the FFS (CDM Smith 2009) was based on modeling of historical soil data collected between 1985 and 2004. The ISTR treatment zone finally selected was noticeably different from that presented in the FFS. With the addition of the pre-design investigation soil data, the modeled soil plume had shifted to the west such that the majority of the treatment area (approximately 76%) was located within the footprint of the former Time Oil building. The majority of the soil contaminant mass was found to be located in two distinct zones. The vadose zone and saturated zone beneath and in the vicinity of the former Time Oil building account for an additional 27% of the soil VOC mass >5,000 µg/kg. In general, the predesign investigation served to better bound the soil plume to the east and south and to confirm its presence beneath the Time Oil building, resulting in a significant reduction in uncertainty associated with the delineation.

The modeling performed to date suggests that, together, the EAB and ISTR treatment zones contain approximately 90% of the total VOC mass >5,000 µg/kg (see Figure B-9). While the Qpf silt unit contains approximately 63% of the contaminant mass in soil, it contributes approximately half the contaminant mass discharge from the site as measured using the GETS pumping evaluation. Likewise, the total contaminant mass near the Time Oil Building area is a much smaller area—13,000 square ft (sf) compared to 162,000sf—but contributes approximately the remaining half of the contaminant mass discharge to the GETS (measured by taking discharge to EW-5 plus half the discharge going to EW-3).

Therefore, ISTR treatment was mapped to the zone covering an area of approximately 13,000sf and extends from the ground surface (approximate elevation 254 ft amsl) to a depth of 55 ft bgs (elevation 199 ft amsl). This zone contains an estimated 27% of the VOC mass in soil and the majority of remaining mobile NAPL; for the reasons noted above, it is also believed to be responsible for approximately half of the contaminant mass discharge from the site. Approximately 74% of the treatment area is within the footprint of the former Time Oil building, with 30% beneath the older southern portion of the former Time Oil building. Although the ISTR treatment volume was similar to what had initially been conceptualized, the location of the area changed significantly with the majority of it being beneath the Time Oil building.

The EAB treatment zone was delineated to address additional isolated hotspots and the secondary source of contamination in the Qpf silty clay. This area is much larger (approximately 162,000 sf vs. 13,000 sf) compared to the ISTR treatment zone, and contains approximately 63% of the remaining mass responsible for approximately half of the mass discharge to the GETS. The mass flux evaluation with the transect evaluation demonstrated that an estimated 96% of the mass discharge in the high-concentration groundwater plume could be addressed by focusing treatment on the 10 ft–15 ft interval around the Qpf silt secondary source. Therefore, the vertical treatment interval for EAB (interval targeted for amendment injection) was refined from 50 ft to approximately 10 ft–15 ft. This provided substantial cost savings in reduced amendment volumes required for treatment.

Table B-9 summarizes the projected cost of the EAB remedy based on the actual implementation cost, but adjusted over the treatment volume (assuming the 50 ft treatment zone), compared to the approximate total final costs with revised treatment strategy (based on a more robust CSM informed by high-resolution characterization). In this case, the characterization did not result in a significant change in the target treatment area, but did result in a significant change in the vertical interval for treatment. Reducing the target vertical interval for treatment from 50 ft to 12 ft (average), with a deeper treatment zone with a 5 ft thickness in a smaller portion of the site, reduced the overall treatment volume by approximately 70%. This lowered the overall cost of the remediation by reducing costs for amendment, well installation, and labor for amendment injection for one full-scale injection event—from an estimated from $4.66 million to $1.66 million. The cost of the high-resolution characterization for the site was approximately $350,000. Even with this additional characterization cost, however, the project saved an estimated $2.65 million due to the substantial reduction in treatment volume.

Table B-9. Example of return on investigation for source zone remediation

Costs	Pre-ISC	Post-ISC	Notes
Characterization			
Predesign investigation	$250,000	$250,000	Phase I/II
High-resolution source area investigation with mass discharge estimate (transect method)		$350,000	
Mass discharge evaluation (GETS pumping test)	$150,000	$150,000	
Subtotal	**$400,000**	**$750,000**	
EAB Remediation			
EAB – Treatment Volume			
Target area (sf)	52,000	52,000	No change
Target thickness (ft)	50	17	Two intervals, shallow 12 ft thick and deep is 5 ft thick
Target volume (cy)	300,000	90,000	~70% reduction in treatment volume
EAB – Amendment Injection			

Table B-9. Example of return on investigation for source zone remediation (continued)

Costs	Pre-ISC	Post-ISC	Notes
Amendment	$1,600,000	$450,000	
Drilling	$1,320,000	$740,000	
Injection labor	$1,740,000	$470,000	
Subtotal	**$4,660,000**	**$1,660,000**	
Overall Costs (Characterization + EAB Remediation)			
	$5,060,000	**$2,410,000**	
Cost Savings From ISC	**$2,650,000**		

B.4.8 Conclusions

High-resolution vertical profiling to evaluate contaminant distribution in heterogeneous media and assessing mass flux and mass discharge provided significant benefits to the project that aided in making key decisions and cost savings. Some key conclusions are as follows:

- Treatment technologies could be mapped effectively to address the contaminant mass discharge coming from the site.
- The primary NAPL source near the Time Oil building was relatively discrete in area and volume, but was responsible for nearly half the mass discharge coming into the GETS. Therefore, an aggressive (and expensive) treatment technology, ISTR, was mapped to this volume.
- The architecture of the contaminant mass of the Time Oil building source area was significantly different than that presented in the previous CSMs. Although the area of the ISTR treatment zone did not change significantly, the location changed dramatically.
- A significant secondary source area was determined to be associated with a discrete silty-clay layer present across a large area of the site. This area actually contained more contaminant mass in soil than the area near the Time Oil building, but was present in a very discrete interval of the aquifer, and discharge significantly less contaminant mass to the GETS. Therefore, EAB was mapped across a relatively large area, which was similar to that originally conceptualized; however, the vertical treatment interval was reduced from 50 ft to approximately 12 ft (with an additional 5 ft interval included in a deeper zone in a much smaller footprint of the area). This resulted in an approximately 70% reduction in the treatment volume.
- Innovative EAB amendments, using shear-thinning fluids, were designed and used for full-scale injections that allow fluids to be delivered more effectively in and around the Qpf silt layer.
- The pumping test method using the GETS was determine to be the best way to measure contaminant mass discharge reductions to achieve the compliance goal for the interim remedy.

Table B-10. Objectives-based site characterization – Example 4

Goal or problem	• Collect data necessary to delineate the horizontal and vertical extent of the soil contamination, including NAPL, beneath and in the vicinity of the former Time Oil building to support delineation of treatment zones for the multi-component remedy. • Collect the data necessary to evaluate contaminant mass discharge methods for selection of a compliance metric.
Uncertainties/Deficiencies with CSM	• Extent of contaminant mass within the Time Oil source area, including areas containing NAPL • Presence of secondary sources, residual NAPL, and diffused mass in low-conductivity zones • Contaminant mass flux and discharge within each stratigraphic units • Capture of source area and contaminant discharge to GETS from different areas within the source
Data Collection Objectives	• Describe the major stratigraphic units. • Quantify the hydraulic properties of the stratigraphic units. • Map the contaminant distribution. • Estimate the contaminant volume and mass. • Estimate the contaminant mass discharge within stratigraphic units. • Map the contaminant mass discharge delivered to the extraction wells of the GETS.
Data Needs/Gaps	• Vertical intervals (elevations) of stratigraphic units • Properties (grain size distribution, porosity, hydraulic conductivity) of stratigraphic units • Extent of DNAPL within each stratigraphic unit • Contaminant levels and extents in soil and groundwater within source area • Transects near boundary of source area with sampling for hydraulic conductivity, contaminant concentration, and gradient • Evaluation of source area capture and of contaminant discharge for each of the GETS extraction wells
Resolution Required	• A pre-design characterization that included 34 soil borings was conducted, beginning with areas near the known NAPL source and stepped out based on high concentrations observed. • Soil samples were collected based on high-resolution screening with a minimum interval of one analytical sample every five ft to 60-95 ft bgs based on results. • Twelve vertical profile borings were advanced every 100 ft along the suspected boundary of the source area. Temporary well screens were initially emplaced every 5 ft from groundwater surface to 95 ft bgs, sampled for contaminant concentrations, and slug tested. Sample intervals were reduced. One sample was collected in each of the five primary stratigraphic units identified. • Pumping test was conducted at variable pumping rates to evaluate drawdown at monitoring wells, with samples collected for contaminant levels daily to biweekly until equilibrium was achieved.
Investigation Tools	• Geoprobe® 8140 track-mounted Rotosonic drill rig and Gus Pech RS 400 truck-mounted Rotosonic drill rig • Soil core logging and subsampling from cores for geotechnical, hydraulic, and chemical analysis

Table B-10. Objectives-based site characterization – Example 4 (continued)

Data Evaluation and Interpretation	• High-resolution screening, including visual logging, PID evaluation, and NAPL dye testing • Physicochemical testing (density, viscosity) from recovered NAPL • Physicochemical testing (density, viscosity) from recovered NAPL • After soil logging, two-jacket drive point screen or Johnson Screen—attached to the core barrel and installed in the boring to create a temporary well for the collection of groundwater samples and slug testing • Soil logging was used to identify five major stratigraphic units. The elevation contacts were recorded and input into MVS to develop a 3D model for geologic extents. • Hydraulic conductivities measured for each stratigraphic unit varied by approximately 5 orders of magnitude between the most permeable gravel units and a low-conductivity silty clay. • Filter cake and NAPL was delineated in soils beneath and around the former Time Oil building. • Observed LNAPL was sampled and profiled and determined not to contain a significant amount of chlorinated solvents. • Chlorinated solvent DNAPL samples collected were collected; samples primarily contained 1,1,2,2-PCE and TCE, with lower concentrations of entrained chlorinated compounds and petroleum hydrocarbons. • Contaminant concentrations were loaded into the MVS^{ATM} 3D model, along with the geologic information, to evaluate contaminant extents, volumes, and masses across the site. A Qpf silty clay unit present throughout most of the high-concentration source area was determined to be a significant secondary source of contamination. • Contaminant mass discharge was found to primarily occur in the permeable intervals in and around the Qpf silty clay unit at the boundary of the source area. A 10 ft vertical interval was found to be responsible for an estimated 96% of the contaminant mass discharge. • Capture was estimated for each extraction well and used to evaluate where most of the contaminant mass discharge was occurring within different parts of the source area. The primary NAPL source area around the Time Oil building was determined to be responsible for approximately 50% of the total discharge going to the GETS. The remaining mass discharge was attributed to the secondary sources.
Comments	• Adaptive site characterization was required to respond to findings in real time. Data were communicated to interpretation team, and investigation borings and sampling locations revised as necessary. • An evaluation of the contaminant mass in soil across the site using different threshold criteria was used to compare the contaminant mass in different potential volumes. • The ISTR treatment volume was delineated based on the presence of NAPL, high concentrations of soil contaminants that extended over a relatively large vertical interval throughout transmissive stratigraphic units, and the volume contributing ~50% of the contaminant discharge. • EAB treatment volume was delineated to target the area where significant secondary soil contamination was present, and where high concentrations of contaminants were observed in permeable zones. In addition, EAB was used to target treatment of some residual NAPL hot-

Table B-10. Objectives-based site characterization – Example 4 (continued)

	spots observed across other areas of the site. • The vertical interval of the EAB treatment zone was refined to target the area above, within, and below the Qpf silty clay. This reduced the target interval from 60 ft to 10–15 ft, depending on the thickness of the Qpf silty clay. • The pumping test method was determined to be best for evaluating the compliance of the Well 12A remedy in meeting the mass discharge reduction goal. • The mass discharge evaluation concluded that approximately half of the total mass discharge coming to the GETS originated from the ISTR treatment zone and the other half from the EAB treatment zone.

APPENDIX C. SPREADSHEET FOR ESTIMATING CONTAMINANT MASS IN THE 14 COMPARTMENT MODEL

The 14-Compartment Model is a graphic decision tool that "provides a new and holistic view of the problem of NAPL and associated dissolved phase contamination in subsurface environments that blends hydrogeology, contaminant phases, and location" (Sale and Newell 2011). This tool aids in understanding the distribution of contaminants in the following areas:

- source versus plume
- transmissive units, such as sands, versus "low-k" units, such as clays ("k" refers to the permeability of the material, thus a low-k unit is typically a clay or silt in unconsolidated media)
- different phases

With four phases, four locations, and the assumption of no nonaqueous phase liquid (NAPL) in the plume locations (by definition), the result is a matrix with 14 different compartments, as shown in Figure C-1.

Phase	Source		Plume	
	Low Permeability	Transmissive	Low Permeability	Transmissive
Vapor				
NAPL			■	■
Aqueous				
Sorbed				

Figure C-1. 14-Compartment matrix.

The following three tools are available to describe the use of the 14-Compartment model:

- *Decision Guide: A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvent Sites* (Sale and Newell 2011). This document, developed by the Environmental Security Technology Certification Program (ESTCP), was designed to assist decision makers in selecting remedies for subsurface chlorinated solvent releases. The decision guide reviews the nature of the problem, considers the critical components of setting objectives, provides an overview of available options, and offers suggestions for developing comprehensive remedial packages.
- *14-Compartment Model Toolkit* (Marquardt et al. 2014) and *User's Guide for 14-Compartment Model* (Vanderkooy et al. 2014). This web-based tool and associated user's guide, prepared for the Strategic Environmental Research and Development Program (SERDP), can be used to assess sites contaminated with chlorinated solvents and to compare the likelihood of success for potential remedies.
- *Management of Contaminants Stored in Low Permeability Zones, A State-of-the-Science Review* (Sale et al. 2013). This SERDP document is a state-of-the-science review of contaminant management in low-permeability zones of aquifers. It was developed by research-

ers from Colorado State University, the University of Guelph, GSI Environmental, and the University of Kansas.

The above-described tools stress a concentration-based approach to applying the 14-Compartment Model in site management; in other words, the relative concentrations use an order-of-magnitude approach (for example, concentrations in the 100-part-per-billion range are referred to as “2” [as in 10^2 parts per million]). Some remediation problems, however, also benefit from use of a mass-based approach. As stated in the decision guide:

> …it is also important that a conceptual site model include a mass balance that addresses the spatial distribution of the mass of contaminants, and the fluxes of contaminants within the site, as well as the hydrogeologic and biogeochemical information needed to evaluate fate and transport.

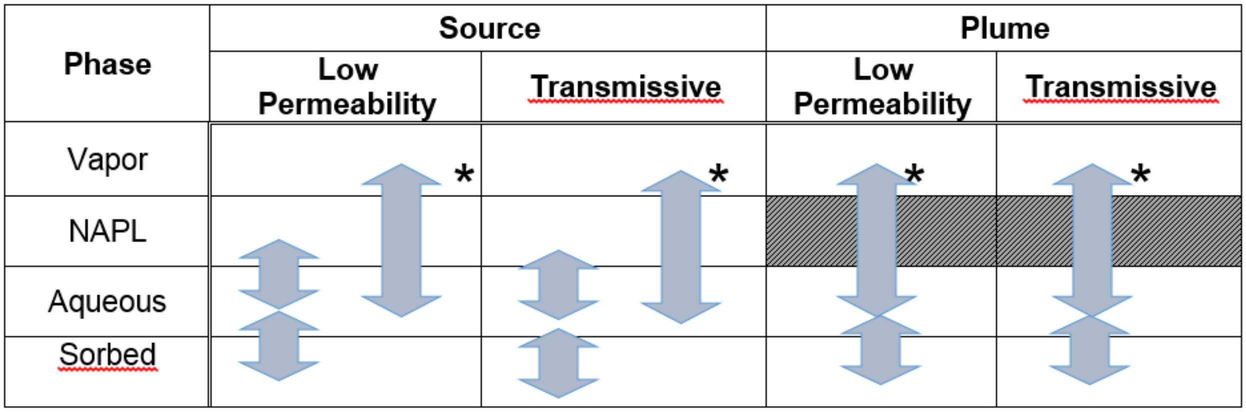
C.1 Estimating Contaminant Mass in the 14 Compartments

The following sections discuss how to collect the necessary data and how to use simple-phase (water, solid, gas, NAPL) partitioning relationships to estimate the relative masses in the 14 compartments. The new Phase Distribution Spreadsheet (PDS), a tool developed by Dr. Kurt Pennell, provides a framework for understanding the distribution of contaminant mass between several key compartments that are related by partitioning relationships, and gives the users a computational platform for estimating contaminant mass in each phase or compartment.

The general approach described in the following sections is based on the following assumptions:

1. You have a sampled soil core as well as a total concentration (in milligrams per kilogram [mg/kg]) for the contaminant of interest.
2. There are physical and chemical properties of interest.
3. All of the different phases are in chemical equilibrium with each other.

With these assumptions, the PDS will help calculate the contaminant mass in all of the 14 compartments (see Figure C-2) for the particular soil core sampled.



**Note: The sampled core(s) must be from the unsaturated zone, as the aqueous phase concentration is the pore water in the unsaturated zone, not the groundwater in the aquifer. Thus, two cores are needed for the source transmissivity column (one from the unsaturated zone and one from the saturated zone).*

Figure C-2. Contaminant mass calculations using the 14-Compartment model.

Warning: The resulting masses are likely accurate for a particular soil core, but may not be representative of the masses even a few feet away, as explained below.

- A core collected in the saturated zone will not have a vapor phase; therefore, this core should not be used to estimate the mass of contaminant in the vapor phase (you should collect soil cores in the unsaturated zone and apply the spreadsheet or, preferably, measure the vapor concentrations in the unsaturated zone directly). In other words, the partitioning calculations do not do the following:
    - extend across the water table
    - link the transmissive and low-k zones
    - go from source to plume
- Nonlinear soil desorption at low concentrations will result in lower groundwater concentrations than predicted by the linear partitioning model in the spreadsheet. At this point in the remediation field, these nonlinear effects are not often considered, but they can be important at some sites.
- Soil concentrations in one location, in one compartment, can be dramatically different than another core collected a short distance away in the same compartment. This variability needs to be considered when estimating masses in a compartment across an entire site.

C.2 Contaminant Phase (Mass) Distribution: The Phase Distribution Spreadsheet

Following is a step-by-step guide on how to apply the PDS.

Step 1. Collect a soil core and submit it to a laboratory to obtain data (in mg/kg) for one or more contaminants. Although the PDS calculates only one component at a time, if you have X component, you can run the PDS X times (once for each component) to get the partitioning values for every contaminant of interest. Enter the concentration(s), in mg/kg, in the top yellow cell (row 10).

Step 2. Fill in the physical and chemical parameters of interest for the contaminant(s). The Texas Risk Reduction Program provides most of the required chemical properties for over 100 compounds—download the file and search for “chemical/physical properties.” Note: be sure that you are using the same units as specified in the PDS.

Note: The spreadsheet provides published physical and chemical parameters for chemicals of interest. These published values, however, are generally for pure chemicals, and may not be fully representative of the weathered or mixed contaminants found at your site. If possible, collecting a sample of the site-specific NAPL to be analyzed will allow for a more accurate assessment—that is, one that considers the actual chemical and physical parameters of the contaminants at the site in question.

Step 3. Enter the soil/core properties and the physical size of the core. Remember, this is a partitioning exercise for a single core collected at the site, and the PDS assumes that the calculation is for an actual core sample. While some soil parameters can be estimated (more accurate results are obtained from a soil analysis to get bulk density, particle density), others demand a soil analysis (water content in the pore space, fraction organic carbon [f_{oc}]). Be sure that you are using the same units as specified in the PDS (for example, f_{oc} is entered as a percent, not a fraction). If the soil sample or boring was collected from the saturated zone, the measured water content (entered in cell G17; % wt.) should result in a gas phase saturation that is equal or close to zero (see cell D27). However, if there still is a gas phase, you can increase the water content value in cell G17 until the gas phase saturation is zero. In most soils, complete water saturation corresponds to gravimetric water content of about 20% wt.

Step 4. The spreadsheet will automatically calculate all of the cells needed for partitioning under two cases: Assuming NAPL is present (Step E and Step A1), and then determining if NAPL is present. Based on the calculated threshold concentration (the maximum concentration in soil that the sample can hold in all phases without any NAPL being present), the PDS will determine whether NAPL is likely present and will adjust the resulting masses accordingly. Do not change any of the blue cells; these are intermediate calculations.

Step 5. Look at the red cells for the results, which show (a) the actual masses of the contaminant in milligrams, and (b) the percentage distribution in the bottom red box. The pie chart then reports these values.

Step 6. If you have multiple core samples from a particular compartment at a site, you can multiply each one by the volume of soil that the sample represents (in cubic yards, cubic meters, or any volumetric unit) and then average the results to get the total mass in that compartment.

APPENDIX D. TOOLS DESCRIPTIONS

D.1 Geophysics

Table D-1a. Geophysics tools: surface geophysics

Tool/References	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Ground Penetrating Radar • Annan 2005 • Bayer et al. 2011 • Beres et al. 1999 • Bradford 2006 • Bradford and Deeds 2006 • Bradford, Dickins. and Brandvik 2010 • Bradford and Babcock 2013 • Clement, Barrash, and Knoll 2006 • Guerin 2005 • USEPA 2004	Ground penetrating radar (GPR) creates a cross-sectional imaging of the ground based on the reflection of an electromagnetic (EM) pulse from boundaries between layers of different dielectric properties. The quality depends on soil and water conditions as penetration is reduced by clay, water, and salinity. GPR is useful in resolving stratigraphic layers; however, independent confirmation of lithology is required. GPR generates a 2D profile, but it can be run with multiple lines in a grid pattern to generate a pseudo-3D image. Penetration and resolution of features depend on antenna frequency and material conductivity and interferences, and are generally limited to 20 meters (m) deep. GPR can identify internal structures between material-bounding reflectors (e.g., cross-bedding) in some cases. GPR can be used to locate geologic material or property contacts associated with dielectric property contrasts (e.g., proxy for porosity in some water-saturated clastic sediments) as well as subsurface infrastructure (e.g., pipes, tanks, cavities).	Data Quality • varies with antennas and subsurface EC • relatively sharp boundaries • qualitative to quantitative depending on field conditions, prior knowledge/subsurface calibration, experimental quality, appropriate modeling Applicability/Advantages • relatively fast to acquire, and processing methodology well established • primarily used in materials with low EC (sand, gravel, or rock except shales) • can be run repeatedly in time-lapse mode to track changes in moisture (above water table) or EC or dielectric properties (plume or spill bodies, including several experiments tracking presence and changes in dense nonaqueous phase liquid [DNAPL] in sandy aquifers)	• minimal penetration in electrically conductive (silts and clay-rich or conductive pore water) units • interpretation of features and depths semiquantitative without independent reference (well or cone penetrometer [CPT])
High-Resolution Seismic Reflection (2D or 3D) • Excel Geophysical Services 2010 • USEPA 2004	With high-resolution seismic reflection, 2D cross-sectional imaging of the ground is based on the reflection of a seismic pulse from the boundaries between the layers of contrasting mechanical properties. The image can be broadened to 3D to account for off-section changes.	Data Quality • varies depending on site conditions Applicability/Advantages • identification of lithological layering, but not necessarily material type • patterns can be diagnostic of depos-	• difficult to get reflections from shallow (<10m deep) boundaries • resolution varies with input frequency and geometric and acoustic characteristics

Table D-1a. Geophysics tools: surface geophysics (continued)

Tool/References	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	This type of imaging evaluates both compression (P) waves and shear (S) waves, and profiles multiple stratigraphic layers to large depths.	itional environment - can be used in some cases to identify water table depth - can be used with marine seismic survey to assess below-water bodies - imaging at greater depths than refraction and surface waves - potential high resolution of large voids, faults, and fractures at depth; S-wave surveys allow shallower surveys, but are still limited by near surface noise	- labor intensive, slow, relatively expensive - difficult to implement in areas with extensive infrastructure
Seismic Refraction - Technos 2004 - USEPA 2004	With seismic refraction, 2D cross-sectional interpretation of layering is based on estimating travel of seismic energy down to, along, and up from boundaries between layers of increasing seismic velocity. This type of imaging evaluates both P-waves and S-waves.	Data Quality - varies depending on site conditions - low detail Applicability/Advantages - identifies lithological layering, but not necessarily material type - works on shallow layers - identifies geologic boundaries (overburden layers, bedrock depth) - in some cases, can identify water table - identifies potential topographically influenced DNAPL flow pathways	- only identifies boundaries of progressively increasing velocity - limited to maximum of three to four layers - maximum depth generally 40m–50m (requires long arrays) - cannot be implemented in areas with high levels of background vibrations
Multichannel Analyses of Surface Wave (Seismic Surveys) - Technos 2005	The multichannel analysis of surface waves method uses the dispersive characteristics of surface waves to determine the variation of S-wave velocity with depth. S-wave data are calculated by analyzing the seismic surface waves generated by an impulsive source recorded by an array of geophones. 2D imaging is cross-sectional imaging of the ground-based reflection of a seismic pulse from the boundaries between layers of contrasting	- evaluates shallow features that serve as DNAPL transport and groundwater flow paths - minimal impacts by buried piping or utilities - data to aid in monitoring well selection zones for vertical characterization - identifies karst terrain, voids, waste pits, and surface bedrock features	- limited to depths >100 ft - can be difficult to implement in some areas due to access restrictions

Table D-1a. Geophysics tools: surface geophysics (continued)

Tool/References	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	mechanical properties. S-wave velocity is a function of the elastic properties of the soil and rock, and is directly related to the hardness and stiffness of subsurface materials.		
Electrical Resistivity Tomography • Binley and Kemna 2005 • Loke et al. 2013 • Telford et al. 1990	2D imaging is cross-sectional imaging of the ground-based variations in electrical resistivity. 3D imaging expands the 2D result into a third dimension.	Data Quality • varies with ground contact configuration (e.g., Wenner, dipole-dipole) and electrode spacing • boundaries are gradational Applicability/Advantages • indicates broad-scale lithologic variations • identifies water table depth • maps electrically conductive pore water	• resolution decreases with depth • deep applications require long straight line access • can be difficult to implement in some areas due to access restrictions
Very Low Frequency • USEPA 2014b	This type of imaging uses the magnetic components of the EM field generated by long-distance radio transmitters in the very-low-frequency band. It maps local EM variations induced by low-frequency distant primary EM antennas.	Data Quality • generally, a reconnaissance-level survey (qualitative) Applicability/Advantages • variations in primary field orientation can be used to identify discontinuities (faults and large fractures) • can be used to map lateral variations in electrical resistivity down to approximately 25m–40m • quick, inexpensive survey	• military transmitters are becoming obsolete • relatively coarse survey • orientation sensitive; multiple line directions may be necessary • conductive structures affect local measurement of direction and strength of field

Table D-1a. Geophysics tools: surface geophysics (continued)

Tool/References	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Electromagnetic Conductivity - USEPA 2014b	This type of imaging maps variations in EC using a local primary field. It is either a frequency-based (lateral variations to a set depth) or time-based system (vertical sounding).	Data Quality - primarily reconnaissance mapping (qualitative) Applicability/Advantages - can be used to map lateral variations in EC from <1m deep to >40m deep - identifies broad geologic variations or conductive plumes - shallow high-resolution systems can be used to map infrastructure - quick, inexpensive survey	- resolution decreases with volume sampled (penetration) - can be subject to interference from surface infrastructure and power sources - penetration can be varied by changing coil orientation and spacing, but vertical resolution of layers is poor - generally qualitative rather than quantitative result - vertical modeling of data very limited; bulk measurement reduces void resolution potential to large, shallow voids; depth of investigation reduced by low-resistivity materials

Table D-1b. Geophysics tools: Downhole geophysics

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Magnetometric Resistivity - USGS 1987	Magnetometric resistivity measures the induced magnetic field created by a current passing between two electrodes. The investigation depth is controlled by electrode spacing.	Data Quality - qualitative - less sensitive to small conductivity variations near the measurement point - less influenced by conductive overburden Applicability/Advantages - mapping preferential pathways in fractured or unconsolidated media - more sensitive to conductive targets under moderately conductive overburden than other EM methods	- requires surface access for measurements
Induction Resistivity (conductivity logging) - Keys 1990 - Kobr, Mares, and Paillet 2005 - McNeill 1986 - McNeill, Bosner, and Snelgrove 1990	This tool performs inductive measurements of apparent conductivity. Given the appropriate contrasts, variations in lithology (especially relative clay or silt content) and water (relative porosity, relative total dissolved solids or conductivity/resistivity) can be recognized. With this tool, the formation without borehole and very-near borehole effects can be sensed.	Data Quality - qualitative to quantitative depending on field conditions, prior knowledge/subsurface calibration, and experimental quality - generally good detail and consistent except in low-conductivity environments Applicability/Advantages - focused beyond borehole, and thus relatively unaffected by diameter or borehole fluid conductivity - fewer corrections needed for quantitative result - can operate in polyvinyl chloride (PVC), not metal casing or screen	- can give poor response in low-conductivity/high-resistivity subsurface environments - vertically averages over approximately 1 m–2 m - metallic minerals (pyrite) or objects (e.g., centralizers) interfere with results

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Resistivity • COLOG 2012 • USEPA 2011b • Keys 1997	This is a galvanic measurement of resistivity, with various configurations of current and potential electrodes. It averages over electrode spacing, typically 0.5m–2m.	Data Quality • sensitivity to borehole diameter and fluid conductivity make results most often qualitative • works best in highly resistive environments Applicability/Advantages • primarily characterizes lithology in terms of EC (i.e., water/clay content) and conductivity of pore water • sensitive to borehole diameter, and thus can be used to detect large fractures; however, technique with typical electrode spacing (0.5m–2m) too unreliable for unsupported fracture detection	• results depend highly on borehole diameter, grounding, and electrode configurations • only works in open hole and below water table • large historical database, but varying electrode configurations can make comparison problematic

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Ground Penetrating Radar Cross Well Tomography - Annan 2005 - Chen, Hubbard, and Rubin 2001 - Dafflon et al. 2011 - Day-Lewis et al. 2003 - Ernst et al. 2007 - Irving et al. 2007	This type of imaging requires wells of appropriate diameter, casing/screen material (nonmetallic), spacing, and depth depending on the problem and aquifer dimensions and subsurface materials. The lateral penetration distance and resolution are functions of antenna frequency and EC and dielectric properties.	Data Quality - qualitative to quantitative depending on field conditions, prior knowledge/subsurface calibration, experimental quality, and appropriate modeling Applicability/Advantages - can provide subsurface structure and proxy property information in an aquifer below conductive surface soil (i.e., where surface GPR may not be useful)	- calibration of features more controlled where independent direct measurement information (contacts, material types, porosity, water chemistry) available for wells used in tomographic survey
Optical Televiewer - COLOG 2012 - USEPA 2004 - Keys 1997	This is an oriented visual image of the borehole wall. It aids in the evaluation of fracture orientation and aperture size in bedrock investigations. The image is originally in a downward direction, and undergoes restoration to correct for optical distortion.	Data Quality - depends on water clarity Applicability/Advantages - identifies fractures and voids - some lithologic information is interpretable from the data - potentially finer resolution than acoustic televiewer - works above the water table	- borehole diameter must be assumed - difficult to interpret when water is cloudy - clear water and clean borehole wall necessary to determine lithologic and structural characteristics - original view is oblique and distorted, requiring digital restoration; some features can be lost in processing

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Acoustic Televiewer • COLOG 2012 • USEPA 2011b • Keys 1997 • USEPA 2004	This tool obtains a highly detailed measurement of borehole diameter by timing the return reflection of an acoustic pulse off the borehole wall back to the probe. It provides a record of the location, character, and orientation of features in the casing or borehole wall that alter the reflectivity of the acoustic signal.	Data Quality • varies depending on condition of borehole and careful data collection Applicability/Advantages • primarily measures fractures and their orientation • measures borehole rugosity • some lithologic information is interpretable • provides borehole diameter • provides borehole orientation • can measure actual fracture dip • independent of water clarity • structural features like bedding, fractures, and solution openings	• only works below water table • requires experience to interpret well • must be well centralized • some thin bed exaggeration • not likely to detect DNAPL directly or indirectly

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Natural Gamma Logging • Keys 1990 • COLOG 2012 • Keys 1997 • USEPA 2004	This tool is most commonly used for identification of lithology and stratigraphic correlation. It is sensitive to the natural gamma radiation from minerals, detected at a sodium iodide crystal in the logging tool. Relatively higher counts in noncarbonate clastic sediments are commonly associated with fines (clay, silt), but also with K-feldspar, micas, and some mineral deposits (e.g., uranium, thorium, potash, phosphate). Sensitivity is related to crystal size and logging speed.	Data Quality • qualitative to quantitative depending on field conditions, prior knowledge/subsurface calibration, and experimental quality Applicability/Advantages • can indicate lithology and changes in lithology • can indicate relative abundance of silt or clay in sands • can log in air or water and in metal or PVC cased or screened wells or uncased wells • natural gamma logging can be combined with other sensors (e.g., fluid resistivity, temperature, caliper) in one tool • relatively fast operation with fast turnaround on information • information can help guide subsequent characterization work	• requires field confirmation • not sensitive to DNAPLs • can be influenced by well construction (e.g., bentonite, feldspathic sand in filter pack, casing material, borehole diameter)

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Neutron (Porosity) Logging • Keys 1990 • Hearst and Nelson 1985 • Barrash and Clemo 2002 • Keys 1997 • USEPA 2004	Neutron porosity probes with a large source and long spacing are used to measure saturated porosity and moisture content in a wide range of borehole diameters, above and below the water table. The neutron source emits known flux at known energy. Collisions with hydrogen are highly moderated because of similar mass, so reduced count rates at a detector(s) in the tool indicate the presence of hydrogen (commonly water in shallow environmental applications) in the volume of influence. Water content in pores below the water table can be converted to porosity. Well-known transforms can quantitatively convert count rates to porosity if calibration information is available from calibration wells, samples, or literature.	Data Quality • qualitative to quantitative depending on field conditions, prior knowledge/subsurface calibration, and experimental quality Applicability/Advantages • can provide semi-quantitative or quantitative information on porosity in wells • can indicate relative abundance of silt or clay in sands and changes in lithology related to porosity or bound water content • can log in metal or PVC cased or screened wells or uncased wells • relatively fast operation with fast turnaround on information • information can help guide subsequent characterization work	• nuclear source tool requires licensed handling and commonly written consent for use in wells • requires field confirmation for lithologic interpretation • can be influenced by hydrogen sources in well construction (e.g., bentonite seals) • PVC casing and large water-filled diameter reduces signal strength, but generally that is not a major problem as a constant influence along a borehole • cannot alone distinguish between hydrogen sources (bound water in clay, water, DNAPL)

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Nuclear Magnetic Resonance Logging - Daughney, Bryar, and Knight 2000 - Grunewald and Knight 2011 - Maliva, Clayton, and Missimer 2009 - Walsh, Grunewald, and Turner 2010	The measured nuclear magnetic resonance (NMR) signal is generated directly by hydrogen nuclei in pore fluids, and it conveys detailed information about the physical and chemical pore environment in which the water resides. The NMR signal amplitude is linearly proportional to the volumetric water content; thus, NMR methods can be used to determine porosity in the saturated zone or moisture content in the unsaturated zone, without any site or lithology-specific calibration. Relaxation or decay behavior of the NMR signal is strongly sensitive to the pore size distribution—i.e., mobile water in large pores exhibits long decay time and water in small pores exhibits short decay time. Decay time behavior is commonly used to estimate a relative pore size distribution and, with porosity estimates based on the signal amplitude, form the basis for robust permeability estimation with the Kozeny-Carman relationship.	Data Quality - emerging technique; quantitative analysis subject of ongoing research - qualitative to quantitative depending on field conditions, prior knowledge/subsurface calibration, experimental quality, and appropriate modeling Applicability/Advantages - borehole tool now available for PVC screened wells - provides quantitative profiles of porosity and permeability in aquifers, and of moisture content in the vadose zone - physically based for unconsolidated sandy sediments - may be able to identify DNAPL (in progress)	- requires non-metallic well screen, casing, or both - quantitative permeability application without calibration or site-specific relationship is limited currently to unconsolidated sandy sediments

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Video Log • COLOG 2012	This is a typically digital video camera that records down the length of a borehole.	Data Quality • varies and requires clear borehole fluid; resolution decreases in cloudy conditions Applicability/Advantages • primarily fracture and void detection • water movement into borehole above water table and in some cases into and out of fractures • rugosity and rock competence • casing length and screen conditions • basic interpretation is simple, but refined interpretation requires experience • real-time inspection of borehole conditions	• analysis is mostly qualitative, although semi-quantitative estimates of aperture and orientation are possible

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Caliper Log • COLOG 2012 • Keys 1997	A caliper log is a mechanical measurement of borehole diameter based on the extension of three or four caliper arms. It is used to guide the interpretation of other downhole geophysical logs, because most types of logs are affected by changes in borehole diameter. It can provide information on lithology and secondary porosity.	Data Quality • average borehole diameter based on three or four point measurements Applicability/Advantages • borehole diameter and rugosity • fracture/void detection • casing depth • simple direct quantitative measurement of hole diameter • uninfluenced by other activities in borehole or by water clarity	• measures only at fixed points within borehole circumference and may not quantitatively represent all features • narrow, deep features are not accurately measured

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Temperature Profiling - COLOG 2012 - Keys 1997	Temperature profiling involves the direct measurement of borehole fluid temperature. It provides information on the movement of water through a well, including the depths that produce or accept water.	Data Quality - sensors measuring to within .001 degree Celsius (°C) - older sensors with lower (0.1°C) resolution have limited applicability Applicability/Advantages - highlights critical flow zones under heterothermic conditions - used to estimate infiltration - heat can be used as an innocuous tracer between boreholes	- borehole must be water filled and preferably allowed to stabilize without other probes or testing prior to logging - typically compromised when collected in open boreholes, but can be collected in lined boreholes - requires thermal disequilibrium between water in fracture and rock (can be induced where not naturally present)

Table D-1b. Geophysics tools: Downhole geophysics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Full Wave Form Seismic • Fichtner 2011	A seismic pulse is created by the full wave form seismic probe and measured at a series of transducers on another part of the Sonde. Travel time and character of the pulse varies as it travels along borehole wall and the immediately surrounding rock mass.	Data Quality • varies with rock competence and borehole quality Applicability/Advantages • measures P-waves, S-waves, and Stoneley seismic waves • quantitative and highly detailed measurement of material properties • calculates bulk modulus • general rock competence and lithology • detects tube waves indicative of some transmissive fractures	• wave forms can be difficult to interpret in irregular boreholes • relies on algorithms to identify events in real time • resolution can vary depending on signal frequency

D.2 Hydraulic Testing

Table D-2a. Hydraulic testing: single-well tests

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Packer Testing • Bliss and Rushton 1984 • Gale 1982 • Lapcevic et al. 1999 • Maini 1971 • National Research Council 1996 • Nielsen 2005 • Price 2009 • Sara 2005 • US Bureau of Reclamation 1977 • Zeigler 1976 • Quinn et al. 2012	Packer testing involves isolating a depth discrete section of the borehole with straddle packers and conducting any of the hydraulic tests (slug tests, constant head step test, pumping/recovery tests). Note: Packers can also be used in an overburden well if the well is constructed properly to allow meaningful data to be obtained.	Data Quality • quantitative to semi-quantitative depending on the presence of nonideal behavior Applicability/Advantages • obtain depth discrete T and S values • high precision values are obtained with lower flow rates • conducting more than one type of test gives greater confidence in the T value	• time consuming • short circuiting to open hole can interfere with test results • non-Darcian flow causes T to be underestimated • for wells with large screened intervals and when filter pack materials are placed outside of the well screen: this high permeability material can and will provide a preferential flow path for contaminants to move either up or down from zones outside of the straddle packer interval. This "short circuiting" can lead to erroneous contaminant distribution data.
FLUTe™ Profiling http://www.flut.com	This is a newer method in which a continuous T profile is obtained for an entire hole by driving a liner down the hole with water pressure and measuring the descent velocity.	Data Quality • quantitative to semiquantitative depending on the presence of nonideal behavior Applicability/Advantages • obtain T profile • rapid test • no water injected or withdrawn • can be performed in conjunction with other FLUTe installments	• large downward gradients can interfere with test results • borehole diameter changes can interfere with test results

Table D-2a. Hydraulic testing: single-well tests (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Borehole Dilution Tests • Drost et al. 1968 • Lee 1985 • Brainerd and Robbins 2004	These tests determine the Darcy flux out of a well based on the dilution of a tracer placed in a well over time.	Data Quality • quantitative to semi-quantitative depending on the presence of nonideal behavior Applicability/Advantages • obtain values for Darcy flux • semiquantitative to quantitative depending on the presence of nonideal behavior • inexpensive	• vertical gradients can affect data
Flow Metering • Rushton and Weller 1985 • Theis 1935 • Warren and Root 1962 • Paillet 2000 • Paillet 2001 • Paillet et al. 2010	With flow metering, vertical flow (ambient or pumping induced) in a well or borehole is measured with depth.	Data Quality • quantitative to semi-quantitative Applicability/Advantages • identifies inflow and outflow from hole	• low-flow zones cannot be identified

Table D-2a. Hydraulic testing: single-well tests (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Partitioning Interwell Tracer Test • Hartog et al. 2010 • Cain et al. 2000 • Jin et al. 1995 • Annable et al. 1998 • Nelson et al. 1999 • Young et al. 1999 • Mariner et al. 1999 • Rao et al. 2000 • Londergan et al. 2001 • Dai et al. 2001 • Meinardus et al. 2002 • SERDP-ESTCP 2012 • Brooks et al. 2002 • Istok et al. 2002 • Davis, Istok, and Semprini 2002 • Werner and Hohener 2002 • Imhoff et al. 2003 • Jalbert et al. 2003 • Brusseau et al. 2003 • Moreno-Barbero and Illangasekare 2006	The partitioning interwell tracer test (PITT) method is used to more accurately characterize the amount of nonaqueous phase liquid (NAPL) in the subsurface. Injection wells release multiple tracers that partition into the NAPL to different degrees, and the chromatographic separation is observed at the extraction wells, which provides a fairly accurate measurement of the volume of NAPL. More than 50 PITTs were used at contamination sites to derive quantitative estimates of saturation and volume of DNAPL in subsurface. In most cases, tests were performed to assess remediation performance. During a PITT, a suite of conservative and partitioning tracers injected via wells migrate with groundwater to the extraction wells. Partitioning tracer velocities are retarded to various degrees depending on their affinity to partition; thus, tracer travel times, in conjunction with laboratory measurements of NAPL-water partitioning coefficients, are analyzed to estimate saturation of NAPL in the interwell zone during the test. Single-well push-pull tests have been proposed to characterize near-well NAPL presence, and gas-phase PITTs have been applied to estimate NAPL volume in the vadose zone.	Data Quality • quantitative to semi-quantitative Applicability/Advantages • assesses contaminant distribution and remedial performance • provides alternative means of estimating NAPL volume over relatively large areas, which typically relies on interpolation between point measurements • extensive monitoring (e.g., multilevel samplers) and detailed data analysis can be used to evaluate architecture of subsurface DNAPL	• physical heterogeneities can cause significant tailing of tracer concentrating • degradation of reactive and nonreactive tracers can cause overestimation or underestimation of NAPL saturations, respectively • tracer partitioning to natural organic carbon can cause overestimation of NAPL • nonequilibrium tracer partitioning can result in underestimation of NAPL • PITTs likely to underestimate NAPL present in pools • tracers may bypass low-permeability zones and underestimate NAPL • multiple confounding factors can lead to significant errors • expensive, and may require recovery of tracers
Pumping and Recovery Tests • Bentall 1963 • Boulton and Streltsova 1977	These tests are conducted by pumping a well at a constant rate (injection or withdrawal) while measuring pressure and flow rate. Recovery after pump shut-off is usually better behaved; however, specific storage is traditionally determined from the pumping portion.	Data Quality • quantitative to semi-quantitative depending on the presence of nonideal behavior	• must measure flow rates and pressure responses accurately • longest testing times • withdrawal tests may require treatment of extracted water

Table D-2a. Hydraulic testing: single-well tests (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
• Bourdet et al. 1989) • Cooper and Jacob 1946) • Gringarten and Witherspoon 1972 • Gringarten 1984 • Gringarten 1987 • Horner 1951 • Jacob 1946 • Jacob 1963 • Kazemi 1969 • Pollard 1959 • Rushton and Weller 1985 • Theis 1935 • Warren and Root 1962		Applicability/Advantages • obtain values for T and specific storage • identify dual permeability effects • agreement between both tests increases confidence in the T values	

