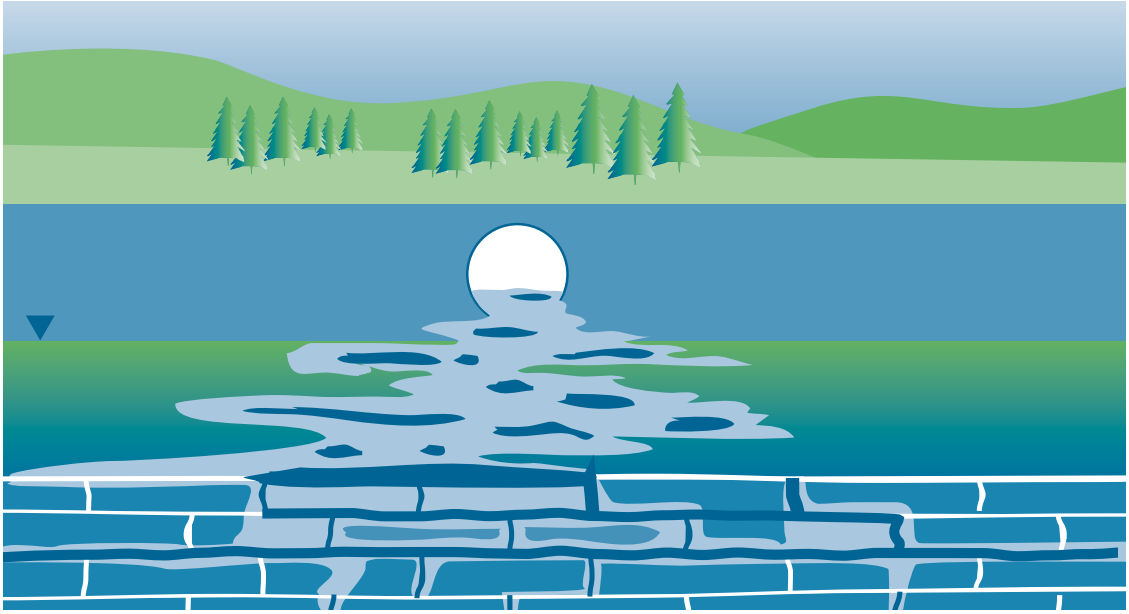
Technical/Regulatory Guidelines

Strategies for Monitoring the Performance of DNAPL Source Zone Remedies



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The Interstate Technology & Regulatory Council
Dense Nonaqueous-Phase Liquids Team

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Strategies for Monitoring the Performance of DNAPL Source Zone Remedies

August 2004

Prepared by
The Interstate Technology & Regulatory Council
Dense Nonaqueous-Phase Liquids Team

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EXECUTIVE SUMMARY

Introduction

The environmental problems associated with DNAPLs (dense, nonaqueous-phase liquids) are well known—they can be extremely difficult to locate in the subsurface; small amounts of DNAPL can contaminate large volumes of an aquifer; they are not amenable to conventional groundwater extraction technologies (e.g., "pump and treat"); restoration of DNAPL sites to drinking water standards or maximum contaminant levels is considered unattainable. These problems are the foundation of many technical and regulatory barriers to DNAPL cleanup attempts. Since 1999, the DNAPLs Team has been trying to ease some of these barriers by informing the regulatory community of developments in innovative approaches to DNAPL source zone characterization and remediation. To this end we have written four guidance documents that provide an overview of the problem and guide the reader through the process of site characterization, technology selection, and implementation. This, our fifth document, provides guidance on assessing the performance of DNAPL source zones remedies.

DNAPLs can be treated by implementing one of several or a combination of aggressive in situ technologies, including surfactant/cosolvent flushing, in situ chemical oxidation, and in situ thermal remediation. Less aggressive technologies for treating DNAPLs, such as bioremediation, are typically designed to address the dissolved plume but show some promise in treating sources. Although the long-term containment option will likely remain a viable remedial strategy at most complex DNAPL sites, the advent of aggressive source zone treatment technologies has caused a reevaluation of the conventional wisdom that significant source removal is "technically impracticable" at all DNAPL sites. Despite the ever-increasing number of field applications of DNAPL removal technologies, many unanswered questions remain regarding the effectiveness of these technologies and how best to measure their performance with respect to site-specific remedial objectives. Furthermore, there is no consensus on the most appropriate set of performance metrics with which to evaluate the benefits of mass removal from the DNAPL source zone, particularly the short and long-term impacts on the rate of contaminant mass discharge or flux emanating from the source zone.