Table D-2a. Hydraulic testing: single-well tests (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Slug Tests (see Discrete Interval Sampling and Constant Head Step Test) - Barker and Black 1983 - Butler 1998 - Greene and Shapiro 2001 - Hvorslev 1951 - Levy et al. 1998 - McElwee 2001 - Murdoch and - Germanovich 2006 - Patchett 1993 - Schwartz 1975 - Schweisinger et al. 2009 - Shapiro and Hsieh 1998 - Svenson et al. 2007 - Zenner 2009	A cross-well slug test involves instantaneously changing the head in the well and monitoring the recovery. This test is commonly initiated by submerging or removing a physical slug or by pneumatic means, by pressurizing or depressurizing the air column above the water. Well development effects can be identified if the results from rising head tests are significantly different than falling head tests with similar initial displacements.	Data Quality - quantitative to semi-quantitative depending on the presence of nonideal behavior Applicability/Advantages - obtain value for T - rapid test - no water is injected or withdrawn	- must measure pressure accurately - must conduct more than one test to pseudo-validate Darcian flow conditions - must conduct both rising and falling head tests to identify well development issues
Constant Head Step Tests - Atkinson, Gale, and Dudgeon.1994 - Doe et al. 1980 - Elsworth and Doe 1986 - Haimson and Doe 1983 - Mackie 1982 - Price et al. 1977 - Price et al. 1982	This tool involves a series of constant rate tests conducted at increasing flow rates by either injecting or withdrawing water. Darcian flow is validated by the flow being directly proportional to the head change.	Data Quality - quantitative to semi-quantitative depending on the presence of nonideal behavior Applicability/Advantages - obtain value for T - ensures results are free from errors due to non-Darcian flow	- must measure flow rates and pressure responses accurately - withdrawal tests may require treatment of extracted water

Table D-2a. Hydraulic testing: single-well tests (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
• Quinn, Cherry, and Parker 2011			

Table D-2b. Hydraulic testing: cross-borehole testing

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Tracer Testing • Horner 1951 • Jacob 1946 • Jacob 1963 • Kazemi 1969 • Lapcevic et al. 1993 • Novakowski and Lapcevic 1994 • Lapcevic et al. 1999 • Novakowski et al. 2004	A tracer added to one well and an observation well is monitored to identify breakthrough. This test can be conducted under ambient flow conditions, or under the stress of pumping.	Data Quality • semiquantitative to quantitative depending on the presence of nonideal behavior and the tracer recovery Applicability/Advantages • obtain Darcy flux and average groundwater velocity	• erroneous values can be obtained if wells have long screens due to vertical flow in hole • difficult to obtain 100% mass recovery
High-Resolution 3D Hydraulic Tomography • Berg and Illman 2011 • Brauchler, Dietrich, and Sauter 2011 • Cardiff, Barrash, and Kitanidis 2012 • Cardiff, Barrash, and Kitanisis 2013 • Illman et al. 2009 • Hsieh, Neuman, and Simpson 1983 • Illman and Tartkovsky 2006 • Illman, Craig, and Liu 2008	This is a cross-well hydrologic testing method that uses systematic short-term pump testing and numerous combinations of pump intake elevations and locations coupled with multiple elevation and location pressure head measurement. The approach is similar in concept to medical imaging or geophysical imaging and leverages advances in data processing and mathematical methods from related fields to identify the most likely hydraulic conductivity distribution within the test domain. A series of pumping tests are run successively in isolated intervals of one or more wells while pressure changes are measured in numerous isolated intervals in surrounding observation wells or direct-push (DP) borings. Follow-up inverse modeling finds the distribution of K that	Data Quality • semiquantitative to quantitative depending on field conditions, prior knowledge of well and subsurface conditions, experimental quality, and appropriate modeling Applicability/Advantages • provides estimates of K distribution in 3D for a heterogeneous investigated volume with a spatially continuous solution (rather than an interpolated solution from separated discrete measurements) • K estimates at cubic meter (m^3) scale can be generated with uncertainty quantification • can be applied in unconsolidated or consolidated/fractured environments given appropriate well configuration	• requires wells and/or DP bores in appropriate configuration • requires sufficient equipment and software for subdividing wells and monitoring numerous zones simultaneously • tomographic inverse modeling is specialized and computing intensive, but is accessible and becoming progressively more accessible • emerging technology with limited com-

Table D-2b. Hydraulic testing: cross-borehole testing (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	best fits the measured disturbances passing through the investigated volume from all the tests observed at all the zones. 3D hydraulic tomography has been demonstrated in the field for unconsolidated sedimentary and fractured hard-rock aquifers and for unconfined and confined aquifers. Aquifer storage properties also can be estimated.		mercial availability
Pumping and Recovery Tests • McElwee 2001 • Murdoch and Germanovich 2006 • Patchett 1993 • Schwartz 1975 • Schweisinger, Svenson, and Murdoch 2009 • Shapiro and Hsieh 1998 • Svenson, Schweisinger, and Murdoch 2007 • Zenner 2009 • Bentall 1963 • Boulton and Streltsova 1977 • Bourdet, Ayoub, and Pichard 1989 • Cooper and Jacob 1946 • Gringarten and Witherspoon 1972 • Gringarten 1984, 1987	These tests are conducted by pumping a well at a constant rate (injection or withdrawal) while measuring the pressure in an observation well and monitoring the recovery after the pump has been shut off. This is the traditional method for determining aquifer parameters.	Data Quality • semiquantitative to quantitative depending on the presence of nonideal behavior in both the pumping and observation wells Applicability/Advantages • obtain values for T and S • identify dual permeability effects • identify boundaries (constant head, no flow) • identify anisotropy if more than one observation well is used • agreement between both tests increases confidence in the T values	• must measure flow rates and pressure responses accurately in both the pumping and observation wells • longest testing times • withdrawal tests may require treatment of extracted water
Cross Borehole Slug	A slug test involves instantaneously changing	Data Quality	• must measure pres-

Table D-2b. Hydraulic testing: cross-borehole testing (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Tests • Atkinson, Gale, and Dudgeon 1994 • Doe, Remer, and Schwarz 1980 • Elsworth and Doe 1986 • Haimson and Doe 1983 • Mackie 1982 • Price, Robertson, and Foster 1977 • Price, Morris, and Robertson 1982 • Quinn, Cherry, and Parker 2011 • Barker and Black 1983 • Butler 1998 • Greene and Shapiro 2001 • Hvorslev 1951 • Levy, Pannell, and Dadoly 1993 • McElwee and Zenner 1998, McElwee 2001	the head in the well and monitoring the recovery in the well and adjacent monitoring well. The test is commonly initiated by submerging or removing a physical slug, or by pneumatic means by pressurizing or depressurizing the air column above the water. Well development effects can be identified if the results from rising head tests are significantly different than falling head tests with similar initial displacements.	• semiquantitative to quantitative depending on the presence of nonideal behavior in both the pumping and observation wells Applicability/Advantages • obtain value for T and S • identify anisotropy if more than one observation well is used • agreement between both tests increases confidence in the T values	sure responses accurately in both the pumping and observation wells • initial displacement must be large enough to see response at observation well • difficult to attain Darcian flow conditions with large displacements

D.3 Discrete Air Sampling

Table D-3. Discrete air sampling

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
- Passive Soil Gas Sampling - ASTM 2011 - ASTM 1993 - Byrnes 2009	Passive soil gas (PSG) samplers can target a wide range of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) to identify source areas and vapor intrusion pathways, track groundwater contamination, and delineate the lateral extent of contaminants (e.g., Beacon BeSure PSG Samplers™ and Gore-Sorber®). PSG sorbent samplers consist of hydrophobic adsorbents housed in glass vials or membranes that are typically installed in shallow, small-diameter holes (e.g., 2.5 cm diameter and less than 1m deep) in uniform grid patterns or in transects. Compounds in soil gas diffuse through the soil pore spaces and are adsorbed by the sorbent samplers, which are exposed to soil gas for a few days to weeks to collect time-integrated measurements. Following exposure, samplers are analyzed at a fixed laboratory using accredited gas chromatography (GC) or GC/mass spectrometry (MS) methods that can achieve very low detection limits of individual compounds with documented accuracy. Passive soil gas surveys are performed to collect high-resolution data sets to identify source areas, track groundwater contamination, and delineate the lateral extent of contaminants.	Data Quality - semiquantitative data – compound-specific quantitative measurements based on traceable standards but in units other than concentrations (e.g., nanograms or micrograms [μg]). Applicability/Advantages - enables collection of high-resolution data sets - can provide indirect evidence of volatile NAPL present in the vadose zone, capillary fringe, and water table - provides evidence of source areas and vapor intrusion pathways - delineates groundwater contamination - focuses and minimizes subsequent soil and groundwater sampling - targets VOCs, as well as SVOCs - detects contamination present at low concentrations - effective in low-permeability soils and when soil is highly	- does not provide vertical profiling - data reported as mass and not in units of concentration for risk assessments - not likely to detect contamination below water table due to limited volatilization - not suited for targeting methane and other non-adsorbable compounds

Table D-3. Discrete air sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
		moist • allows for rapid collection of samples • requires only basic hand tools to install samplers • minimal impact to sites • not affected by the temporal variability of soil gas concentrations	

Table D-3. Discrete air sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
• Active Soil Gas Sampling • ASTM 1993 • Marrin and Thompson 1987 • Devitt et al. 1987 • Marrin 1988 • Marrin and Kerfoot 1988 • Cohen and Mercer 1993 • Rivett 1995 • Pankow and Cherry 1996 • USEPA 1997b • USEPA 1998 • Lewis et al. 2004	Active soil gas surveys are performed to target VOCs in the vadose zone, including compounds that cannot be targeted with sorbents (e.g., methane and acetylene). Typically, a hollow probe with an expendable or retractable tip connected to tubing is driven to the target depth using a hammer drill, slide hammer, or direct-push technology. A vacuum is applied to the tubing to withdraw soil gas, which is captured in metal canisters, Tedlar bags, or a syringe. Sorbent tubes with low-flow pumps or syringes can also be used to sample the soil gas and target both VOCs and SVOCs. Analysis is performed on site or at a fixed laboratory using accredited GC or GC/MS methods. Active soil gas surveys are performed to identify source areas, measure soil gas concentrations for risk assessment, track groundwater contamination, and delineate the lateral and vertical extent of contaminants.	Data Quality • quantitative to semi-quantitative data – compound-specific values in units of concentration based on traceable standards—e.g., micrograms per liter (µg/L), parts per million (ppm), and parts per billion (ppb) by volume Applicability/Advantages • enables collection of high-resolution data sets • can provide indirect evidence of volatile NAPL present in the vadose zone, capillary fringe, and water table • provides evidence of source areas and vapor intrusion pathways • reports data in units of concentration • may be able to delineate groundwater contamination • focuses and minimizes subsequent soil and groundwater sampling • allows for rapid collection of samples	• not effective in low-permeability soils or when soil is highly moist • not likely to detect contamination below water table due to limited volatilization • not appropriate for SVOCs

D.4 Solid Media Sampling and Analysis Methods

Table D-4. Solid media sampling methods

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Split Spoon Samplers • ASTM 2013a • ASTM 2013b • ASTM 2013d • ASTM 2013e • ASTM 2013f • ASTM 2013g	The split spoon is typically 24 inches (in) long and 2in outside diameter. The cutting shoe and drive head hold the split barrel of the sample tube together as it is pushed or driven into unconsolidated soils and sediments for sampling. It is often used through hollow-stem augers incrementally as the augers are advanced (e.g., one 2ft spoon sample for every 5ft of boring). It can be run continuously, and plastic liners can be used. Spoons can be driven with a drop hammer to obtain standard penetration test (SPT) data if required for the investigation. Spoons may be hydraulically pushed or hammered with hydraulic hammers to collect samples if SPT data are not required. Split spoons can be used through DP installed casing to collect samples. Split spoon samples are inspected and characterized in the field for geology using standard methods such as the Unified Soil Classification System (USCS) and qualitatively sampled with field instruments such photoionization detectors (PIDs) and field test kits (e.g., Hach). Split spoon samples can be containerized and submitted to a laboratory for chemical and physical analysis (e.g., grain size).	Data Quality • qualitative field inspection by visual, manual methods • samples can be submitted for quantitative chemical analysis or other lab methods (e.g., sieve analysis) Applicability/Advantages • widely available • generally used in unconsolidated formations for lithologic samples and SPT data • spoon samples can be subsampled for chemical and physical analysis in the lab	• split spoon samples considered disturbed due to minor deformation where the cutting shoe and split barrel have been driven around the soil • sample recovery may be poor in saturated sands and other poorly cohesive formations • catchers can be used in cutting shoe to enhance recovery in some materials • difficulty penetrating or collecting coarse gravels or cobbles; not for use in rock • when run through hollow-stem augers, driller must maintain hydraulic control in noncohesive saturated formations so sand heave does not fill lead auger (sand heave can result in collection of nonrepresentative samples); often must add water to augers to prevent/control sand heave • nonrepresentative slough remaining from shallower interval should be recognized • sampling below light nonaqueous phase liquid (LNAPL) or DNAPL zones can lead to cross contaminated samples due to trapped fluids inside augers

Table D-4. Solid media sampling methods (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Single-tube Solid Barrel Samplers - ASTM 2013d - ASTM 2013e - ASTM 2013a - ASTM 2013h - Geoprobe 2011a - Robbins et al. 1997 - Ohio EPA 2005	The single-tube solid barrel sampler is available in several lengths and diameters. Lengths are typically 3 ft–5 ft and sample diameters are approximately 1 in–4 in. Typical designs have a cutting shoe and drive head that hold a PVC sample liner inside the sample barrel. The sample is advanced incrementally into unconsolidated materials to recover samples. An outer casing is not used, so the sample tube is tripped in and out of the open borehole at increasing depths for continuous sampling. It is best used in cohesive formations. These samplers are most often used with direct-push machines and methods, and can be used through hollow-stem augers.	Data Quality - qualitative field inspection by visual manual methods most common - samples can be submitted for quantitative chemical analysis or other lab methods (e.g., sieve analysis) - best if used in cohesive soils and sediments Applicability/Advantages - widely available - generally used in unconsolidated formations for lithologic samples and contaminant distribution assessment - single-tube collected samples may be subsampled for chemical and physical analysis in lab - rapid and cost-effective method under appropriate field conditions	- single-tube solid barrel samples considered disturbed due to minor deformation where cutting shoe and barrel have been driven around the soil - sample recovery may be poor in saturated sands and other soft or poorly cohesive formations; catchers may be used in cutting shoe to enhance recovery of some noncohesive materials - difficulty penetrating or collecting coarse gravels or cobbles; not for use in rock - solid drive point or piston point must be used in samplers to prevent collection of slough or cave-in as deeper intervals are sampled - contaminated materials may fall down borehole (considered open borehole technique)

Table D-4. Solid media sampling methods (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Dual-Tube Samplers • ASTM 2013a • ASTM 2013d • ASTM 2013e • ASTM 2013h • Geoprobe 2011b • Geoprobe 2013b	These systems use an outer and inner casing or rods to advance the borehole and recover samples. The larger diameter outer casing is equipped with a cutting shoe and stays in place as the inner rod is retracted with the soil/sediment sample in a liner or sample tube. The outer casing controls the borehole wall, preventing formation collapse and increasing sample integrity as compared to single-single tube methods. Dual-tube techniques are used with DP methods, sonic methods, and hollow-stem auger methods in unconsolidated formations.	Data Quality • qualitative field inspection by visual manual methods most common • samples can be submitted for quantitative chemical analysis or other lab methods (e.g., sieve analysis) Applicability/Advantages • widely available • generally used in unconsolidated formations for lithologic samples and contaminant distribution assessment; dual-tube collected samples may be subsampled for chemical analysis in lab • outer casing controls borehole wall and eliminates potential for downhole collapse of formation materials • rapid, cost-effective method under appropriate field conditions	• sample recovery may be poor in saturated sands and other soft or poorly cohesive formations; catchers may be used in sample liners or sample tubes to enhance recovery of some noncohesive materials • difficulty penetrating or collecting coarse gravels or cobbles; not for use in rock • outer casing controls borehole wall and eliminates potential for downhole collapse of formation materials • driller must maintain hydraulic control in noncohesive saturated sands formation so sand heave does not enter outer casing as sample is retrieved; often necessary to add water to casing to prevent/control sand heave • sampling below LNAPL or DNAPL zones can lead to cross-contaminated samples due to trapped fluids inside outer casing

Table D-4. Solid media sampling methods (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Rock Coring • ASTM 2013c	Rock coring is achieved through conventional or wire line tooling systems. Conventional systems require the entire rod string to be retrieved to access the core, while wireline systems allow core retrieval with a wire rope and winch. The purpose of both systems is to recover competent rock cores in a wide variety of diameters. Industry standard tooling system sizes are designated with the letters A, B, N, H, and P, the most common of which are N (1.8in core) and H (2.5in core). Most commonly, the sampling system consists of an outer barrel and inner barrel. Drill rods advance the outer barrel and cutting bit, while the inner barrel remains rotationally stationary and encompasses and grips the core for retrieval. Various carbide and diamond bits are manufactured to cut a wide range of rock types. Rock coring requires high rotational speeds for good penetration rates. Most multipurpose geotechnical drill rigs perform well for shallow cores, while dedicated core rigs are used for deeper hole exploration work.	Data Quality • high-quality samples can be retrieved with known orientation, allowing for accurate visualization with intact grain structure • most accurate method for collecting competent rock samples for defining and assessing stratigraphy or rock type Applicability/Advantages • widely available • used for investigation of contamination in fractured and competent rock formations • used in consolidated formations to confirm bedrock in foundation investigations or for mineral exploration • may be adapted to many different conditions ranging from dense sands and fractured formations to hard competent rock	• specialized tooling must be used for good sample recovery in unconsolidated formations • water must typically be used to cool bit and flush cuttings out of hole • slower penetration rates in dense or difficult formations result in higher cost per foot
Solid Media Evaluation and Testing Methods			

Table D-4. Solid media sampling methods (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Core Logging • Kelleher 2003 • Lockman, George, and Hayes 1997 • Parker, Gillham, and Cherry 1994 • Parker, Chapman, and Cherry 2011, 2010 • Spence et al. 2005	Core is logged by a geologist for lithology and any small-scale heterogeneities. The information that can be gathered by this method includes the following: • unconsolidated–color, grain size, sorting, roundness, plasticity, wetness, USCS class, laminations, and secondary material • sandstone–color, grain size, sorting, roundness, wetness, secondary material, sedimentary structures, bedding, cementation index, and fractures • carbonates–color, crystallinity, fossils (type and abundance), vugs and voids (size and abundance), sedimentary structures, bedding, cementation index, and fractures • bedrock–lithology, lithologic changes, lithologic contacts, mineralogy, crystal size, texture, fractures, fracture orientation, fracture interconnectivity, and weathering	Data Quality • quantitative Applicability/Advantages • widely available • obtain the highest resolution of geologic units • assists in understanding style of small-scale heterogeneities • assists in understanding paleoenvironment conditions of subsurface and estimating vertical and lateral continuity of strata	• mechanical fractures (e.g., end of core runs, breaks to fit core into boxes) and natural fractures should be identified and labeled immediately upon retrieval to avoid misinterpretation • difficult to complete logging during coring • core should be revisited when more time can be allocated
Percent Recovery and/or Rock Quality Designation • ASTM 2008b	Preliminary rock mass quality can be quickly estimated by measuring core recovery and calculating the rock quality designation. Core recovery is a percentage of the measured length of core in the core barrel divided by the length of the core run. Rock quality designation is a calculated percentage of the sum of recovered core pieces that are a minimum of 4in long (measured at core center) divided by the length of the core run.	Data Quality • quantitative Applicability/Advantages • information essential to constructing complete borehole log • low recovery commonly indicates high-permeability zones (i.e., sands and gravel, highly fractured rock)	• measurements are taken during drilling/core retrieval and calculations are made afterwards

Table D-4. Solid media sampling methods (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Contaminant Analysis • Camel 2000 • Dincutoiu, Gorecki, and Parker 2003, 2006 • Ganzler, Salgo, and Valko 1986 • Hewitt 1998 • Kennel 2008 • Kinniburgh and Miles 1983 • Lawrence et al. 1990 • Lopez-Avilla, Young, and Beckert 1994 • Richter et al. 1996 • Spence et al. 2005 • USEPA 1999	Contaminant analysis is best achieved by sampling the soil/rock core; however, the core can be screened using field instruments to minimize the number of samples analyzed in the laboratory.	Data Quality • quantitative to qualitative depending on analytical method Applicability/Advantages • obtain vertical contaminant mass distributions • identify soil/rock where contaminant resides	• expensive • most efficient to conduct transects perpendicular to groundwater flow
Geochemical Composition and Mineralogy • Nicholson, Cherry, and Reardon 1983 • Nelson and Sommers 1982	This method involves testing for solid-phase organic carbon, reactive minerals (e.g., pyrite), carbonates, iron and manganese oxides, clay mineralogy, and leachable chloride.	Data Quality • quantitative Applicability/Advantages • determine cation exchange capacity • estimate sorption and other contaminant reactions • understand contaminant retardation and degradation • determine oxidant demand for remediation	• take samples from core soon after drilling to avoid oxidation and other influences • in some cases, porosity, density, and surface area measurements are needed

Table D-4. Solid media sampling methods (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Physical Properties - ASTM 2008a, 2010, 1986, 2001 - Cooper and Jacob 1946 - Byers, Mills, and Stewart 1978 - Churcher and Dickhout 1987 - Tanikawa and Shimamoto 2009	The soil/rock core is sampled for physical and mineralogical analyses (e.g., permeability, porosity, fraction of organic carbon, mineralogy).	Data Quality - quantitative Applicability/Advantages - obtain values for matrix K in rock core - obtain values of other parameters needed for mass calculations and transport models	- difficult to obtain valid permeability measurement on unconsolidated core samples
Microbial and Molecular Diagnostics - Parker, Chapman, and Cherry 2011	This method involves identifying the indigenous microbe population and/or conducting microcosm studies.	Data Quality - qualitative to semiquantitative metrics Applicability/Advantages - knowledge of indigenous microbe population to aid in studies of natural attenuation	- short holding times

D.5 Direct-Push Logging

Table D-5. Direct-push logging

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Hydraulic Profiling Tool • Binder 2008 • Kober et al. 2009 • McCall 2010, 2011 • McCall et al. 2009 • McCall et al. 2014 • Geoprobe 2013c	The hydraulic profiling tool (HPT) is a direct-push probe with a screened injection port on the side of the tool where water is injected into unconsolidated formations as it is advanced—at 2 centimeters per second (cm/sec)—through virgin materials. A pressure sensor located in the probe assembly measures the pressure required to inject water into the formation at a flow rate of 200–300 milliliters (mL)/minute (min). A flow module at the surface contains a pump and flow meter that measures the injection flow rate. The HPT probe includes an electrical conductivity (EC) array that provides an EC log of the bulk formation. A notebook computer with Acquisition software provides real-time viewing of pressure, flow rate, and EC logs as the tool is advanced. Dissipation tests may be performed to evaluate hydrostatic pressure at multiple intervals and determine water levels. The HPT pressure log and EC log provide detailed information about lithology and hydrostratigraphy. Cross sections based on HPT pressure logs may be used to interpret hydrostratigraphy and define migration pathways and aquitards. The HPT flow rate and pressure data can be used to calculate a log of estimated hydraulic conductivity for the local formation. It takes about 1 hour to complete a 60ft (20m) log. Logs to depths of over 100ft (30m) have been obtained.	Data Quality • high-resolution logs of HPT pressure and EC provide detailed information on lithology and hydrostratigraphy Applicability/Advantages • rapid, high-resolution (15 millimeter [mm]) hydrostratigraphic characterization tool capable of penetrating 300ft–600ft/day • typically applied up to >100ft • probe can be pushed and driven with a hydraulic hammer to penetrate difficult formations • retraction grouting with 2.25in tools can be used to reduce risk of cross contamination • compared to conventional CPT, Geoprobe® is less expensive, more maneuverable, and readily available • greater depth penetration than push-only CPT tools • small, maneuverable direct-push machines advance tools; can be used on slopes • HPT probe includes EC array	• data should be confirmed at targeted locations and depths with soil sampling • for penetration of unconsolidated materials only; no rock penetration • penetration limitations in dense or cemented formations; usually will not penetrate cobble-rich materials • HPT pressure logs provide relative permeability data

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Electrical Conductivity Logging • Christy, Christy, and Wittig 1994 • USEPA 2000 • Beck, Clark, and Puls 2000 • McCall and Zimmerman 2000 • Schulmeister et al. 2003 • Schulmeister et al. 2004 • Wilson, Ross, and Acree 2005 • Sellwood et al. 2005 • McCall et al. 2006 • Harrington and Hendry 2006 • Binder 2008 • www.geoprobe.com	This robust DP probe can be pushed and advanced under a percussion hammer into unconsolidated formations to depths in excess of 100ft (30m) in amenable formations. The Wenner array probe has four evenly spaced electrodes where current is applied to the formation and the resultant voltage is measured. The probe can be advanced at rates as high as 5ft/min and EC data are acquired on a 15mm spacing for the log. A simple string pot tracks the depth of the probe and the rate of penetration. Uphole electronics process the analog signal and provide digital output to a notebook computer. The Acquisition software provides a live-time view of the EC log and speed/depth log as the probe is advanced. The EC log provides an indication of lithology and permeability in fresh water formations. The EC of unconsolidated materials is primarily a function of clay content; high clay content yields higher EC readings, while sand and gravel formations yield lower EC readings. Some clays have low electrical conductance while electrically conductive fluids (e.g., salt water, sodium persulfate) can impart a very high conductance to low-EC materials.	Data Quality • accurate soil stratigraphy at high resolution in fresh water formations Applicability/Advantages • rapid, high-resolution (15mm), stratigraphic characterization tool capable of penetrating 400ft–700ft/day • typically applied to up to 100ft (30m) in unconsolidated formations; can go deeper in amenable materials • an expendable dipole probe allows for retraction grouting to reduce risk of cross contamination; re-entry grouting with nonexpendable tools • generally, greater depth penetration than push-only CPT methods • small, maneuverable DP machines advance tools, can be used on slopes • EC logs can be used to track-/map ionic contaminants such as salt water or sodium permanganate	• EC is non-unique value; many materials display similar EC values, so targeted soil sampling needed to verify logs • penetration limitations in dense or cemented formations; usually will not penetrate cobble-rich materials • interference by electrically conductive fluids (e.g., salt water, potassium permanganate) can mask formation identity

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Cone Penetrometer - ASTM D3441 - ASTM D6067-10 - Campanella and Robertson 1986 - Robertson et al. 1986 - Berzins 1993 - Lutenegger and DeGroot 1995 - Lunne et al. 1997 - McCall et al. 2006 - www.vertek.ara.com	Hydraulic rams, supported by the reaction weight of a 10- to 40-ton truck, are used to push a narrow-diameter (1.44in or 1.77in) rod with a conical point into the ground at a maximum steady rate of 2 cm/sec. An instrumented cone probe measures penetration tip resistance, sleeve (side) friction, and pore pressure. The tip resistance and friction values, which are measured using load cells, are then related to soil behavior type. Sandy soils have high tip resistance and low sleeve friction; clayey soils have low tip resistance and high sleeve friction. Pore pressure is measured using a pressure transducer connected to a ceramic screen mounted just above the cone tip. Pressure exerted on water by cone advancement dissipates more quickly in permeable media (e.g., sand) than in finer grained units. Hydraulic conductivity of tight media can be estimated in situ using the CPT pore pressure dissipation test. Penetration depth is measured using a linear displacement transducer. The soil behavior data are transmitted uphole via cabling, typically recorded each second (providing a spatial resolution of 2 cm), and compiled to generate logs, which are interpreted to delineate stratigraphy and estimate hydraulic conductivity.	Data Quality - highly accurate soil stratigraphy at high resolution Applicability/Advantages - rapid, high-resolution (to 2 cm), stratigraphic characterization tool capable of penetrating 200ft–500ft/day - typically applied to up to 300ft - inclinometer measurements can be used to indicate if rods are bending (and push should be terminated) - retraction grouting and grouting during advancement can be used to reduce risk of cross contamination - greater depth penetration than percussion probing methods	- data must be calibrated against conventionally logged borehole(s) - penetration resistance limitations - heavier trucks (which allow deeper penetration) more difficult to maneuver off road - cannot be used on steep slopes

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Laser Induced Florescence • ASTM D3441 • ASTM D6067-10 • Campanella and Robertson 1986 • Robertson et al. 1986 • Berzins 1993 • Lutenegger and DeGroot 1995 • Lunne et al. 1997 • USEPA 1997b • McCall et al. 2006 • www.vertek.ara.com	Laser-induced fluorescence (LIF) tools employ a laser excitation light that pulses down fiber-optic cable within drill rods to a sapphire window, which is typically employed with a CPT tool on a DP (or similar) rig. The excitation light induces fluorescence of two-ring and higher polycyclic aromatic hydrocarbon (PAH) compounds and other fluorophores (e.g., naphthalene) located across the sapphire window. This fluorescent light is transmitted uphole through a second cable to a surface detection system. Fluorescence intensity and spectral waveforms are recorded continuously in real time and interpreted to infer NAPL presence and distribution. LIF systems that have been deployed on DP units include: SCAPS, ROST™, UVOST™, and TarGOST™. UVOST and TarGOST™ probe are percussion tolerant and able to be advanced using DPT rigs (e.g., Geoprobe®). Alternative types of downhole fluorescence probe include the fuel fluorescence detector, which uses a downhole mercury lamp for its ultraviolet (UV) light source, and the UV-induced florescence tool, which uses a UV lamp instead of a laser. Addition of fluorescing compounds to enhance DNAPL detection in situ is discussed under Dye-LIF™.	Data Quality • semiquantitative, high-resolution NAPL detection Applicability/Advantages • used for continuous logging/detection of petroleum products (gasoline, diesel fuel, and jet fuel), coal tar, and creosote • possible use for chlorinated solvent DNAPLs, commingled with fluorescing petroleum compounds or through addition of fluorescing compounds into DNAPL during probing (see Dye-LIF™) • CPT/LIF provides concurrent delineation of stratigraphy and fluorescent contamination • typical daily probing of 10 0m–16 0m • with proper calibration, LIF waveforms allow product identification and rejection of non-contaminant fluorescence • reduced investigation-derived waste and exposure to site contaminants	• primarily applicable to PAHs; very limited use/-experience at chlorinated solvent sites • subject to interferences • NAPL must be adjacent to sapphire window • penetration resistance limitations • limited availability globally • unconsolidated tool

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Membrane Interface Probe - Christy 1996 - ESTCP 2002, 2011 - USEPA 2004 - Griffin and Watson 2002 - Bumberger et al. 2011 - ASTM D 7532 - Considine and A. Robbat 2008 - Geoprobe 2009 - Costanza & Davis 2000 - Kurup 2009, McAndrews, Heinze, and DiGuiseppi 2003 - Ravella et al. 2007 - Kober et al. 2009 - McCall et al. 2014 - Adamson et al. 2014	The membrane interface probe (MIP) is a volatile organic compound (VOC) screening tool that provides real-time data at the foot scale as it is advanced using DP methods. The MIP probe includes an EC array, and more recently has been combined with the HPT in the membrane interface probe hydraulic profiling tool (MiHpt) probe that provides both detector data for VOCs and HPT pressure data for permeability/lithology. The MIP tool uses heat to enhance the diffusion of VOCs through a membrane. The MIP membrane is made of semipermeable polymer impregnated into a stainless steel screen that is seated in a steel plate for heating to 100°C–120°C. The MIP membrane allows for the diffusion of VOCs, but resists the migration of water vapor or liquid phases. A clean, inert carrier gas (typically nitrogen) sweeps across the membrane and entrained VOCs are carried to the surface by the trunkline. The sample gas is directed to gas phase detectors at the surface. Detectors commonly used include a PID for aromatic hydrocarbons, a halogen specific detector (XSD) for halogenated compounds, and a flame ionization detector (FID) for aliphatic hydrocarbons. Detection limits vary, but are approximately as follows: 200 ppb for chlorinated compounds using an XSD; 500 ppb for individual benzene, toluene, ethylbenzene, and xylene (BTEX) compounds using a PID; and 1 ppm for BTEX and aliphatic hydrocarbons using a FID. The new low-level MIP system provides detection limits for many VOCs below 50 ppb. Results are reported as detector response in microvolts and reflect relative total VOC concentrations. The MIP also records and graphs sample depth, soil EC, and probe temperature.	Data Quality - Qualitative to semiquantitative Applicability/Advantages - commonly available - simultaneous log of VOCs and soil EC - operates in vadose and saturated zones - useful for delineating or focusing investigation to sources, NAPL, and elevated concentration zones - rapid site screening, typically 200ft–400ft/day (60m–120m/day) - using three detectors in tandem enables operator to identify different contaminant groups - using combined MiHpt probe provides information about formation hydrostratigraphy and VOC distribution simultaneously - new low-level MIP system provides detection limits below 50ppb for many VOC analytes	- high detection limits for standard MIP, but well below the levels required for NAPL and high-level plume characterization - qualitative analytical data; results reported as detector microvolt readout vs. depth on log - no analyte specificity - designed for VOCs (boiling points <250 degrees Fahrenheit (°F) (121°C) - Contaminant carryover likely in NAPL or high-concentration zones - penetration limitations due to larger soil sizes, high-density or cemented soils - Shallow use (generally <100ft) - unconsolidated tool only - cannot readily distinguish between high-concentration soil levels and free-phase NAPL - hole abandonment completed following removal of probe, thus hole collapse possible prior to grouting

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Hydrosparge • Davis et al. 1998 • Davis et al. 1997 • Kram et al. 2001	Hydrosparge integrates a customized CPT probe with a small sampling port, a sparging device, and an above ground detector situated in a truck. The probe is advanced into the groundwater to a target depth and a liquid sample is allowed to enter the sample port. A direct sparging device bubbles helium carrier gas through the sample to purge VOCs. The stripped VOCs are carried to the surface for analysis using an ion trap mass spectrometer (ITMS) or GC spectrometer. The ITMS Hydrosparge system has demonstrated good correlation with United States Environmental Protection Agency (USEPA) Method 8260 for dissolved halogenated contaminant concentrations ranging from one to several thousand µg/L. Confirmation samples will be required when using a Hydrosparge probe for DNAPL source zone evaluation; however, a DNAPL source zone characterization approach incorporating the Hydrosparge probe techniques, when coupled with lithological sensors, will allow investigators to rapidly reach the t2 stage	Data Quality • quantitative to semi-quantitative Applicability/Advantages • indirect evidence based on VOC partitioning into carrier gas • can be coupled with lithological sensors for correlation • can use different types of detectors (FID, PID, ITMS)	• user required to determine appropriate depths in the moment, which can be difficult in zones of ganglia • system purge not always rapid • clogging can occur • limited by lithology

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
CPT In Situ Video Camera (GeoVIS and ARA/Vertek) • Lieberman et al. 2000 • Udell, Heron, and Heron 2000 • www.vertek.ara.com	The GeoVIS probe, developed by the Navy, is a real-time, in situ, microscopic soil video imaging system consisting of a miniature charge-coupled device video camera with magnification and focusing lens system integrated into a CPT platform. Soil in contact with the probe is illuminated with an array of white-light-emitting diodes and imaged through a sapphire window mounted on a probe. The video image from the camera is returned to the surface, displayed in real-time on a video monitor, and captured digitally with a frame grabber installed on the computer. The digital image can be incorporated into the SCAPS operation and data processing software to allow for depth-specific video clip recall. The standard GeoVIS optics system provides a viewing field of approximately 2 mm x 3 mm and a magnification factor of 100 when viewed on a standard 13in monitor. The system can be advanced at a rate of approximately 4 in/min. GeoVIS had been combined with a standard LIF probe to produce images of DNAPL globules known to yield fluorescence. For GeoVIS to be most effective, a recognizable color or textural contrast must exist between the DNAPL and the soil matrix. Another version of a CPT-deployed downhole video camera is sold by ARA/Vertek.	Data Quality • quantitative to semi-quantitative Applicability/Advantages • can provide direct evidence of NAPL presence and distribution based on video image processing • provides continuous, high-resolution view of soil with depth • can be used to identify geologic materials and delineate stratigraphy	• unless NAPL is black or highly colored, it may be difficult to detect • penetration resistance limitations • slow rate of probe advancement (1ft every 3 min–5 min) • area viewed is small • pressure or heat front may drive NAPL droplets away from window • limited availability

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Raman Spectroscopy • USDOE 1999 • Rossabi et al. 2000 • Nielsen 2005 • Mosier-Boss, Newbery, and Lieberman 1997	Raman spectroscopy (Raman) is similar in concept and deployment to LIF spectroscopy, except that the laser used to raise the excitement state of the contaminant molecules. Raman uses a longer (785 nanometer) wavelength infrared laser and a different analytical method to identify the compounds of interest. Raman measures the light inelastically scattered from the incident light remediation. The energy shifts in the scattered light are correlated to the vibrational modes of the particular compound and constitute the Raman spectrum for the compound. As the material outside the sapphire window of the probe is exposed to laser light, the molecules in the compound present scatter light, vibrate in a distinctive way creating a vibrational fingerprint. The fingerprint is transmitted via fiber-optic cable to the analyzer where it is compared to a database of vibrational signals. The Raman system has been used to detect metals, organic compounds, oxidizers, and radionuclides in a complex mixture of waste, DNAPLS such as tetrachloroethylene and trichloroethylene, and a variety of other compounds	Data Quality • quantitative to semi-quantitative Applicability/Advantages • direct evidence based on Raman scatter • fluorescence may be due to commingled materials (indirect evidence for DNAPL) • sensitivity may be enhanced through surface coating (requires sample in contact with substrate for this configuration)	• noncontinuous stream of data • fluorescence due to organic material can interfere • detection threshold depends on probability of droplets appearing on sapphire window, amount of contaminant in soil/sediment, type of soil/sediment, soil moisture content, and heterogeneity

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Co-Solvent Injection/Extraction or Precision Injection/Extraction PIX Probe - Looney, Jerome, and Davey 1998 - MSE Technology Applications 2000	The PIX method functions by solubilizing, mobilizing, and recovering NAPL in contact with a single well or specialized probe. The probe is advanced to a target depth, or the monitoring well is screened at a target depth and a known amount of water with a conservative tracer of fixed concentration is injected a few inches into the formation and is recovered by overextraction. Then, a known amount of alcohol is injected and overextracted. Differences in component concentrations, alcohol concentrations, and tracer concentrations are compared to determine the potential presence of DNAPL using a mass-balance approach. Lithologic sensors can be used to help identify candidate DNAPL zones based on potential migration pathways.	Data Quality - qualitative Applicability/Advantages - potential direct evidence of presence of DNAPL - can be coupled with lithologic sensors	- difficult to ensure direct contact between co-solvent and DNAPL - density differences between co-solvent and DNAPL could pose challenges - best-guess approach for sampling location/depth - requires relatively long sampling times (approximately two hours or more per sample)

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Targost® - Ferland et al. 1994	Visible wavelength LIF Tar-specific Green Optical Screening Tool (TarGOST®) is another LIF tool invented by Dakota Technologies for use on coal tar creosote, as well as bunker fuel or other multicomponent PAH-containing DNAPLs (“heavies”). TarGOST® uses visible wavelength fluorescence spectroscopy to yield monotonic response in the presence of heavies in soil. TarGOST® is a time-resolved front-face fluorometer that is fiber-optically connected to a sapphire window probe. The probe is advanced into the ground by a DP rig, and fluorescence measurements are made directly on the soil surface as the sapphire window passes by. TarGOST® can be combined with EC when using percussion DP or, when deployed on a CPT rig, geotechnical sensors that measure the mechanical properties of the soils. As the probe advances, very fast pulses of laser light are delivered by fiber-optic cable and reflected though the sapphire window by a mirror. The light is absorbed by the heavies and PAHs are driven to an electronically excited state. When the excited-state PAHs return to ground state, they emit visible and infrared fluorescence that is collected by the mirror and transmitted back up to the surface via the collection fiber-optic. Data are generated on ~1 in increments from the DP borings. The average daily production rate achieved (based on over 166 sites since 2004) is 330 ft/day. TarGOST® logging data can be used to develop high-resolution conceptual site models (CSMs) depicting the location of sites contaminated with heavy PAH DNAPLs. TarGOST® can be calibrated using DNAPL samples collected from the site.	Data Quality - qualitative Applicability/Advantages - highest production heavy PAH NAPL logging technology available - available throughout North America with 2–4 week lead times - calibration results in accurate mapping of heavy PAH NAPL - integration of data into GIS and other graphics systems is straightforward - data-density reduction tools available from Dakota Technologies, Inc.	- limited availability in Europe/Asia - direct-push delivery prohibits use in consolidated materials - “blind” to the dissolved phase (often considered an advantage)

Table D-5. Direct-push logging (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Dye-LIF™ (Emerging) • Einarson et al. 2012 • SERDP 2002	Dakota Technologies, Inc. has been working with geologists at Haley and Aldrich (formerly at AMEC Geomatrix) to develop a LIF tool that responds to chlorinated solvent DNAPL, even when DNAPL does not contain sufficient PAHs or other fluorophores to allow for direct detection. This new tool, referred to as the DYE-LIF™ optical screening tool, works by injecting fluorescent hydrophobic dye through a small injection port located several inches below the detection window of a standard LIF probe (the current Dye-LIF™ system is built onto a standard TarGOST backbone). As the probe is advanced through the subsurface, the injected dye partitions almost instantly into the DNAPL (if present), ensuring that the DNAPL is now fluorescent and detectable by LIF (in much the same way the oil red makes DNAPL observable in sample jar dye shake tests). Field testing verification of the new tool (funded by the Environmental Security Technology Certification Program) SERDP/ESTCP Project 201121 Direct Push optical Screening Tool for High-Resolution, Real-Time Mapping of Chlorinated Solvent DNAPL Architecture. 2013is underway and scheduled for completion at the end of 2013. Limited commercial projects have also been proposed for 2013. Results of preliminary field testing have been very successful and Dakota is committed to full commercialization by the first quarter of 2014.	Data Quality • qualitative Applicability/Advantages • available in North America in 2014 • high production rate of 200ft–300 ft/day • works either by direct LIF detection of DNAPL co-contaminants (such as PAHs) or the dye labeling enhancement • continuous data of ~0.5in vertical data density • deliverable by both CPT and percussion	• no availability in Europe/Asia • direct-push delivery prohibits use in consolidated materials • “blind” to the dissolved phase (sometimes considered an advantage)

D.6 Discrete Groundwater Sampling

Table D-6a. Discrete groundwater sampling

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Discrete Interval Groundwater Sampling • ASTM 2012a • USEPA 1997a, 2003, 2005 • Robbins et al. 1997 • Ohio EPA 2005	DP and occasionally sonic drilling methods are used to install a variety of small-diameter groundwater sampling tools in unconsolidated formations. These tools are installed for short periods and recovered for decontamination and multiple reuse. These tools range from simple exposed screen tools (e.g., mill slotted rods) to protected screen tools and dual-tube systems. These devices are advanced directly into virgin soil and sediments without a preexisting borehole or well. Generally screens are 1in or less in diameter and screen lengths can be varied from as little as a few inches to about 5 ft Screen options include tool steel (mill slotted rods), slotted PVC, wire wound stainless steel screens, and stainless steel screened ports. Variable screen lengths of several tools enable the investigator to target specific intervals within a complex formation for sampling. In these devices, the screen is in intimate contact with the formation and no filter pack is used. This means that minimal development of the screens is required to obtain representative samples of the groundwater over discrete intervals. These devices may be used to sample for most environmental contaminants of concern and many can be slug tested to measure hydraulic conductivity. Small bladder pumps may be used for low-flow quality samples. No significant cuttings waste is generated, and minimal purge/development water is generated in the operation of these devices. These tools are very effective for high-resolution site characterization programs. Most tools can be grouted as they are removed to protect groundwater integrity.	Data Quality • quantitative to qualitative • project manager uses the project data quality objectives (DQO) to select the appropriate tool and sampling technique to achieve the DQO requirements Applicability/Advantages • for use in unconsolidated formations • have been used at depths exceeding 200 ft • single-depth sampling or multidepth profiling capabilities • used to sample discrete intervals to define vertical variations in contaminant distribution and aquifer geochemistry • small-diameter tools are easy and simple to advance with mobile DP machines • eliminates problems with long screened wells that result in water quality averaging that masks true contaminant distribution	• may encounter regulatory restrictions; coordinate with site-specific regulators to verify acceptability for project goals and DQOs • certain tools may have analyte limitations, e.g., steel screens should not be used to sample for chromium • not for use in rock • may not penetrate thick layers of coarse gravel or cobbles or very dense or cemented formations • may not provide sufficient groundwater for sampling from low-permeability formations (e.g., sandy clays and silty clays) • dual-tube profiling methods subject to formation heave in flowing saturated sands; added