This document is intended for regulators and others interested in learning about approaches to performance monitoring while implementing various in situ technologies for the treatment of DNAPLs. In this document, we present a number of ways in which the success or failure in treating a DNAPL source zone has been measured. Because the vast majority of experience in DNAPL source zone remediation has been in unconsolidated geologies, such as sands and silts, many of the conclusions, recommendations, and lessons learned presented in this document do not necessarily transfer to performance assessment in fractured bedrock, karst, or other consolidated geologies.

What Is Performance Assessment?

The task of evaluating the efficiency and effectiveness of a remedial action in meeting the remediation and operational objectives established for the project is termed "performance assessment." System effectiveness is the ability of the system to achieve remediation goals at a given site, while "efficiency" refers to the optimization of time, energy, and cost toward the

achievement of effectiveness. The EPA defines performance monitoring as "the periodic measurement of physical and/or chemical parameters to evaluate whether a remedy is performing as expected." In terms of DNAPL source zone treatment, performance assessment involves the collection and evaluation of conditions following treatment and the comparison of that information to pretreatment or baseline conditions.

Measuring performance can be a difficult undertaking, particularly when clear, measurable goals or metrics are not specified. According to the National Research Council (NRC), verifying the effectiveness of a remedial action typically involves quantifying reductions in "contaminant mass, concentration, mobility, and/or toxicity" following implementation and evaluating whether the performance objectives established for the project were achieved. Consistent with the NRC's definition of technical performance, we consider effectiveness to be the degree to which a technology application achieves risk reduction goals by reducing contaminant mass, concentration, mobility, and/or toxicity while preventing the uncontrolled mobilization or further spread of contaminants.