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
		• no permanent well left in place that requires quarterly sampling and long-term maintenance	water may be required for hydraulic control

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Screen Point 22 Groundwater Sampling Tool - ASTM 2012a - USEPA 1997a, 2003, 2005 - Geoprobe 2010, 2011a - McCall 2011 - Robbins et al. 1997 - Ohio EPA 2005	This tool is usually installed by DP or sonic drilling methods. The Screen Point 22 may be used as a single-depth discrete interval sampling device or as a multilevel sampling device. The screen is installed through the drive rods after they are driven to the desired depth to minimize the potential for screen damage. Screens are available in PVC and wire wound stainless steel materials. Screens of approximately 1 ft and 4 ft lengths are available. The screen may be partially deployed to target a specific zone of a formation. Slug testing to measure hydraulic conductivity may be performed. Sampling with a small-diameter bladder pump can provide high-quality samples and water quality data for dissolved oxygen, oxidation reduction potential (ORP), pH, specific conductance, and turbidity. After sampling is completed, the tool may be grouted from bottom-up as the tool string is retracted. The Stainless Steel screens and drive rods are recovered for multiple reuse following decontamination. PVC screens are generally used as one-time, disposable parts. PVC risers may be used as the inner rod/casing to minimize sample contact with steel drive rods if preferred.	Data Quality - quantitative to qualitative - project manager uses the project DQOs to select the appropriate tool, screen and sampling technique to achieve the DQO requirements Applicability/Advantages - eliminates problems with long-screened wells, i.e., water quality averaging that masks true contaminant distribution and changes in aquifer geochemistry - for use in unconsolidated formations; have been used at depths exceeding 200 ft - single-depth or multi-depth profiling - used to sample discrete intervals to define vertical variations in contaminant distribution and aquifer geochemistry - small-diameter tools are easy and simple to advance with mobile DP machines	- may encounter regulatory restrictions; coordinate with site-specific regulators to verify acceptability for project goals and DQOs - certain tools may have analyte limitations; e.g., steel screens should not be used to sample for chromium - not for use in rock - may not penetrate thick layers of coarse gravel or cobbles or very dense or cemented formations - may not provide sufficient groundwater for sampling from low-permeability formations (e.g., sandy clays and silty clays) - sample turbidity may be elevated in formations with significant fines content

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
		• no permanent well left in place that requires quarterly sampling and long-term maintenance	

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Screen Point 16 Groundwater Sampling Tool • ASTM 2012a, b • USEPA 1997, 2003, 2005 • Geoprobe 2006, 2010, 2011a • McCall 2011 • Robbins et al. 1997 • Ohio EPA 2005	This tool is usually installed by DP methods. The Screen Point 16 is a single-depth, discrete interval sampling device. It may be installed at multiple increasing depths at one location to conduct profiling. Top-down profiling is recommended to obtain the best sample quality. The screen is enclosed in a protective sheath as the tool is driven to the desired depth to prevent cross contamination. Screens are available in PVC and wire wound stainless steel materials. Screens approximately 1m long are available. The screen may be partially deployed to target a specific zone of a formation. Slug testing to measure hydraulic conductivity may be performed. Sampling with a small-diameter bladder pump can provide low-flow quality samples and water quality data for dissolved oxygen, ORP, pH, specific conductance, and turbidity. After sampling is completed, the tool may be grouted from bottom-up as the tool string is retracted. The SS screens and drive rods are recovered for multiple reuse following decontamination. PVC screens are generally used as one-time, disposable parts.	Data Quality • quantitative to qualitative • project manager uses the project DQOs to select the appropriate tool, screen, and sampling technique to achieve the DQO requirements Applicability/Advantages • eliminates problems with long-screened wells, i.e., water quality averaging that masks true contaminant distribution • for use in unconsolidated formations; have been used at depths exceeding 200 ft • single-depth or multi-depth profiling of discrete intervals • sample discrete intervals to define vertical variations in contaminant distribution and aquifer geochemistry • small-diameter tools are easy and simple to advance with mobile DP machines • no permanent well left	• may encounter regulatory restrictions; coordinate with site-specific regulators to verify acceptability for project goals and DQOs • certain tools may have analyte limitations; e.g., steel screens should not be used to sample for chromium • not for use in rock • may not penetrate thick layers of coarse gravel or cobbles or very dense or cemented formations • may not provide sufficient groundwater for sampling from low-permeability formations (e.g., sandy clays and silty clays) • sample turbidity may be elevated in formations with significant fines content • dual-tube pro-

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
		in place that requires quarterly sampling and long-term maintenance	filing methods subject to formation heave in flowing saturated sands; may must add water for hydraulic control

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Hydraulic Profiling Tool-Groundwater Sampler • USEPA 2003 • Geoprobe 2011b, 2013a	This recently developed tool is installed by DP methods and is used in unconsolidated formations. The Hydraulic Profiling Tool-Groundwater Sampler (HPT-GWS) is a combined logging and groundwater sampling tool. The probe contains an EC array and an HPT pressure sensor downhole to provide information on lithology and relative permeability. Four screened ports on the side of the probe allow for injection of water into the formation as the probe is advanced at 2 cm/sec. The downhole pressure sensor measures the pressure required to inject water into the formation at a flow rate of 200 mL–300 mL/min. The EC and HPT pressure logs are plotted on screen as the probe is advanced. The logs are used to guide selection of zones in the formation with sufficient permeability for groundwater sampling. To sample groundwater, probe advancement is halted and HPT injection flow is turned off. Either a peristaltic pump at the surface or a small bladder pump installed in the probe is used to purge and sample groundwater. Water is pulled in through the four screened ports on the side of the probe and pumped to the surface. Water quality parameters, such as dissolved oxygen, ORP, pH, and specific conductance may be monitored in a flow cell until stabilized to verify representative samples are obtained. Samples may be collected for most environmental analytes.	Data Quality • quantitative to qualitative • project manager uses the project DQOs to select the appropriate materials and sampling technique to achieve the project DQO requirements Applicability/Advantages • eliminates problems with long-screened wells, i.e., water quality averaging • for use in unconsolidated formations; has been used at depths up to 100 ft and can be used deeper • used for multidepth profiling • used to sample discrete intervals to define vertical variations in contaminant distribution and aquifer geochemistry • small-diameter tools are easy and simple to advance with mobile DP machines • no permanent well left in place that requires quarterly sampling and long-term maintenance	• may encounter regulatory restrictions; coordinate with site-specific regulators to verify acceptability for project goals and DQOs • certain tools may have analyte limitations; e.g., steel screens should not be used to sample for chromium • not for use in rock • may not penetrate thick layers of coarse gravel or cobbles or very dense or cemented formations • will not provide sufficient groundwater for sampling from low-permeability formations (e.g., sandy clays and silty clays) • sample turbidity may be elevated in formations with significant fines content • reentry grouting

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
			is required with this combined sampling-logging tool

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Waterloo Advanced Profiling System (Waterloo APS) - Pitkin et al. 1999 - Cho et al. 2004 - Guilbeault, Parker, and Cherry 2005 - Parker et al. 2003 - Pitkin, Ingleton, and Cherry no date	The Waterloo^{APSTM} is a DP groundwater sampling tool that also generates a high-resolution log of the index of hydraulic conductivity (I_K) during borehole advancement. The downhole portion of the equipment is provided in three diameters: 1.5 in, 1.75 in, and 2.25 in. The large-diameter version is used with the new large direct-push rigs (e.g., Geoprobe® 8040). The hole can be grouted during retraction of the tool string. The I_K is determined by measuring the flow rate and pressure of water injected into the formation as the tool is advanced. The vertically continuous I_K data provides high-resolution information on stratigraphic changes in real-time. Groundwater samples are collected at depth-discrete measurements of the depth to the potentiometric surface (relative to ground surface) via standard low-flow sampling techniques using a peristaltic pump or a downhole nitrogen gas positive displacement pump, which allows sample collection when the water table is below the suction limit of the peristaltic pump or where peristaltic pumps are not suitable for sampling. Using either pumping system, groundwater samples are collected into 40 mL VOA vials, filled from the bottom with zero head space in a stainless steel via holder. When the peristaltic pump is used, the samples are collected on the suction side of the pump and are not exposed to either the pump head or the atmosphere. The vertical interval (i.e., screened interval of the Waterloo $^{APS\ TM}$ is approximately 5 cm (2 in). The tool and sample tubing are all stainless steel, resulting in virtually no sorption/desorption. The tool string is not tripped between vertical samples. The sample spacing is variable as needed by the investigator. At each selected sampling depth, a volume of water is drawn from a narrow depth interval into the tool through small screened ports. The use of a nitrogen gas-drive pump allows sample col-	Data Quality - I_K – qualitative to semi-quantitative - chemistry – quantitative Applicability/Advantages - collection of vertically continuous hydrostratigraphic data in vadose zone and below the water table - distinction between relatively low-permeability zones (commonly consisting of fine sand, silt, or clay) from relatively high-permeability zones (commonly consisting of medium or coarse sand and gravel) - identification of fine-scale hydrostratigraphic changes critical to understanding of contamination flow/distribution - collection of depth to potentiometric surface (hydraulic head) at each sample depth for the evaluation of hydraulic gradients - collection of rep-	- inability to efficiently collect discrete-interval groundwater samples from low-permeability geologic media (silt and clay) - inefficiency if large sample volumes required (although reliable I_K logs can still be generated in most low-permeability geologic environments) - Waterloo^{APSTM} can be driven through silt or clay layers, but groundwater samples cannot be collected from these geologic materials - for analytes requiring the collection of large sample volumes, this tool is relatively costly given the amount of time required to obtain sufficient sample

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	lection when the water table is below the suction limit and the samples can be analyzed in the field with a mobile field laboratory for contaminants of concern (see field laboratory section). Depending on project objectives, samples can be sent instead for analysis to a fixed laboratory. The samples can be analyzed in the field with a mobile laboratory for contaminants of concern (see field laboratory section) or using a fixed laboratory. The Waterloo $^{APS\ TM}$ is uniquely offered by Stone Environmental, Inc. It is a proprietary modification of the original Waterloo Profiler® developed by Dr. John Cherry's research team at the University of Waterloo.	resentative groundwater samples (formation groundwater stabilized at the time of sampling) for laboratory analysis of organic and inorganic contaminants of concern • collection of depth-discrete samples rather than flow-weighted average samples from long well screen intervals, resulting in development of high-resolution contaminant distribution data from the same borehole • selection of optimum sampling depths based on detailed knowledge of hydrostratigraphy (I_K) rather than relying on preset intervals • compilation of hydrostratigraphic data sets consistent/comparable across a whole site (not dependent on different geologists' interpretations) • data easily exported/imported for the creation of clear 2D and	volume • typically advanced using DP drill rigs and limited by the capabilities of these rigs to advance tooling through certain geologic media (e.g., glacial till) • tips can become clogged when silt is pulled through screen within the tip but cannot be entrained up stainless steel tube to sample box • tips may also become clogged when screen size within the tip is sufficiently small to allow for caking of silt onto outside of screen and preclude sample collection • screen mesh size can be changed in response to particle size distributions • Waterloo^{APSTM} can

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
		3D CSMs • results often used to design effective long-term monitoring well networks • collection and analysis of real-time data in the field (commonly referred to as a dynamic site investigation process), which enables real-time refinement of CSMs and reduction in the number of field campaign iterations • no drill cuttings are generated and a limited amount of purge water and decontamination waste are generated • retraction grouting of the borehole can be completed using a sacrificial tip to reduce the potential for vertical contaminant migration • hybrid drive profiling capability enables profiling to depths of over 500 ft below ground surface • portable system allowing easy transport and use at distant locations	be driven through silt of clay layers, but samples cannot be pulled in these layers (long time required to obtain sufficient sample volume) • compounds requiring collection of large volumes (longer time required to obtain sufficient sample volume) • common limitations of drill rigs used to advance boring; Geoprobe™ commonly used • duration of tool decontamination when driving across NAPL (although contractor often has two tool boxes to address that issue) • presence of sandy layers should be highly suspected prior to mobilization to ensure that water

Table D-6a. Discrete groundwater sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
		(national and international projects), in tight spaces, or in remote portions of a site (wetlands or woodlands)	samples can be collected • tips can become clogged when silt is pulled through screen within tip but not able to be entrained up stainless steel tube to sample box • Tips may also become clogged when screen size within tip is sufficiently small to allow for caking of silt on outside of screen and preclude sample collection

Table D-6b. Discrete groundwater sampling (part 2)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Grab Samplers; Hydrasleeve™ and Snap Sampler™ - ITRC 2006 - ITRC 2007 - HydraSleeve website http://www.hydrasleeve.com - Snap Sampler website http://www.snapsampler.com	The HydraSleeve™ grab sampler consists of a reusable weight attached to the bottom of a long lay-flat disposable polyethylene sleeve with a self-sealing valve. Under water, the HydraSleeve™ can remain flat and sealed for indefinite time periods. It is opened for sample collection by pulling a suspension cord upward. The valve closes when the sampler is full. Samples are transferred to containers (e.g., 40 mL vials) at the surface. HydraSleeve™ samplers have been made to retrieve from 80 mL to >4,000 mL and for use in wells as small as 1 in diameter. The Snap Sampler™ employs a cable to trigger release of a spring and close Teflon end caps on double-opening 40 mL VOA vials or polyethylene bottles (125 mL or 325 mL) in situ without headspace vapor. Once retrieved from the well, standard screw caps and preservatives can be added to the sample container. Up to six samplers can be attached in series to one trigger cable. Snap Samplers fit in 2 in or larger monitoring wells.	Data Quality - quantitative - semi-quantitative Applicability/Advantages - allow analysis for all common analytes (such as VOCs, SVOCs, and metals)	(See above) - patented methods with sales/support available from a limited number of vendors

Table D-6b. Discrete groundwater sampling (part 2) (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Accumulative Samplers - ITRC 2006 - ITRC 2007	Accumulative samples are passive sampling devices that rely on diffusion and sorption to accumulate analytes into the sampler. Samples are a time-integrated representation of conditions at the sampling point over the deployment period. The accumulated mass and duration of deployment are used to calculate analyte concentrations in the sampled medium. Examples include: - Semipermeable Membrane Devices (SPMDs) - GORE™ Sorber Module - Polar Organic Chemical Integrative Samplers (POCIS) - Passive In Situ Concentration Extraction Sampler (PISCES) All of these samplers involve the diffusion of chemicals, primarily VOCs and SVOCs, across a membrane from the environment into a medium that is then extracted and analyzed for contaminants of concern. SPDMs, POCIS, and PISCES are primarily designed for deployment in surface water and are used to measure bioaccumulation and toxicity, a variety of wastewater, and to identify sources of contamination. These tools are not directly relevant to DNPL site characterization.	Data Quality - qualitative to semi-quantitative Applicability/Advantages - simple to use and cost-effective - can deploy in any setting - wide range of VOCs and SVOCs - sensitive to parts per trillion - built-in duplicates - disposable; no decontamination required	- gives total mass desorbed, calibration required to convert to concentrations - single-source supplier and lab - no field parameters of inorganics - cannot use where NAPL is present

Table D-6b. Discrete groundwater sampling (part 2) (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Membrane Diffusion Samplers Polyethylene Diffusion Bag and Rigid Porous Polyethylene Samplers • ITRC 2006 • ITRC 2007 • CAS lab website • Eon Products website	Membrane diffusion samplers rely on groundwater flow through a screened or open well interval and equilibrium diffusion of dissolved chemicals through polyethylene film. Polyethylene diffusion bag (PDB) samplers are a simple and inexpensive way to sample groundwater monitoring wells for a variety of VOCs. A typical PDB sampler consists of low-density polyethylene lay-flat tubing filled with distilled, deionized water and heat-sealed at both ends. The bags are suspended by a weighted line at the target horizon in monitoring wells and allowed to equilibrate with the surrounding water. Retrieved after the equilibration period (typically two weeks), the enclosed water is immediately transferred to appropriate sample containers for analysis. PDB samplers are typically 18 in–24 in long and 1.25 in–1.75 in diameter and provide 200 mL–300 mL of sample. One or more samplers are set at desired depths in screened or open well intervals and are left in place for at least two weeks. PDB samples, which are typically representative of adjacent well water quality during the last few days of deployment, are transferred to 40mL VOA vials for subsequent analysis. Designed for sampling/analysis of a broader range of analytes than PDB samplers, rigid porous polyethylene (RPP) samplers are made of thin sheets of foam-like porous polyethylene with pore sizes of 6–20 microns. The pores allow a water-water interface facilitating equilibrium of water-soluble groundwater analytes with deionized water in the RPP sampler. RPP samplers can be used to sample all water-soluble analytes, including perchlorate, 1,4-dioxane, inorganic anions and cations, most metals, MEE parameters, methyl tertiary butyl ether (MTBE), hexavalent chromium, explosives, dissolved gases, and many SVOCs.	Data Quality • qualitative to semi-quantitative Applicability/Advantages (See above) • used for analysis of VOCs and other parameters	(See above) • PDB samplers generally not applicable for sampling SVOCs, ions, and MTBE • patented methods with sales/support available from limited number of vendors

Table D-6b. Discrete groundwater sampling (part 2) (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
FACT FLUTe - FLUTe, Flexible Liner Underground Technologies, Ltd. L.C. 6 Easy St., Santa Fe, NM 87506. 505-455-1300 www.flut.com	The FLUTe Activated Carbon Technique (FACT) is a method developed by FLUTe for mapping the distribution of contamination in the pore space and fractures of a borehole wall. The technique incorporates a 0.125 in x 1.5 in strip of activated carbon felt into the typical hydrophobic cover of the NAPL FLUTe system normally used for mapping the subsurface presence of a wide variety of NAPLs. The NAPL FLUTe cover is typically installed into a borehole on the outside of an everting FLUTe blank liner. The installation of a NAPL FLUTe cover with the added activated carbon strip allows one to draw, by diffusion, the dissolved contaminants from the formation into the activated carbon. Recovery of the liner by inversion prevents the carbon from contact with any other portion of the borehole wall. At the surface, the carbon is then sectioned for chemical analysis. With the combination of the NAPL cover and the FACT, one can map both the NAPL and the dissolved phase of many other contaminants.	Data Quality - qualitative Applicability/Advantages - direct evidence - excellent screening tool - fast, inexpensive, and direct method for identifying NAPL presence in soil or water boreholes - capable of detecting clear, colorless NAPL at low saturations	- false positive (i.e., obvious stain with no NAPL present) very unlikely - no stain means cover did not contact NAPL; does not indicate that NAPL is not nearby - works to 2,000 ft - must have open borehole without material casing

Table D-6b. Discrete groundwater sampling (part 2) (continued)

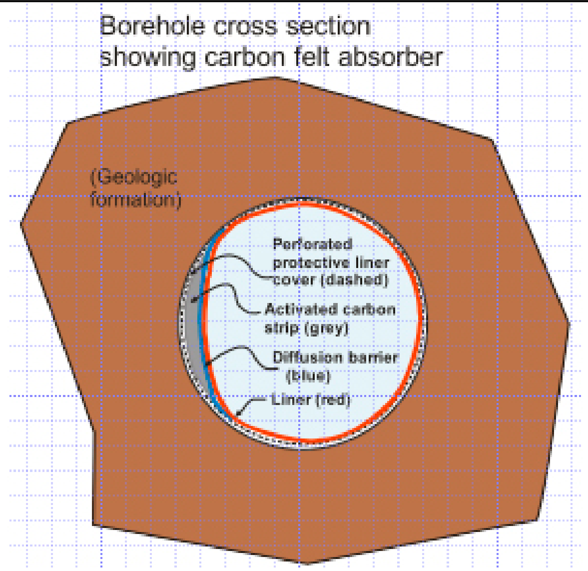
Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
			
Straddle Packer Sampling - Gefell, Hamilton, and Stout 1999 - Holloway and Waddell 2008 - Shapiro 2002 - Taylor et al. 1990 - Swiger and Boll 2009	Straddle packer sampling involves isolating a depth discrete section of the borehole with straddle packers and collecting a discrete groundwater sample. Field properties (pH, temperature, specific conductance, and dissolved oxygen) should be monitored and recorded during purging. After three purge volumes have been removed and field properties have stabilized, a ground-water sample is collected. Packers can also be used to collect discrete samples from an overburden well if the well is constructed properly to allow meaningful data to be obtained. In addition, discrete depths may be isolated within a large well screen (e.g., 20 ft) with packers.	Data Quality - quantitative - Applicability/Advantages - obtain depth-discrete groundwater concentrations - minimize purge volumes - compares well with other sampling methods	- if sampling an interval with multiple fractures, may be bias to pull water from largest fractures with highest head

Table D-6c. Passive flux meter, Hydropunch, and ZONFLO

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Passive Flux Meter (emerging) • Hatfield et al. 2004 • Annable et al. 2005 • www.enviroflux.com • ITRC 2010	The EnviroFlux Passive Flux Meter™ (PFM) is designed to simultaneously measure contaminant and groundwater fluxes. It uses a sorptive permeable medium (a nylon mesh tube filled with sorbent/tracer mixture) that is placed in a borehole or monitoring well to passively intercept contaminated groundwater and release resident tracers. After a specified residence time (typically one to four weeks) in the flow field, the sorbent/tracer tube is retrieved for extraction and analysis. Detected contaminant masses are used to calculate time-averaged contaminant fluxes, and the residual tracer mass data are used to determine cumulative groundwater flux. By selecting appropriate sorbents, PFMs can be used for a wide variety of contaminants. For common organic contaminants, such as chlorinated solvents, activated carbon and a suite of different alcohols are used as the sorbent and tracers, respectively. Depth variations of groundwater and contaminant fluxes are measured by vertically segmenting sorbent/tracer mixture in a well or borehole. Fluxes across a transect perpendicular to flow are measured by placing PFMs in multiple wells.	Applicability/Advantages • time-averaged measurements are increasingly less sensitive to short-term fluctuations in groundwater flow and contaminant concentrations • only two site visits required • can be used to measure vertical variations in horizontal fluxes • passive technique requires no electrical power or pumping • precise prior knowledge about local aquifer hydraulic conductivities not required	• limited application of this recently developed method • each PFM interrogates a small volume of formation, thus multiple PFMs must be deployed, and resultant data must be integrated to estimate mass flux across a plane • competitive sorption or rate-limited sorption may affect ability of PFM to capture and retain contaminants • as with other methods, requires proper placement in groundwater flow field • method assumes horizontal flow
Hydropunch™ • Edge and Cordry 2007 • ITRC 2007	Hydropunch™ is a stainless steel and Teflon sampling tool that can collect discrete interval groundwater samples through a small-diameter drive pipe.	Data Quality • quantitative to semi-quantitative Applicability/Advantages • unconsolidated terrain, rapid, cost effective	

Table D-6c. Passive flux meter, Hydropunch, and ZONFLO (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
ZONFLO - Harte 2013b	ZONFLO (zonal flow) is based on hydraulic control of borehole flow conditions to isolate flow from discrete fracture zones. Hydraulic containment with use of multiple pumps is achieved by balancing flow in the borehole and confirming directions of borehole flow. In rough-faced boreholes where physical containment such as packers may fail, hydraulic containment offers an alternative solution to obtain discrete samples.	Data Quality - quantitative; discrete sampling Applicability/Advantages - deployment easier than packer deployment in some cases	- pump rates must match rates of borehole flow; high yielding wells require high pumping rates - current depth limitation of 400ft

Table D-6d. Multilevel sampling

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Multilevel Sampling • http://www.slb.com/services/additional/water/monitoring/multilevel_well_system/multilevel.aspx • Black, Smith, and Patton 1986 • Patton and Smith 1988	**General Description** This method involves a single multilevel sampler (MLS) device assembled on surface and then installed in an open borehole or a casing with multiple screens, each isolated at a different depth to divide the hole into many depth-discrete segments for data acquisition. It can be used in overburden or bedrock. An MLS is used to obtain vertical profiles of hydraulic head, dissolved contaminants, or natural geochemistry in the saturated zone. It can also be used in the unsaturated zone for soil gas profiling. An MLS can be equipped for single use (fluid sampling or head measurements) or dual use (both fluid sampling and head measurements). Monitoring wells are not definitive tools for detecting the presence of DNAPL; however, because concentrations measured with MLS relative to conventional monitoring wells are the least diluted and therefore most representative of actual concentrations in the formation, MLS-derived water chemistry is best for inferring the presence of DNAPL based on water concentrations relative to DNAPL solubility in water.		

Table D-6d. Multilevel sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	Westbay Systems[a] (Schlumberger) First used in groundwater applications in 1978, it is a modular system using PVC or stainless steel casing with valves at the sampling point. Ports are most commonly isolated using packers that can be installed in 3 in–6.3 in (7.6 cm–16 cm) diameter boreholes. For holes ≥5 in (≥13 cm), it can be installed with backfilling option.[e] To date, the maximum installation depth achieved with the PVC version is 4,035 ft (1,235 m), and with the stainless steel version the maximum depth is 7,128 ft (2,173 m); however, deeper installations are feasible with the stainless steel version.[h]	Data Quality • quantitative Applicability/Advantages • least chemically reactive[c] • can be easily installed through temporary drill casing in weak rock or soils to prevent borehole collapse interfering with installation • can monitor largest number of zones in deep boreholes • can quality control (QC) individual packer seals from installation data and testing after MLS installation • some design modifications can be made in the field • can conduct hydraulic tests with the least restrictions when using the pumping port[f] • discrete sampling without repeated purging[g] • no fixed downhole (dedicated) instruments avoids irreplaceable instrument failure	• can only monitor head in one port at a time with single MOSDAX probe; however, string of MOSDAX probes can be used to monitor continuously in multiple ports at same time • when sampling using a measurement port, maximum amount of water obtained in a single trip is 1 liter; if greater volume required, more downhole trips are needed • current version of pumping port not intended for repeated use; however, an improved version is under development

Table D-6d. Multilevel sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	Waterloo Systems[a] (Solinst) First used in groundwater applications in 1984, it is a permanent, modular system using PVC casing. Ports are isolated in 3 in–4.5 in (7.6 cm–11.4 cm) diameter boreholes using packers and in boreholes ≥5 in (≥13 cm) by backfilling option.[e] To date, the maximum installation depth achieved is 1,000 ft (305 m).[h] • http://www.solinst.com/Prod/Lines/MultilevelSystems.html • Cherry and Johnson 1982 • Parker, Cherry, and Swanson 2006	Data Quality • quantitative Applicability/Advantages • minimally reactive option available • largest number of monitoring zones in shallow holes (<100 ft) • Self-inflating permanent packers • two options available: (1) dedicated pumps and transducers; and (2) peristaltic pump and water level tape • wide selection of tubing materials available • can be installed through casing using all drilling techniques • more monitoring points can be used if only measuring head • some design modifications can be made in the field	• most difficult to decommission due to stainless steel ports • packer option restricts hole diameter to ≤5 in (13 cm) • cannot identify if self-inflating packers rupture, but chemical self-sealing effect minimizes leakage

Table D-6d. Multilevel sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	FLUTe Systems[b] (FLUTe) First used in groundwater applications in 1994, this system uses a continuous flexible urethane-coated nylon fabric tube (liner) to seal the borehole with spacers between the liner and the borehole wall to create monitoring zones. The entire system is pressed against the borehole wall with water or grout, and can be used in 3 in–20 in (7.6 cm–50 cm) diameter boreholes. To date, the maximum installation depth achieved is 850 ft (260 m); however, deeper installations are feasible.[h] • http://www.flut.com/sys_1.html • Cherry, Parker, and Keller 2007 • Keller 2009	Data Quality • quantitative to semiquantitative Applicability/Advantages • most easily removable for repair/replacement or reuse of borehole[d] • smallest sampling reservoir volume • seals entire borehole except for monitoring intervals; general overall seal is confirmed by water level measurement inside liner, except for zones with head larger than excess head in liner • design is not restricted by individual component lengths • simultaneous rapid high volume purging of all monitoring intervals • more monitoring points can be used if only measuring head • most easily installed in artesian holes • most convenient for angled holes and holes in karst	• most chemically reactive[c]; however, high-volume rapid purging system minimizes contact time for reactions to occur • zone with significantly higher head than blended head may result in weak seal for this zone • extremely low head at depth may cause liner rupture

Table D-6d. Multilevel sampling (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
	CMT Systems (Solinst) First used in groundwater applications in 1999, this system uses polyethylene tubing with three or seven chambers, and each chamber is converted into a depth-discrete monitoring tube in 4 in–8 in (10 cm–20 cm) diameter boreholes using the backfilling option.[e] Bentonite packers can be used for three-channel systems in boreholes of 2.5 in–3.5 in (6.1 cm–9 cm). To date, the maximum installation depth achieved is 300 ft (100 m). • Einarson and Cherry 2002 • http://www.solinst.com/Prod/Lines/MultilevelSystems.html	Data Quality • quantitative Applicability/Advantages • lowest capital cost • simple installation procedure does not require advanced training • can be installed through casing using all drilling techniques • most versatile system for design modifications in the field • continuous tube; no joints minimizes potential leaking • heads measured using narrower diameter water level tape, or option for dedicated pumps/transducers • several methods for water sampling (such as double-valve pump, peristaltic pump, and inertial lift) • simple surface completion with minimally intrusive infrastructure	• moderately chemically reactive[c] • limited to a maximum of seven monitoring zones • bentonite and sand cartridges only available for three-channel systems, but additional CMT packer options are being developed

Notes:

[a] Westbay and Waterloo systems have three options: 1) using packers to isolate multiple screens in a cased well; 2) using packers to isolate borehole sections in an open hole in bedrock; and 3) using sand backfill in monitored sections with bentonite seals between sections in an open hole. When using packers, the Westbay system is removable, but may be difficult if the hole collapses on the system.

[b] FLUTe systems have two options: (1) install in hole that has multi-screened casing; and (2) install in open borehole.

[c] Chemical reactivity refers to the system components being prone to sorption and diffusion of organic contaminants. Purging is more important for systems with greater reactivity to avoid adsorption/diffusion effects.

[d] Waterloo and CMT can be removed by overdrilling, or the CMT system can be decommissioned by grouting in place.

[e] The backfilling option is not attractive for karstic rock with large zones that require too much sand or bentonite.

[f] Hydraulic tests can be conducted with all MLS; however, permeability can only be measured to a certain point, depending on the tubing size or other flow restrictions.

[g] The Westbay system does not include any components that isolate water from the sampling point (e.g., tubing to the surface), and thus does not require purging to remove stagnant water from tubing before a relatively undisturbed sample is obtained.

[h] The Westbay and Waterloo systems can be installed to the greatest depths using packers; the FLUTe system can be installed in holes with diameter >4 in.

D.7 NAPL Presence

Table D-7. NAPL presence

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
NAPL FLUTe - Keller 2012 - FLUTe, Flexible Liner Underground Technologies, Ltd. L.C. 6 Easy St., Santa Fe, NM 87506. 505-455-1300 www.flut.com	The NAPL FLUTe is a hydrophobic cover installed over the standard impermeable liner that, following eversion, is in contact with the borehole wall. When NAPL comes in contact with the FLUTe, it penetrates the cover, resulting in a visually distinct stain that can be correlated to depth upon inversion and removal of the liner. 	Data Quality - qualitative Applicability/Advantages - direct evidence - complex method for identifying NAPL presence directly in contact with borehole - capable of detecting clear, colorless NAPL at low saturations	- false positive (i.e., obvious stain with no NAPL present) very unlikely - no stain means cover did not contact NAPL; does not mean NAPL is not nearby - costs approximately about $17/ft

Table D-7. NAPL presence (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Dye Techniques (e.g., Sudan IV dye, Red Oil DNAPL-Lens-Detect) - Parker et al. 2003 - Cohen and Mercer 1993 - www.oilin-soil.com - Cohen and Mercer 1993 - Pankow and Cherry 1996	Direct visual detection of NAPL in soil or water may be difficult where the NAPL is clear and colorless, present at low saturation, or distributed heterogeneously. Hydrophobic dye can assist visual detection of NAPL. The test involves adding a very small amount of a hydrophobic dye (e.g., 2 mg), such as Sudan IV, soil (e.g., ~20 cc), and a small volume of clean water (~15 mL) in a sealed plastic or glass jar (e.g., a 40 mL vial), which is then capped and shaken by hand. Sudan IV is a reddish-brown powder that dyes organic fluids red upon contact, but is practically insoluble in water at ambient temperatures. If NAPL is present in a sample (and contacts the dye), it will appear as red globules, a red meniscus, or a red film. Background and NAPL-contaminated samples should be examined to check for interference and site-specific response. A similar test can be made on water samples by adding dye. Test kits with enhancements are available commercially.	Data Quality - qualitative Applicability/Advantages - direct evidence - excellent screening tool - fast, inexpensive, and direct method for identifying NAPL presence in soil or water samples - capable of detecting clear, colorless NAPL at low saturations	- best-guess approach for sampling location/depth - volume not easily quantifiable - soil type and moisture condition may influence accuracy - potential for false negatives; can only detect NAPL if present in subsample examined - visual contrast can be difficult to see in dark soil - precaution should be taken to avoid complete evaporation of highly volatile NAPL from sample - many solvent dyes are irritants and possible mutagens; skin and eye contact should be prevented

Table D-7. NAPL presence (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Ultraviolet Fluorescence - Kram et al. 2001 - Kram and Keller 2004a, 2004b - www.ptslabs.com	Fluorescence refers to the spontaneous emission of visible light resulting from a concomitant movement of electrons from higher to lower energy states when excited by UV radiation. Samples and core can be inspected in a dark space under UV light (e.g., using a small portable UV light box) for fluorescence, which may indicate the presence of NAPL containing PAHs or other commingled fluorophores. Fluorescent response depends on UV excitation wavelength. Known background soil and NAPL-contaminated samples should be checked for interference and site-specific NAPL response.	Data Quality - semiquantitative Applicability/Advantages - can illuminate NAPLs that fluoresce, including those that contain PAHs (coal tar, creosote, and petroleum products) and those mixed with fluorescent impurities (e.g., oil and grease removed by solvent during degreasing, humic compounds from natural organic matter) - can provide detailed information on relationship between stratigraphy and fluorescent NAPL distribution - can guide selection of subsamples for chemical or saturation analyses	- chlorinated solvents generally do not fluoresce when exposed to UV-visible light unless commingled with sufficient fluorescent impurities - indiscriminant - interference from nontarget fluorescent materials (such as shell fragments in coastal sediment) - significant potential for false positives and false negatives

Table D-7. NAPL presence (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
NAPL Interface Probe - Solinst 2009	This is a down-well electronic measurement tool, similar in format to a standard electronic water level meter. The interface probe is capable of measuring both LNAPL and DNAPL thickness to an accuracy of 1mm. Interface meters generally detect the oil/water interface by distinguishing the different angles of refraction of water and NAPL using an infrared beam. They also measure conductivity of the liquids and signal differently for conductive liquids (water) and nonconductive liquids (NAPLs). To measure the thickness of a product layer, the probe is lowered into the well until the signals activate. If there is an oil/product layer on top of the water (LNAPL), a specific signal is made by the instrument, indicating an air/product interface. The depth is read off the permanently marked tape. The probe is then lowered further and the signal changes at the product/water interface. The thickness of the product layer is then determined by subtracting the first reading from the second. The presence or absence of dense (sinking) nonaqueous layers (DNAPL) is determined by continuing to lower the probe to the bottom of the well. If the signal changes, this indicates a nonconductive liquid. The depths should be measured the probe continued to be lowered until it touches bottom and the tape goes slack. To determine the thickness of the DNAPL layer, the first reading from the bottom depth is subtracted.	Data Quality - qualitative Applicability/Advantages - simple, accurate, cost-effective measurement of both LNAPL and DNAPL product thickness in monitoring wells	- product-level thickness measured in monitoring wells not a reliable measurement of product presence, thickness, and location in formation

D.8 Chemical Screening

Table D-8. Chemical screening

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Membrane Interface Probe - Christy 1996 - ESTCP 2002, 2011 - Griffin and Watson 2002 - USEPA 2004 - ESTCP 2011 - SERDP 2002 - USACE 2002 - www.geoprobe.com	The MIP is a screening tool that provides real-time, near-continuous data on VOCs. The MIP tool uses heat to enhance the diffusion of VOCs through a membrane. The MIP membrane is made of semi-permeable thin film polymer impregnated into a stainless steel screen that is seated in a steel plate for heating to 100°C–120°C. The MIP membrane allows for the diffusion of VOCs, but resists the migration of vapor or liquid phases. A clean, inert carrier gas (typically nitrogen) sweeps through tubing attached behind the membrane and carries VOCs that have diffused through the membrane to gas phase detectors at the surface. Gas phase detectors commonly used include a PID for aromatic hydrocarbons, an electron capture detector (EC or ECD) for halogenated compounds, and a FID for aliphatic hydrocarbons. Detection limits vary, but are around 200ppb for chlorinated compounds using an ECD, 1 ppm for BTEX compounds using a PID, and 1 ppm for BTEX and chlorinated compounds using a FID. Results are reported as detector response in microvolts and reflect relative total VOC concentrations. The MIP also records and graphs sample depth, soil conductivity, and temperature.	Data Quality - qualitative to semi-quantitative Applicability/Advantages - commonly available - simultaneous log of VOCs and soil conductivity - operates in vadose and saturated zones - useful for delineating or focusing investigation to sources, NAPL, and elevated concentration zones - rapid site screening (typically 50 m–100 m/day)	- high detection limits - designed for VOCs (boiling points <250°F (121°C) - contaminant carry-over likely - nonphase descript, only VOC monitor regardless of phase or where within formation

Table D-8. Chemical screening (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Background Fluorescence Analysis - Otz 2005 - Otz et al. 2005	Background fluorescence analysis (BFA) can be successfully applied to identify and understand preferential groundwater flow pathways as well as to delineate extent of contaminated areas. It relies on the principle that most mixtures of organic compounds emit at characteristic patterns of fluorescence when exposed to specific frequencies of EM radiations and BFA can fingerprint such fluorescence patterns. The fluorescence of a water sample has therefore a unique fluorescence fingerprint, which is based on the dissolved organic content of that water sample (resulting from naturally occurring and manmade organic substances). When fluorescence fingerprints show similar patterns (similar slope and peaks in the scan), one averted BFA analyzer can conclude that the freight is also similar and a hydraulic connection is probable. In a homogenous isotropic aquifer, all fingerprints would be the same. Increasing fluorescence intensities also correspond with increasing concentrations of a contaminant plume. A useful supplement to the basic BFA is the introduction of artificial fluorescence drug- and cosmetic-grade dyes in a fluorescent dye-tracing test. Seven different fluorescent dyes may be implemented to quantitatively evaluate preferential groundwater flow paths.	Data Quality - qualitative to semi-quantitative Applicability/Advantages - analysis of water samples, minimum volume requirement of two 40 ml vials per location - location of preferential groundwater flow paths - identification of presence or absence of hydraulic connections between areas or monitoring wells - potential separation of organic plumes resulting from releases at different locations and dates, identification of degradation products, and natural attenuation processes - differentiation between impacted and non-impacted groundwater - outline of degree of affected groundwater within a single plume - nondetections are not an issue as many organic substances can be detected in lower parts per trillion	

Table D-8. Chemical screening (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Colorimetric Screening - http://www.aqrcolortec.com - Triad Central 2011a	Color-Tec is a field-based analytical method that combines sample purging with colorimetric gas detector tubes to detect total chlorinated volatile organic halocarbon compounds in any ex situ liquid or solid sample at concentrations from ~3 µg/L or µg/kg. Samples are analyzed in 2 min or less by purging the volatile compounds from the sample directly through the colorimetric tube, which is designed to produce a distinct color change when exposed to chlorinated compounds. Estimated sample concentrations are obtained by comparing the tube readings to a conversion table, which was developed based on comparison of the method values to GC/MS analysis of split samples.	Data Quality - semiquantitative Applicability/Advantages - on-site, real-time analysis - low-cost analysis - able to develop high-density data sets - decision quality data	- potential false positive from nontarget compounds - not compound specific - applicable to only halocarbon, providing total halocarbon estimates

Table D-8. Chemical screening (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Direct Sampling Ion Trap Mass Spectrometer - USEPA Method 8265 - Wise et al. 1997 - Wise and Guerin 1997 - www.triad-env.com - Davis et al. 1998 - Costanza and Davis 2000 - Davis and Hayworth 2006	The direct sampling ion trap mass spectrometer (DSITMS) is a field portable instrument used for real-time, on-site analysis of VOCs. The DSITMS is the basis of USEPA SW-846 Method 8265. The method involves direct analysis of VOCs from field samples without chromatographic separation. The DSITMS has sample introduction capabilities for analysis of water, soil extracts (USEPA Method 5035), and vapor samples. The analysis times are 3 min/sample for water and soil samples and 6 min/sample for vapor samples. The short analysis time allows a single instrument and operator to analyze up to 80 samples/day for water and soil and 60 samples/day for vapor, plus full QC analyses.	Data Quality - quantitative Applicability/Advantages - compound specific analysis in real-time - limits of detections of single µg/L for water, 10–20 µg/kg for soil and <10 µg/m^3 for vapor - accurate and precise due to use of high-level QC - due to the very short analysis time, extra QC beyond the minimum requirements are routine - support rapid, on-site development of high-density data sets - support real-time decisions for optimization of allocation of sampling resources	- compounds with identical mass spectra reported as group, e.g., cis- and trans-1,2-DCE and 1,1-DCE
Organic Vapor Analysis for Screening Samples - Cohen et al. 1992 - Feenstra, Mackay, and Cherry 1991 - Griffin and Watson 2002	Organic vapor analysis (OVA) measurements are made using an FID and/or PID to screen soil/rock samples for VOC contamination (and to monitor air quality). Soil core is typically screened every 6 in–12 in by inserting an OVA probe tip into a freshly opened void space in the core and recording peak readings, or by measuring vapors in the headspace of sample jars or bags. Vapor concentrations emitted from a NAPL may be much less than the saturated vapor concentration of a pure chemical. Very high OVA readings (e.g., >1,000 ppm by volume) may suggest NAPL presence.	Data Quality - semiquantitative Applicability/Advantages - rapid and inexpensive - high concentrations of VOCs may suggest NAPL presence - useful to focus sampling	- readings sensitive to effective contaminant volatility, water content, sample temperature, and sample handling

D.9 Environmental Molecular Diagnostics

Table D-9. Environmental molecular diagnostics

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Fluorescence In Situ Hybridization - Aman and Fuchs 2008 - Pernthaler and Amann 2002 - Wagner, Horn, and Daims 2003 - ITRC 2013	Fluorescence in situ hybridization (FISH) is a molecular biology method used to visualize and enumerate specific types of microorganisms or groups of microorganisms in an environmental sample. The method does not require isolation or cultivation of microorganisms and allows for examination of microorganisms in complex environmental samples with minimal disruption of the natural microbial community. Since its introduction in the late 1980s, FISH has been used in medical and developmental biology and environmental bacteriology. Today, FISH is considered to be a powerful tool for phylogenetic, ecological, diagnostic, and environmental microbiology studies. FISH is a technique used to detect and locate a particular genetic sequence (DNA or RNA) on a chromosome by using a complimentary fluorescently-labeled genetic probe. This probe is designed to only bind to areas of the chromosome that have significant sequence similarity.	Data Quality - qualitative Applicability/Advantages - for environmental applications, FISH typically used to identify microorganisms known to degrade a particular contaminant - FISH results typically used with other lines of evidence in natural attenuation studies	- not high throughput method - when microbial population density is low (<10^6 cells/mL) or in stationary phase of growth sensitivity is reduced

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Compound Specific Isotope Analysis - ITRC 2011a - USEPA 2008 - Kuder and Philip 2008 - Schmidt et al. 2004 - Kuder et al. 2005 - McHugh et al. 2011	Compound-specific isotope analysis (CSIA) is used to directly examine individual contaminants to learn both about their original isotopic composition and about any degradation the compound has undergone. CSIA establishes mass loss (biotic or abiotic degradation) as the mechanism for decreasing concentrations of contaminants. A key feature of CSIA is that degradation processes produce distinct isotopic enrichments that are not caused by mass transfer processes such as dilution or adsorption. CSI can be used to demonstrate degradation by measurement of an isotopic shift in the ratio of stable isotopes of elements such as carbon and hydrogen when multiple degradation processes are occurring. Fractionation results from degradation of lighter isotopes as compared to heavier isotopes due to thermodynamics and low bond energy within the former; therefore, an enrichment of the heavier isotopes occurs following degradation of the lighter isotopes of the parent compound (i.e., less negative δ13C values).	Data Quality - quantitative to semiquantitative Applicability/Advantages - assessment of contaminant sources when multiple sources possible - identification and quantification of degradation at lab- and field-scales vs. mass transfer - estimating natural attenuation rates	- in some cases, fractionation slight and difficult to validate/interpret without large number of samples - limited number of labs that can analyze these samples; high cost per sample - units of measure unfamiliar to many environmental professionals and stakeholders

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Enzyme Activity Probes • ITRC 2011a • Clingenpeel et al. 2005 • Gu et al. 2011	Enzyme activity probes (EAPs) are chemicals used to detect and quantify specific activities of microorganisms in environmental samples (e.g., soil, water, or sediment). EAPs are transformed by the target enzyme into a readily detectable product that can be measured and predicted. Most microbial enzymes are not functional outside of a cell; therefore, EAP response provides direct evidence that microorganisms in the sample are active. There is also a strong positive correlation between the rate of transformation of an EAP and the number of microorganisms actively producing the enzyme, so the microorganisms' abundance in the environment can be estimated. Some EAPs are designed to have a fluorescent product so that the cells with active enzymes will fluoresce when viewed on a fluorescence microscope. Other EAPs result in a readily detectable product that can be quantified by other means.	Data Quality • quantitative to semiquantitative Applicability/Advantages • can be used to estimate the concentration of active microorganisms with the active enzyme of interest, e.g., responsible for biodegradation • proven technology • many EAPs available for both anaerobic and aerobic metabolic processes • EAPs can be used to establish degradation rates • total cells vs. active cells can be counted on same slide with two different fluorophores	• uncharacterized/ unknown enzymes can also react with an EAP • quantification is by microscopy, and therefore can be labor intensive with manual counting • microbial enzymatic transformations not always detectable because products are either not identified or not detectable • limited commercial availability

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
DNA Microarrays	Environmental samples can contain thousands of different microorganisms and many different functional genes, some of which can serve as process-specific biomarkers. Phylogenetic microarrays evaluate community composition based on the presence/absence of microbial 16S rRNA genes present in a sample. A microarray is a solid surface upon which microscopic spots of DNA probes are attached. These probes are designed to represent genes that, when expressed, indicate a microbial activity. A gene is expressed when it produces messenger RNA (mRNA) – the genetic sequence of the messenger RNA produced is copied as cDNA (complementary DNA) using fluorescently labeled nucleotides. This cDNA is then exposed to the microarray and sequences that are complementary hybridize to the gene probes and fluoresce. A single microarray can be used to compare expressed genes in different microorganisms by using different colors of fluorescent nucleotides.	Data Quality • qualitative and semiquantitative Applicability/Advantages • test for many thousands of different microorganisms and many different functional genes, some of which can serve as process-specific biomarkers • in addition to DNA microarrays, many other types (e.g., protein, cellular, tissue, antibody) are available • detection and relative quantification of thousands of organisms or functional genes in a single analysis • information about gene expression (i.e., activity) can be obtained	• limited commercial availability • rapid advancements in both production techniques and reference database of microorganisms and functional genes • quantification of results can be difficult • interpretation of data typically requires significant expertise

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Microbial Fingerprinting • ITRC 2011a • Muyzer et al. 1993 • Hedrick et al. 2000 • Osborn, Moore, and Timmis 2001 • Bent, Pierson, and Forney 2007	Fingerprinting methods are used to provide an overall view of the microbial community, indications of microbial diversity, and insight into the types of metabolic processes occurring in the aquifer (e.g., notably the terminal electron-accepting processes such as sulfate reduction). Microbial fingerprinting methods differentiate microorganisms or groups of microorganisms based on unique characteristics of a universal component or section of a biomolecule (such as phospholipids, DNA, or RNA). Microbial fingerprinting methods provide an overall profile of the microbial community, indications of microbial diversity, and insights into the types of metabolic processes occurring. In some cases, they can be used to identify subsets of the microorganisms present. Methods include: denaturing gradient gel electrophoresis (DGGE), terminal restriction length polymorphism (T-RFLP), and phospholipid fatty acid analysis (PLFA). PLFA analysis provides total microbial biomass and a general characterization of the microbial community. The relative abundance of several different microbial functional groups (e.g., sulfate-reducing bacteria) is measured based on the concentrations of membrane lipids. DGGE and T-RFLP are both genetic fingerprinting methods. DGGE provides a genetic fingerprint of the microbial community based on melting rates during electrophoresis. T-RFLP is similar to DGGE except that the separation is based on the sizes of the DNA/RNA fragments produced by digesting the DNA/RNA with restriction enzymes.	Data Quality • qualitative to semiquantitative Applicability/Advantages • all three methods are commercially available • does not require growth of measured microbial communities during testing; therefore robust compared to other EMDs • identify predominant bacteria or group of organisms present in sample to family or even genus level • requires little prior knowledge about which microorganisms are of interest • evaluate whether the subsurface biogeochemistry at a site is conducive to known bioremediation pathways	• these methods (phospholipid fatty acid analysis [PLFA]) may not identify specific microorganisms • number of microorganisms that can be identified depends on complexity of microbial community • relevant microbial processes may not be detected in DGGE profile • interpretation is somewhat subjective and less straightforward than for other Environmental Molecular Diagnostics

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Polymerase Chain Reaction • ITRC 2011a • Pavlov et al. 2006 • Saiki et al. 1988 • USEPA 2004 • Bartlett and Stirling 2003	Polymerase chain reaction (PCR) is a technique that can test for the presence of the specific microorganism, family of microorganisms, or expressed genes in environmental samples such as soil, water, or sediment. PCR is a category of laboratory methods that can be used to detect the presence of either (a) a specific microorganism or group of microorganisms that are known to be able to biodegrade a specific contaminant or group of contaminants or (b) DNA sequences (genes) that regulate the production of enzymes (proteins) that biodegrade or partially biodegrade these contaminants. PCR capitalizes on the ability of DNA polymerase (the enzyme that copies a cell's DNA before it divides in two) to synthesize new strands of DNA complementary to a template DNA strand. A DNA primer linked to a particular bacterium or microbial activity is amplified (30–40 times) to generate enough copies of the DNA so that it can be visualized to confirm the presence of that DNA and therefore that bacteria or metabolic capability in that environment.	Data Quality • qualitative to semiquantitative Applicability/Advantages • mature technology (1960s) • capable of detecting specific microorganisms or target genes within diverse microbial communities • results are available within days • can be performed on a variety of sample types (e.g., water, soil, sediment)	• results limited to known pathways and gene sequences • some metals or humic acids may influence results

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Quantitative Polymerase Chain Reaction • ITRC 2011a • Peirson and Butler 2007 • Davis et al. 2008 • Hendrickson et al. 2002 • Lee et al. 2008 • Baldwin et al. 2010 • DeBruyn, Chewning, and Sayler 2007 • Hristova et al. 2003 • Amos et al. 2007	Quantitative polymerase chain reaction (qPCR) and reverse transcriptase quantitative polymerase chain reaction (RT-qPCR) are used to quantify the abundance and activity of specific microorganisms or expressed genes in pathways capable of biodegrading contaminants at a contaminated site. Quantitative PCR is a method for estimating the concentration of a particular genetic sequence in an environmental sample. The concentration of that genetic material is then related to the concentration of a particular microorganism or class of microorganisms.	Data Quality • quantitative to semiquantitative Applicability/Advantages • commercially available • quantify abundance of specific microorganisms capable of biodegrading identified contaminants • identify whether or not specific genes are being expressed for contaminant biodegradation	• qPCR analyses based on known biodegradation pathways and gene sequences • RT-qPCR must be used to distinguish between dead cells containing target gene and live cells

Table D-9. Environmental molecular diagnostics (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Stable Isotope Probing • Kuder and Philip 2008 • Kreuzer-Martin et al. 2007 • ITRC 2011a	Stable isotope probing (SIP) techniques are used to determine whether biodegradation of a specific contaminant does or could occur. SIP can identify the microorganisms responsible for this activity. SIP involves exposing the microbial community to an isotopically labeled substrate (e.g., contaminant) and using the detection of that heavy isotope in a biomarker molecule to indicate microbial metabolism (biodegradation). This is typically implemented by baiting a microcosm with an isotopically labeled contaminant of concern. These microcosms can be lowered into a well to be populated by the indigenous groundwater bacteria, or the groundwater and sediment from the aquifer can be put into an enclosed microcosm. The nucleic acids or phospholipids of the microbial population colonizing the microcosm are subsequently analyzed for the isotopic label. Degradation is confirmed by the production of $^{13}CO_2$ and the organisms responsible are identified by examining the incorporation of ^{13}C into the DNA (or RNA) or PLFA of the degrading organisms.	Data Quality • qualitative to semiquantitative Applicability/Advantages • commercially available • proven technology • does not require prior knowledge of microorganisms, genes, or enzymes involved in biodegradation processes • DNA-SIP can link functionality to phylogeny • applicable to different environmental media (water, soil, sediment)	• contaminants artificially enriched with high levels of stable isotopes such as ^{13}C and ^{15}N • not appropriate for contaminants used as terminal electron acceptors, such as chlorinated ethenes or perchlorate • DNA/RNA SIP can identify organisms only if they have been identified in the past • extrapolating results of SIP studies to field conditions (i.e., lower than lab conditions) must be done carefully

D.10 Stable Isotopic and Environmental Tracers

Table D-10. Stable isotopic and environmental tracers

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Stable Isotopes - Coplen, Herczeg, and Barnes 1999 - Harte 2013a	Deuterium, oxygen-18, and carbon-13 isotopes provide qualitative information on the origin of water that can be used to infer age in some cases.	Data Quality - qualitative estimate of age and processes Applicability/Advantages - help identify environmental processes that affect water such as climate and vegetation	- isotopic compositions of water may be derived from non-unique processes and may require additional geochemical information
Radioactive Tracers - Cook and Böhlke 1999 - McKinley 1994	Radioactive isotopes can be used to calculate the age of groundwater based on the rate of decay of a radioactive isotope and input concentration at the time of recharge into the groundwater system. Some common radioactive isotopes include hydrogen (tritium), helium, carbon-14, and chlorine-36.	Data Quality - quantitative to semi-quantitative Applicability/Advantages - independent assessment of fracture connectivity based on age of groundwater - could be used to identify dual permeability or bimodal ages of multiple water origins - assessing well integrity	- tritium signal has decreased since reduction of atmospheric nuclear detonation and was absent prior - helium ratios provide higher resolution of age determination

Table D-10. Stable isotopic and environmental tracers (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Anthropogenic Chemical Tracers - Cook and Böhlke 1999	Chemical tracers typically have distinct input concentrations at the time of recharge, from being in contact with the atmosphere, that can be used to estimate age. Some examples of chemical tracers include chlorofluorocarbons and sulfur hexafluoride.	Data Quality - semiquantitative Applicability/Advantages - independent assessment of fracture connectivity based on age of groundwater - identify dual permeability or bimodal ages of multiple water contributions	- interactions with DNAPL may affect estimates of groundwater age - requires sampling for dissolved nitrogen and argon
Accumulation Tracers - Cook and Böhlke 1999 - Semprini et al. 1998	Isotopes of the uranium and thorium decay series such as radium and radon have been used to identify locations of DNAPL given the differential tendency of DNAPL and water relative to daughter products uptake (e.g., radon flux rate). This tool is similar to partitioning tracer tests with increased sensitivity to radionuclide detection.	Data Quality - qualitative Applicability/Advantages - identification of DNAPL saturations or pool geometry	- not commercially available - may require information on background uptake of uranium and thorium

D.11 Analytical Options

Table D-11. On-site analytical options

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Mobile Laboratory	Mobile laboratories can be equipped to use the same reference methods as fixed base laboratories. These could include purge and trap GC/MS methods (e.g., USEPA Methods 5035 / 8260) or extraction based GC/MS methods (e.g., USEPA methods 3550 / 8270). Data can be uploaded to the fixed laboratory information management system with reports provided in a wide variety of media and formats.	Data Quality • quantitative to qualitative Applicability/Advantages • can provide fixed laboratory quality assurance when needed • can use reference methods with years of regulatory acceptance history	• mobilization expense can be high, thus most cost effective for large projects • mobilization can require significant lead time
Portable Gas Chromatograph • https://www.clu-in.org/characterization/technologies/gc.cfm	Portable GCs with halogen- or hydrocarbon-sensitive detectors can be used to produce screening, semiquantitative, and quantitative results in the field. These systems are hand portable and weigh 2 kg–20 kg. The GC is most commonly coupled with headspace or purge and trap sample preparation when used for DNAPL in water or soil.	Data Quality • quantitative to qualitative Applicability/Advantages • GC separation prior to detection increases specificity and discrimination among similar compounds • smallest portable GCs are handheld; can be taken to sample collection point and produce results in a few minutes	• may not be possible to meet quality assurance expectations commonly applied to laboratory-based GCs • may not be as sensitive as laboratory-based GCs

Table D-11. On-site analytical options (continued)

Tool	Description	Data Quality and Applicability/Advantages	Limitations/Difficulty
Portable Gas Chromatograph / Mass Spectrometer - https://www.clu-in.org/characterization/technologies/gc.cfm	Portable GC/MS systems can be used to produce screening, semi-quantitative, and quantitative results in the field. These systems are hand portable and weigh 10 kg–20 kg. The GC/MS is most commonly coupled with headspace or purge and trap sample preparation when used for DNAPL in water or soil.	Data Quality - quantitative to qualitative Applicability/Advantages - GC separation coupled with MS detection is very selective and sensitive, approaching laboratory quality - smallest systems can be carried by hand or as a backpack to the sample collection point and produce results in a few minutes	- may not be optimized to meet quality assurance expectations commonly applied to laboratory based GC/MS when in most rapid turnaround mode - expensive

APPENDIX E. DATA TYPES AND DEFINITIONS

Understanding the types of data that must be collected for a dense nonaqueous phase liquid (DNAPL) site characterization is crucial in selecting the appropriate tools (see the Tool Selection Worksheet). The data types for DNAPL investigations generally fall into three categories – geologic, hydrogeologic, and chemical – as described below.

E.1 Data Quality

Data quality can be described as follows:

- **Quantitative = Q** , tool that provides compound-specific values in units of concentration based on traceable standards (such as µg/L, ppm, or ppbv)
- **Semi-quantitative = SQ**, tool that provides compound-specific quantitative measurements based on traceable standards but in units other than concentrations (such as ng or µg) or provides measurements within a range
- **Qualitative = QL**, tool that provides an indirect measurement (for example, LIF and PID measurements provide a relative measure of absence or presence, but are not suitable as stand-alone tools for making remedy decisions)

E.2 Sample Location

Sample locations are defined as follows:

- *Subsurface*. The subsurface terrain (geology) is categorized as :
  - Unconsolidated - Sampling heads can often be pushed through an unconsolidated subsurface (for example, a poorly cemented sedimentary subsurface).
  - Bedrock – Bedrock is the general type of subsurface terrain that requires rotatory drilling methods (for example, intrusive igneous rock types such as granites, diorites, or extrusive igneous rocks such as basalt, rhyolite, or andesite and metamorphic rock terrains).
- *Hydrologic Zones*. The subsurface consists of two hydrologic zones:
  - Unsaturated (vadose zone), where the pores are saturated by groundwater
  - Saturated (groundwater zone), where the pores of the rock terrain are completed filled with groundwater

E.3 Geology

Geologic data provide a means to describe the physical matrix and structure of the subsurface and to classify the sedimentary, igneous, or metamorphic environment. Data related to lithology and distribution of strata and facies changes are generated through a variety of qualitative and quantitative collection tools and methods.

Initial methods and tools used to characterize site geology include site walkovers to help gain a preliminary understanding of the site prior to a major field mobilization, which can involve the use of both intrusive and nonintrusive tools. Outcroppings offer insight into structural features of the bedrock, and much information can be obtained through basic geologic mapping techniques (for example, measuring strike and dip of planar features and plotting on a stereonet).

Following a surface investigation, the next step in site characterization commonly involves collecting a continuous core of sediments and bedrock. Data provided by this core sampling may include lithology, grain size and sorting, crystalinity, geologic contacts, bedding planes, fractures and faults, depositional environment, porosity, and permeability. Generally, numerous boreholes are drilled to determine the vertical and horizontal variability of the site-specific geology. The depositional environment and facies changes should also be mapped as much as possible, and these data may be combined with surface and borehole geophysical data to interpolate conditions between the holes. Downhole geophysical tools and direct-push tools – for example, membrane interface probe (MIP), hydraulic profiling tool (HPT), and Waterloo profiler – can provide detailed information on the geology and contaminant distribution at a site.

Effective site geology characterization requires that personnel are trained and experienced in field geology and are able to accurately assess the collected data. It is also important that the team use consistent investigative methods – for example, characterizing soil or rock type using the same, agreed upon classification system. The team must determine the level of data resolution necessary to adequately characterize a specific site and whether surface and borehole geophysical data are of sufficient resolution.

Unfortunately, collection efforts at contaminated sites often yield insufficient geologic data, leading to a high degree of uncertainty in subsurface interpretation. Historically, there has been a tendency to oversimplify conceptual site models (CSMs), which has led to the misperception that physical (geologic) conditions of the site can be engineered around – that is, limitations in site characterization data can be compensated by overdesigning remediation systems. However, remedy performance success rates have been poor under such circumstances, whereas investing in adequately detailed site characterization has provided a positive return on investigation in terms of improved remedy success rates and reduced life cycle costs.

Oversimplification of CSMs is particularly relevant to glaciated regions with complex depositional environments. In the northeast and Midwest, many glaciated sites contain both bedrock and glacial aquifers that have DNAPL issues. Under such conditions, hydrogeological and geological expertise specific to glacial environments and their depositional characteristics is required for developing an accurate and complete CSM, and is key to the success of a DNAPL remedy.

E.3.1 Lithology

Lithology describes a rock unit or unconsolidated deposit, including the physical characteristics of the rock and unconsolidated materials such as mineral composition, grain size, shape, sorting, texture, and origin of the rock (sedimentary, igneous, or metamorphic). Grasping the lithology of a site is important in understanding the geology in three dimensions, and this provides insight into the heterogeneity of the subsurface. Heterogeneity is often a controlling factor in contaminant fate and transport, and, when mapping lithology, it is important to understand that the physical properties of a geologic unit are not always unique to that unit. Thus, further information may be required to define flow units, typically referred to as hydrogeologic units. Hydrogeologic units often group different lithologic units or parts of adjoining lithologic units with similar flow and transport properties (that is, permeability and porosity).

E.3.2 Lithologic Contacts

A lithological contact is the surface between different lithological units. Lithologic changes may be defined by sharp boundaries (lithologic contact) between sediments or rock of different type (for example, shale and sandstone), or they can be transitional, changing from one sediment or rock type into another over several inches or feet (for example, sand grading to silty sand to silty-clay to clay). This may be a conformable contact (similar geologic history, not representing an erosional surface) or a nonconformable contact (representing a change in geologic history and erosional/nondepositional period). Lithologic contact data are important in site characterization as they delineate lithological units for the geological model and identify the potential for contaminant flow and transport and DNAPL pooling at the contacts.

E.3.3 Porosity

Porosity is the ratio of void volume of open space to total volume within sediment or rock. Porosity is generally expressed as a percentage of the total rock or sediment volume that is open space.

Primary porosity is the volume of void space that results from sediment deposition, settling, and lithification. Primary porosity is generally most important in sediments, unconsolidated formations, and sedimentary rocks. Igneous and metamorphic rocks generally have significantly less primary porosity, except for some igneous rocks such as vesicular basalts. Secondary porosity is represented by the open voids created after sediment deposition, settling, and lithification processes by a variety of mechanisms: (1) structural activities, including mineral alignment during metamorphosis (foliation); (2) faulting and fracturing of rock or sediments through plate tectonics; (3) fracturing caused by stress imbalances, such as those involved in isostatic rebound; and (4) chemical dissolution of limestones.

Porosity can change over time due to a variety of mechanisms such as chemical precipitation of minerals (for example, calcium carbonate and silicates in pore spaces) or dissolution along fluid flow paths. Porosity values are important for understanding the fluid storage capacity of the system. High porosity values may indicate the potential for significant mass storage at contaminated sites.

E.3.4 Permeability

Permeability is a physical property of a porous medium describing the ability of the medium to transmit fluids under a hydraulic gradient. Small-scale differences in permeability that may be indiscernible to the naked eye can have a significant bearing on the distribution and migration of

DNAPL and dissolved contamination. High porosity does not always indicate high permeability. The pore spaces must be interconnected to have permeability. One example of a high-porosity but low-permeability rock is vesicular basalt in which the vesicles (large pores) are not interconnected. Contrasts in permeability can result in diffusion from high-permeability strata to low-permeability strata (matrix diffusion) and from low-permeability strata to high-permeability strata (back-diffusion).

E.3.5 Dual Permeability

Dual permeability refers to the two different permeabilities that relate respectively to the primary and secondary porosity of a porous media and that, combined, result in the total permeability of the media. For example, a bedded limestone may have low primary permeability (intergranular or intercrystalline) and porosity within the matrix of the rock, but dissolution of the limestone along bedding planes or fractures can result in the formation of cavities and conduits, creating very high permeability.

The influence of the lower permeable matrix is not usually discernable in hydraulic test results unless the test is of very long duration. In a fracture network, there is often a significant contrast between the highly permeable large fractures or dissolution voids intersecting the borehole and the smaller peripheral fractures connected to these large fractures. These will affect hydraulic test results, especially in shorter-term hydraulic tests.

E.3.6 Faults

A fault is created when a rock mass undergoes failure due to stresses or strains. When a rock mass fails, two masses of rock move past each other at a low angle (thrust fault) or high angle (normal or reverse faults). In the process of these two masses shifting by each other, part of the rock is fractured, brecciated, and pulverized along a fault plane. The pulverized material commonly creates a fine-grained material along the fault plane, known as fault gouge, which usually has low permeability. Conversely, coarse-grained fault breccias (larger clasts) may exhibit very high permeability unless secondary mineralization has filled the voids and pore spaces. The two rock masses are also highly fractured for a certain distance from the failure point, commonly referred to as the fault damage zone. Depending on the distribution of the rock gouge and the geometry of the fault damage zone, faults can act as barriers to flow perpendicular to the fault or enhance flow parallel to the fault, or as complicated combinations of barrier with enhanced flow in both directions. Understanding a fault's effects on groundwater flow is important in developing a CSM for a site that contains faults.

E.3.7 Fractures

A fracture is a planar feature in rock in which brittle deformation (separation or cracks) has occurred. A fracture generally forms in rock when external stresses exceed the strength of the rock. Fractures in clays can occur through desiccation and associated shrinkage. In low-permeable media, fractures dominate the flow system and can act as the primary contaminant transport pathways (NRC 1996). Individual fractures may constitute a significant groundwater flow pathway and contaminant conduit; however, fractures must be interconnected to form a continuous flow path to act as preferential flow zones. It is therefore important to determine which fractures act as continuous features and which are nontransmissive; this determination is usually made through hydraulic testing.

E.3.8 Fracture Density

Fracture density is the number of fractures in a unit length of a rock hole. This is a poorly defined term; however, the number of fractures in a given length of matrix can be an indicator of the potential effect of secondary porosity and even permeability.

E.3.9 Fracture Sets

Fracture sets are groups of similarly oriented fractures in a rock. Fracture sets are often associated with other fracture sets that have cut across each other at consistent, definable angles. It is important to characterize fracture sets, as they constitute critical elements of the structural fabric of bedrock aquifers and may strongly cause preferential effects on contaminant transport.

E.3.10 Rock Competence

Rock competence reflects the degree of fracturing, where a highly competent rock has very few fractures. Determining where the rock is competent is important in defining hydrogeologic flow units.

E.3.11 Mineralogy

The mineral composition of rock or sediment plays a significant role in determining its physical properties. Mineralogy of a rock includes the study of the chemical compositions of each mineral and its origin. In igneous and metamorphic rocks, the crystal structure, crystal size, modality, and physical mineralogy of the rock controls physical properties such as hardness, competence, and microstructure. In sedimentary rocks, mineralogy can influence grain size, roundness/angularity, distribution, cementation, and intergranular contacts, and these mineralogic characteristics can control rock hardness, competence, sedimentary structures, porosity, and permeability. Knowing these physical properties helps in assessing the degree of fracturing, and can also explain the role of matrix diffusion in a fractured bedrock system. Knowing the clay content and clay mineralogy, as well as the organic carbon content, also helps in understanding the potential for matrix diffusion from a fine-grained sediment.

E.4 Hydrogeology

Hydrogeology is branch of geology that studies groundwater flow. The main hydrogeologic parameters in Darcy's Law are hydraulic conductivity and hydraulic gradient. Hydraulic conductivity is usually determined by in situ hydraulic tests, while hydraulic gradient is determined from hydraulic head measurements at three or more points in the flow system. Both of these parameters can vary vertically and horizontally in all groundwater systems. In particular, hydraulic conductivity can vary by orders of magnitude vertically over short distances in some geologic environments. Lateral changes in hydraulic conductivity within a sediment or rock unit also may occur. Often this is due to a facies change across the unit (for example, sand grading laterally to sandy silt, to silty clay, to clay over distances of a few to many meters). This lateral change is often less dramatic, but still may have significant influence on contaminant fate and migration. Hydrogeologic units are commonly created by combining the geology and hydraulic data sets relying on head distributions in the system. While hydraulic head patterns may be relatively uniform throughout a hydrogeologic unit, the hydraulic conductivity can vary.

Knowing the flow distribution is fundamental in predicting the potential fate and transport of the contaminant. Interfaces between media of differing hydraulic conductivity can determine the migration of DNAPL and the diffusion of contaminants from high-conductivity units into adjacent low-conductivity units. Sufficient hydrogeologic data must be collected to minimize the uncertainty of the CSM with regard to contaminant flux (see ITRC 2010). Direct-push logging methods – for example, HPT, electrical conductivity, cone penetrometer, laser-induced fluorescence (LIF), and MIP – can be key in defining hydrostratigraphic facies and contaminant relationships in unconsolidated hydrostratigraphic units.

E.4.1 Open Hole Flow

Open hole flow occurs in a vertical hole drilled through porous media. Vertical flow occurs inside the borehole due to differences in hydraulic head with depth. There are many cases in which boreholes intersecting two aquifers create vertical migration of contaminants from the upper to lower aquifer (that is, cross connection). This phenomenon often occurs in fractured rock boreholes and care must be taken to minimize the time the hole is left open at contaminated sites to prevent this cross connection. Even short periods of cross connection can cause long-term effects due to matrix diffusion (Sterling et al. 2005).

Open hole flow measurements can be made to determine the direction and magnitude of vertical groundwater flow within the borehole and identify the contribution of individual fractures to flow into and out of the borehole. However, the highest flow zones in the open hole dominate the response, and moderate- to low-flow zones (where contaminants may be stored) will not be identified.

E.4.2 Ambient Flow and Vertical Head Gradients

Ambient flow reflects the normal horizontal and vertical flow of groundwater under natural gradient conditions. This forms the baseline for further testing of fate and transport of a contaminant. It is especially important at fractured rock sites because zones exhibiting high conductivity, based on forced gradient tests, may not be well connected to contaminated or recharge zones, and therefore will not provide very active migration pathways under natural conditions.

Vertical head gradients may be present in unconsolidated sediment and rock aquifer systems. A significant upward gradient may inhibit the downward migration of contamination, while a significant downward gradient may accelerate the downward movement of contaminants. The installation of multilevel piezometers, FLUTe liners, or Westbay systems may be needed to define vertical gradients in consolidated aquifers. In unconsolidated formations, multilevel piezometers, HPT logs, or Waterloo Profiler logs can be used to define vertical gradients, if present.

E.4.3 Groundwater Isotope Analysis

Isotope analysis can be used to identify recharge areas and estimate the travel time of the water from the recharge source. For example, if the groundwater sample is young, the aquifer presumably is being replenished with modern water from the surface; therefore, the aquifer is vulnerable to contamination from above. Relative aging along a flow path is also used to determine the travel time between two points in the flow system; however, the geometry of the flow system, including recharge and discharge areas, is essential for reliable interpretation.

The stable isotopes deuterium (^{2}H) and oxygen-18 (^{18}O) serve mainly as indicators of groundwater source areas, and as evaporation indicators in surface-water bodies. Radioactive isotopes are used to infer age by measuring the amounts of the isotope in the sample and knowing the rate of decay. Common radioactive isotopes, including tritium (^{3}H) and carbon-14(^{14}C), are produced naturally in the atmosphere by the interaction of cosmic rays and nitrogen; ^{3}H was naturally incorporated into water molecules and ^{14}C into carbon dioxide. When these isotopes enter groundwater, they become isolated from the atmosphere, and thus the radioactive decay process dominates the change in concentrations over time. However, calcite and dolomite, which are generally of much older origins and present in many groundwater systems, can dilute the isotope concentrations in groundwater samples; they must be accounted for to obtain accurate ages. These isotopes may also be useful in indirectly estimating bimodality in water sources. This could be an indication of dual permeability and fracture connectivity (Coplen, Herczeg, and Barnes 2000; Cook and Böhlke 2000).

E.4.4 Fracture Aperture

The aperture is the width of a fracture. The three main types of fracture aperture measurements are as follows:

1. Mechanical aperture – The mechanical aperture is the actual measured fracture width, which can vary significantly throughout the fracture, and represents the true aperture distribution throughout the fracture. This aperture can change if the fracture is pressurized or depressurized. Hydromechanical well testing attempts to measure this change (Rutqvist et al. 1998; Schweisinger et al. 2009).
2. Hydraulic aperture - Hydraulic apertures are the theoretical fracture widths calculated with the cubic law using transmissivity (T) values determined from hydraulic tests. Hydraulic apertures represent the size of the fracture based on the hydraulic behavior.
3. Transport aperture - Solute transport apertures can also be determined based on the behavior of solute transport through the fracture.

Typically, these three types of apertures conflict, and there is still discussion about which apertures is most applicable for inputs into discrete fracture network models for contaminant transport.

E.4.5 Fracture Connectivity

Fracture connectivity in concert with the aperture and density of fractures determines the overall bulk hydraulic conductivity of the formation. Poorly connected fractures result in relatively low hydraulic conductivity. Conversely, well-connected fractures result in higher hydraulic conductivity.

E.4.6 Hydraulic Conductivity

Hydraulic conductivity (K) is related to the permeability of a porous medium, but it is specific to the moving fluid.

$$K = \frac{Cd^2\rho g}{\mu}$$

K can also be expressed as:

$$K= \frac{k\rho g}{\mu}$$

Where:

C is dimensionless shape factor that relates to the shape of the pore spaces.

d is the average diameter of the matrix grains.

ρg is the specific weight of the fluid.

μ is the viscosity of the fluid.

Cd^2 is equal to k which is the permeability of the porous medium.

K is most often used to describe the movement of water and is often considered the proportionality constant (K) in Darcy's Law; however, the conductivity of any liquid can be determined in this manner if the permeability of the porous medium and the properties of the fluid are known.

The transmissivity (T) of an aquifer is a measure of how much groundwater can be transmitted horizontally over a unit thickness of the saturated aquifer. It is expressed as:

$$T= Kb$$

Where:

K is the hydraulic conductivity.

b is the saturated thickness of the aquifer.

K or T (transmissivity) values are commonly determined from hydraulic tests, and are important for developing a flow system model to assess the migration of contamination being carried by the moving water. The K value is the maximum velocity at which the fluid could flow through the given porous medium.

Velocity (v) is the rate groundwater flows through the aquifer proportional to the K and hydraulic gradient (Fetter 1994):

$$v = \frac{Ki}{n_e}$$

Where:
K is the hydraulic conductivity.
i is the hydraulic gradient.
n_e is the effective porosity.

Although a unit may have high hydraulic conductivity and good permeability, contaminant migration may be limited if the hydraulic gradient at the site is small. However, human activity (such as water supply extraction or fluid injection) and natural phenomena such as tides and seasonal climate variations (such as spring snow melt, floods, or droughts) can significantly influence local gradients; for example, a drought can change what was a gaining stream into a losing stream and reverse the groundwater gradient.

E.4.7 Hydraulic Head

The hydraulic head is the sum of the elevation head, pressure head, and velocity head (Fetter 1994), although the velocity head is generally negligible in groundwater unless in karst terrains. In an open hole that is screened over an entire aquifer or an entire hydrogeologic unit, the water level in the open hole represents the total head in that unit and can be used to determine hydraulic gradients, the natural driving force for groundwater flow. However, if the hole penetrates more than one aquifer or hydrogeologic unit, the water level in the open hole is a blended head that results from the cross-connected units that have different heads and conductivities. This is especially important to understand in fractured rock systems or layered aquifers where head profiles with depth are instrumental in defining hydrogeologic units to improve accuracy in gradient calculations and for defining contaminant migration pathways.

E.4.8 Borehole Condition

The physical condition of a borehole – including its diameter; depth; structural integrity; degree of collapse; physical, chemical, or biological clogging or fouling; condition of installed structures such as well screens, sand packs, and seals – is often assessed upon installation to determine whether specifications have been met and to establish a baseline condition. It is then measured periodically for monitoring and maintenance or to troubleshoot a performance deficiency. Borehole condition is generally measured with a downhole camera.

In fractured rock boreholes, optical or acoustic televiewer logs can be used to create a virtual caliper log that can be very useful for identifying breakout zones where part of the rock has been dislodged from the wall, and to select good locations for setting inflatable packers to maximize the likelihood of creating a good seal.

E.5 Chemistry

Chemical data provide information on the site's contaminants and geochemical conditions and contaminant distribution. Parameters include contaminant concentrations, system biogeochemistry (for example, microorganisms and total organic carbon), and water quality parameters (for example, oxidation reduction potential [ORP], pH, dissolved oxygen [DO], alkalinity, and temperature). These data types provide direct measurement of the chemical conditions in the subsurface. Most data analysis and interpretation methods rely on the chemistry of the groundwater; however, chemistry data are not limited to one type of media. Soil gas and porous media samples can be collected and analyzed to help complete or round out the picture of the source zone(s) in the CSM. The chemical composition of the geologic media may have a significant impact on contaminant fate (for example, carbon, alkali minerals) and how effective some remediation fluids may be under the ambient geochemistry conditions (for example, the abundancy of ferric iron when a reductive dechlorination process is to be applied).

Chemistry data methods can be divided into three primary categories: quantitative, semi-quantitative, and qualitative. Quantitative methods are usually defined as using formal laboratory analytical methods and equipment to compound specific values in units of concentration based on traceable standards (for example, µg/L, ppm, ppbv). Because of the high cost, the number of samples that can be analyzed may be very limited. Limiting the number of samples due to analytical costs has often resulted in CSMs that cannot provide the necessary resolution to understand contaminant distribution, degradation, and migration. Sometimes a well-equipped on-site mobile laboratory can provide the same or similar chemical data quality as a fixed lab at a reduced price. This will often provide for more samples and higher data density, giving better resolution of conditions for the CSM.

Semiquantitative (compound-specific quantitative measurements based on traceable standards but in units other than concentrations (for example, ng or µg) or provides measurements within a range) to qualitative (indirect measurement (for example LIF and PID measurements provide a relative measure of absence or presence, but are not suitable as stand-alone tools for making remedy decisions) methods often provide results in relative concentrations and may not provide analyte specificity. Several of the direct-push logging tools fall into this category (for example, MIP, LIF, OSTs). Although they do not specifically identify contaminants, these tools can provide valuable semiquantitative data on contaminant concentration, at the much higher resolution needed to understand their distribution and migration, so that an effective CSM can be developed.

E.5.1 Soil Gas

Data on contaminants in the vapor phase in the vadose zone are an important component of many DNAPL CSMs. Soil gas measurements may indicate the presence of a contaminant source in the unsaturated zone or help to define the extent of groundwater contamination. Soil gas measurements are also used to assess potential or actual contaminant vapor intrusion into structures. The concentration of a volatile contaminant in the pore space in the vadose zone may also indicate the composition and concentration of these volatile contaminants in the adjacent shallow groundwater.

E.5.2 Groundwater

Groundwater chemistry is described in several distinct categories, including geochemistry, microbiology, field or indicator parameters, and contaminant measurements. However, the resolution of the measurement is always a function of the sample size. Many studies have shown that wells with long screens produce blended concentration values that can be orders of magnitude less than wells with multiple short screens at the same location. Multilevel monitoring systems are invaluable for measuring depth-discrete groundwater samples over time to fully understand the contaminant distribution in the groundwater.

E.5.3 Geochemistry

Geochemical parameters, often referred to as water quality parameters, include those that typically define the suitability of groundwater for consumption. Geochemical parameters include alkalinity, hardness, pH, DO, and minerals such as iron, magnesium, calcium. These parameters can inform an investigator of general groundwater conditions at a site, and can indicate groundwater contamination as well as assist with the evaluation of remedial alternative. During a site investigation, field parameters are often collected by low-flow purging of groundwater through a multiprobe sonde that typically measures pH, specific conductance, temperature, DO, ORP, and turbidity.

E.5.4 NAPL Presence

The presence of DNAPL represents a potentially persistent reservoir of contaminant mass that can continue to degrade groundwater quality over long periods. Therefore, understanding the potential presence and distribution of DNAPL in the subsurface is critical to long-term site environmental management. NAPL confirmation requires direct observation. However, there are a variety of chemical and physical techniques are available to provide evidence of the presence of NAPL (some of which provide direct evidence that NAPL is present), as follows:

- measurement of contaminant concentration in bulk soil samples (may provide direct evidence or an indication of NAPL presence)
- sorption techniques (such as NAPL FLUTe, which provides direct evidence of NAPL when it reacts with the coating on the FLUTe)
- tracers (such as Partitioning Interwell Tracer Test), which provide an indication of NAPL presence
- fluorescence (such as LIF), which provides direct evidence of NAPL
- dye (such as Sudan IV and Oil Red O), which provides direct evidence of NAPL
- optical (such as GeoVIS), which provides direct evidence of NAPL
- conductivity (such as NAPL interface probes), which provides direct evidence of NAPL)

See Chapter 2 and Chapter 3 for more thorough descriptions of NAPL and NAPL behavior in the subsurface.

E.5.5 Contaminant Concentration

The contaminant concentration in the solid matrix of the aquifer can be used to indicate the presence of DNAPL or light nonaqueous phase liquid (LNAPL), via partitioning calculations (Feenstra, Mackay, and Cherry 1991; Mariner, Jin, and Jackson 1997), which can serve as an ongoing source of mass to the aquifer. This can be either mobile NAPL or immobile NAPL. High contaminant concentrations in the source area can indicate an early-stage release from an ongoing source of a DNAPL versus lower concentrations, which may be more indicative of a diffusive source from a middle- or late-stage release.

Because of the high cost of completing boreholes at contaminated fractured rock sites, analyzing samples from the rock core at adequate frequency is important for understanding the contaminant mass distribution in the rock, and is a major factor in designing a multilevel system for measuring groundwater that will be installed at a later date. In addition, because of open hole flow, a multilevel sampler may show groundwater contamination at locations where the rock core did not; therefore, rock core concentrations are necessary to fully understand the contaminant distribution measured in the groundwater.

At sites where volatile organic contaminants are present in unconsolidated formations, several direct-push logging methods can be used to qualitatively define contaminant concentrations and distribution. Some of these logging methods are LIF, MIP, and ROST. These logging methods can provide detailed information on contaminant distribution at a relatively low cost. The logs may be used to guide the targeted collection of expensive laboratory samples, thus optimizing the information gained while reducing overall costs.

E.5.6 Solid Media

Solid media consists of the subsurface material of unconsolidated or bedrock geologic terrains.

E.5.7 Solids Geochemistry

Chemical analysis of solid geologic material is important because contaminants can be sorbed or sequestered on fine grained or weathered particles. Many secondary minerals occur as very fine-grained rock particles or crystalline material that can sorb and desorb metals and organic constituents. This fine-grained material may be very transient in that they can precipitate and dissolve over short periods depending on the local environment. Chemical analyses of solid geologic material can delineate sinks for subsurface contaminants.

E.5.8 Fraction of Organic Content, F_{oc}

Fraction of organic content, f_{oc}, is a measure of the fraction of organic carbon in the subsurface solid material. The higher the f_{oc} the more organic matter is available to adsorb contaminants. The higher the organic content of the soils, the more contaminant can be adsorbed and less is available to leach to groundwater. In transport models, f_{oc} is an important parameter because the organic carbon content of the soils in part determines the degree of retardation of a contaminant in groundwater. Physical test are required to identify f_{oc} (see Appendix I for more information regarding f_{oc}).

The ability of an organic chemical/contaminant to sorb to the aquifer matrix is a function of the f_{oc} of the aquifer and the affinity of the contaminant to the organic carbon. This is known as the organic carbon partitioning coefficient, which is represented as K_{oc}.

E.5.9 Presence in Solid Material

The presence of NAPL represents a potentially persistent reservoir of contaminant mass that can continue to degrade groundwater quality over long time periods. Therefore understanding the potential presence and distribution of DNAPL in the subsurface is critical to long-term site environmental management. NAPL confirmation requires direct observation of NAPL; however, there are a variety of chemical and physical techniques available to confirm the presence of NAPL.

- measurement of contaminant concentration in bulk soil samples (may provide direct evidence or an indication of NAPL presence)
- sorption techniques (such as NAPL FLUTe, which provides direct evidence of NAPL when it reacts with the coating on the FLUTe)
- tracers (such as Partitioning Interwell Tracer Test), which provide an indication of NAPL presence
- fluorescence (such as LIF), which provides direct evidence of NAPL
- dye (such as Sudan IV and Oil Red O), which provides direct evidence of NAPL
- optical (such as GeoVIS), which provides direct evidence of NAPL
- conductivity (such as NAPL interface probes), which provides direct evidence of NAPL)

See Chapter 2 and Chapter 3 for more thorough descriptions of NAPL and NAPL behavior in the subsurface.

E.5.10 Contaminant Concentration in Solids Material

The contaminant concentration in the solid matrix of the aquifer can be used to indicate the presence of DNAPL or LNAPL, which can serve as an ongoing source of mass to the aquifer. This can be either mobile NAPL or immobile NAPL. High contaminant concentrations in the source area can be an indication of an early stage release from an ongoing source of a DNAPL, versus lower concentrations, which may be more indicative of a diffusive source from a middle or late stage release.

Because of the high cost of completing boreholes at contaminated fractured rock sites, analyzing samples from the rock core at adequate frequency is important for understanding the contaminant mass distribution in the rock and is a major factor in designing a multilevel system for measuring groundwater that will be installed at a later date. In addition, because of open hole flow, a multilevel sampler may show groundwater contamination at locations where the rock core did not, and therefore rock core concentrations are necessary to fully understand the contaminant distribution measured in the groundwater.

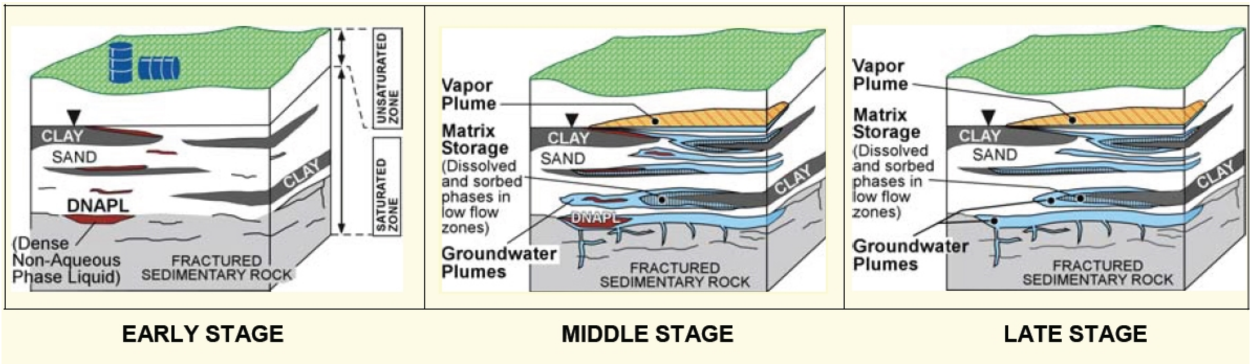
E.5.11 Microbial Community

Knowledge of the microbial community from any solid material is important since some types of bacteria can degrade the contaminant of concern even in the unsaturated zone. However there must be moisture for a microbial community to survive. Several varieties are known to degrade contaminants and identification of them will help to assess the applicability of active degradation. In other cases, the degree of microbial diversity can be an indicator of the toxicity of an environment.