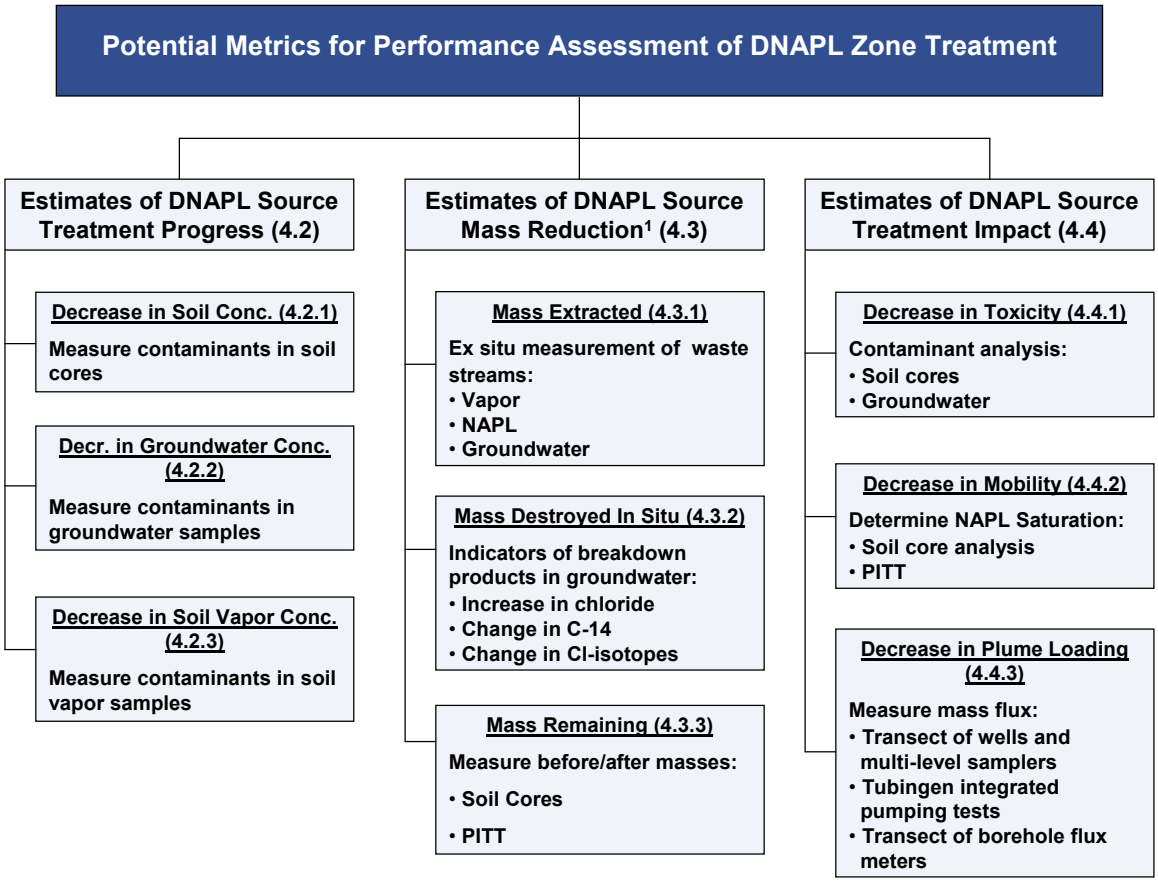
Establishing Performance Goals

Goals for a DNAPL source zone cleanup generally fall into three categories: short-term, intermediate, and long-term performance goals. Short-term goals focus on controlling DNAPL mobility and mitigating the potential for further contaminant migration. Long-term goals typically target the achievement of compliance with regulatory criteria applicable to contaminated media at the site, such as restoration of groundwater to drinking water standards. Intermediate performance goals are appropriate when guiding cleanup at a DNAPL source zone, where complete removal of the source in one aggressive remedial effort is typically not feasible yet the levels of contamination left behind are unacceptable. Examples of intermediate performance goals might include depleting the source sufficiently to allow for natural attenuation, preventing the migration of contaminated fluids beyond the treatment zone, reducing dissolved-phased concentrations outside the source zone, or reducing the mass discharge rate or flux emanating from the source. According to EPA, a "phased approach" to site cleanup generally accelerates risk reduction and achievement of long-term goals. For each phase, performance goals should be selected to guide the interim remedial action. Selection of an appropriate set of performance goals is discussed in Section 3 of the document.

Categories of Performance Metrics

Depending on the goals of the remedial project, different field parameters or metrics are measured and used to confirm attainment of those objectives or to evaluate progress. Typically, this process involves collecting groundwater or soil samples before and after treatment and comparing contaminant concentration levels. Applying these metrics and designing a performance monitoring program are discussed in Section 4. Although concentration data are useful, there are serious deficiencies to relying solely on such point measurements to evaluate the effectiveness of a source zone remedy. Fortunately, there are numerous other metrics for measuring performance which are discussed in terms of their utility in estimating source treatment progress, source mass reduction, and source treatment impact. Each metric has its advantages and limitations; no one metric is appropriate for all cases. To offset the limitations and uncertainties in relying on any one measure of success, it is suggested that several lines of evidence be used.

Figure 4-1 in the document (reproduced below) illustrates the various categories of performance metrics for assessment of DNAPL source zone treatment and directs the reader to the applicable section of the document where further details and references can be found.



Performance Monitoring Tools

Although standard protocols for measuring the performance of DNAPL source zone treatment technologies have not been established, a variety of assessment tools have been applied to making performance measurements and are the focus of this document. Groundwater sampling, soil core analysis, and partitioning tracer tests are just a few examples of methods currently being used to evaluate the effectiveness of source treatment. These tools yield information about changes in the concentration of contaminants in groundwater or the amount of mass remaining in the source zone following treatment, but they do not provide direct evaluation of the flux of contaminants being released from the source following treatment. Attempts to determine this latter property have led to a new type of performance measure—contaminant mass flux—that currently is the subject of intensive research, development, and field evaluation.