APPENDIX F. SCREENING METHOD TO ESTIMATE IF A CHLORINATED SOLVENT RELEASE IS IN THE EARLY, LATE, OR MIDDLE STAGE

The chlorinated solvent FAQ (Sale et al. 2008) presents the idea that chlorinated solvent sites go through various stages during their life cycle. In the early stage, chlorinated solvent releases are dominated by dense nonaqueous phase liquid (DNAPL); over time, DNAPLs slowly dissolve, plumes develop, and contaminants accumulate in permeable zones. Eventually, little to no DNAPL remains, and plumes are sustained by the release of contaminants from low-permeability zones via diffusion (Chapman and Parker 2005). Although recoverable, DNAPL can still be found within some source zones; it is very difficult to find DNAPLs at the heads of many persistent plumes. At some sites (see the “late stage” depiction in the graphic below), DNAPL may no longer be present, even though the source zone [see question 4 in Sale et al. (2008)] is still active. Key factors controlling the rate at which chlorinated solvent releases age include the amount of DNAPL released, the solubility of the constituent in the DNAPL, the rate of groundwater flow, and the architecture of transmissive and low-permeability zones.

Described below is a methodology used by site managers, consultants, remediation specialists, and regulators to determine whether they are working on an early-, middle-, or late-stage site. The method is based on work experience in chlorinated solvent source zones, with some assistance from recently developed matrix diffusion models that form the basis of the Environmental Security Technology Certification Program’s Matrix Diffusion Toolkit (Farhat et al. 2012). This method is an initial classification system, and the approach may change as more is discovered about how chlorinated solvent sites age.



EARLY STAGE MIDDLE STAGE LATE STAGE

Figure F-1. Aging of a chlorinated solvent release.

Examples are as follows:

- My regulatory guidance says I must remove DNAPL if present (for example, DNAPL is considered a primary threat waste).
- I want to consider using a DNAPL-specific technology (such as injection-based technology).

Some key considerations about the screening method are as follows:

- It is designed for chlorinated solvent sites, although it may be possible to adapt it for other contaminants.
- Although the method can be applied to other DNAPL constituents, it is mainly derived from experience with trichoroethene (TCE) sites.
- It is relatively general and relies on several interpretations when compiling the required data; thus, different users may generate different answers.
- The method may be time intensive as it requires careful consideration about the site and the data required.

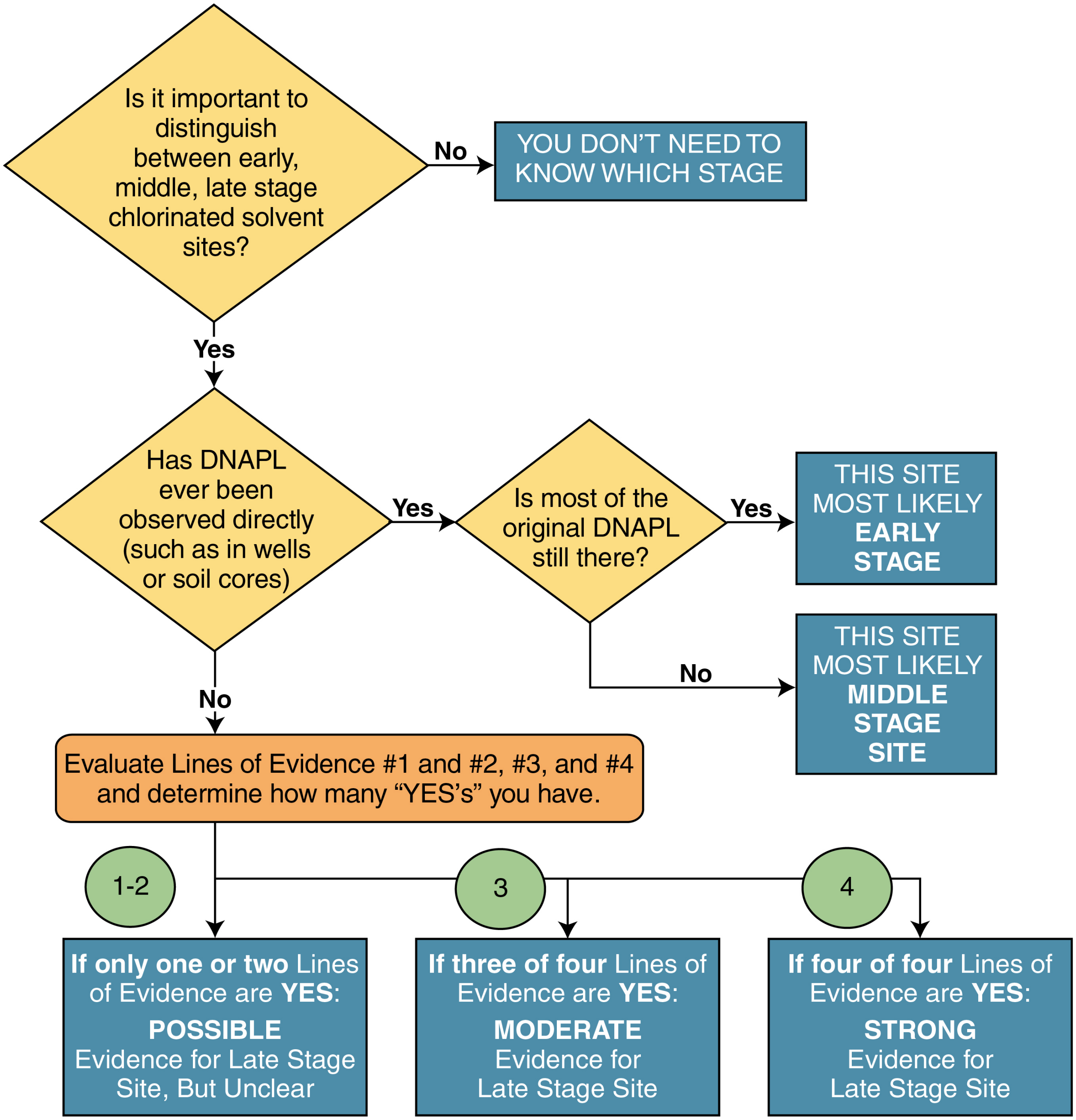


Figure F-2. Screening method decision chart.

Examples are as follows:

- I'm going to use containment.
- I'm going to use a DNAPL technology that is not DNAPL (type) specific (such as thermal remediation).

F.1 Is Most of the Original DNAPL Still There?

It can be difficult and controversial to answer questions as to whether DNAPL is still present. Some observations and speculations are presented below; these may change over time as better methods for understanding DNAPL source zones are developed. In this application, references to DNAPL mean DNAPL chemicals rather than an insoluble oil or other chemicals in the original release.

Knowing whether the original DNAPL is still present depends on several variables that can be difficult to determine, such as the amount of the release, the composition of the DNAPL, and the source architecture, as well as more commonly measured geochemical and hydrogeologic variables. Simple dissolution models can be used as guidance; however, if the DNAPL is mainly in ganglia or blob form, the resulting dissolution times are often just a few years. DNAPL pools, particularly long ones (tens of meters), can last for several decades.

In general, the answer is more likely to be "No" if the site has more of the following characteristics:

- There are only a few indicators of DNAPL presence (for example, a couple of stains on just a few cores).
- No significant DNAPL accumulation in groundwater monitoring wells has been observed.
- The source release is small (a few hundred or few thousand kilograms or less).
- The source release mechanism and the geology will spread the DNAPL into a large volume in the subsurface.
- Groundwater seepage velocities are moderate to high (tens of meters per year or more).
- An in situ remediation technology has successfully removed much of the DNAPL mass from the transmissive zone.
- The key constituents are more soluble (several hundred or thousand milligrams per liter [mg/L] or more).
- It has been several decades since most of the DNAPL was released.

In general, the answer is more likely to be "Yes" if the site has more of these characteristics:

- There are multiple indicators of DNAPL presence (for example, many cores with positive dye test results, several monitoring wells with DNAPL accumulations).
- Significant DNAPL accumulation in monitoring wells has been observed.
- The release was very large (hundreds of thousands or millions of kilograms).
- The release point and subsurface geology result in the formation of large DNAPL pools.
- Groundwater seepage velocities are low (meters per year or less).
- No remediation or DNAPL removal has occurred.
- The key constituents have relatively low solubility (tens or a few hundreds of mg/L).
- It has been just a few years since most of the DNAPL was released.

At most sites, DNAPL is never observed, so the lines of evidence outlined below must be followed.

F.1.1 Line of Evidence 1- Adequate DNAPL Search?

Was a *thorough* direct DNAPL investigation conducted, in which one or more of the following was performed:

- Interfaces above low-permeability zones were sampled.

  OR

- A vertical transect was used to identify high flux zones that were then sampled for DNAPL.

  OR

- Soil samples were investigated using enhanced techniques such as hydrophobic dye.

  OR

- Other DNAPL-specific characterization technologies were used.

If ANY of these were done, Line of Evidence 1 is **YES**.

If NONE were done, Line of Evidence 1 is **NO**.

(**IMPORTANT:** the “1% rule” should not be used to indicate the presence of DNAPL).

F.1.2 Line of Evidence 2 - Old Plume + Heterogeneity?

Does the site meet both of these qualitative conditions?

- The site has low–k zones (such as silts, clays, sandstone, limestone) with hydraulic conductivity of at least 100 times lower than the fastest transmissive zones that is, or was, in contact with the plume.

  AND

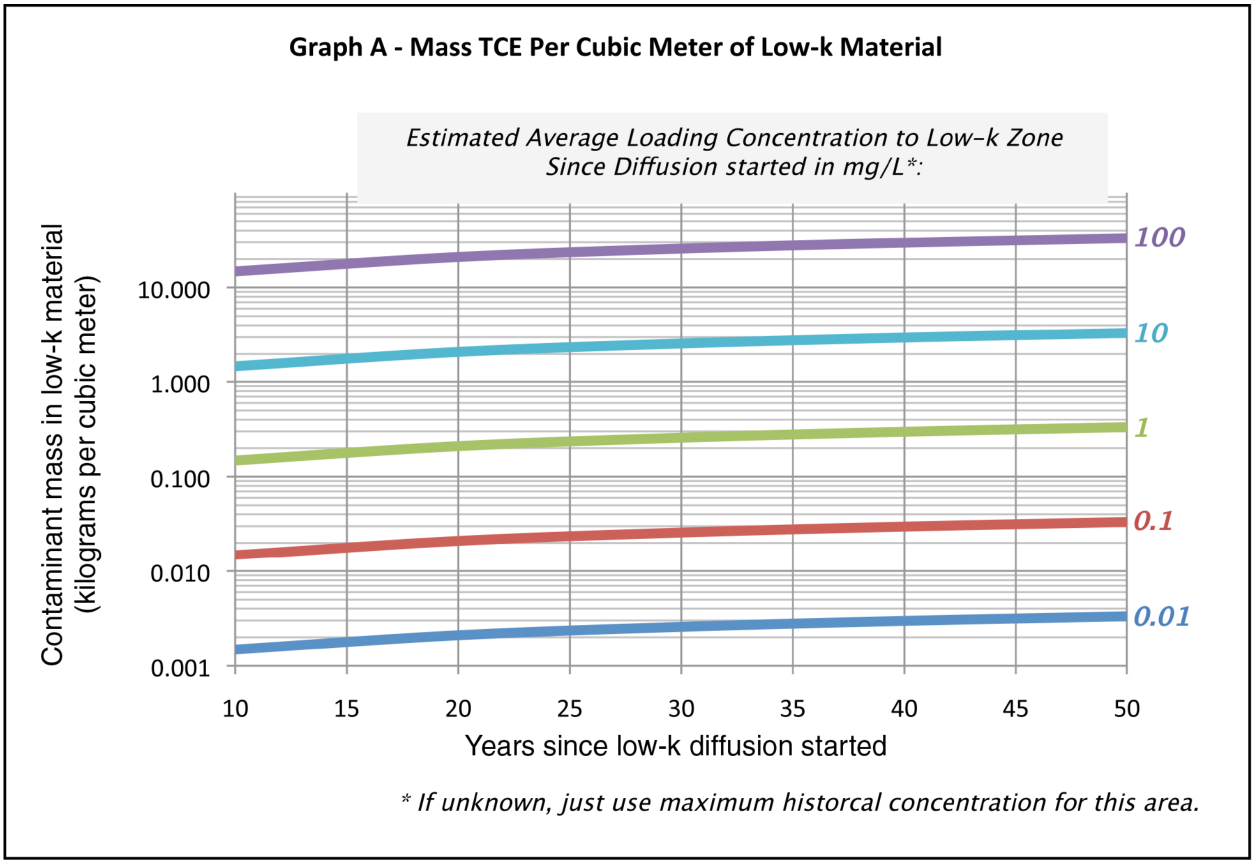
- The original release likely occurred more than 30 years ago.

If BOTH of these are TRUE, Line of Evidence 2 is **YES**.

If EITHER IS FALSE, Line of Evidence 2 is **NO**.

F.1.3 Line of Evidence 3 - Can the Low-k Zone Hold Enough Mass?

Calculate TCE mass per cubic meter of low-k material using Figure F-3, and estimate the volume of low-k material at the site using Figure F-4 (see figures below).


Graph A - Mass TCE Per Cubic Meter of Low-k Material

* If unknown, just use maximum historcal concentration for this area.

Figure F-3. Mass TCE per cubic meter of low-k material.

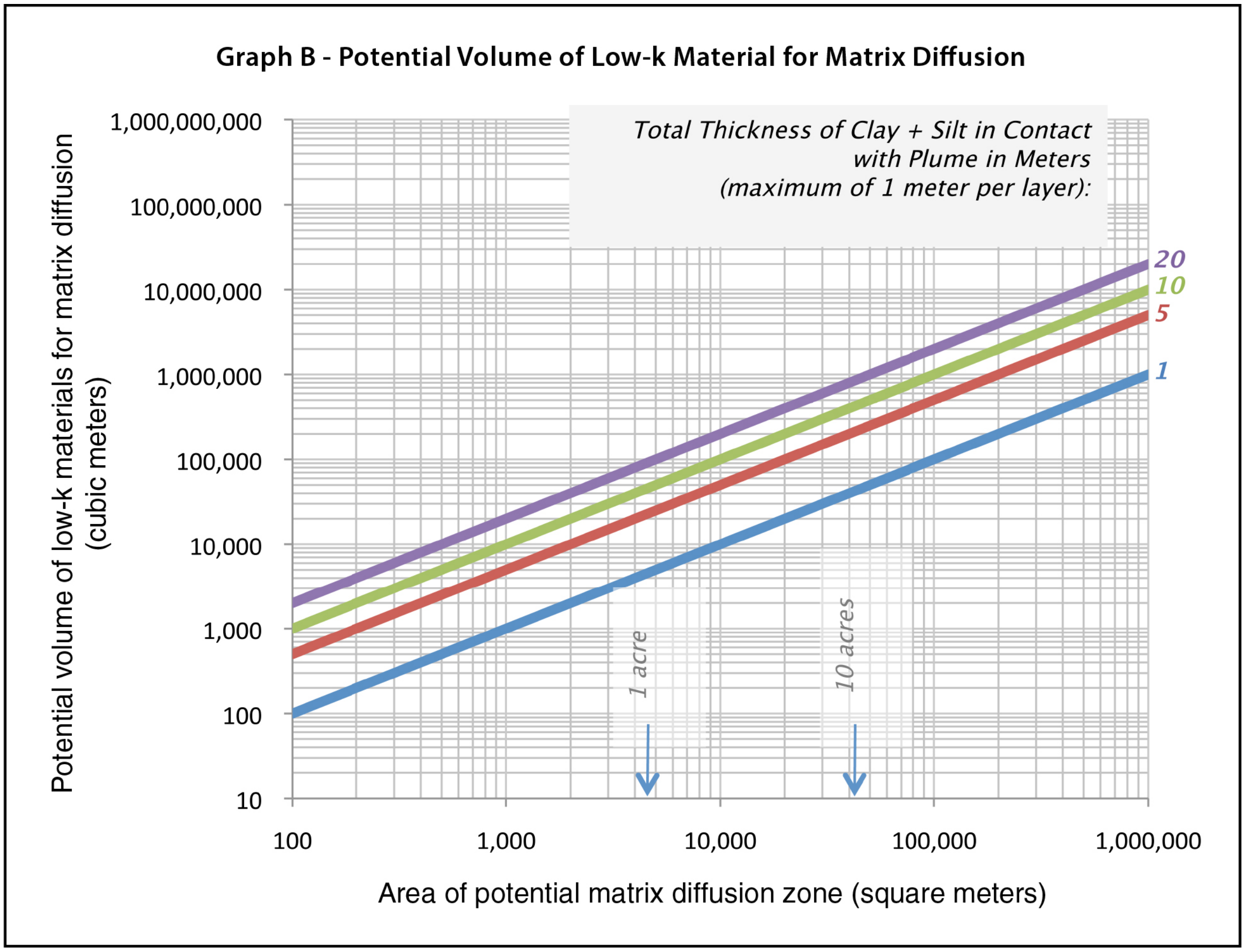


Figure F-4. Potential volume of low-k material for matrix diffusion.

Multiply the two values from Figure F-3 and Figure F-4 to get an estimated mass in low–k unit in kilograms.

This particular chart is designed for TCE and for a source zone, but can be applied to other chlorinated solvents by multiplying by the pure-phase solubility of the specific DNAPL chemical in mg/L and dividing by 1,000 mg/L (value used for TCE).

This can be done for different parts of the site – such as the original source zone; a high-concentration part of the plume and a low-concentration area, each with a different concentration; year since low-k diffusion started; and areas – and then the numbers can be added.

If the mass is >100 kg, Line of Evidence 3 is **YES**.

If the mass is <100 kg, Line of Evidence 3 is **NO**.

F.1.4 LINE OF EVIDENCE 4 - Can Low-k Zones Create High Enough Concentrations?

Estimate the length of the low-k zone parallel to groundwater flow that might have been in contact with a high-strength plume. Enter the graph and select the line for the subject contaminant. If the contaminant is not represented, find the line for the chemical with the solubility closest to the subject contaminant (for this graph, the solubility of 1,2-dichloroethane (DCA), cis-dichloroethene (DCE), TCE, and tetrachloroethene (PCE) were assumed to be 8,690, 1,000, 800, and 143 mg/L, respectively. Alternatively, the Matrix Diffusion Toolkit can be run to evaluate potential monitoring well concentrations from low-k zones.

At the y-axis, find the potential maximum concentration in groundwater in a monitoring well with a 10 ft screen in mg/L (note: log scale).

If the potential maximum concentration in Step 3 is greater than the maximum historical concentration for that contaminant at the site, Line of Evidence 4 is **YES**.

If the potential maximum concentration in Step 3 is less than the maximum historical concentration for that contaminant at the site, Line of Evidence 4 is **NO**.

If the mass in Step 3 is <100 kg, Line of Evidence 4 is **NO**.

If the calculated maximum theoretical concentration from Figure F-5 below is less than the observed maximum concentration in site monitoring wells, a late-stage site is possible and Line of Evidence 4 is YES; otherwise, Line of Evidence 4 is **NO**.

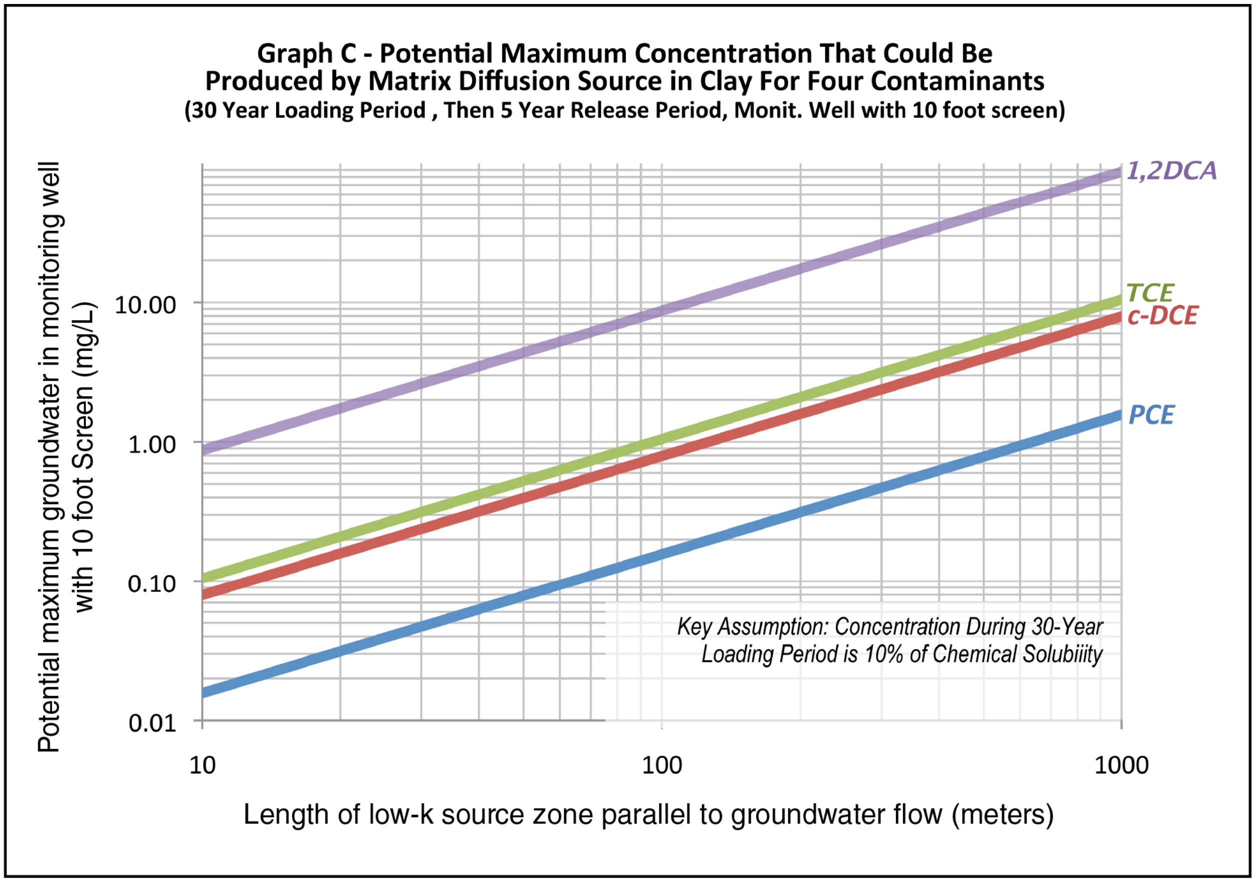


Figure F-5. Potential maximum concentration that could be produced by matrix diffusion source in clay for four contaminants (30-year loading period, then 5-year release period, monitoring well with 10 ft screen).

F.2 Technical Basis- How Does This Work?

The methodology for matrix diffusion modeling is discussed in the following sections.

F.2.1 Overall Basis – Assume Simple Geometry, One Low-k Unit, One Transmissive Unit

This methodology is designed for sites with unconsolidated hydrogeologic settings (sand, silt, clay), with a single low-k unit in contact with a plume in a transmissive zone. For those familiar with matrix diffusion modeling, the methodology can be adapted to other configurations such as multi-layered systems and fractured rock sites by multiplying the results in Lines of Evidence 3 and 4 (below) by the number of contacts between transmissive and low-k units.

F.2.2 Line of Evidence 1 – Adequate DNAPL Search?

A strong but not conclusive line of evidence of a late-stage site is that a thorough search for DNAPL using current DNAPL-specific techniques did not reveal any evidence of DNAPL in the source zone. Determining if a particular field program rates a YES or NO is somewhat subjective, but the main criterion is that a DNAPL-specific field investigation to find direct evidence of

DNAPL in wells and soil cores was performed. Use of the 1% should not be used for Line of Evidence 1 because matrix diffusion modeling indicates that strong matrix diffusion sources can create concentrations greater than 1% of the effective solubility of DNAPL.

F.2.3 Line of Evidence 2 – Old Plume + Heterogeneity?

There are two key ingredients for a strong, long-lived matrix diffusion source: (1) heterogeneity, considering that a 100-fold difference in hydraulic conductivity leads to matrix diffusion processes (B. Parker, University of Guelph, personal communication); and (2) old sites loading more mass in low-k zones.

F.2.4 Line of Evidence 3 – Can the Low-k Zone Hold Enough Mass?

The square root model in the Matrix Diffusion Toolkit (Farhat et al. 2012) is used to estimate a contaminant mass that could diffuse into a single low-k layer at least 1 m thick. The total thickness of the clay and silt in contact with a plume is then applied to the calculated potential mass per cubic meter. A site can be broken up into different zones. This method can then be used to estimate the mass separately— in high-, medium-, and low-concentration zones—and then the masses are added together.

Why 100 kg? This is the amount that can sustain an average plume (Mag 5 plume in the plume magnitude system) for 50 years (Newell et al. 2011).

F.2.5 Line of Evidence 4 – Can Low-k Zones Create High Enough Concentrations?

This line of evidence assumes that a plume with concentrations at 10% of the pure-phase solubility of the contaminant was in contact with a low-k zone for 30 years. If unknown, assume the length of the low-k zone is the length of the source zone at the site parallel to groundwater flow. The low-k zone was assumed to be clay with a fraction organic carbon (f_{oc}) of 0.002 grams per gram, giving retardation factors for DCA, DCE, TCE, and PCE of 1.4, 1.7, 1.2, and 2.1 in the clay, respectively. The Matrix Diffusion Toolkit's square root model (Farhat et al. 2012) was used to generate the concentrations as a function of the length of the low-k zone.

Different contaminants can be evaluated by picking the lines with the solubility closest to the subject contaminant. If there is process knowledge that the concentration during the loading period is different than the 10% solubility assumed above, the final result can be adjusted by the ratio of the solubility to 10% (for example, if the loading concentration was equal to 50% of TCE pure-phase solubility, multiply the concentrations on the y-axis by 5).

APPENDIX G. FIELD APPLICATION OF TOOLS CASE STUDIES

G.1 Case Study 1. Field Application of the Combined Membrane Interface Probe and Hydraulic Profiling Tool to Assess Hydrostratigraphy and Contaminant Distribution – Skuldelev, Denmark

The combined membrane interface probe (MIP) and hydraulic profiling tool (HPT) is designated as the MiHpt probe (Figure G-1). The MIP part of the system includes the downhole probe with semi-permeable membrane, trunkline strung through the probe rods, and uphole gas chromatograph (GC); the GC typically includes a photoionization detector (PID), flame ionization detector (FID), and halogen specific detector (XSD). The HPT part of the system contains the screened port on the side of the probe, downhole pressure transducer, and uphole pump with flow meter and trunkline. The MiHpt probe includes an electrical conductivity (EC) array.

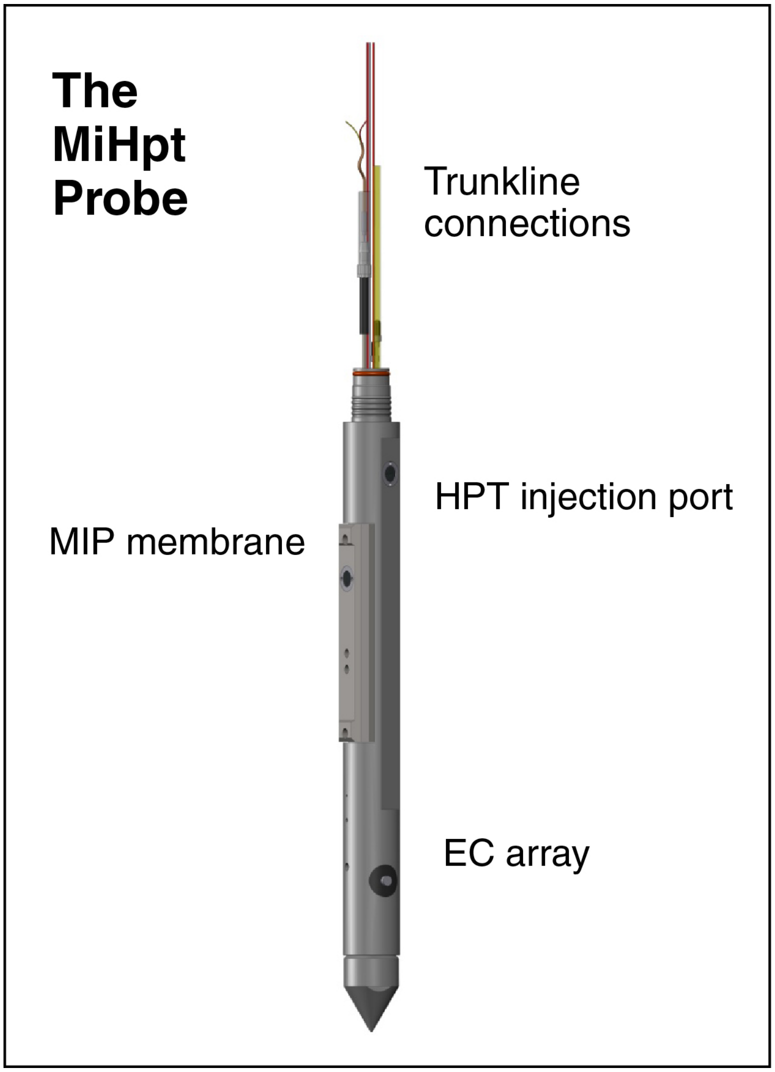


Figure G-1. Schematic of an MiHpt probe (combined MIP and HPT).

The semipermeable membrane on the side of the probe allows volatile organic compounds (VOCs) to pass from the soil into the clean carrier gas stream under a concentration gradient (Figure G-2). The nitrogen carrier gas sweeps the VOCs up the trunkline to the GC detectors at the surface. A heater block at the membrane is heated to about 100 degrees Celsius to enhance VOC migration from the soil across the membrane. The probe is advanced incrementally into the formation. Advancement is stopped for approximately 60 seconds at each 1 ft (30 cm) increment. This allows time for the VOCs to cross the membrane and be swept up to the GC detectors. A stringpot mounted on the mast of the direct-push machine tracks depth as the probe is advanced. The acquisition software plots the detector response at the correct depth on the computer screen as the log is being run.

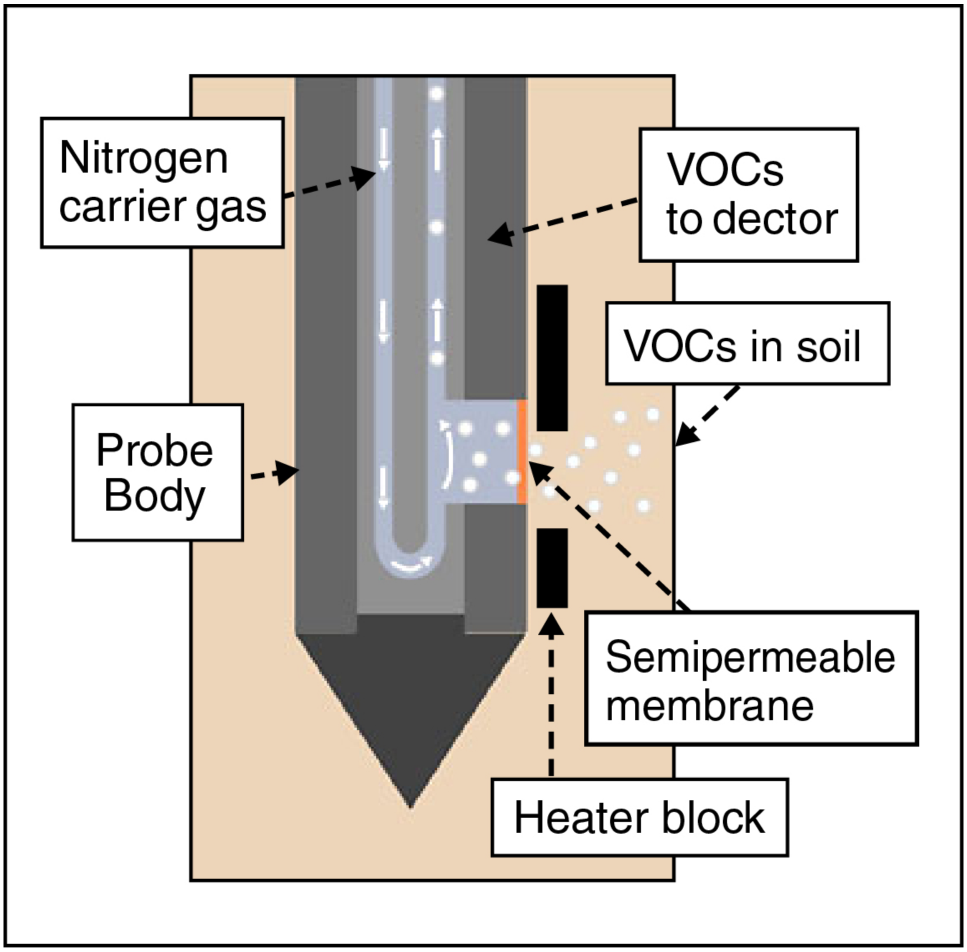


Figure G-2. Operating principles for the MiHpt probe.

In Figure G-3, a pump (B) at the surface pumps clean water down the trunkline and out the screened port (F) on the side of the probe into the unconsolidated formation. A flow meter (B) measures the injection flow rate. The downhole pressure sensor (E) measures the pressure required to inject water into the formation. The injection pressure and flow are plotted on screen vs. depth as the probe is advanced. An electrical conductivity array (G) also provides an EC log of the formation.

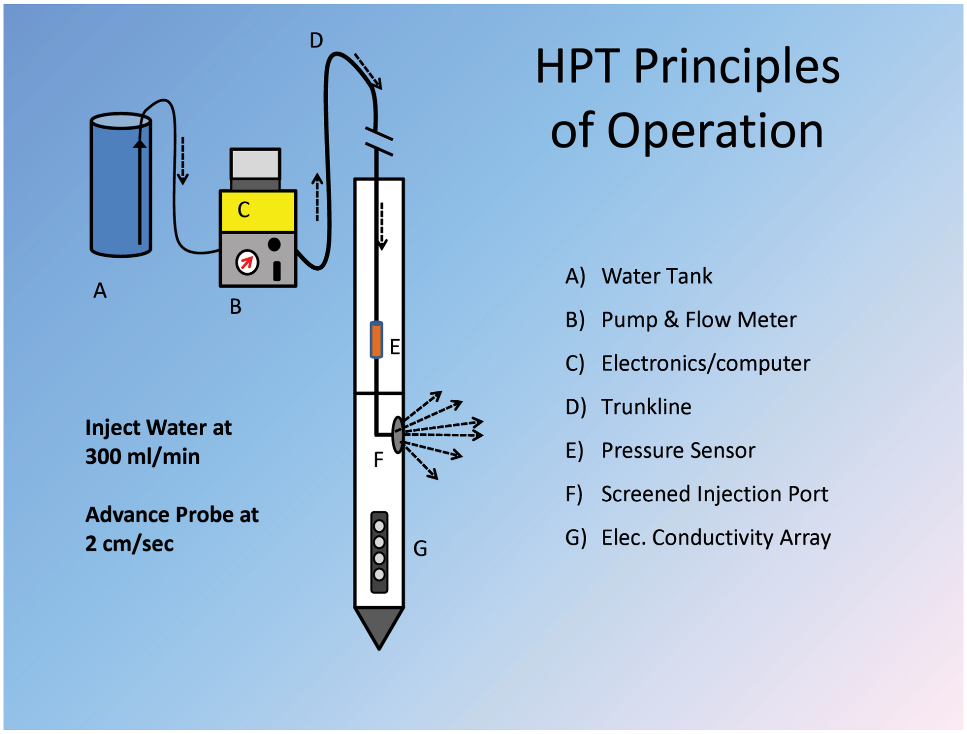


Figure G-3. HTP operation.

MiHpt log interpretation is relatively simple. On the EC and detector data log (Figure G-4) for Case Study 1—a tetrachloroethene (PCE)-contaminated site in Skuldelev, Denmark—the left graph plots the EC log vs. depth. In fresh water formations, low EC values generally indicate coarse-grained materials (sand and gravel), while higher EC values usually indicate elevated clay content. This EC log indicates primarily sand and gravel to a depth of about 7 m. The graph in the center plots the PID detector response vs. depth, and the graph on the right plots the XSD detector response vs. depth. Higher detector response indicates higher concentrations of contaminants.

The detector logs show that, above 3 m, there is little or no contamination, while the contaminant concentrations increase significantly at 3 m–6 m and then drop off again. The XSD is sensitive to chlorinated VOCs such as PCE and trichloroethene (TCE). The PID is sensitive to aromatic compounds like benzene and toluene, but also responds to the double bond present in the chlorinated ethenes (for example, PCE, TCE, and dichlorothene [DCE]). Thus, from the combined PID and XSD data, it can be inferred that the primary contaminants are chlorinated ethenes, although sampling is required to confirm this initial interpretation. The combined data from the EC log and detector responses indicate that the contaminants are primarily in the permeable and transmissive sand and gravel of the local formation.

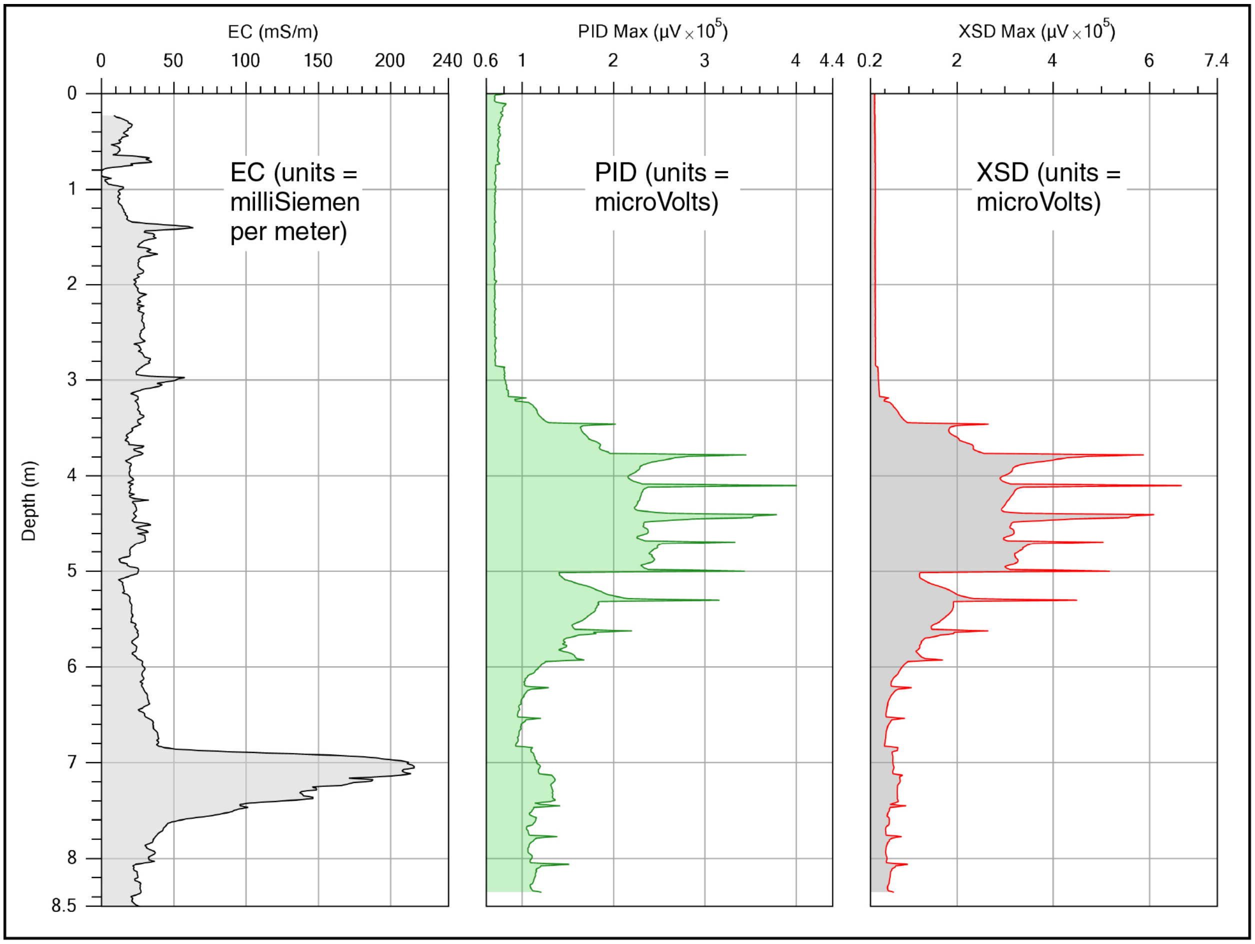


Figure G-4. SK05 MiHpt log EC and detector response data: Skuldelev, Denmark.

After this log (Figure G-5) was completed, a direct-push, discrete-interval sampling tool was used to collect groundwater samples at targeted intervals based on the detector response log. Only 1 ft (30 cm) of screen was opened at each depth interval. The samples were analyzed at a fixed lab by gas chromatography/mass spectrometry for the typical suite of VOC contaminants. The results for PCE+TCE+DCE are plotted over the PID and XSD logs at the depths where they were collected (red triangles). Duplicate samples were collected in the field at a couple of intervals and those results are plotted with the original sample results. The PID and XSD detector logs correlate well with the groundwater sample results.

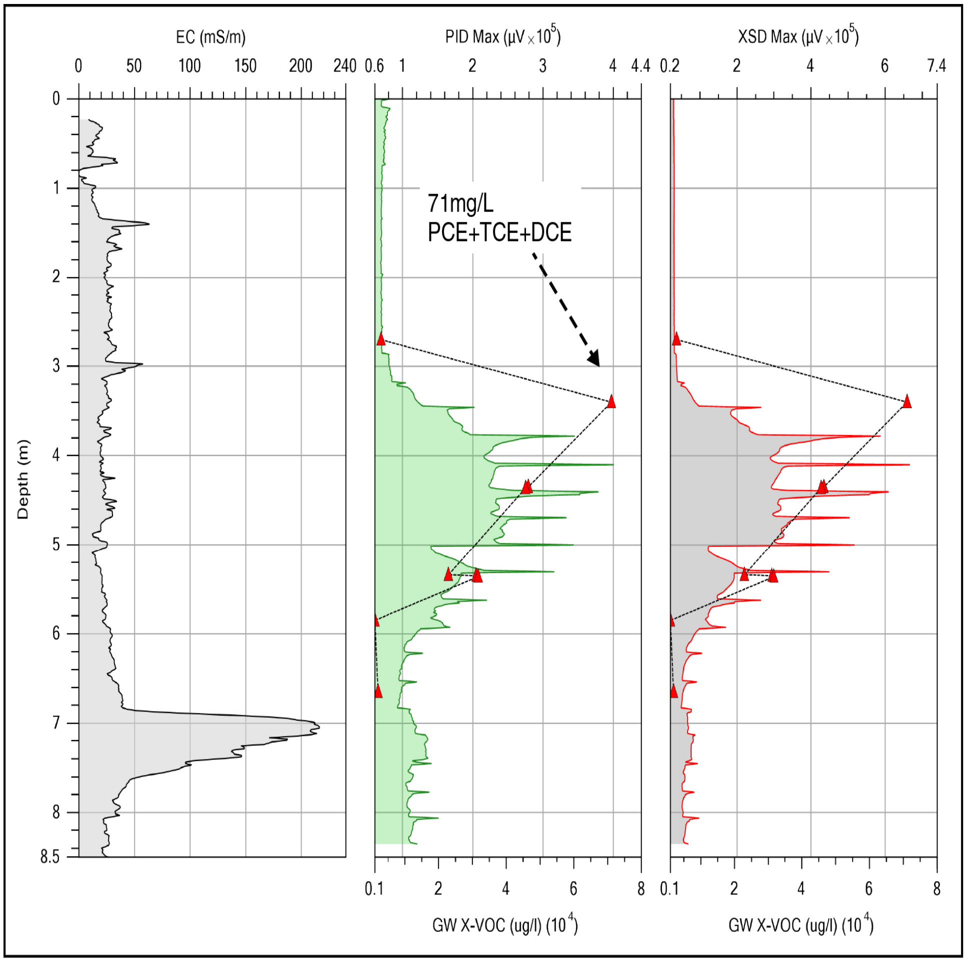


Figure G-5. SK05 MIP log data with groundwater X-VOC results.