Technology-Specific Monitoring Considerations

Ideally, the effectiveness of any one DNAPL remediation technology should be evaluated using the same performance goals and metrics as other technologies being considered so their relative performance and benefits can be evaluated independent of the technology. Methods for monitoring system efficiency, however, must address technology-specific considerations. For instance, the effectiveness of a thermal technology like steam injection should be judged based on technology-independent criteria such as how much the source strength was depleted or how much contaminant mass was removed from the ground, but the program for monitoring system efficiency must be technology specific.

Section 5 provides a brief description of some technologies employed for DNAPL source zone remediation and offers some suggestions on the types of monitoring that may be appropriate for each technology. The information in Section 5 is intended as "suggested monitoring requirements" for planning purposes—actual monitoring varies depending on site-specific conditions and the technology being deployed.

Case Studies

Appendix B is intended to highlight the various approaches to performance assessment being used to measure success at some recent DNAPL source zone treatment projects. It contains several succinct case studies that cover remedial goals and objectives, performance monitoring and verification, and lessons learned. The reader is encouraged to contact the technical or regulatory person listed at the end of each case study for more detailed information.

Summary

Currently, there is no clear consensus based on objective guidelines as to the best way to evaluate treatment performance and balance performance objectives against site-specific stratigraphy, measurement uncertainties, regulatory acceptance, and cost. At present, the best approach is for site owners, regulators, and stakeholders to understand the options available and the benefits and limitations of each so that informed decisions can be made. The primary purpose of this document is to provide that knowledge base.

It is essential to recognize that development of effective DNAPL source treatment assessment tools is a work in progress. Every assessment tool discussed in this document has both strengths and weaknesses that must be considered when selecting a performance assessment strategy for a site. There is a significant amount of research currently under way at the federal level, much of it funded through the Department of Defense's Strategic Environmental Research and Development Program, which is focused on developing assessment tools for measuring the impacts of DNAPL source zone treatment that cut across technologies and allow objective comparisons of performance and cost among remedial alternatives to be made.

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STRATEGIES FOR MONITORING THE PERFORMANCE OF DNAPL SOURCE ZONE REMEDIES

1.0 INTRODUCTION

This document describes various performance assessment strategies and methods being used in field situations to measure the performance of in situ DNAPL source zone remediation systems. In addition, it presents new tools and approaches under development to measure the site-specific impacts of source treatment on contaminants emanating from the source zone.

1.1 Problem Statement

In recent years, technologies for treating DNAPL (dense, nonaqueous-phase liquid) sources have been employed under a variety of scenarios (demonstrations, pilot scale, and full scale) and geologic conditions. As a result of this experience, many lessons have been learned and useful information obtained on how to design, construct, and operate these systems. Despite the number of deployments, many unanswered questions remain regarding the effectiveness of these technologies and how best to measure their performance. There is no consensus on the most appropriate set of metrics with which to gauge success or the benefits of DNAPL source zone remediation, particularly its impact on mitigating the environmental problem at hand (Rao, et al. 2001; SERDP, 2002a).

DNAPLs are defined as separate-phase, slightly water-soluble liquids having a specific density greater than 1 (meaning they will sink in water). Examples of DNAPLs include chlorinated solvents, coal tar, creosote, and polychlorinated biphenyls (PCBs). This document is intended for the reader who is familiar with DNAPLs and their physical characteristics.

Every DNAPL site is different and requires tailoring a site-specific approach to implementing an effective treatment technology and verifying its performance. It is recommended that as new advances in treatment technologies are published, the reader continue to explore these new technologies. Studies are being conducted that constantly improve upon current understandings of how DNAPLs can be treated.

1.2 Scope of Document

1.2.1 Intent

This document is intended for regulators and others with an interest in learning about performance verification as applied to the treatment of DNAPLs and the strategies used in designing a remediation performance monitoring program. It is assumed that a decision to implement some type of source zone remedy has already been made or is being considered and that the reader is interested in developing an appropriate DNAPL removal performance monitoring program. Although some of the methods may be applicable to source containment remedies, our focus is on measuring performance of source treatment technologies, particularly in unconsolidated sediments within the saturated zone.