For the HPT log data from the SK05 location (Figure G-6), the EC log is again plotted on the left, while the HPT pressure is in the center graph and the HPT flow rate is on the right; all are presented versus depth. For HPT logs, lower injection pressure indicates higher permeability and higher injection pressure indicates lower permeability. For this log, the pressure peak between the surface and the 1m depth indicates some fine-grained soils. This is followed by relatively low HPT pressure down to just above 7m, indicating a good permeability formation. Below 7m, the HPT pressure increases, indicating lower-permeability materials. The HPT flow rate is relatively constant down the log, with some flow decrease as the probe passes through the higher-pressure material below 7m. The slow rise in the HPT pressure from about 1m deep to just below 7m where the fine-grained material is penetrated indicates the increase in hydrostatic pressure (dashed line) as the probe advances below the water table. During this log probe, advancement was stopped at about 3m and 5m to run dissipation tests. The HPT injection flow was turned off and the ambient piezometric pressure was measured. With this information, the piezometric pressure line could be plotted and the local water level calculated.

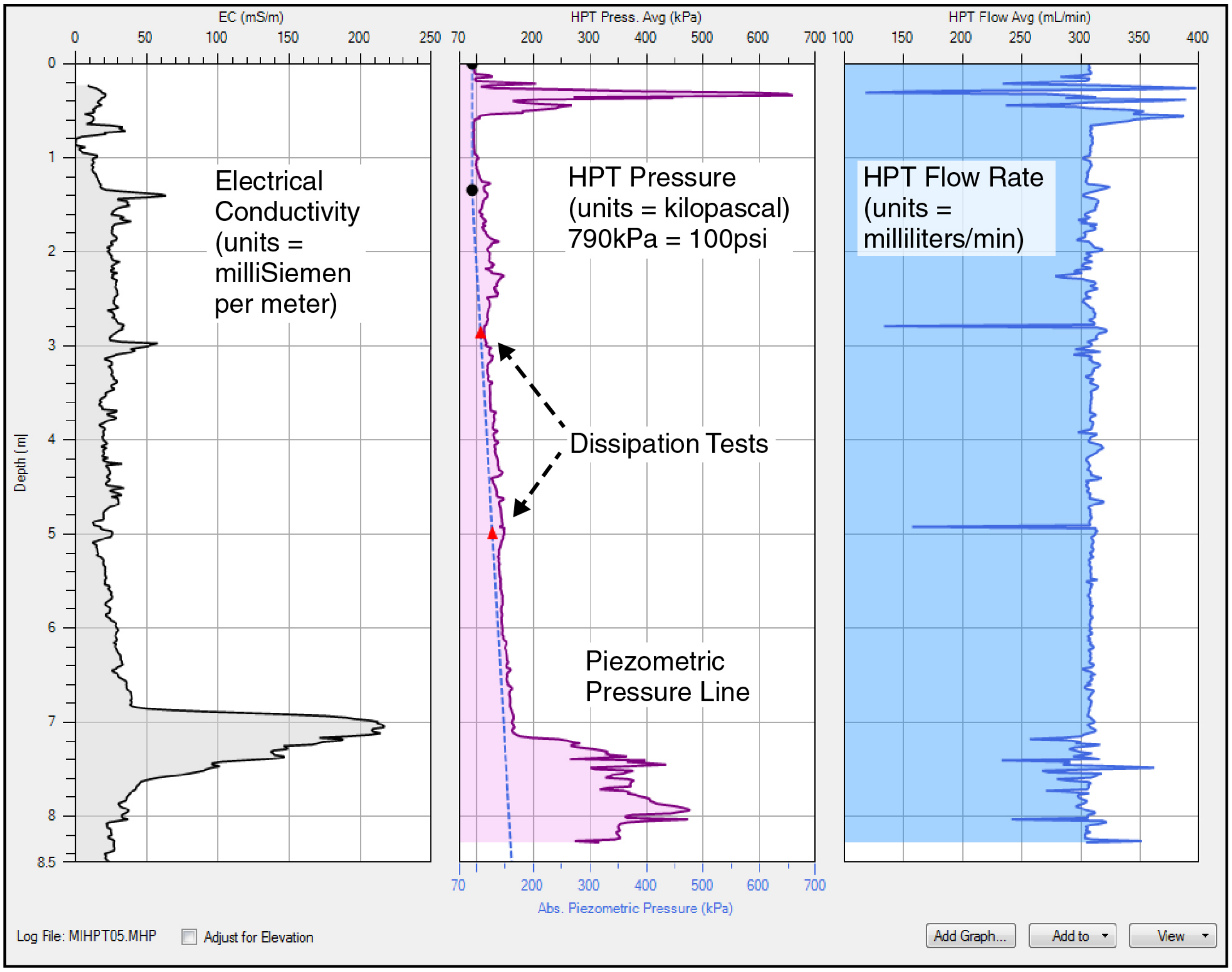


Figure G-6. EC, pressure, and flow data for the SK05 MiHpt log.

Continuous soil cores were collected next to the SK05 location (Figure G-7). Photos of some of the core samples are shown next to the HPT pressure and flow rate logs. The cores from the upper 7m are composed mostly of sand and gravel with minor amounts of silt and clay. Below 7m, the core samples contain primarily fine-grained, silty clay with a little sand and occasional gravel sized clasts. It is thus evident that the HPT pressure data provide a good representation of the local lithology and formation permeability.

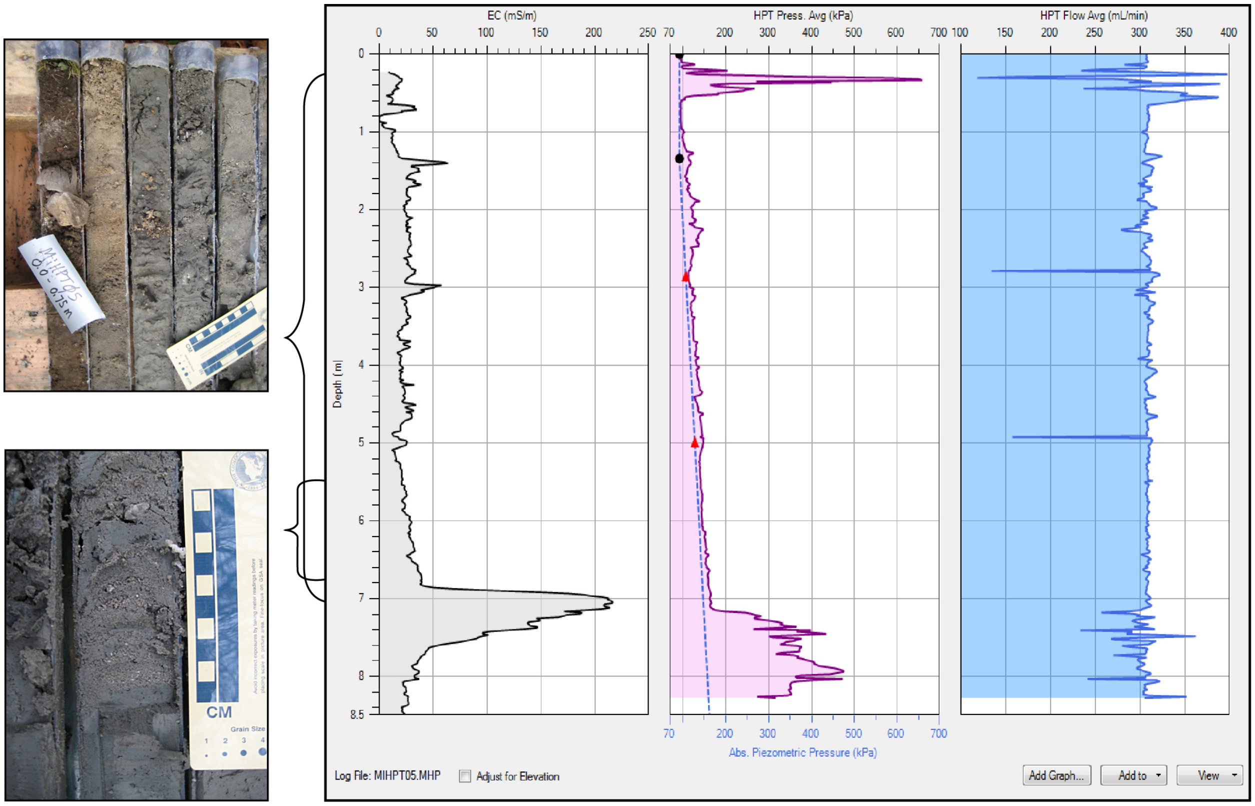


Figure G-7. SK05 HPT log data.

All of the MiHpt data from the SK05 location are combined in one log (Figure G-8). The HPT flow data (blue dash) are shown on the same graph as the HPT pressure data. The axis for the flow rate data is provided on the bottom of the graph. These data show that the chlorinated volatile organic compound (X-VOC) contamination at this location is present in the permeable formation materials and could readily migrate in the groundwater.

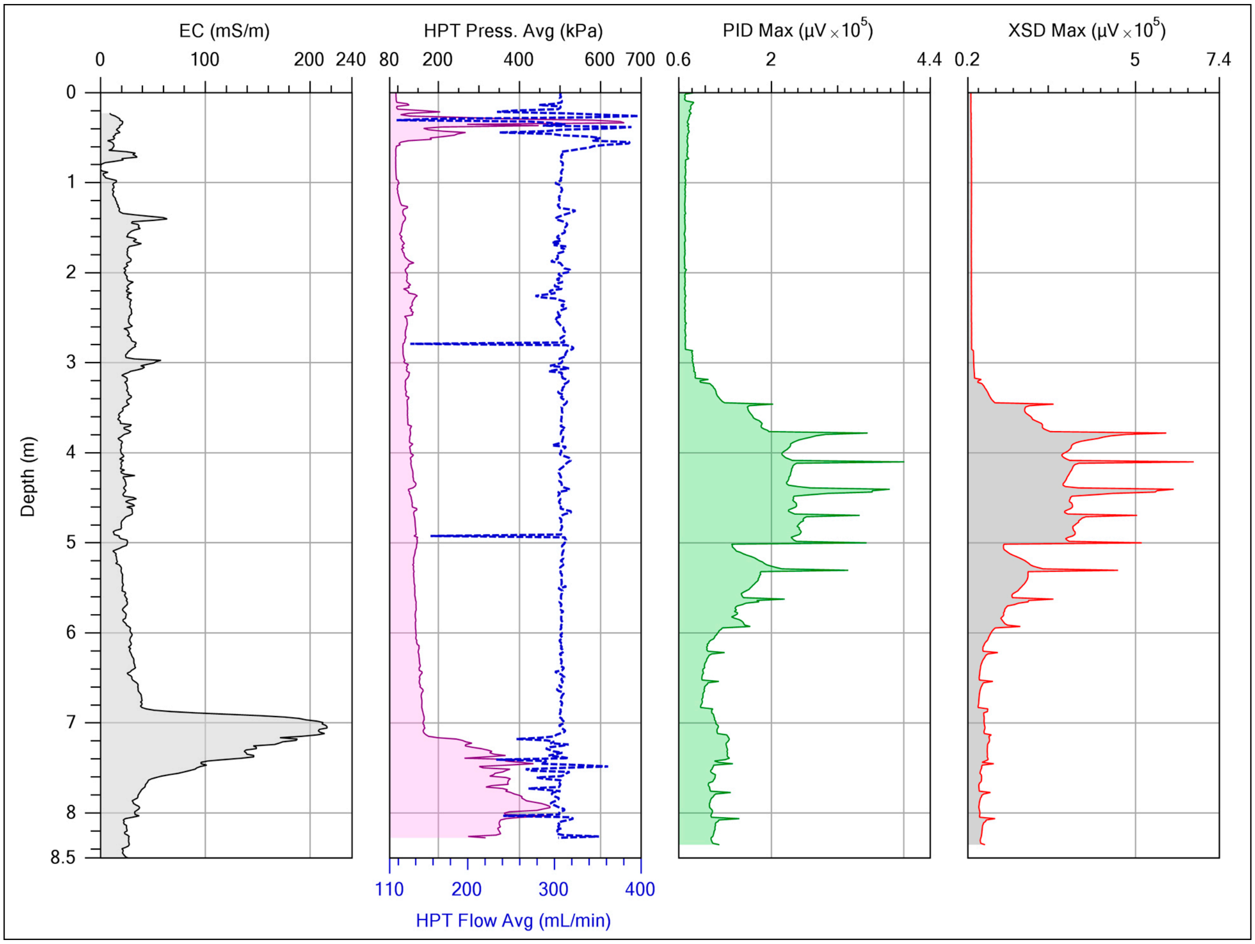


Figure G-8. Complete SK05 MiHpt log.

The small town of Skuldelev is located about an hour west of Copenhagen in the pastoral countryside of Denmark (Figure G-9). This region was glaciated and the town is underlain by glacial deposits and related sediments. A manufacturing facility located adjacent to the town's community park used PCE as a cleaning solvent, and it was released to the environment (Figure G-10). Previous investigations had delineated at least three DNAPL hot spots and a groundwater plume extending more than a kilometer off site; however, the groundwater plume followed an irregular course, and the results of the earlier investigations did not determine the reason for this type of plume migration.

MiHpt logs were run in a transect across the site to study the contaminant distribution and evaluate the local hydrostratigraphy. The SK05 log is one of the logs along this transect (blue circle).

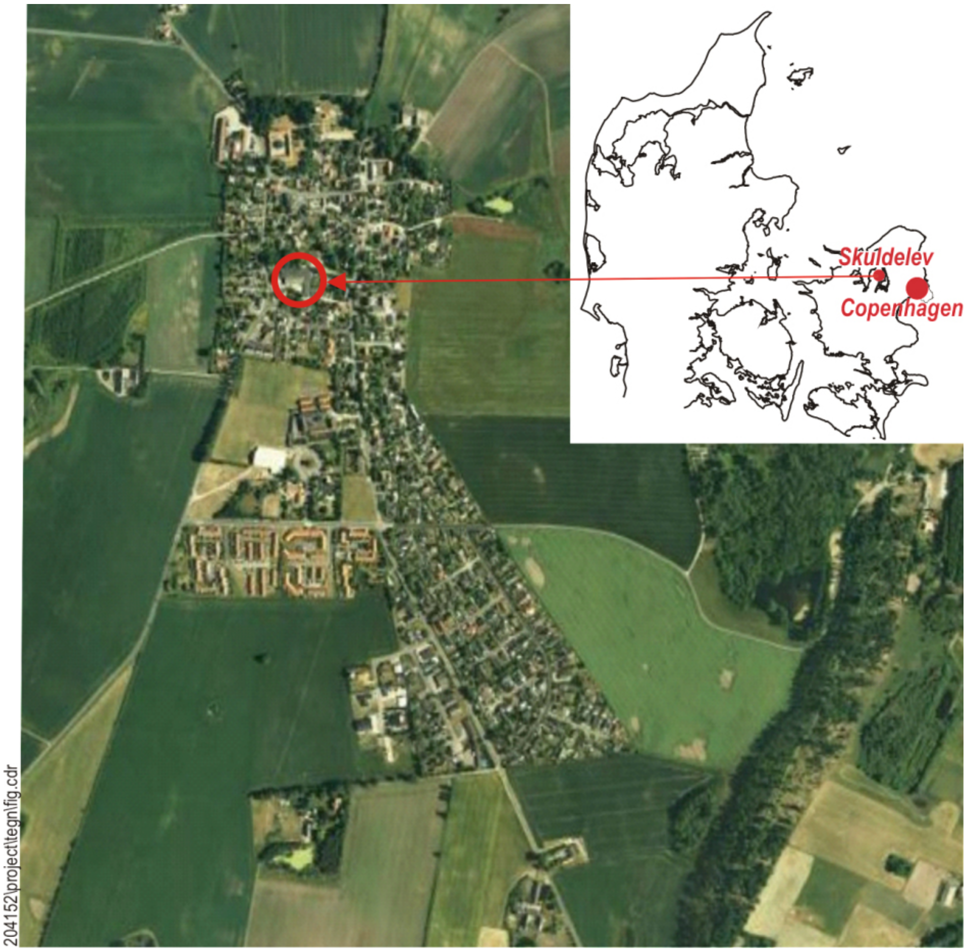
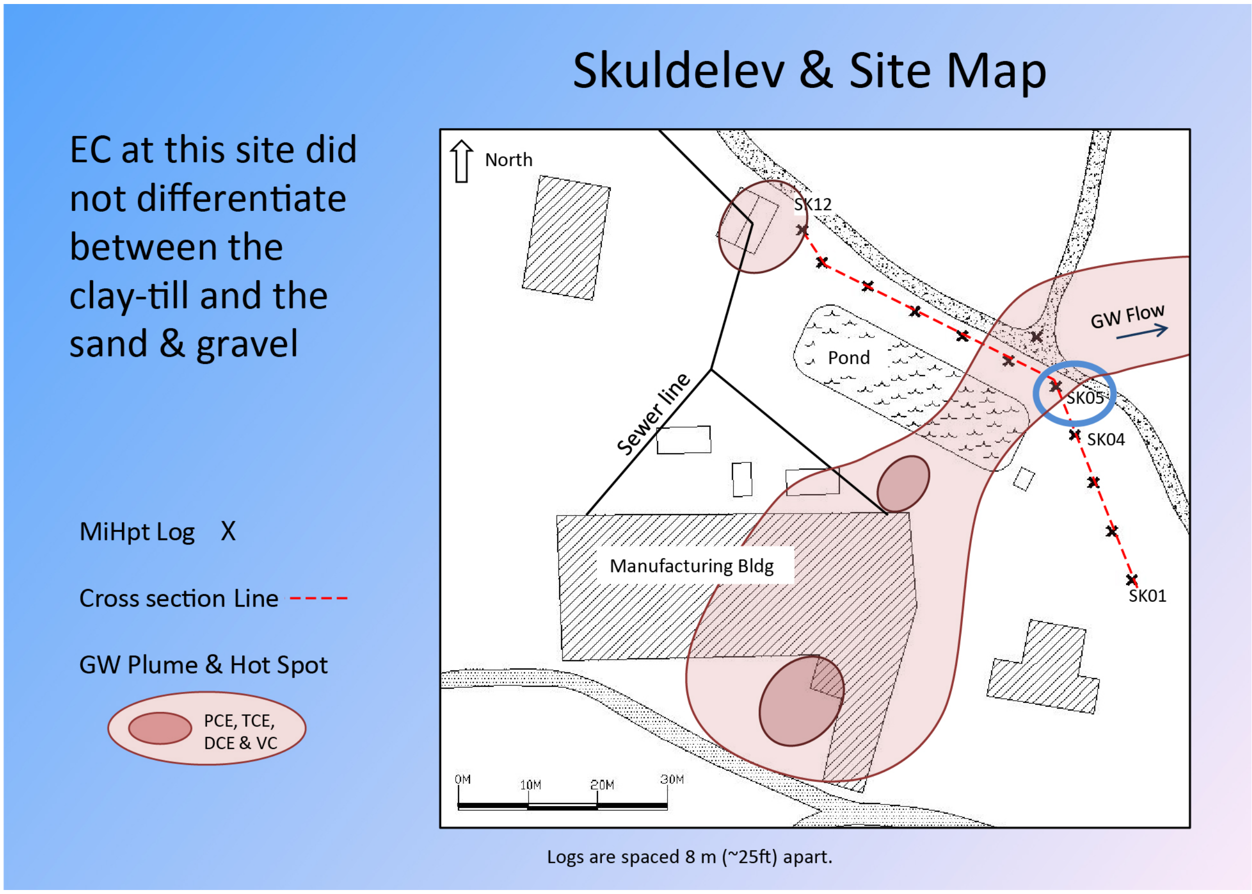


Figure G-9. Site location map, Skuldelev, Denmark.



Skuldelev & Site Map

EC at this site did not differentiate between the clay-till and the sand & gravel

MiHpt Log X

Cross section Line ----

GW Plume & Hot Spot

PCE, TCE, DCE & VC

Logs are spaced 8 m (~25ft) apart.

Figure G-10. Skuldelev site map.

Figure G-11 provides a cross section of the HPT pressure logs, with perspective facing south. As shown, the increase in HPT pressure in each log corresponds to the top of the clay-till; thus, below this HPT pressure increase, the formation is primarily clay-till, and the lower HPT pressure above corresponds to the sand and gravel formation. The dashed line connecting the point where HPT pressure increases in each log provides an outline of the surface of the clay-till at depth. This cross section shows what appears to be a small valley cut into the clay-till, possibly by a late-post-glacial stream. Later, this small valley was filled with sand and gravel (glacial outwash?). The HPT logs and a few collocated core samples from across the site have provided an interpretation of the local geologic depositional environment and hydrostratigraphy.

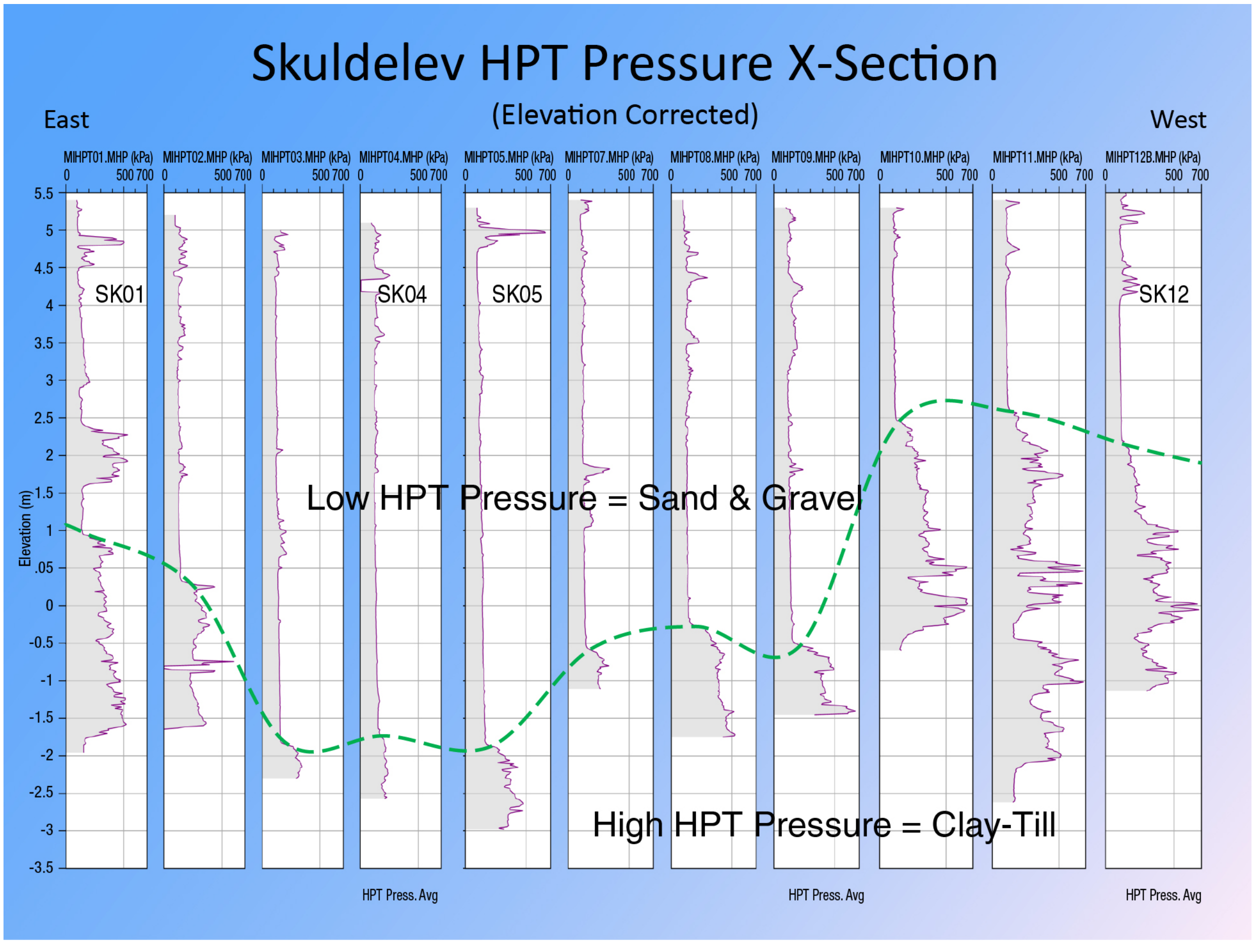


Figure G-11. Skuldelev HPT pressure cross section.

In Figure G-12, the HPT pressure logs (black lines) have been overlaid with the XSD detector logs (red with blue fill), indicating elevated XSD responses at the SK05 and SK07 logs near the center of the buried stream valley. Thus, it appears that the groundwater plume is migrating off site by following the migration pathway created by the buried stream valley. More than 10 years of investigative work had been conducted at this facility; however, not until completion of the MiHpt logs was the controlling factor for the groundwater plume migration understood.

On the west side of the cross section are very high XSD responses down in the clay-till, with little or no contamination in the overlying sand and gravel (Figure G-13).

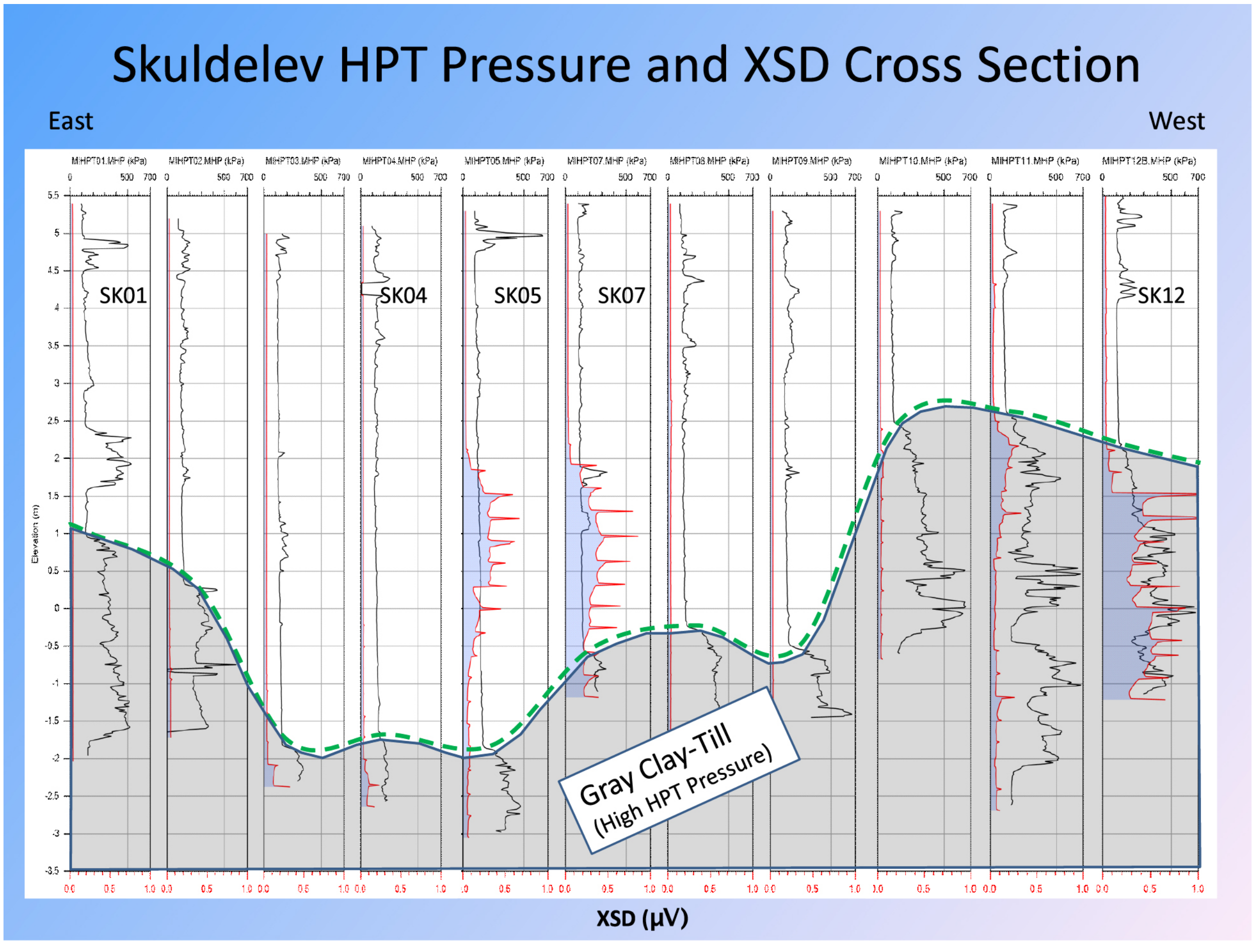


Figure G-12. Skuldelev HPT pressure and XSD cross section.

By plotting the sewer lines on the site map (black dash) (Figure G-13), a sewer line junction is evident next to the SK12 log at the location of a DNAPL hot spot. An earlier investigation revealed that waste solvent (PCE) had been poured down the drain at the facility, and a leak in the sewer line junction next to the SK12 location led to development of this hot spot with DNAPL. Additionally, migration of PCE vapors through the sewer lines and in the sewer trenches led to vapor intrusion into several homes at the site. Several of the old sewer lines have been replaced and mitigation of the vapor intrusion is underway.

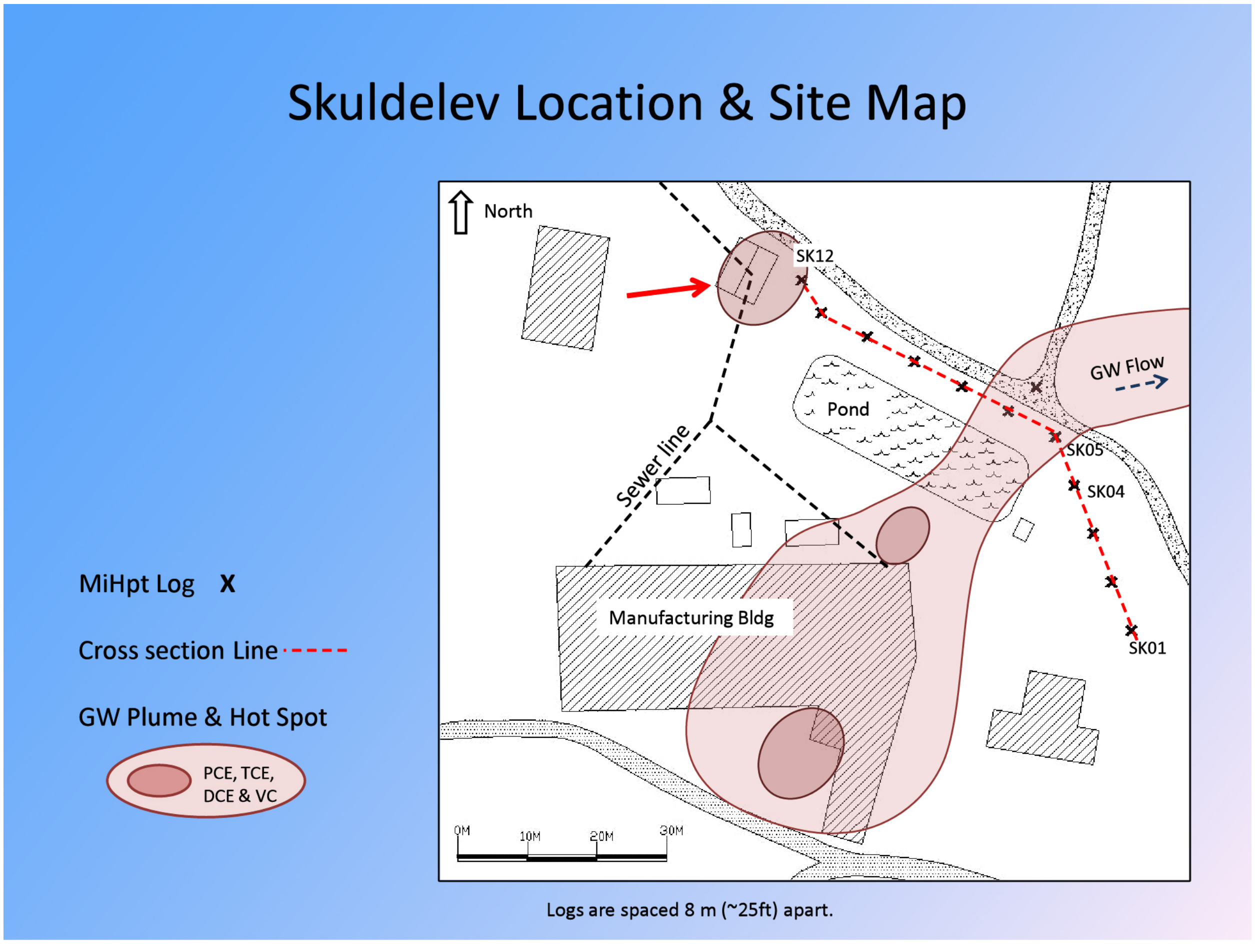


Figure G-13. Skuldelev location and site map.

G.2 Case Study 2 – Observing Contaminant Distribution and Back-Diffusion Using Low Level MiHpt – DNAPL Source Area and Plume, Salina, Kansas

Two municipal wells at a site in Kansas were found to be impacted by 1,2-dichloroethane (DCA) at concentrations above the USEPA maximum contaminant level, and an investigation revealed a large X-VOC plume, originating at a former grain storage facility. Contaminants observed in the plume and at the source area included carbon tetrachloride (CCl_4), CCl_4's primary degradation product chloroform, and 1,2-DCA. The site map (Figure G-14) shows the extent of the 1,2-DCA plume, the location of sampling points, and the impacted municipal wells. After further investigation, extraction wells were installed to begin remediation; two of these wells are plotted on the site map. Shortly after the remediation program began, logs were run using the low-level MiHpt system to assess subsurface conditions across part of the plume. After the logs were run, groundwater profiling was conducted with the hydraulic profiling tool-groundwater sampler (HPT-GWS) system. The groundwater profiles were located adjacent to the MiHpt log locations, and sampling depths were guided by the XSD results of the logs. The site is located within the Smoky Hill River alluvial aquifer. The thickness of the aquifer ranges from less than 20 ft to over 80 ft, and the aquifer is underlain by Permian Age shale bedrock.

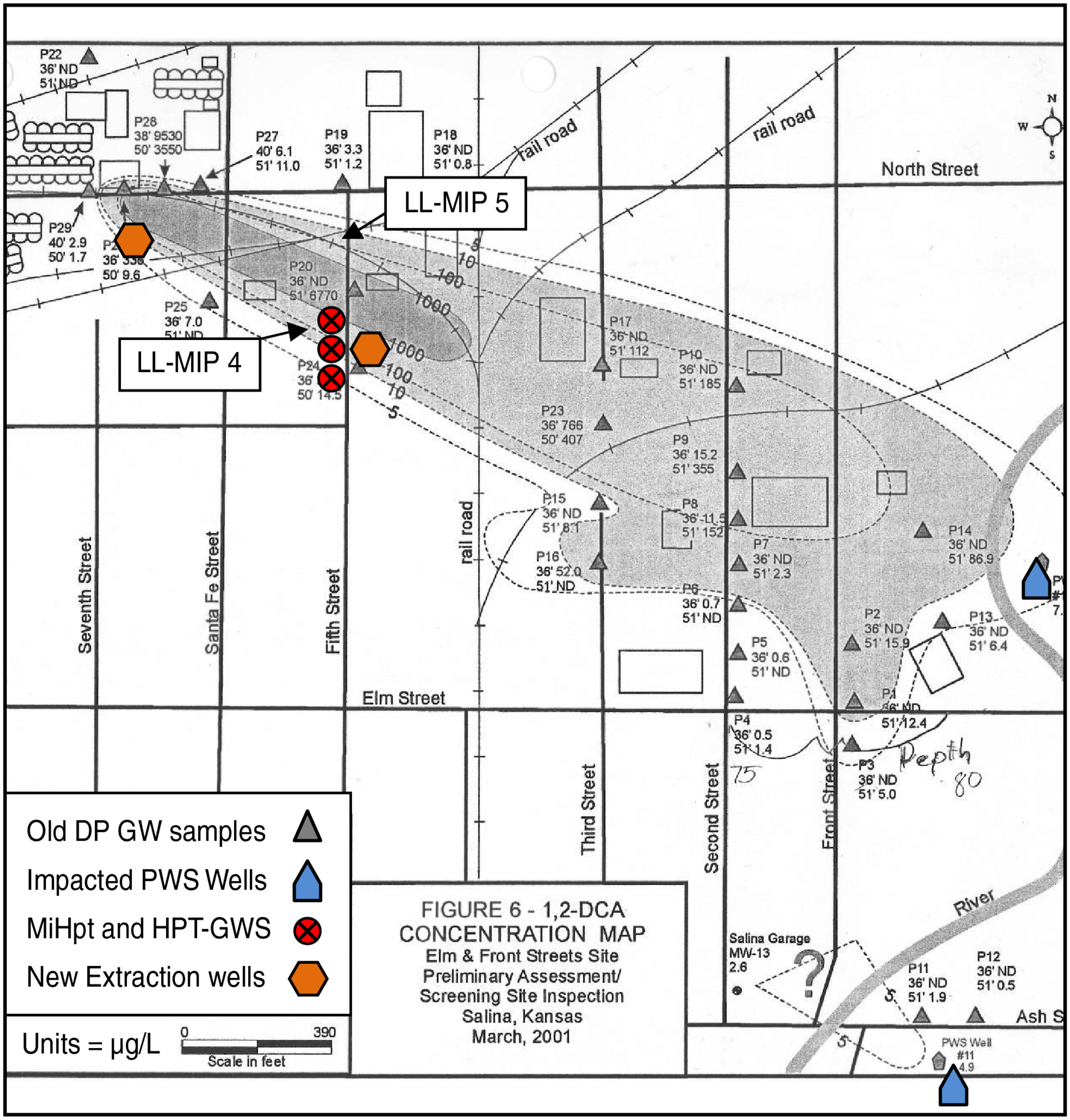
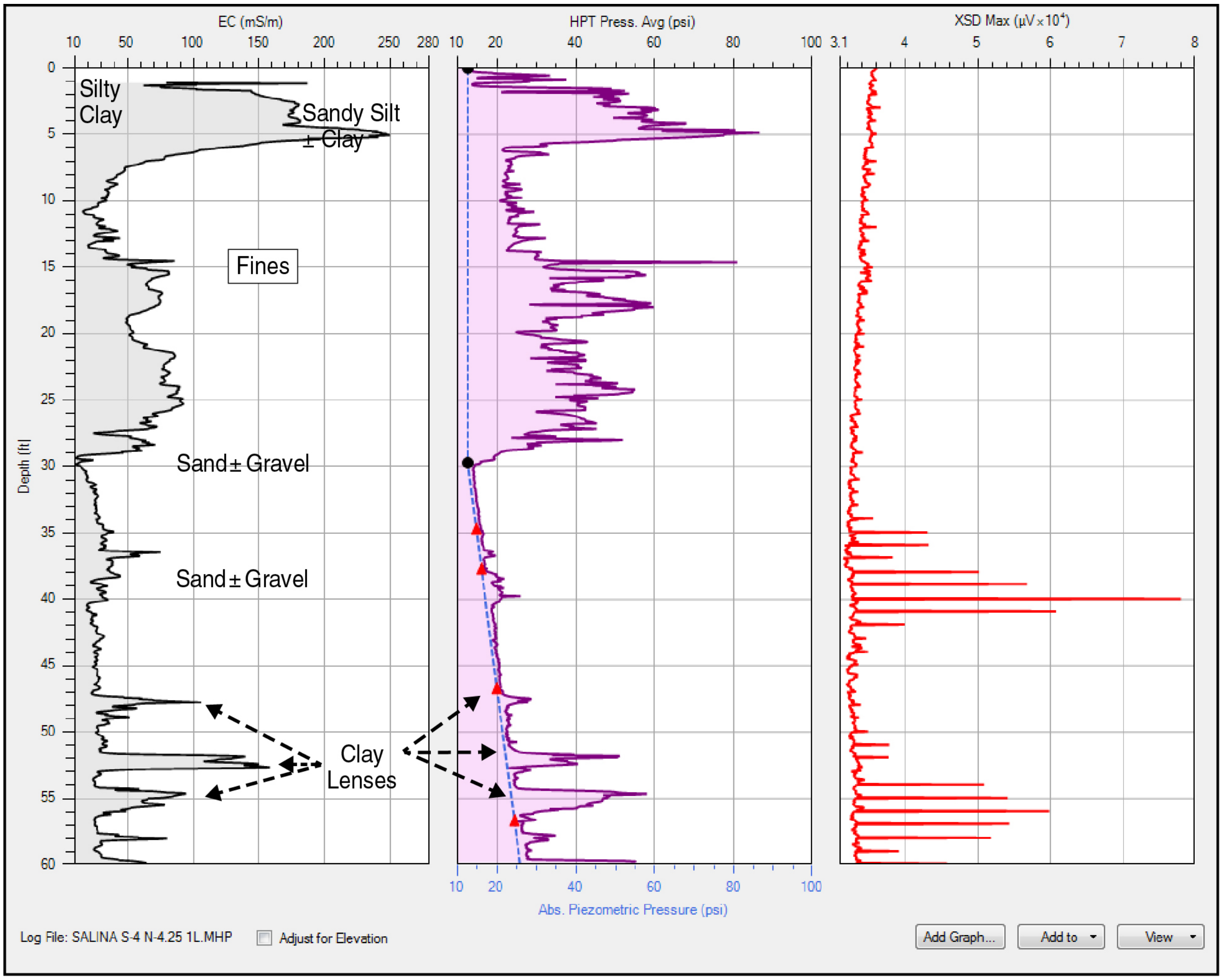


Figure G-14. Site map.

The log shown in Figure G-15 is the one in the center of the short three-log transect depicted in Figure G-14. From the surface to a depth of about 30 ft below grade, both the EC log (left) and HPT pressure log (center) are relatively high, indicating a large amount of clay and silt in the formation with relatively low permeability. Where the EC and HPT are lower (~7 ft–4 ft), there is an increase in the silt and sand content in the formation. Below 30 ft, the EC is generally below 50 millisiemens per meter, indicating mostly sand and gravel. The peaks and spikes in EC across this zone suggest an increase in clay content (clay lenses), and it is evident that the HPT pressure increases over most of these same intervals, indicating lower permeability. The right graph provides the log of the XSD detector. The XSD is sensitive to X-VOCs; thus, the presence of X-VOCs in the formation is evident by the elevated responses over the two zones in the log.

The red triangles on the HPT pressure log mark the depths at which the probe advancement was stopped, the HPT injection flow turned off, and dissipation test run to determine the local hydrostatic pressure. The blue dashed line below 30 ft indicates the piezometric pressure line, showing how the water pressure increases below the static water level. The black circle just above 30 ft represents the calculated water level based on the dissipation test results.

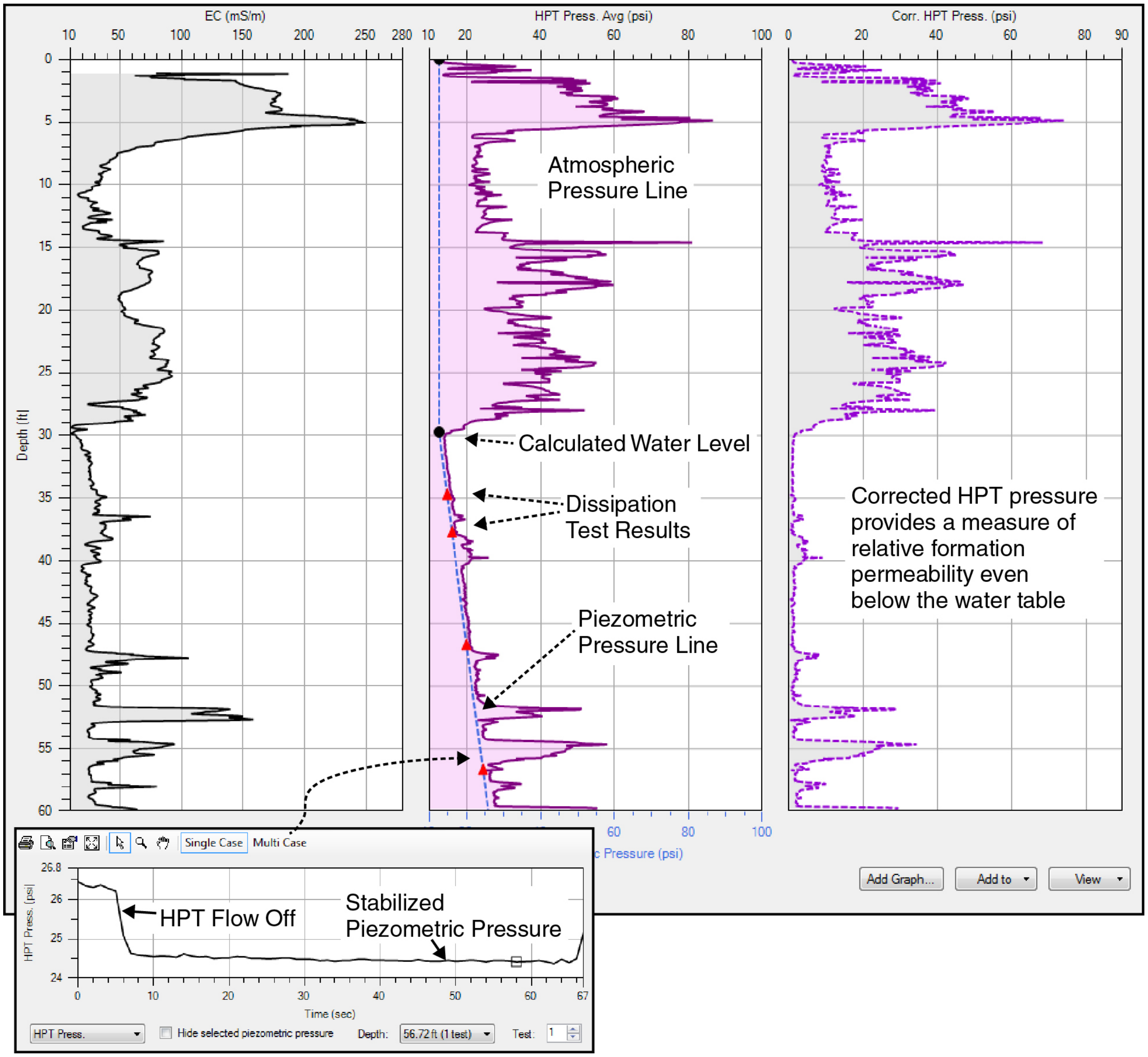


Log File: SALINA S-4 N-4.25 1L.MHP ☐ Adjust for Elevation

Figure G-15. EC log left, HPT log center, and XSD log right.

Figure G-16 illustrates the same log as Figure G-15, but with the XSD detector log replaced by the corrected HPT pressure (right graph). The corrected HPT pressure log is obtained by subtracting the atmospheric pressure and piezometric pressure from the HPT pressure log at each depth interval. The corrected HPT pressure shows the actual pressure required to inject water into the formation, without the atmospheric and piezometric pressure influences. Thus, the pressure required to inject water into the formation at 34 ft, 44 ft, and 54 ft is approximately equal in this formation, as is the permeability at the three depth intervals.

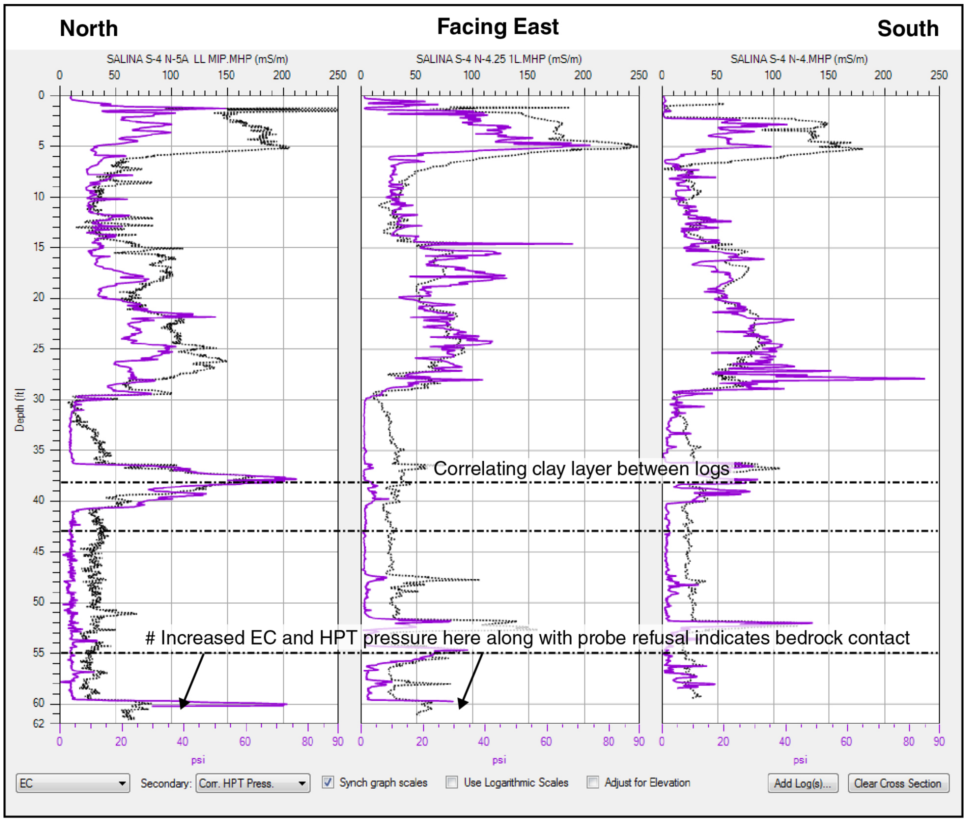
The inset box below displays the dissipation test run at the 56.72 ft depth, along with the stabilized piezometric pressure for that depth.



Corrected HPT pressure provides a measure of relative formation permeability even below the water table

Figure G-16. Corrected HPT Log from Figure G-15.

Figure G-17 is a simple cross section of the three logs obtained across the plume. The logs were run about 30ft apart in an N-S transect. The corrected HPT pressure is depicted by the solid purple line and the EC is depicted by the dashed black line. The EC and HPT pressure measure two different physical parameters of the soil–bulk EC of the formation and permeability, respectively. The EC responds primarily to the clay content of this formation. At this site, the clay content and the HPT pressure correlate well, indicating that clay content is the primary influence on formation permeability. In general, as the EC increases, the HPT pressure increases and vice-versa. This cross section shows that the upper 30 ft of the formation is primarily fine-grained material with low to moderate permeability at best and that, below 30 ft, the formation is primarily sand and gravel with lenses of clay (higher EC and HPT pressure). The clay-rich layer at depths of approximately 36 ft–40 ft (between dot-dash lines) appears to be continuous across the area logged; however, the clay content appears to be lower and the permeability higher at the center log (N425) than at the other two locations.



Correlating clay layer between logs

Increased EC and HPT pressure here along with probe refusal indicates bedrock contact

EC

Secondary: Corr. HPT Press.

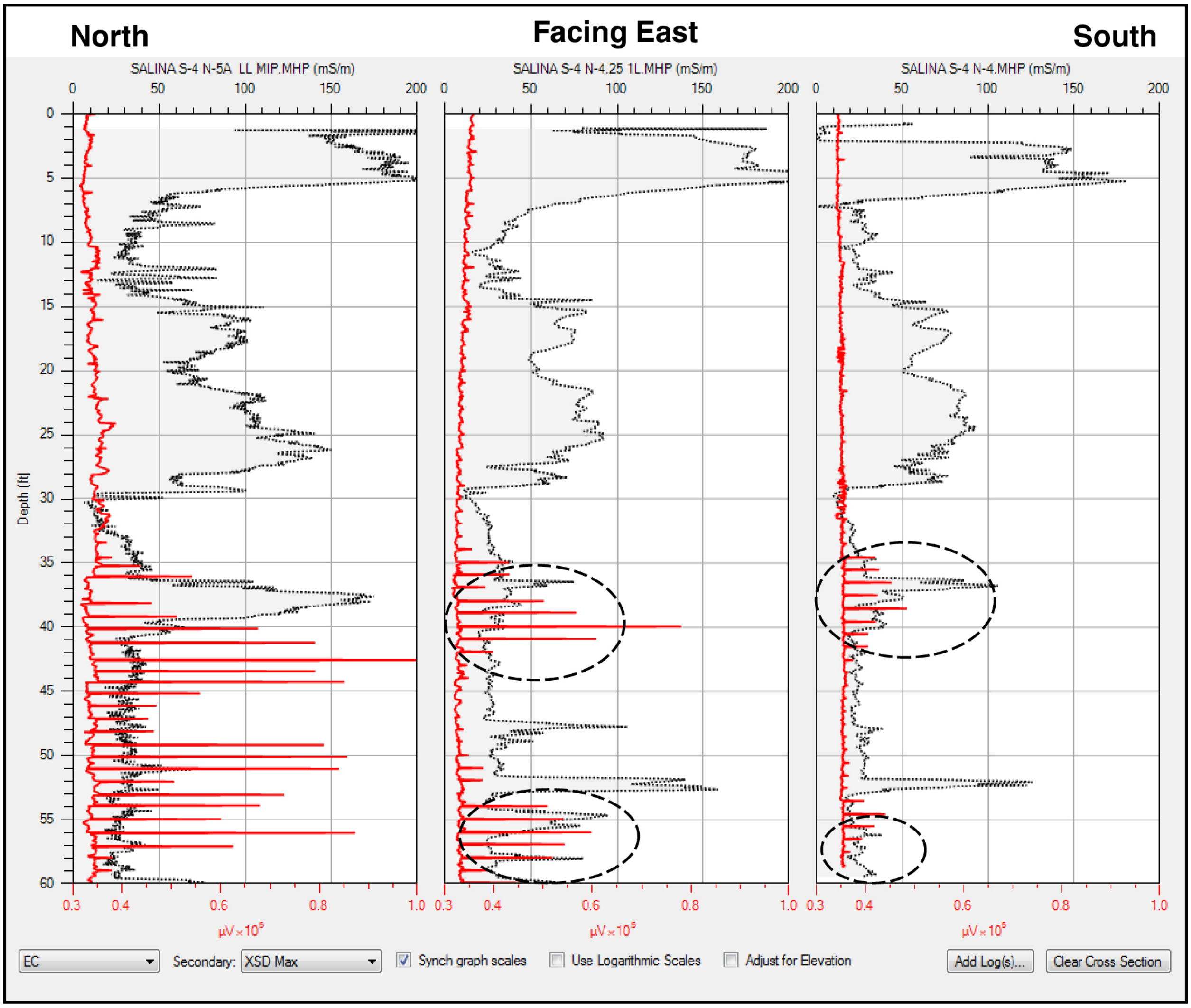
☑ Synch graph scales

☐ Use Logarithmic Scales

☐ Adjust for Elevation

Figure G-17. Cross section of the three MiHpt logs showing corrected HPT pressure and EC (dashed).

In Figure G-18, the XSD response (solid red line) is laid over the EC log (black dash with gray fill). These logs were obtained with the low-level MiHpt system, which provides lower detection limits (about 10X) so that lower concentrations of X-VOCs at the edge of the plume are detectable. The horizontal scales for EC and XSD are the same for each log, so the magnitude of the XSD response is consistent across the logs. The core of the plume is to the north (log N-5A) and the edge of the plume is to the south (log N-4). This is apparent as the magnitude of the XSD response decreases from north to south along the transect. In the core of the plume (log N-5A), the X-VOC contamination is generally dispersed across the sandy aquifer materials. There is an upper zone (~38 ft–45 ft) and lower zone (~48 ft–57 ft) at which detector response is high, with a decrease in response between these zones. Moving south away from the core of the plume, the XSD response (and thus X-VOC concentrations) are focused around some of the clay lenses (dashed ovals). It therefore appears that, as the plume ages and remediation progresses, X-VOC contaminants in the sandy aquifer materials are removed while those sorbed into the clay lenses remain. Further, the relationship between the clay lenses defined by the EC logs and the surrounding XSD response indicates that the contaminated clay lenses are behaving as a low-permeability source, slowly feeding X-VOCs back into the sandy aquifer materials around the clay lenses.



EC

Secondary: XSD Max

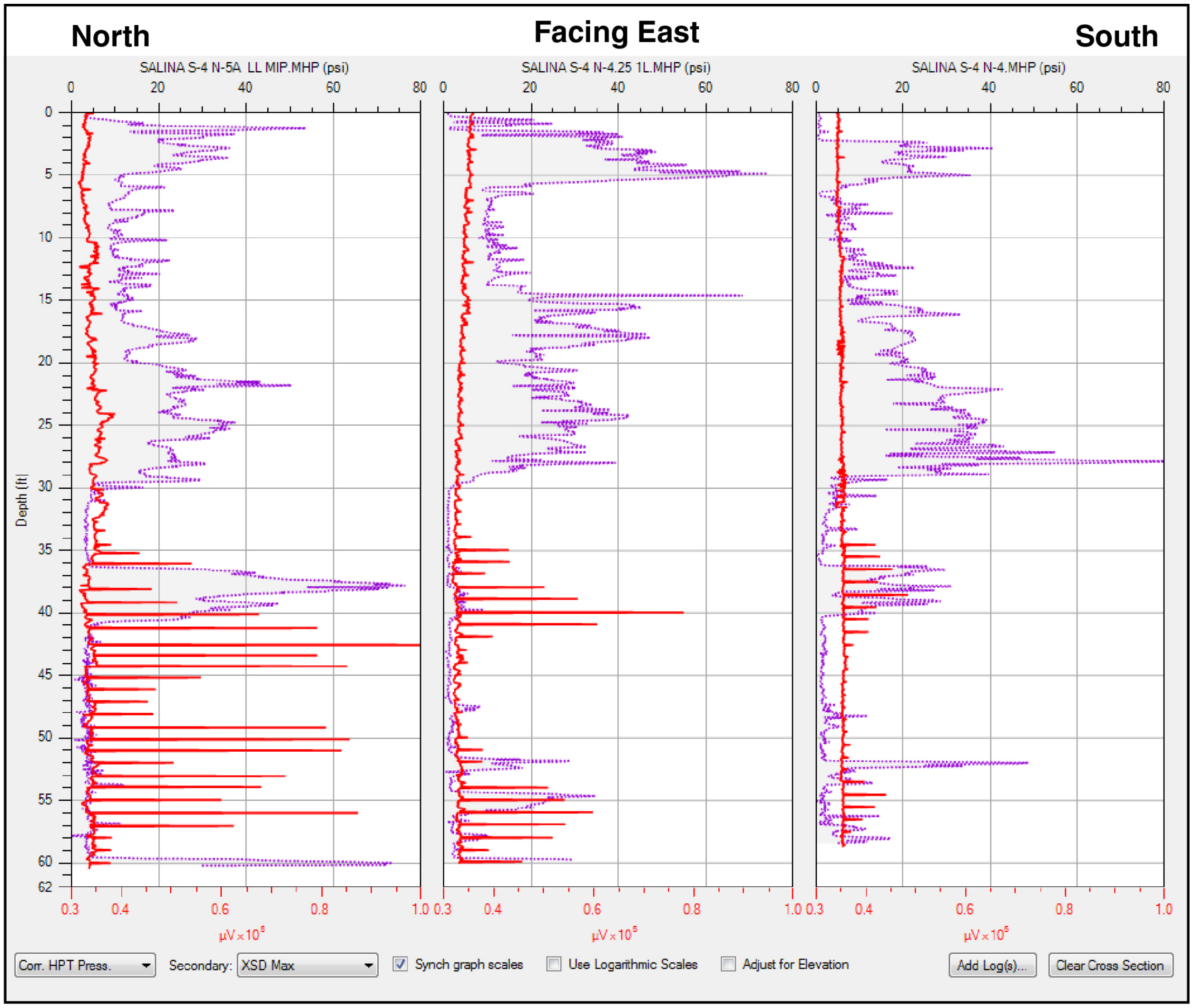
☑ Synch graph scales

☐ Use Logarithmic Scales

☐ Adjust for Elevation

Figure G-18. Cross section with EC and XSD response indicating back-diffusion from clay lenses.

The Figure G-19 cross section, with corrected HPT pressure and XSD detector response, suggests the same relationship between the lower-permeability (higher HPT pressure) clay lenses and the X-VOC contamination as that observed in Figure G-18. South of the plume core, the clay lenses behave as low-permeability sources, bleeding X-VOCs back into the surrounding sandy aquifer materials.



Corr. HPT Press.

Secondary: XSD Max

☑ Synch graph scales

☐ Use Logarithmic Scales

☐ Adjust for Elevation

Figure G-19. Cross section with corrected HPT pressure and XSD response.

Once the low-level MiHpt logs were completed and reviewed, depth intervals were selected for groundwater profiling with the HPT-GWS system. Depths for groundwater sampling were selected based on the XSD detector response and HPT pressure. The HPT-GWS probe has four screened ports over a 4 inch vertical interval along the side of the probe. This provides for discrete interval samples. Groundwater samples cannot be collected from the high-pressure/low-permeability clay lenses, but can be obtained from the lower-pressure/higher-permeability sandy aquifer materials. Figure G-20 illustrates the HPT pressure and EC log in the left graph for the

N-5A log. The other three graphs are repeats of the XSD detector response for this log with plots of the 1,2-DCA, CCl_4, and chloroform concentrations from the groundwater samples collected next to the log location. This plot shows that 1,2-DCA is the primary contaminant in the upper zone (~38 ft–45 ft) while CCl_4 and its degradation product chloroform are the primary contaminants in the lower zone (~48 ft–57 ft) at this location.

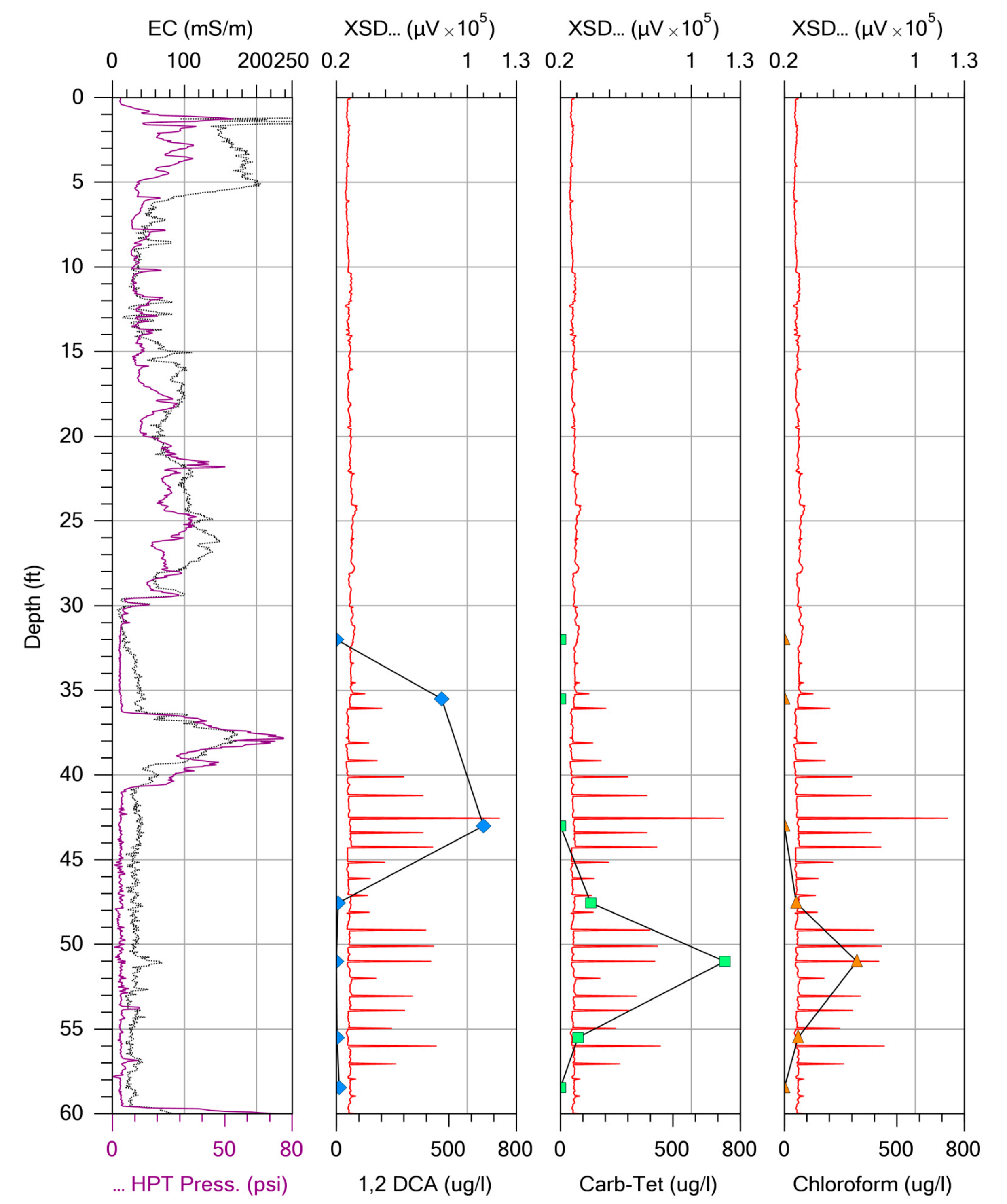


Figure G-20. The N-5A log with plots of 1,2-DCA (blue diamonds), CCl_4 (green squares), and chloroform (orange triangles) plotted over the XSD log. Note that 1,2-DCA dominates in the upper zone while CCl_4 and chloroform dominate in the lower zone, as defined by the XSD detector response.

Logs for the N425 and N4 locations are shown on Figure G-21, with the groundwater sample results plotted over the XSD detector response. As above, the blue diamonds represent 1,2-DCA, the green squares represent CCl_4, and the orange triangles represent chloroform. Again, 1,2-DCA dominates in the upper zone while CCl_4 and chloroform dominate in the lower zone, as defined by the XSD detector response.

The horizontal axes for contaminant concentration varies on these logs so that lower concentrations near the edge of the plume can be viewed at a useable scale.

On the N4 log, a sample interval at 55 ft was missed, leaving a gap in the data for this log.

For all three logs, where groundwater samples show total X-VOC concentrations increasing, the XSD detector response generally increases and vice-versa.

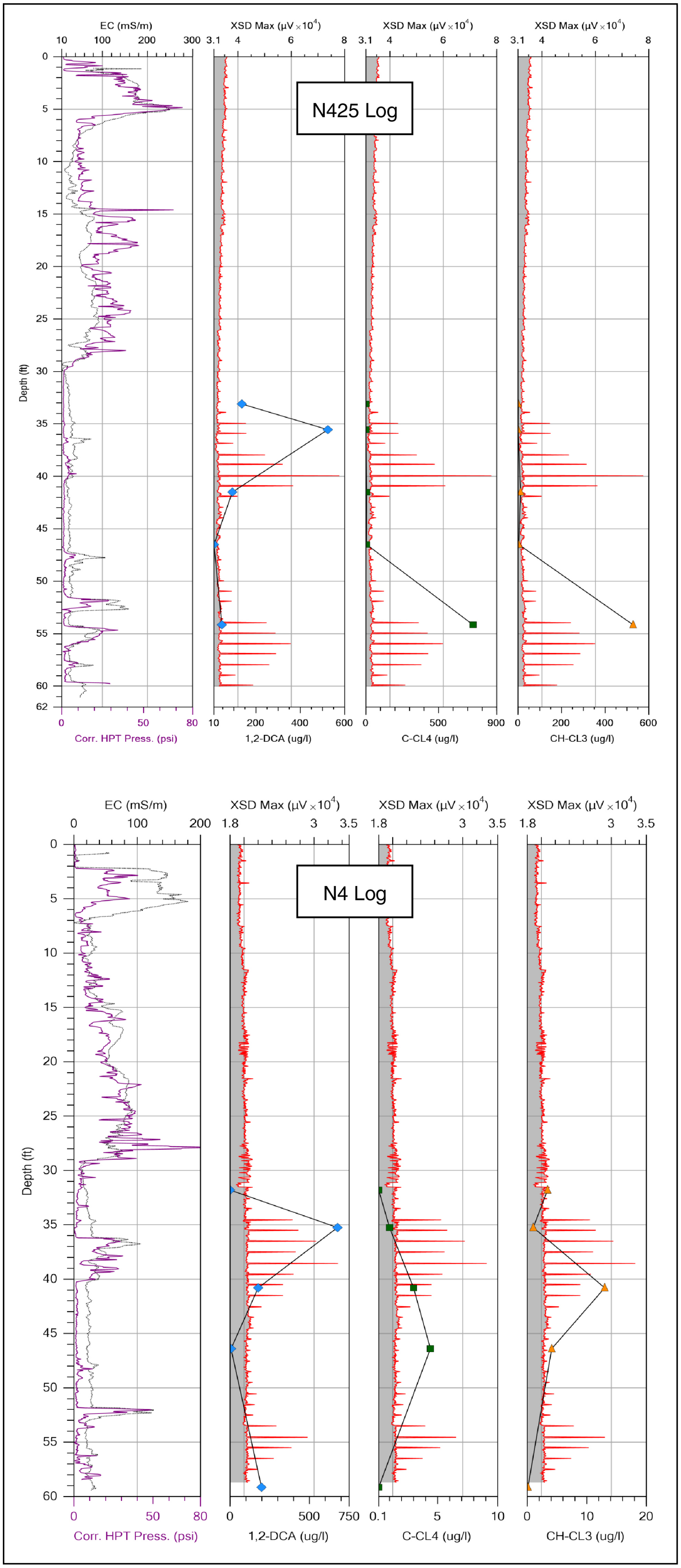

N425 Log
EC (mS/m)
10 100 200 300
XSD Max (µV × 10^4)
3.1 4 6 8
3.1 4 6 8
3.1 4 6 8
Depth (ft)
0 5 10 15 20 25 30 35 40 45 50 55 60 62
0 50 80
Corr. HPT Press. (psi)
10 200 400 600
1,2-DCA (ug/l)
0 500 900
C-CL4 (ug/l)
0 200 400 600
CH-CL3 (ug/l)
N4 Log
EC (mS/m)
0 100 200
XSD Max (µV × 10^4)
1.8 3 3.5
1.8 3 3.5
1.8 3 3.5
Depth (ft)
0 5 10 15 20 25 30 35 40 45 50 55 60
0 50 80
Corr. HPT Press. (psi)
0 500 750
1,2-DCA (ug/l)
0.1 5 10
C-CL4 (ug/l)
0 10 20
CH-CL3 (ug/l)

Figure G-21. Groundwater sample results plotted over XSD detector responses.

Figure G-22 shows all of the groundwater analyte results plotted over the N-5A XSD detector log. This more clearly defines the upper zone with 1,2-DCA, while the lower zone consists mostly of CCl_4 and its primary degradation product chloroform. The MIP XSD detector response provides a clear indication of total X-VOC contaminant load vs. depth, but not specificity; however, the groundwater profile samples provide the specificity (analyte ID) necessary for discerning the contaminant zones.

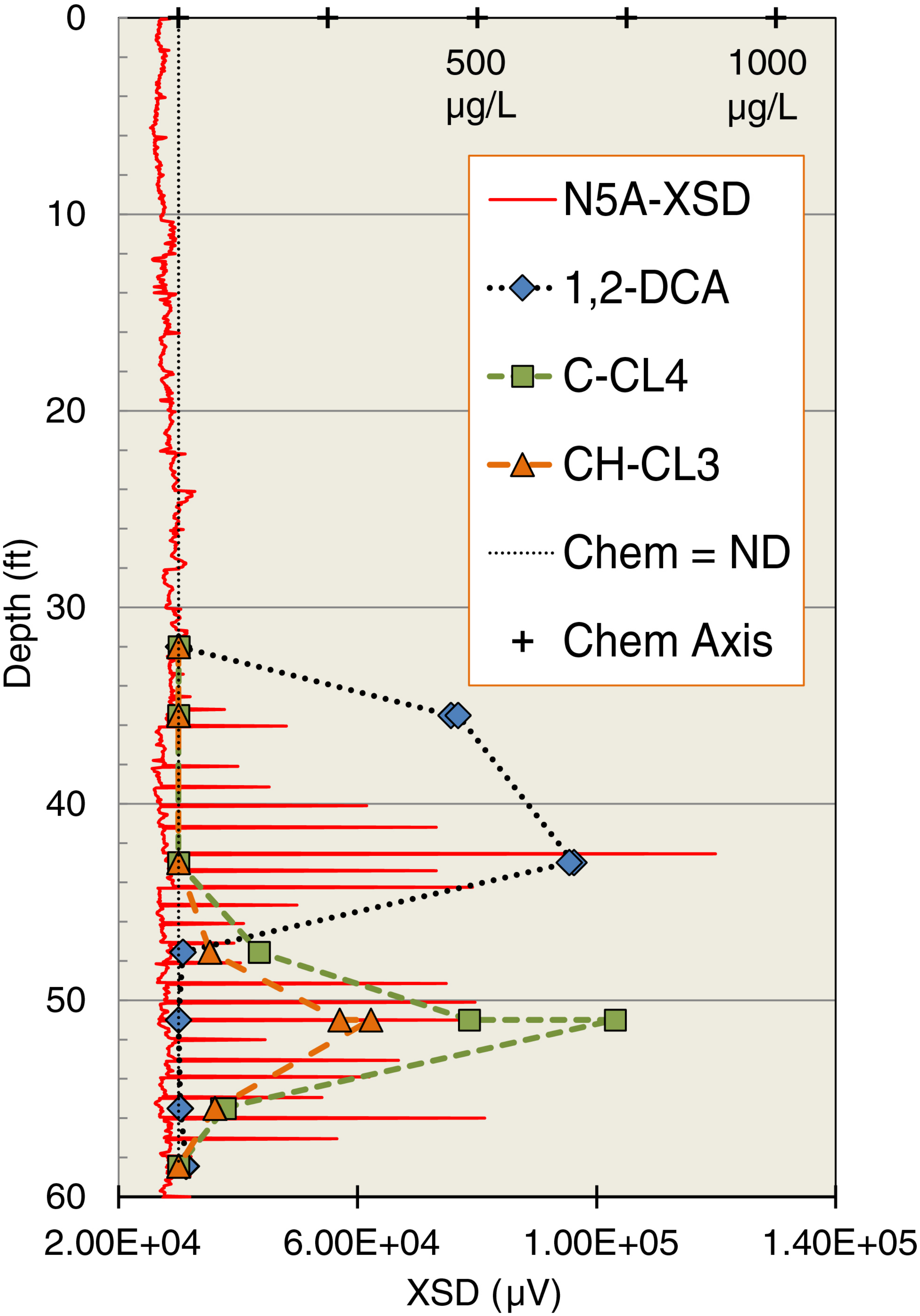
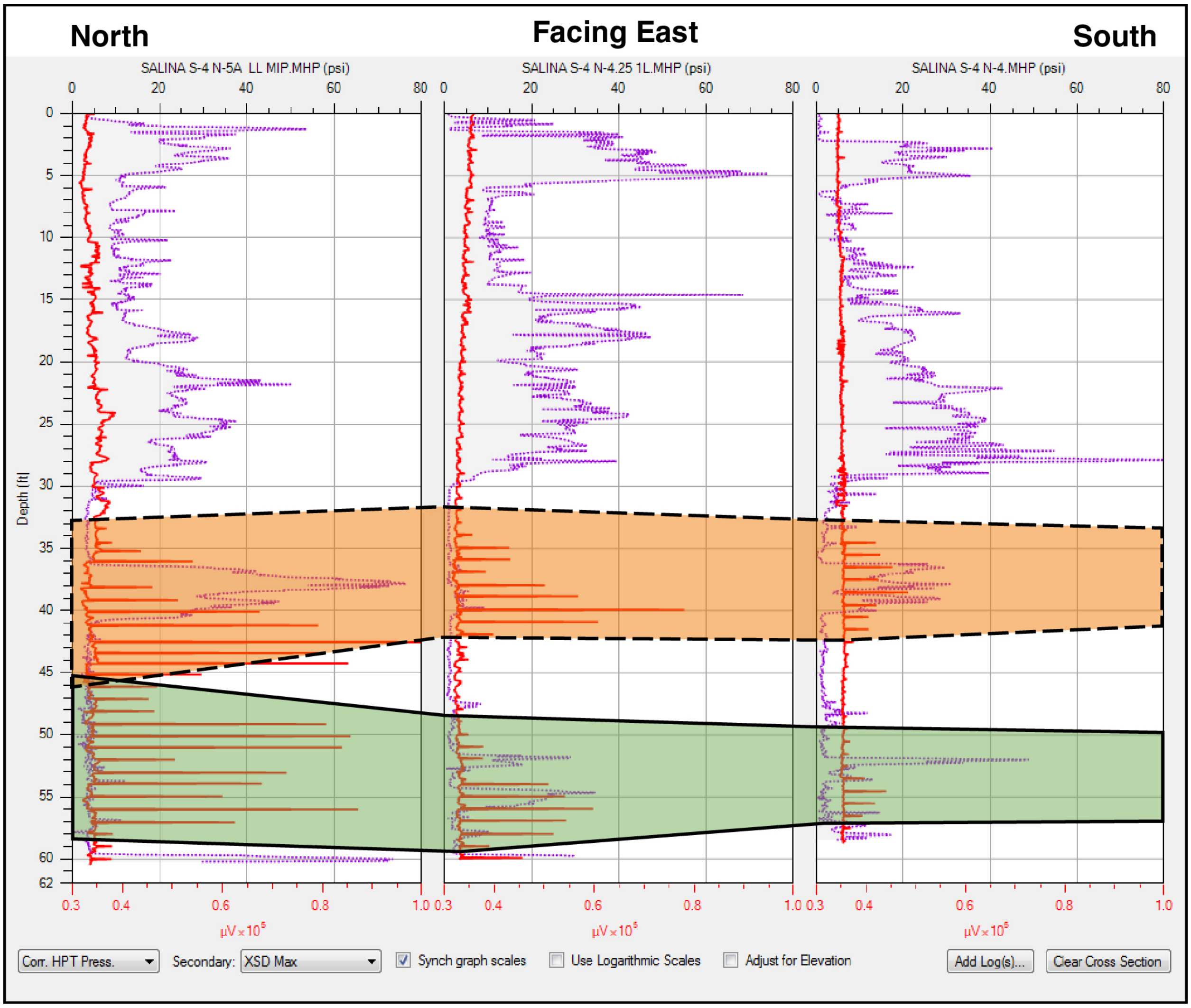

0
10
20
30
40
50
60
Depth (ft)
500 µg/L
1000 µg/L
N5A-XSD
1,2-DCA
C-CL4
CH-CL3
Chem = ND
Chem Axis
2.00E+04
6.00E+04
1.00E+05
1.40E+05
XSD (µV)

Figure G-22. Groundwater analyte results plotted over XSD detector log.

With the groundwater profile sample results, Figure G-23 shows the distribution of the contaminants in the subsurface. There is an upper groundwater plume consisting primarily of 1,2-DCA (dashed line with orange fill) and a deeper groundwater plume consisting primarily of CCl_4 and chloroform (solid line with green fill). Figure G-23 covers only a small portion of the contaminant plume, which does not allow for extrapolation too far beyond the cross section shown; however, additional transects of the plume farther downgradient could provide additional insight into plume migration, contaminant distribution, and fate. Because only the 1,2-DCA is affecting the municipal wells, it may be useful to focus additional work primarily on that plume; however, the CCl_4-chloroform plume is extensive at this site and will require additional investigation/remediation to prevent further impacts to the municipal wells and the valuable groundwater resource.



Corr. HPT Press. ▾ Secondary: XSD Max ▾ ☑ Synch graph scales ☐ Use Logarithmic Scales ☐ Adjust for Elevation

Figure G-23. Cross section with corrected HPT pressure and XSD response.

APPENDIX H. EMERGING TECHNIQUES FOR SITE CHARACTERIZATION—RECONSTRUCTING SOURCE HISTORY

Adapted from *Frequently Asked Questions about Monitored Natural Attenuation in Groundwater* (Adamson and Newell 2014)

One of most common lines of evidence for evaluating monitored natural attenuation (MNA) is using long-term contaminant monitoring data to determine attenuation rates, with positive evidence illustrating the loss of contaminant mass and plume stabilization. Monitoring records may be relatively short at many sites, however, covering perhaps only a few years and only rarely extending to the time of the release. Given the natural variability in groundwater monitoring data, these limited and temporary records may be insufficient for establishing decreasing concentration trends that support the use of MNA, or to demonstrate long-term source zone attenuation.

There are two innovative characterization methods that can, in some cases, reconstruct a concentration history that predates groundwater monitoring. These methods involve collecting high-resolution data in a diffusion-based medium, either from trees or low-permeability zones. These two methods are discussed below.

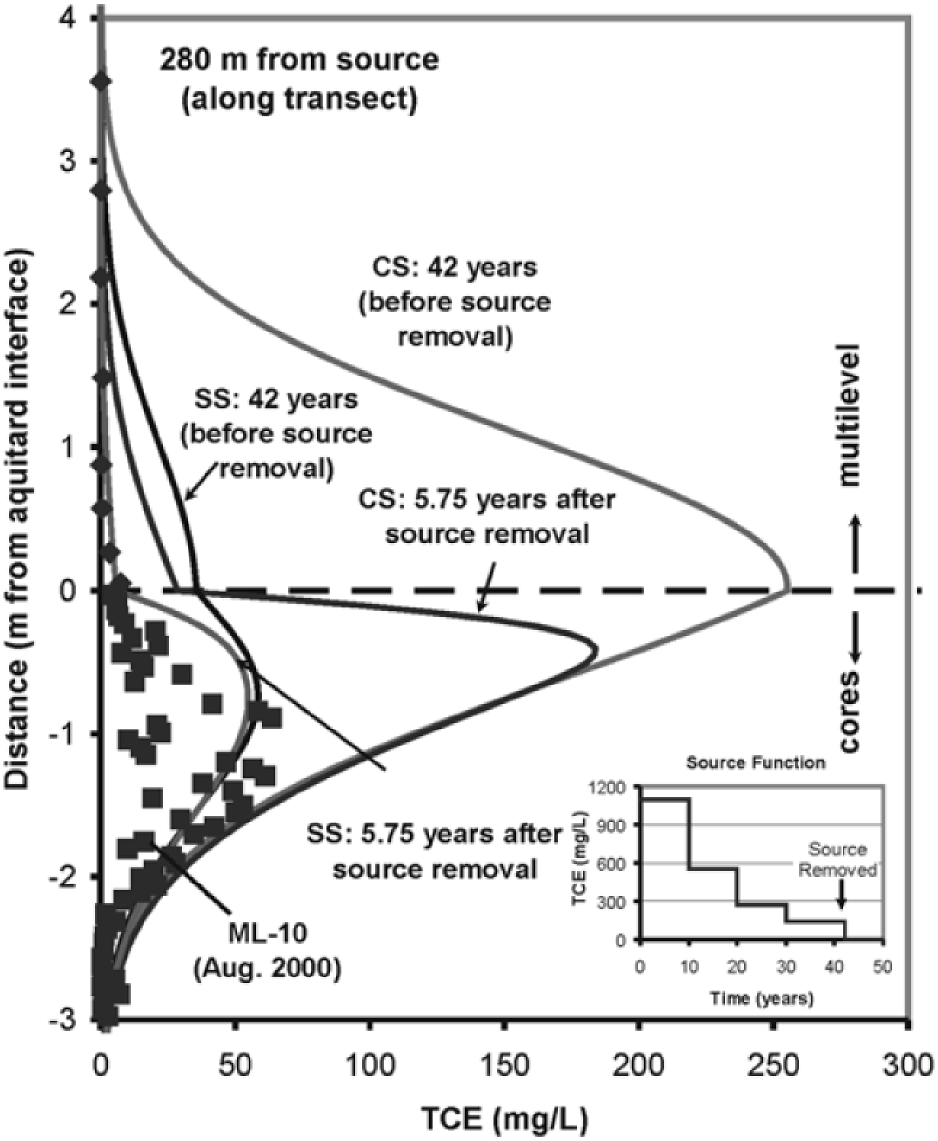


Figure H-1. Example of source history derived from coring an aquitard. The soil profile from the silty clay interval (black squares) is used to estimate the concentration vs. time in the overlying aquifer. Four different inputs to a one-dimensional diffusion model were used to make the four solid lines: CS = constant source; SS = stepped declining source. The concentration history shown as an inset resulted in the best simulated match to the data, and is labeled "SS: 5.75 years after source removal." This SS starts out at near solubility concentrations, but declines by half every 10 years ($t_{1/2}$ = 10 years).

Source: Chapman and Parker 2005

H.1 Source History Using Low-Permeability Zone Soil Data

This method makes use of the contaminant mass that has migrated (via diffusion and slow advection) into and out of low-permeability geologic strata within a source zone or plume during the period following release (Chapman and Parker 2005; Newell et al. 2013; Liu et al. 1999). Detailed high-resolution soil concentration profiles within the low-permeability zones are obtained and serve as fingerprints of the source loading (concentration versus time), extending back to the origin of the source. The shape of the soil concentration profile can be used to reconstruct this source history using simple analytical or more complex numerical models. These methods are being demonstrated as part of an ongoing project funded by the Environmental Security Technology Certification Program (ESTCP 2013), a user-friendly source history software tool and field manual.

H.2 Phytoforensics Using Tree Core Data

Trees in contact with shallow groundwater can take up contaminants during transpiration such that accumulation of these contaminants can occur during the year(s) of exposure. As a result, annual tree ring data can provide a quantitative indicator of changes in contaminant concentration over time (Vroblesky 2008; Balouet et al. 2009; Burken et al. 2011). The study of historical effects on tree ring chemistry, known as dendrochemistry, is one of several phytoforensic methods that can rapidly generate valuable site characterization data at some sites. The depth of the tree roots and depth to groundwater are very site-specific, however, and this technique is not applicable for all sites.

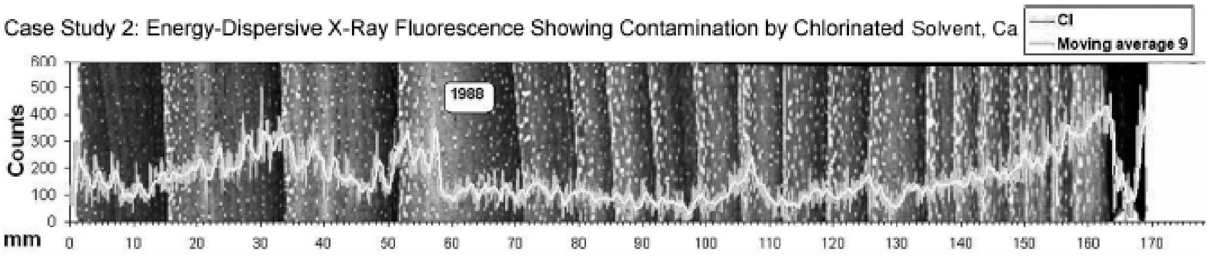


Figure H-2. Chloride patterns (shown on y-axis as x-ray fluorescence counts) over time in tree core (shown on x-axis in millimeters of core). The pattern identifies potential exposure events (releases) in 1988 and 1993/1994, along with continuing impact at dates when the core was collected (far right hand side) (Balouet et al. 2009).

Dendrochemical investigations require the collection of deep cores from trees that are scanned using energy diffusive x-ray fluorescence. Elements are quantified and used as surrogates of particular contaminants—including chlorine for halogenated contaminants (chlorinated solvents) and sulfur for crude oil and petroleum products. While factors such as degradation and naturally occurring variation can confound data interpretation, controls are used to better understand background patterns of targeted elements. The methodology is generally well developed and has been applied at more than 20 sites.

APPENDIX I. REPRESENTATIVE VALUES FOR FOC

Table I-1 provides examples of the fraction of organic carbon (f_{oc}) in various geologic media.