It is important to note that we are not attempting to predict the effectiveness of a particular source zone reduction technology or forecast its performance. Answers to questions such as, "Should DNAPL source zone mass removal be attempted?", "Will reducing source strength by removing mass be beneficial?", or "What are the limitations of X technology?" can be answered only through careful analysis of site-specific conditions and may require numerical modeling. We will, however, discuss possible alternatives to the question "How can performance be verified?"and provide guidance on developing a system performance monitoring program tailored to a specific source mass reduction approach.

While this document does describe several performance assessment approaches and methodologies, including a discussion of their applicability and limitations, its purpose is not to define or recommend standard protocols for measuring performance of in situ remediation technologies. Source zone treatment technologies are, in many cases, still under development, and there are no guarantees with any of the current technologies that DNAPL will be completely removed. Likewise, none of the performance assessment technologies described in this document can completely remove all the uncertainty associated with measuring performance or gauging success.

1.2.2 Organization

This document is organized into seven major sections. This section (Section 1) introduces the topic of remedial performance and stresses the importance of performance assessment. Section 2 defines some fundamental concepts relating to DNAPL source zone remediation that must be considered when designing or approving a performance monitoring program. In Section 3, some basic strategies for performance assessment are covered, including establishing performance goals and metrics, attaining data quality objectives, and developing an exit strategy. Section 4 describes various measures of success that have been used to evaluate DNAPL source treatment progress and impact, while Section 5 presents technology-specific monitoring parameters and tools. Section 6 discusses other issues that must be considered or may be encountered when designing or approving plans for a DNAPL source zone remediation. Finally, Section 7 lists references used in developing this document.

In addition, there are six appendices: a list of acronyms (Appendix A); several case studies highlighting performance monitoring approaches (Appendix B); discussion on the role of pilot studies (Appendix C); the use of statistics (Appendix D); responses to reviewers' comments (Appendix E); and Interstate Technology & Regulatory Council (ITRC) contacts (Appendix F).

1.3 Defining Performance Assessment

Performance can be perceived differently depending on the "eye of the beholder." For example, to a regulator charged with protecting public health and the environment, performance may be based strictly on whether the project conforms to applicable state and federal rules and regulations. To property owners responsible for reducing risk and future liability, performance is not only a measure of technical success of a technology but also defined by a business decision that allows them to cost-effectively achieve regulatory criteria and successfully manage risk. Depending on the contract

mechanism and method of payment, remedial contractors responsible for building and operating a treatment system are interested in achieving performance specifications goals as outlined in their contract. They may also want to achieve regulatory criteria to facilitate future business opportunities. Public stakeholders may define performance based on other concerns such as the potential for disruption to the community, the production of secondary emissions, or avoidance of post-remediation land use controls.

There are two primary criteria to be addressed in a remediation performance assessment: effectiveness and efficiency. Box 1-1 presents some terminology used in this document that may help the reader to, among other things, discern between measurements used for assessing remedial effectiveness and those for optimizing system efficiency.

1.3.1 Effectiveness

System effectiveness refers to the ability of the system to achieve remediation goals at a given site. For example, if plume remediation is the primary goal for the site, system effectiveness may be determined by the cumulative mass of contaminant removed from the aquifer or a permanent decrease in contaminant concentrations observed at specified compliance monitoring wells. Or where reduction in DNAPL mobility is the goal, effectiveness may be expressed in terms of whether continued DNAPL migration has been halted as a result of source treatment.

Measuring performance in terms of effectiveness can be a difficult undertaking, particularly when clear, measurable goals or metrics are not specified. According to the National Research Council's (NRC's) 1997 report, verifying the effectiveness of a remedial action typically involves quantifying reductions in contaminant mass, concentration, mobility, and/or toxicity following implementation and evaluating whether the performance objectives established for the project were achieved (NRC, 1997). Consistent with the NRC's definition of technical performance, we consider effectiveness to be the degree to which a technology application achieves risk reduction goals by reducing contaminant mass, concentration, mobility, and/or toxicity while preventing the uncontrolled mobilization or further spread of contaminants.