Table I-1. Representative natural f_{oc} values determined in soils, sediments, and rocks

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Silty clay sediment (EPA-4), dark grayish, from Missouri River, Stanton, ND	Near surface	0.021		Hassett, J.J., J.C. Means, W.L. Banwart, and S.G. Wood. 1980. *Sorption Properties of Sediment and Energy-Related Pollutants*. EPA 600/3-80-041. USEPA, Athens, GA.
Clay loam sediment (EPA-5) from Missouri River near Linton, ND	Near surface	0.023		
Clay (EPA-6) sediment, grayish, from Missouri River near Pierre, SD	Near surface	0.0072		
Loamy sand (EPA-8) sediment from Missouri River near Onawa, IA	Near surface	0.0015		
Silty loam loess (EPA-9) from bluff north of Turin, IA	Near surface	0.0011		
Clay (EPA-14), red soil from hillside near Ceredo, WV	Near surface	0.0048		
Silty clay loam (EPA-15) sediment from Ohio River near Leavenworth, IN	Near surface	0.0095		
Clay loam (EPA-18) sediment from Mississippi River near Columbus, KY	Near surface	0.0066		
Silty clay loam (EPA-20) soil from near Ferne Clyffe State Park, IL	Near surface	0.013		
Loam sediment (EPA-21) from creek near Lorenzo, IL	Near surface	0.019		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Silty loam (EPA-22) sediment from bay in Illinois River near Lacon, IL	Near surface	0.017		
Clay (EPA-23) sediment from Crane Lake in Sanganois Wildlife Refuge, IL	Near surface	0.024		
Silty loam (EPA-26) sediment from Mississippi River near McClure, IL	Near surface	0.015		
Sandy loam (EPA-B2) sediment from stream near Watkinsville, GA	Near surface	0.012		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Subsoil sample (B horizon, silty loam) of Mollisol from the Drummer soil series in Kane, IL	1 to 4	0.0027	Mollisols form in semi-arid to semi-humid areas, typically below grassland cover. In North America, they are most commonly found east of the Rocky Mountains. Their parent material is typically base-rich, calcareous, and includes limestone, loess, or wind-blown sand. Mollisols' defining feature is their deep, high organic matter, nutrient-enriched surface soil (A horizon), that is typically between 60–80 cm in depth.	Jagadamma, S., M.A. Mayes, and J.R. Phillips. 2012. "Selective sorption of dissolved organic carbon compounds by temperate soils." *PLoS ONE* 7 (11): e50434, 9 p.
Subsoil sample (B horizon, silty clay loam) of Mollisol from the Longford soil series in Washington, KS	1 to 4	0.0029		
Subsoil sample (B horizon, silty clay loam) of Mollisol from the Pawnee soil series in Lancaster, NE	1 to 4	0.0018		
Subsoil sample (B horizon, silty clay loam) of Alfisol from the Malmo soil series in Lancaster, NE	1 to 4	0.0032	Alfisols typically form under hardwood forest cover in semiarid to humid areas. They have undergone only moderate leaching, have a clay-enriched subsoil with >35% base saturation (Ca, Mg, and K relatively abundant), and are commonly found in glaciated areas.	
Subsoil sample (B horizon, silty clay) of Alfisol from the Arispe soil series in Decatur, IA	1 to 4	0.0020		
Subsoil sample (B horizon, silty clay) of Alfisol from the Zanesville soil series in Spencer, IN	1 to 4	0.0019		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Subsoil sample (B horizon, silty clay) of Ultisol from the Jefferson soil series in Anderson, TN	1 to 4	0.0020	Ultisols, commonly identified as red clay soils, are mineral soils which contain no calcareous material, have <10% weatherable minerals in the A horizon, and have <35% base saturation throughout the soil. They are typically acidic (pH <5) and their red and yellow colors result from iron oxide accumulation. Ultisols are considered the ultimate product of continuous mineral weathering in a humid, temperate climate and they are the dominant soils in the southern U.S.	
Subsoil sample (B horizon, clay) of Ultisol from the Collegedale soil series in Anderson, TN	1 to 4	0.0030		
Subsoil sample (B horizon, silty clay loam) of Ultisol from the Wolftever soil series in Anderson, TN	1 to 4	0.0023		
Clay loam (B horizon) sample of the St. Clair soil series from MI	1 to 2	0.0044		Lee, J., J.R. Crum, and S.A. Boyd. 1989. "Enhanced retention of organic contaminants by soils exchanged with organic cations." *Environmental Science & Technology* 23(11): 1365–1372.
Clay loam (B horizon) sample of the Marlette soil series from MI	1 to 3	0.0030		
Sand (B horizon) sample of the Oshtemo soil series from MI	1 to 3	0.0011		
Sand (4 samples) from near a hazardous waste site in Memphis, TN	0 to 1	0.0004 to 0.0006		Johnson-Logan, L.R., R.E. Broshears, and S.J. Klaine. 1992. "Partitioning behavior and the mobility of chlordane in groundwater." *Environmental Science & Technology* 26(11): 2234–2239.
Silt loam (4 samples) from near a hazardous waste site in Memphis, TN	3 to 8	0.0012 to 0.004		
Silt (3 samples) from near a hazardous waste site in Memphis, TN	9 to 10	0.0036		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Silt loam shallow aquifer sample from Tinker Air Force Base near Oklahoma City, OK	16 to 29	0.00010		MacIntyre, W.G., and T.B. Stauffer. 1989. *Liquid Chromatography Applications to Determination of Sorption on Aquifer Materials*. Air Force Engineering & Services Laboratory, Tyndall AFB, FL, 38 p.
Loamy sand shallow aquifer sample from Carswell Air Force Base near Fort Worth, TX	4 to 21	0.00027		
Sandy loam shallow aquifer sample from Barksdale Air Force Base near Shreveport, LA	14 to 46	0.0011		
Sandy loam shallow aquifer sample from Blytheville Air Force Base near Blytheville, AR	28 to 33	0.0016		
Sand shallow aquifer sample from Canadien Forces Base Borden in Ontario	1 to 13	0.00015		
Sand shallow aquifer sample from the Johnson Ranch near Lula, OK	16	0.00020		
Sand aquifer sediment from a site in Tampa, FL	6.5 to 8.2	0.0013		Brusseau, M.L., and P.S.C. Rao. 1991. "Influence of sorbate structure on nonequilibrium sorption of organic compounds." *Environmental Science & Technology* 25(8): 1501–1506.

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Loamy sand, dark brown	10 to 15	0.014	Samples were obtained from intact cores of subsurface solids collected at the former Naval Training Center in Orlando, FL.	Woods, L., R.L. Siegrist, and M. Crimi, 2012. "Effects of in situ remediation using oxidants and surfactants on subsurface organic matter and sorption of trichloroethene," *Groundwater Monitoring & Remediation* 32(2): 96–105.
Sand, orange tan	30 to 35	0.0036		
Loamy sand, gray	50 to 55	0.0024		
Upper layer silty sand terrace deposits of the surficial aquifer	5 to 15	0.0015 to 0.0018	Samples were collected at the U.S. Naval Air Station site in Jacksonville, FL. Specific sample depths are not identified. Two samples were analyzed from the upper layer and four samples were analyzed from the intermediate layer.	Davis, J.H. 2000. *Fate and Transport Modeling of Selected Chlorinated Organic Compounds at Operable Unit 3, U.S. Naval Air Station, Jacksonville, Florida*. USGS Open-File Report 00-255, 36 p.
Intermediate layer of silty sand terrace deposits of the surficial aquifer	30 to 100	0.00071 to 0.0059		
Clay interbed in the surficial aquifer at the Naval Air Station in Jacksonville, FL	~15 to 25	0.0018		Adamson, D.T., S.W. Chapman, S.K. Farhat, B.L. Parker, P. deBlanc, and C.J. Newell. 2015. "Characterization and source history modeling using low-K zone profiles at two source areas." *Ground Water Monitoring & Remediation*. doi: 10.1111/gwmr.12090, 18 p.

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Columbia aquifer Atlantic coastal plain sediments from Virginia Beach, VA	9	0.00019		Rectanus, H.V., M.A. Widdowson, F.H. Chapelle, C.A. Kelly, and J.T. Novak. 2007. "Investigation of reductive dechlorination supported by natural organic carbon." *Ground Water Monitoring & Remediation* 27(4): 53–62.
Columbia aquifer Atlantic coastal plain sediments from Virginia Beach, VA	21	0.0012		
Gray clay in the Kirkwood-Cohansey coastal plain sediment aquifer near Glassboro, NJ	89	0.021	Sample taken at well FSS1-3	Chapelle, F.H., L.J. Kauffman, and M.A. Widdowson. 2014. "Modeling the effects of naturally occurring carbon on chlorinated ethene transport to a public water supply well." *Ground Water* 52:76–89.
White sand in the Kirkwood-Cohansey aquifer near Glassboro, NJ	131	0.0033	Sample taken at well FSS1-4	
White sand in the Kirkwood-Cohansey aquifer near Glassboro, NJ	98	0.0015	Sample taken at well FSS2-2	
Yellow sand in the Kirkwood-Cohansey aquifer near Glassboro, NJ	312	0.0028	Sample taken at well FSS3-4	
Black clay in the Kirkwood-Cohansey aquifer near Glassboro, NJ	141	0.029	Sample taken at well FSS4-4	

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Gravel with sand (<6% silt/clay) alluvium from boring SSA-01 at the Chevron PCPL Superfund Site in Fillmore, CA	11 to 61	.0026 to 0.0088	Analyses were performed on 6 samples collected at 11, 21, 28, 35, 43, and 61 feet bgs.	URS. 2007. *Final Report of Natural Attenuation Characteristics and Soil Vapor Characteristics above Dissolved-Phase Benzene Plume, Pacific Coast Pipeline (PCPL) Superfund Site, Fillmore, California*.
Gravel with sand (<6% silt/clay) alluvium from boring SSA-02 at the Chevron PCPL Superfund Site in Fillmore, CA	14 to 56	.0020 to 0.0075 average = 0.0040	Analyses were performed on 6 samples collected at 14, 21, 28, 35, 43, and 56 feet bgs.	
Gravel with sand, gravel, and silty fine sand from boring NSA-01 at the Chevron PCPL Superfund Site in Fillmore, CA	13 to 90	0.0012 to 0.0057 average = 0.0037	Analyses were performed on 9 samples collected at 13, 13dup, 25, 25dup, 35, 51, 65, 78, and 90 feet bgs.	
Fine to coarse-grained sand and gravel alluvium from Moffett Naval Air Station in Mountain View, CA	15 to 20	0.0011	The organic matter appeared to be concentrated in the clay fraction, which had an organic carbon content 6X greater than that of the bulk material.	Roberts, P.V., G.D. Hopkins, D.M. Mackay, and L. Semprini. 1990. "A field evaluation of in-situ biodegradation of chlorinated ethenes: Part I, methodology and field site characterization." *Ground Water* 28(4): 591–604.

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Glaciofluvial medium to fine sand	4.0 to 8.5	0.00079	The samples were collected from the vadose zone (beyond the area of greatest contaminant concentration) at a dry cleaner site in NY. Each sample was air dried, dry sieved, and pulverized prior to duplicate analysis.	Wang, G., R.M. Allen-King, S. Choung, S. Feenstra, R. Watson, and M. Kominek. 2013. "A practical measurement strategy to estimate nonlinear chlorinated solvent sorption in low f_{oc} sediments." *Groundwater Monitoring & Remediation* 33(1): 87–96.
Glaciofluvial medium to fine sand	9.3 to 12.7	0.00079		
Glaciofluvial medium to fine sand	3.5 to 5.5	0.0012		
Glaciofluvial sand and gravel	10.5 to 14.0	0.0005		
Glaciofluvial sand and gravel	6.5 to 8.0	0.00049		
Glaciofluvial sand and gravel	7.0 to 9.7	0.00054		
Glacial outwash sand from the Cliffs-Dow Superfund site near Marquette, MI	7 to 12	0.0055	Near well cluster B-3	Klecka, G.M., J.W. Davis, D.R. Gray, and S.S. Madsen. 1990. "Natural bioremediation of organic contaminants in ground water: Cliffs-Dow Superfund site." *Ground Water* 28(4): 534–543.
Glacial outwash sand from the Cliffs-Dow Superfund site near Marquette, MI	20 to 27	0.0018	Near well 85-3	
Sand, brown, medium to fine grained, well sorted Wedron IL group Quaternary sediments	19 to 20	0.0024		Weston Solutions, Inc. 2013. *Site Investigation Report, Hoxsey Property, Wedron, LaSalle County, Illinois*. Report prepared for Illinois EPA.
Silty clay (gray, some sand) and sand (fine to coarse grained) Wedron Group Quaternary sediments	19 to 20	0.0075		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Robein silt paleosol (buried A soil horizon) including wood fragments and peat from IL	61 to 194	0.0052 to 0.17 average = 0.039	Analyses were performed on 16 samples.	Glessner, J.J.G., and W.R. Roy. 2009. "Paleosols in Central Illinois as potential sources of ammonium in groundwater." *Ground Water Monitoring & Remediation* 29(4): 56-64.
Sangamon geosol (buried A, B, and C horizons) silty clay loam to sandy loam from Peoria, IL	119 to 200	0.003	Analyses were performed on 4 samples.	
Sandy glacial outwash deposit in Minneapolis-St.Paul area, MN	75	0.00026 to 0.00038 average = 0.00035	Analyses were performed on 4 samples.	Ferrey, M.L., J.T. Wilson, C. Adair, C. Su, D.D. Fine, X. Liu, and J.W. Washington. 2012. "Behavior and fate of PFOA and PFOS in sandy aquifer sediment." *Ground Water Monitoring & Remediation* 32(4) 63–71.
Moderately calcareous, moderately to poorly sorted sandy gravel, gravelly sand, and sand with thin interbeds of silt; glacial outwash deposits near Bemidji, MN	<90	0.0009		Essaid, H.I., B.A. Bekins, W.N. Herkelrath, and G.N. Delin. 2011. "Crude oil at the Bemidji site: 25 years of monitoring, modeling, and understanding." *Ground Water* 49(5): 706–726.
Fine to coarse calcareous sand aquifer on the north shore of Lake Erie, Long Point, Ontario	<23	0.0015		W.D. Robertson. 2008. "Irreversible phosphorus sorption in septic system plumes?" *Ground Water* 46(1): 51-60.

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

<table>
<tr><th>Sample</th><th>Depth (ft bgs)</th><th>f_{oc}</th><th colspan="4">Additional Sample Information</th><th>References</th></tr>
<tr><td>Borden aquifer clean, well-sorted fine to medium sand of glaciofluvial origin in Borden, Ontario</td><td>~5 to 20</td><td>0.0001 to 0.0009
average = 0.0002</td><td colspan="4">Analyses were made on multiple samples taken from undisturbed cores.</td><td>Mackay, D.M., D.L. Freyburg, P.V. Roberts, and J.A. Cherry. 1986. "A natural gradient experiment on solute transport in a sand aquifer: 1. Approach and overview of plume movement." *Water Resources Research* 22(13): 2017–2029.</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td rowspan="10">Borden aquifer clean, well-sorted fine to medium sand of glaciofluvial origin in Borden, Ontario</td><td rowspan="10">1 to 13</td><td rowspan="10">bulk sample:
0.00021</td><td colspan="4">foc was determined on sieve size fractions in addition to a bulk aquifer sample:</td><td>Ball, W.P., and P.V. Roberts. 1991. "Long-term sorption of halogenated organic chemicals by aquifer material, 1. Equilibria." *Environmental Science & Technology* 25(7): 1223–1237.</td></tr>
<tr><td>**Fraction size (mm)**</td><td>**% of bulk mass**</td><td>**# samples**</td><td>**Average foc**</td><td rowspan="9"></td></tr>
<tr><td>1.7-4.75</td><td>0.58</td><td>12</td><td>0.00063</td></tr>
<tr><td>0.85-1.7</td><td>0.91</td><td>8</td><td>0.00099</td></tr>
<tr><td>0.42-0.85</td><td>5.24</td><td>22</td><td>0.00052</td></tr>
<tr><td>0.25-0.42</td><td>16.3</td><td>11</td><td>0.00023</td></tr>
<tr><td>0.18-0.25</td><td>25.7</td><td>11</td><td>0.00014</td></tr>
<tr><td>0.12-0.18</td><td>31.5</td><td>12</td><td>0.00013</td></tr>
<tr><td>0.075-0.12</td><td>16.5</td><td>11</td><td>0.00015</td></tr>
<tr><td><0.075</td><td>34.1</td><td>15</td><td>0.00035</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td>Glaciofluvial outwash interstratified silts, sands, and gravels at the Gloucester Landfill near Ottawa, Ontario</td><td>~30 to 250</td><td>0.001 to 0.006
average = 0.0035</td><td colspan="4"></td><td>Jackson, R.E., and R.J. Patterson. 1989. "A remedial investigation of an organically polluted outwash aquifer." *Ground Water Monitoring & Remediation* 9:119–125.</td></tr>
<tr><td colspan="8"></td></tr>
</table>

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

<table>
<tr><th>Sample</th><th>Depth (ft bgs)</th><th>f_{oc}</th><th colspan="4">Additional Sample Information</th><th>References</th></tr>
<tr><td>Silty sand from the Gloucester Landfill site near Ottawa, Ontario</td><td>49 to 52</td><td>0.0004 to 0.0016 average = 0.00077</td><td colspan="4">Analyses were made on 18 samples taken every 5 cm along a core.</td><td>Priddle, M.W., and R.E. Jackson. 1991. "Laboratory column measurements of VOC retardation factors and comparison with field values." <i>Ground Water</i> 29(2): 260–266.</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td rowspan="6">Cape Cod stratified sand and gravel aquifer USGS research site, MA</td><td rowspan="6">10 to 70</td><td rowspan="6">Range of averages:
0.00005 to 0.0012</td><td>Fraction size (mm)</td><td># of samples</td><td>Average foc</td><td>foc Range</td><td rowspan="6">Barber, L.B., II. 1994. "Sorption of chlorobenzenes to Cape Cod aquifer sediments." <i>Environmental Science & Technology</i> 28(5): 890-897.</td></tr>
<tr><td>0.5-1.0</td><td>28</td><td>0.00005</td><td>0.00002-0.00031</td></tr>
<tr><td>0.25-0.50</td><td>40</td><td>0.00005</td><td>0.00002-0.0020</td></tr>
<tr><td>0.125-0.25</td><td>42</td><td>0.00011</td><td>0.00001-0.00054</td></tr>
<tr><td>0.063-0.125</td><td>42</td><td>0.00028</td><td>0.00007-0.0020</td></tr>
<tr><td><0.063</td><td>45</td><td>0.0012</td><td>0.00020-0.011</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td>Silty clay from NY</td><td>13 to 16</td><td>0.0013</td><td colspan="4" rowspan="5"></td><td rowspan="5">Paviostathis, S.G., and G.N. Mathavan. 1992. "Desorption kinetics of selected volatile organic compounds from field contaminated soils." <i>Environmental Science & Technology</i> 26(2): 532–538.</td></tr>
<tr><td>Silty clay from NY</td><td>2 to 6</td><td>0.0017</td></tr>
<tr><td>Silty clay from NY</td><td>7.8 to 10</td><td>0.014</td></tr>
<tr><td>Coarse sand from NY</td><td>3 to 4</td><td>0.0009</td></tr>
<tr><td>Coarse sand from NY</td><td>11.8 to 14</td><td>0.0004</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td>Glaciolacustrine silty clay from NY</td><td>16 to 20</td><td>0.0013</td><td colspan="4"></td><td>Paviostathis, S.G., and J. Kendrick., 1991. "Desorptive behavior of trichloroethylene in contaminated soils." <i>Environmental Science & Technology</i> 25(2): 274–279.</td></tr>
<tr><td colspan="8"></td></tr>
</table>

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
St. Joseph silty clay till containing dark brown to black shale fragments (believed to be kerogen rich) from near Sarnia, Ontario	40 to 50	0.0068 and 0.020	Two samples were analyzed.	Allen-King, R.M., L.D. MacKay, and M.R. Trudell. 1997. "Organic carbon dominated trichloroethene sorption in a clay-rich glacial deposit." *Ground Water* 35(1): 124–130.
Clay-rich saprolite derived from the Cambrian Dismal Gap Fm. (shale and limestone with lesser sandstone) in eastern TN	4.9 to 6.2	0.001 to 0.006		Lenczewski, M., L. McKay, A Pitner, S. Driese, and V. Vulava. 2006. "Pure-phase transport and dissolution of TCE in sedimentary rock saprolite." *Ground Water* 44(3): 406–414.

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

<table>
<tr><th>Sample</th><th>Depth (ft bgs)</th><th>f_{oc}</th><th>Additional Sample Information</th><th>References</th></tr>
<tr><td>Red mudstone from the upper Triassic Lockatong Fm. at the former Naval Air Warfare Center (NAWC) in West Trenton, NJ</td><td>287</td><td>0.0017 to 0.0020 average = 0.0019</td><td>Three rock core disc samples were analyzed.</td><td rowspan="7">Lebron, C.A., D. Phelan, G. Heron, J. LaChance, S.G. Nielsen, B. Kueper, D. Rodriguez, A. Wemp, D. Baston, P. Lacombe, and F.H. Chapelle. 2012. *Dense Non Aqueous Phase Liquid (DNAPL) Removal from Fractured Rock Using Thermal Conductive Heating (TCH)*. ESTCP Final Report Environmental Restoration Project ER200715, 427 p.</td></tr>
<tr><td>Gray mudstone from the Triassic Lockatong Fm. at the NAWC site</td><td>260</td><td>0.0040 to 0.0042 average = 0.0041</td><td>Three rock core disc samples were analyzed.</td></tr>
<tr><td>Black mudstone from the Triassic Lockatong Fm. at the NAWC site</td><td>50</td><td>0.0075 to 0.0097 average = 0.0087</td><td>Three rock core disc samples were analyzed.</td></tr>
<tr><td>Siltstone from the Devonian Lock Haven Fm. in northern PA</td><td>70</td><td>0.0024 to 0.0031 average = 0.0028</td><td>Three rock core disc samples were analyzed.</td></tr>
<tr><td>Limestone from the Ordovician Gull River Fm. in Frontenac County, Ontario</td><td>70</td><td>0.0023 to 0.0027 average = 0.0025</td><td>Three rock core disc samples were analyzed.</td></tr>
<tr><td>Sandstone from the Cambro-Ordovician Nepean Fm. in Landsdowne, Ontario</td><td>38</td><td>0.00024 to 0.00093 average = 0.00059</td><td>Three rock core disc samples were analyzed.</td></tr>
<tr><td>Dolostone from the Silurian Lockport Dolomite in southern Ontario</td><td>45</td><td>0.0013 to 0.0023 average = 0.0018</td><td>Three rock core disc samples were analyzed.</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td>Silurian age Guelph Fm. tan-gray fine to medium crystallinity sucrosic dolostone aquifer in Guelph, Ontario</td><td>~15 to 330</td><td>Average = 0.0002</td><td><table>
<tr><th>Sample type</th><th># of samples</th><th>Average foc</th><th>foc range</th></tr>
<tr><td>fracture surface</td><td>15</td><td>0.0023</td><td>0.0008-0.064</td></tr>
<tr><td>stylolite layer</td><td>1</td><td>0.035</td><td>--</td></tr>
<tr><td>shale transition</td><td>6</td><td>0.0006</td><td>0.0003-0.0011</td></tr>
<tr><td>dolostone matrix</td><td>74</td><td>0.0002</td><td>0.0001-0.0010</td></tr>
</table></td><td>Kennell, J.R., 2008. "Advances in Rock Core VOC Analyses for High Resolution Characterization of Chlorinated Solvent Contamination in a Dolostone Aquifer." M.S. Thesis, Earth Sciences Department, University of Waterloo, Waterloo, Ontario.</td></tr>
<tr><td colspan="5"></td></tr>
</table>

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

<table>
<tr><th>Sample</th><th>Depth (ft bgs)</th><th>f_{oc}</th><th colspan="4">Additional Sample Information</th><th>References</th></tr>
<tr><td>Cambrian Ledger Fm. dolostone in Montgomery County, PA</td><td>352</td><td>0.0009</td><td colspan="4"></td><td>Golder Associates and Stone Environmental geotechnical testing reports. 2012.</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td>Eocene chalk from the Negev desert, Israel</td><td>Not reported</td><td>0.00042 -white chalk
0.011 - gray chalk</td><td colspan="4">Mean f_{oc} values are reported; number of samples analyzed or range of values not reported.</td><td rowspan="2">Witthuser, K., B. Reichert, and H. Hotzl. 2003. "Contaminant transport in fractured chalk: Laboratory and field experiments." <i>Ground Water</i> 41(6): 806–815.</td></tr>
<tr><td>Upper Cretaceous chalk from Sigerslev, Denmark</td><td>Not reported</td><td>0.00033 -white chalk</td><td colspan="4">Mean f_{oc} value is reported; number of samples analyzed or range of values are not reported.</td></tr>
<tr><td colspan="8"></td></tr>
<tr><td rowspan="9">Upper Cretaceous Chatsworth Fm. composed of thick-bedded medium to coarse-grained arkose and lithic arkose sandstone(60-70%), siltstone (25-35%), breccia (1-2%), and trace limestone derived from turbidite flows at the Santa Susana Field Laboratory near Simi, CA</td><td rowspan="9">13 to 518</td><td rowspan="9">0.00005 to 0.041 (188 samples, including those not categorized by grain size) average = 0.0015</td><td>Sample type</td><td># of samples</td><td>Average foc</td><td>foc Range</td><td rowspan="9">Hurley, J.C. 2003. "Rock Core Investigation of DNAPL Penetration and Persistence in Fractured Sandstone." M.S. Thesis, Earth Sciences Department, University of Waterloo, Waterloo, Ontario.</td></tr>
<tr><td>banded sandstone</td><td>13</td><td>0.0088</td><td>0.0021-0.040</td></tr>
<tr><td>hard sandstone</td><td>8</td><td>0.00012</td><td><0.00005-0.00022</td></tr>
<tr><td>fine sandstone</td><td>14</td><td>0.00049</td><td><0.00008-0.0026</td></tr>
<tr><td>med. sandstone</td><td>31</td><td>0.00026</td><td><0.00008-0.0010</td></tr>
<tr><td>coarse sandstone</td><td>47</td><td>0.00026</td><td>0.00008-0.0015</td></tr>
<tr><td>all sandstone</td><td>134</td><td>0.00028</td><td><0.00005-0.0026</td></tr>
<tr><td>siltstone</td><td>20</td><td>0.0053</td><td>0.00025-0.014</td></tr>
<tr><td>breccia</td><td>11</td><td>0.00019</td><td>0.00013-0.00035</td></tr>
<tr><td colspan="8"></td></tr>
</table>

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Ordovician Prairie du Chien Grp. dolostone in Dane County, WI	77	<0.0001	Analyzed rock samples were derived from core taken at the Hydrite Chemical Company site. All detected foc values were estimated (below the limit of quantitation but above the method detection limit).	Lima, G., Parker, B.L., Meyer, J.R. 2012. "Dechlorinating microorganisms in a sedimentary rock matrix contaminated with a mixture of VOCs." *Environmental Science & Technology* 46(11): 5756–5763. Austin, D.C. 2005. "Hydrogeologic Controls on Contaminant Distribution within a Multi-Component DNAPL Zone in a Sedimentary Rock Aquifer in South Central Wisconsin." M.S. Thesis, University of Waterloo, Waterloo, Ontario, 480 pp. Meyer, J.R. 2005. "Migration of a Mixed Organic Contaminant Plume in a Multilayer Sedimentary Rock Aquifer System." M.S. Thesis, University of Waterloo, Waterloo, Ontario, 313 pp.
Ordovician Prairie du Chien Grp. silty sandstone in Dane County, WI	118	<0.0001		
Cambrian St. Lawrence Fm. dolostone in Dane County, WI	126	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	163	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	163	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	191	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	197	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	197	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	215	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	215	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	222	<0.0001		
Cambrian Tunnel City Group sandstone in Dane County, WI	223	<0.0001		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Cambrian Tunnel City Group Mazomanie Fm. sandstone in Dane County, WI	236	0.00012		
Cambrian Wonewoc Fm. sandstone in Dane County, WI	257	0.00010		
Cambrian Wonewoc Fm. sandstone in Dane County, WI	257	<0.0001		
Cambrian Wonewoc Fm. sandstone in Dane County, WI	317	<0.0001		
Cambrian Eau Claire Fm. silty sandstone in Dane County, WI	346	0.00015		
Cambrian Mt. Simon Fm. sandstone in Dane County, WI	376	<0.0001		
Cambrian Mt. Simon Fm. sandstone in Dane County, WI	465	<0.0001		
Cambrian Mt. Simon Fm. sandstone in Dane County, WI	465	<0.0001		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information			References
			Depth (ft)	**Rock type**	**foc**	
Triassic Stockton Fm. sandstone, siltstone, and shale in Montgomery County, PA	57 to 333	<0.0001 to 0.0022 (15 samples); average = 0.00084	37.8-38.4	reddish-brown fine sandstone	0.0004	Golder Associates and Stone Environmental geotechnical testing reports. 2012.
			57.2-57.8	medium-coarse arkosic sandstone	0.0011	
			76.4-77.0	medium-coarse arkosic sandstone	0.0008	
			98.2-98.8	reddish-brown siltstone	0.0006	
			117.0-117.6	light-brown sandstone	0.0005	
			136.2-136.9	fine-medium gray sandstone	0.0012	
			226.0-226.7	very fine reddish-brown sandstone	0.0007	
			241.6-242.3	medium gray sandstone	0.0022	
			260.6-262.2	fine reddish-gray sandstone	<0.0001	
			280.4-281.0	reddish-brown siltstone	0.0009	
			294.7-295.3	very fine reddish-brown sandstone	0.0017	
			315.4-316.0	greenish-gray siltstone	0.0006	
			332.1-332.9	gray shale	0.0009	
Triassic New Haven Fm. arkose redbeds in CT	Between	0.0002 to 0.01	Analyses were performed on 18 subsamples of bedrock core taken from various depths.			Lipson, D.S., B.H. Kueper, and M.J. Gefell. 2005. "Matrix diffusion-derived plume attenuation in fractured bedrock." *Ground Water* 43(1): 30–39.

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Ordovician age Normanskill Fm. dark-gray shale at the Watervliet Arsenal in Albany County, NY	32 to 147	0.0026 to 0.0068 (23 samples) average = 0.0037		Kavanaugh, M., R. Deeb, and D. Navon. 2011. *Final Report - Watervliet Arsenal: Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent-Contaminated Sites*. ESTCP Project ER-200318, 298 p.
Devonian Dunkirk shale (grayish black to black) in Alleghany County, NY	370 to 514	0.0012		Hill, D.G., and T.E. Lombardi. 2002. *Fractured Gas Shale Potential in New York.* Ticora Geosciences report to New York State Energy Research and Development Authority.
Devonian Hanover shale in Alleghany County, NJ	514 to 983	0.0014		
Ordovician Utica shale (black to grayish black) in central NY	outcrop samples	0.016 to 0.040 average = 0.017		
Organic-rich shale, Tertiary age, Germany		0.27		Grathwohl, P. 1990. "Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{oc} correlations." *Environmental Science & Technology* 24(11):1687–1693.
Organic-rich shale, Jurassic age, Germany		0.097		
Peat, Germany		0.33		
Lignite, Germany		0.19		
Bituminous coal, Germany		0.84		
Anthracite, Germany		0.80		

Table I-1. Representative natural foc values determined in soils, sediments, and rocks (continued)

Sample	Depth (ft bgs)	f_{oc}	Additional Sample Information	References
Metasedimentary bedrock of phyllite grade from bedrock core at MW-203 at a site in northern Maine, MW	13 to 82	0.0011 to 0.0024 average = 0.0018	Analyses were performed on 10 samples collected immediately adjacent to fractures at 13, 23, 27, 38, 42, 47, 52, 58, 69, and 82 feet bgs. The samples analyzed included the fracture surfaces and extended back to <1 cm from the fracture.	Rawson, J.R.Y., and T.R. Eschner. 2007. "Analysis of organic carbon (foc) in fractured bedrock." In: Proceedings of the Fractured Rock Conference, NGWA/USEPA, Portland, Maine, pp. 555–563.
Metasedimentary bedrock of phyllite grade from bedrock core at PW-207 at a site in northern Maine, MW	11 to 90	0.0016 to 0.0024 average = 0.0019	Analyses were performed on 10 samples collected immediately adjacent to fractures at 11, 19, 24, 29, 35, 45, 55, 87, and 90 feet bgs. The samples analyzed included the fracture surfaces and extended back to <1 cm from the fracture.	

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APPENDIX K. ACRONYMS

AFB	Air Force Base
amsl	above mean sea level
BAP	benzo-a-pyrene
BFA	background fluorescence analysis
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylene
CCL_4	carbon tetrachloride
cDCE	cis-1,2-dichloroethene
CF	chloroform
CLP	Contract Laboratory Program
COC	contaminant of concern
CPT	cone penetrometer testing
CSIA	compound specific isotope analysis
CSM	conceptual site model
CT	carbon tetrachloride
1,4-D	1,4-dioxane
2D, 3D	two dimensional, three dimensional
DCA	dichloroethane
DCE	dichloroethene
DDT	dichlorodiphenyltrichloroethane
DGGE	denaturing gradient gel electrophoresis
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DOD	U.S. Department of Defense
DPT	direct-push technology
DQO	data quality objective
DSITMS	direct sampling ion trap mass spectrometer
EAB	enhanced anaerobic bioremediation
EAP	enzyme activity probe
EC	electrical conductivity
ECOS	Environmental Council of the States
EM	electromagnetic conductivity
ERIS	Environmental Research Institute of the States

ESTCP	Environmental Security Technology Certification Program
EtOH	ethanol, ethyl alcohol
FFS	focused feasibility study
FID	flame ionization detector
FISH	fluorescence in situ hybridization
Foc	fraction of organic carbon
GC	gas chromatography/chromatograph
GETS	Groundwater Extraction and Treatment System
GPR	ground penetrating radar
Hg	mercury
HPT	hydraulic profiling tool
HPT-GWS	hydraulic profiling tool–groundwater sampler
HRC	Hydrogen-Release Compound
IBT	internet-based training
IDSS	integrated DNAPL site strategy
ISB	in situ bioremediation
ISC	integrated site characterization
ISCO	in situ chemical oxidation
ISCR	in situ chemical reduction
ISTR	in situ thermal remediation
ITMS	ion trap mass spectrometer
ITRC	Interstate Technology & Regulatory Council
LC34	Launch Complex 34
LIF	laser induced fluorescence
LNAPL	light nonaqueous phase liquid
M	molar
MASW	multi-channel analyses of surface waves
MBT	molecular biological tool
MCL	maximum contaminant level
MEK	methyl ethyl ketone (2-butanone)
MGP	manufactured gas plant
MIP	membrane interface probe
MiHpt	membrane interface probe hydraulic profiling tool
MNA	monitored natural attenuation

MPE	multiphase extraction
MS	mass spectrometry
MTBE	methyl tertiary butyl ether
MVS	mining visualization software
NAPL	nonaqueous phase liquids
NM	not measured
NMR	nuclear magnetic resonance
NR	not recorded
OU	operable unit
OVA	organic vapor analyzer
PAH	polycyclic aromatic hydrocarbons
PBA	tetrabromomethane
PCA	tetrachloroethane
PCB	polychlorinated biphenyls, Aroclor range congeners
PCE	perchloroethene (tetrachloroethylene)
PCP	pentachlorophenol
PCR	polymerase chain reaction
PDB	polyethylene diffusion bag
PDS	phase distribution spreadsheet
PFM	passive flux meter
PID	photo ionization detector
PITT	partitioning Interwell tracer test
PLFA	phospholipid fatty acid analysis
PSG	passive soil gas
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
SQ	Semiquantitative
Q	quantitative
QC	quality control
QL	qualitative
qPCR	quantitative polymerase chain reaction
RAO	Remedial Action Objective
REV	representative elementary volume
RI	Remedial Investigation

ROD	Record of Decision
ROI	return on investigation
RPP	rigid porous polyethylene
SERDP	Strategic Environmental Research and Development Program
SG	specific gravity
SIP	stable isotope probe
SMART	specific, measureable, attainable, relevant, time-bound (referring to goals)
SP	sample port
SPT	standard penetration test
SROI	sustainable return of investigation
SVE	soil vapor extraction
SVOC	semivolatile organic compound
TCA	trichloroethane
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCE	trichloroethene
TMB	trimethylbenzene
1,2,4-TMB	1,2,4-trimethyl benzene
T-RFLP	terminal restriction length polymorphism
TVOC	total volatile organic compounds
USCS	Unified Soil Classification System
USDOE	U.S. Department of Energy
USEPA	U.S. Environmental Protection Agency
UST	underground storage tank
UV	ultraviolet
VC	vinyl chloride
VOC	volatile organic compound
XSD	halogen specific detector
X-VOC	chlorinated volatile organic compound

APPENDIX L. GLOSSARY

A

accuracy

Accuracy of an analytical measurement is how closely the result corresponds to the true value. This normally requires the use of standards in carefully calibrating the analytical methods.

advection

Transport of a solute by the bulk motion of flowing groundwater.

aliphatic compounds

Acyclic or cyclic, saturated or unsaturated, carbon compounds (excluding aromatic compounds).

anisotropy

The property of being directionally dependent (as opposed to isotropy, which means homogeneity in all directions).

aqueous solubility

Aqueous solubility represents the maximum concentration of the dense nonaqueous phase liquid (DNAPL) chemical constituents that can be dissolved in an aqueous solution (groundwater, for the purpose of this document).

C

capillary entry pressure

Capillary entry pressure (Pce) represents the capillary pressure at residual saturation (Sr) of the nonwetting fluid. The value of Pce represents the pressure that must be overcome for DNAPL (as a nonwetting fluid) to initially displace water from initially water-saturated media. The Pce represents the minimum pressure required for DNAPL to be mobilized into any geologic material.

capillary pressure

Capillary pressure (Pc) represents the pressure difference between two fluids sharing pore space within a representative elementary volume (REV). Due to interfacial tension and the formation of a meniscus, the nonwetting fluid develops a greater pressure than the wetting fluid. Pc is a nonlinear function of saturation (S), with Pc increasing at greater saturation of the nonwetting fluid.

chlorinated ethene

Organic compounds containing two double-bonded carbons and possessing at least one chlorine substituent.

chlorinated solvent

Organic compounds with chlorine substituents that are commonly used for industrial degreasing and cleaning, dry cleaning, and other industrial processes.

coal tar

A brown or black liquid of extremely high viscosity. Coal tar is one of the resultant byproducts when coal is carbonized to make coke or gasified to make coal gas. Coal tars are complex and variable mixtures of phenols, polycyclic aromatic hydrocarbons, and heterocyclic compounds.

compliance monitoring

The collection of data which, when analyzed, can allow for the evaluation of the contaminated media against standards such as soil and or water quality regulatory standards, risk-based standards, or remedial action objectives.

conceptual site model

A conceptual site model (CSM) is a hypothesis about how contaminant releases occurred, the current state of the source zone, and current plume characteristics (plume stability).

control plane

The location of the control plane, or response boundary, is defined as a location within the source area, or upgradient or immediately downgradient of the source area, where changes in the plume configuration are anticipated due to the implementation of the DNAPL source zone treatment. The response boundary should not be confused with the term “point of compliance,” which USEPA defines as the point where media-specific standards (such as maximum contaminant levels or risk-based cleanup goals) must be achieved.

creosote

The portion of chemical products obtained by the distillation of a tar that remains heavier than water. Creosote is notably useful for its antiseptic and preservative properties. It is produced in some quantities by wood and coal burning (in blast furnaces and fireplaces).

D

dense nonaqueous phase liquid (DNAPL)

A water-immiscible organic liquid that is denser than water (such as tetrachloroethene).

density

Describes the mass per unit volume of the DNAPL, and is sometimes expressed as specific gravity, which is the density relative to water.

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desorption

The process in which atomic or molecular species leave the surface of a solid and escape into the surroundings.

diffusion

The process of net transport of solute molecules from a region of high concentration to a region of low concentration caused by their molecular motion in the absence of turbulent mixing.

dilution

A reduction in solute concentration caused by mixing with water at a lower solute concentration.

dispersion

The spreading of a solute from the expected groundwater flow path as a result of mixing of groundwater.

F

flux

Rate of flow of fluid, particles, or energy through a given surface.

G

Gaussian distribution

Normal distribution. See http://hyperphysics.phy-astr.gsu.edu/hbase/math/gaufcn.html.

H

hydraulic aperture

Hydraulic apertures are the theoretical fracture widths calculated with the cubic law using transmissivity (T) values determined from hydraulic tests. Hydraulic apertures represent the size of the fracture based on the hydraulic behavior.

hydraulic conductivity

The capability of a geologic medium to transmit water. A medium has a hydraulic conductivity of unit length per unit time, if it will transmit in unit time a unit volume of groundwater at the prevailing viscosity through a cross section of unit area, (measured at right angles to the direction of flow), under a hydraulic gradient of unit change in head through unit length of flow.

I

interfacial tension

Represents the force parallel to the interface of one fluid with another fluid (usually air or water), which leads to the formation of a meniscus and the development of capillary forces and a pressure difference between different fluids in the subsurface.

isotropy

Equal physical properties in all direction.

M

mass balance

Quantitative estimation of the mass loading to the dissolved plume from various sources, as well as the mass transport, phase transfer, degradation, and attenuation capacity for the dissolved plume.

mass discharge

Mass discharge (Md) is a contaminant load past a transect (mass per time). It can also be referred to as cumulative mass flux, mass discharge, or mass flux.

mass flux

Mass flux (J) is a contaminant load (mass) per time per unit area. It is a general term for performing mass-flux- or mass-discharge-type calculations.

mass loading

Contaminant released to the environment (in this case, the aquifer or unsaturated zone) from the source material.

mass transfer

The irreversible transport of solute mass from the nonaqueous phase (that is, DNAPL) into the aqueous phase, the rate of which is proportional to the difference in concentration.

mechanical aperture

The mechanical aperture is the actual measured fracture width, which can vary significantly throughout the fracture, and represents the true aperture distribution throughout the fracture. This aperture can change if the fracture is pressurized or depressurized. Hydromechanical well testing attempts to measure this change (Rutqvist et al. 1998; Schweisinger et al. 2009).

N

nonaqueous phase liquid

A water-immiscible organic liquid that is denser than water (for example, tetrachloroethene).

P

precision

Precision is the reproducibility of multiple measurements, usually described by a standard deviation, standard error, or confidence interval.

R

relative permeability

The actual or effective permeability of a fluid in a REV relative to the intrinsic water permeability of a porous medium. The value of relative permeability (kr) ranges from 0 to 1.0 as a nonlinear function of S, where kr = 1.0 at S = 1.0 and kr = 0 at S= 0.

representative elementary volume

The smallest subsurface element that can be considered to have homogeneous conditions representative of the system being evaluated.

residual saturation

A combined property of the DNAPL and the subsurface formation materials. Sr is the fraction of pore space within a REV that is filled by the DNAPL at the point where it becomes disconnected from DNAPL in an adjacent REV and is no longer mobile. The value of Sr represents the fraction of DNAPL potentially remaining in zones that were previously directly exposed to DNAPL migration (Cohen et al. 1993; Pankow and Cherry 1996).

S

saturation

Represents the proportion of the subsurface pore space within a REV that is occupied by a fluid (either DNAPL, air, or water), ranging from 0 to 1.0. When multiple fluids are present, the sum of all fluid saturations equals 1.0. DNAPL saturation very rarely approaches 1.0, because the NAPL typically shares pore spaces with water or air, and most porous media are water wetting.

secondary porosity

The openings or discontinuities in a rock matrix caused by breakage, fracture, or dissolution, which are further subdivided by origin as faults, joints, or karst channels (ITRC 2011b, p. 12).

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seepage velocity

The rate of movement of fluid particles through porous media along a line from one point to another.

sensitivity

Sensitivity is the smallest amount of a substance in a sample that can accurately be measured by an assay.

sorption

The uptake of a solute by a solid.

source strength

Mass discharge at the source zone.

specific discharge

An apparent velocity calculated from Darcy's law, specific discharge represents the flow rate at which water could flow in an aquifer if the aquifer were an open conduit.

specificity

Analytical specificity is the ability of an assay to measure a particular constituent or parameter rather than others in a sample.

synoptic

A general view of the whole.

T

transport aperture

Solute transport apertures can be determined based on the behavior of solute transport through the fracture.

V

vapor pressure

Vapor pressure is the pressure exerted by the vapor phase of a substance at equilibrium with the pure condensed (solid or liquid) phase in a closed system.

viscosity (dynamic)

Represents the thickness or resistance to shear (flow) of the fluid. For example, honey is more viscous than water, which is more viscous than air.

volatility

Represents the tendency of the DNAPL chemical constituents to evaporate into the vapor phase.

W

wettability

Represents whether a fluid is wicked into or repelled out of the subsurface media, and is defined by the contact angle of the DNAPL fluid against the matrix materials in the presence of water. Wettability is a combined property of the DNAPL and the subsurface formation materials, and can be affected by chemistry and the presence of co-contaminants. In the example in Figure 2-2 of this guidance document, the solid surface has sufficient attractive force to overcome the surface tension of the low-surface-tension droplet on the right, and the droplet is stretched out into a thin wetting layer. The solid surface energy is not high enough to overcome the high surface tension of the droplet on the left and wetting does not occur.