> "Given the unknowns in fully defining the human health and environmental effect of contaminants in ground water and soil, the dilemma is how to define remediation technology performance in a way that is both quantifiable and relevant to the goal of preventing adverse effects." - NRC, 1997

1.3.2 Efficiency

System efficiency refers to the optimization of time, energy, and costs toward the achievement of remediation effectiveness using a specific technology. Efficiency is typically assessed by comparing system operating parameters to design specifications. For example, an in situ chemical oxidation system may be effective at reducing contaminant concentrations initially, but the rate of reduction can become successively lower and less efficient with each injection, in terms of the time, energy, and money expended. Collecting and analyzing system operation and process data to monitor system efficiency is a standard practice at remediation projects.

Box 1-1. Terminology Used in Evaluating Performance

intermediate performance goals: facility-specific goals established for source zones as part of a "phased approach" to cleanup to monitor progress toward final cleanup goals for the site. May include removing DNAPL to the extent feasible, preventing the migration of DNAPL constituents, meeting certain numerical cleanup criteria, or mitigating the risk of exposure.

operational objectives: objectives describing what is to be achieved by the process utilized to effect remediation. These objectives focus on the efficiency of the engineered system.

performance assessment: the task of evaluating the efficiency and effectiveness of a remedial action in meeting the remediation and operational objectives established for the project.

performance metrics: environmental conditions and parameters monitored to evaluate progress or measured to confirm attainment of response objectives and criteria.

performance monitoring: monitoring conducted specifically to collect data in support of the performance assessment program. EPA defines performance monitoring as "the periodic measurement of physical and/or chemical parameters to evaluate whether a remedy is performing as expected."

performance standards: the predicted level of performance achievable under controlled conditions by a particular technology based on experience in field applications. Performance standards are useful for estimating costs and in making comparisons among remedial alternatives.

response boundary: the point or plane at which a facility is expected to monitor and achieve response objectives (e.g., media-specific cleanup levels). Also referred to as a "control plane."

response objectives: qualitative and quantitative objectives describing what is to be achieved by a particular operation. Data collected during effectiveness monitoring are evaluated to assess attainment of these objectives.

termination criteria: measurable, technology-specific parameters used to gauge whether or not the current remedial phase is complete and the system is ready to be shut down or transitioned to the next phase. Termination criteria are typically based on numerical targets or endpoints to which operational monitoring data are compared.

1.4 Goals and Outcomes of Performance Assessment

Below are listed some of the ways performance monitoring data are used. These examples are intended to stress the importance of having an adequate performance assessment plan.

To Optimize System Operation

By monitoring the efficiency and effectiveness of a unit operation or process, the system can be optimized and the site cleaned up faster and/or cheaper. Performance monitoring may also be useful when evaluating whether advances in technologies or implementation approaches could improve the ability of a remedy to achieve cleanup goals, to detect changes in environmental conditions that may reduce the efficacy of the remedy, or to detect conditions in the environment that could impact the effectiveness of the remedy.

When the data indicate that remedial progress has stalled or has reached a point of diminishing returns and simple adjustments in system operating parameters do not improve performance, the project team should consider a remedial process optimization (RPO) evaluation. Guidance on performing RPO evaluations is contained in the *Remedial Process Optimization Handbook*, produced by the Air Force Center for Environmental Excellence (AFCEE, 2001), as well as the ITRC's RPO Team document (ITRC, in preparation).

To Confirm Effectiveness of Cleanup

Confirming effectiveness of the DNAPL treatment technology can be based on achieving regulatory criteria in soil and/or groundwater at predetermined, site-specific points of compliance. Typically, these points of compliance are located well beyond the area undergoing active remediation and may not respond immediately to a reduction in source mass. A long-term monitoring program is therefore usually required once active source zone remediation has ceased to evaluate whether compliance has been achieved in the affected aquifer. Modeling can also be used to predict the decrease in plume longevity if plume restoration is a long-term goal. Assessment of effectiveness can also be based on achieving intermediate performance goals at a control plane or response boundary located within or just beyond the treatment area as part of a phased cleanup.

To Monitor Potential Impacts Beyond the Treatment Zone

The potential for contaminants to migrate beyond the treatment zone during aggressive source removal actions is a concern expressed by regulators and the public at many DNAPL projects. By monitoring pertinent parameters (e.g., groundwater or vapor contaminant concentrations) at the perimeter of the treatment zone, project managers can verify that no unacceptable exposure to down-gradient receptors is occurring. In this way, potential impacts to the environment as a result of treatment can be assessed and timely action taken to prevent further migration or possible exposure during remediation efforts. Performance monitoring data can also be used to identify any potentially toxic and/or mobile transformation products that may have formed and verify that the environmental problem is not being exacerbated.

To Facilitate Efficient Coupling of Remediation Technologies

Evaluation of performance monitoring data gives the remediation professional feedback to determine whether the remedial system is progressing as intended and when it may be time to transition to another technology if necessary. Many of the source zone technologies may be combined in a "treatment train" approach, either sequentially or contemporaneously, to more efficiently reduce source strength or longevity. For instance, cosolvent flushing of a chlorinated solvent source zone with ethanol coupled with enhanced bioremediation at the periphery of the source zone has been demonstrated (Jawitz, et al., 2000). Another example is the coupling of chemical oxidation and bioremediation.

For these and many other combinations, performance assessment is needed on an ongoing basis to optimize the synergy and/or transition between technologies. This optimization can include either managing the application of specific amendments or determining an appropriate time to transition from one coupled treatment process to the other. Knowing when and where to implement specific technologies and approaches requires close monitoring of performance data.

To Implement Performance-Based Contracts

There is typically a trade-off between an investment of resources for assessing performance and that for conducting remedial efforts. A cost-benefit analysis can be performed to evaluate this trade-off. When considering remedial alternatives, the availability of performance guarantees included within the price of technology application may be relevant. Such performance-based contracts are designed to encourage innovation and transfer the financial risk of source zone treatment by making the vendor responsible for meeting performance objectives. The contracted vendor will likely increase the price as appropriate for the level of risk that is being assumed. These types of contracts have been commonly used for in situ thermal treatment to allow greater flexibility in operations and to acknowledge the inherent uncertainties involved in subsurface DNAPL remediation. A decision as to who is responsible for conducting the performance evaluation should be stated contractually in advance, as well as how payment schedules will be impacted by objectives that are not fully met.

To Support the Decision to Close a Site

Site closure is the process of obtaining release from remedial responsibilities under the operable regulatory driver. A regulatory decision supporting "no further action" (NFA) is commonly a conditional release from further remedial requirements based on an agency's determination that the site does not constitute a threat to human health and the environment for the known environmental conditions and for a specified type of land use. Thus, the conditions of NFA decisions are highly site-specific.

Performance assessment results are components of the NFA decision. An assessment may show that while some source mass remains in place, the impact on the dissolved plume does not constitute a significant risk. For example, a former manufacturing facility in Skokie, Illinois performed remediation of DNAPL using electrical resistance heating (EPA, 2003a). Performance assessment

demonstrated that groundwater concentrations were reduced to below the Illinois EPA Tier III groundwater cleanup levels but that residual DNAPL remained in place. Illinois EPA granted an NFA letter based on the performance assessment results, which included total mass removed in extracted vapor and condensate, and a comparison of post-remediation groundwater concentrations to Tier III cleanup levels.

2.0 THE CONCEPTUAL SITE MODEL AND DNAPL ZONE DYNAMICS

We cannot stress enough the importance of understanding the site's history and contaminant distribution/behavior and having a robust performance assessment plan based on that understanding before attempting to remediate a DNAPL source zone. Typically, this process is completed in an interactive manner involving the responsible party, regulators, and public stakeholders. The resulting conceptual site model (CSM), based on a detailed characterization of baseline conditions in the source zone and potential paths of exposure, should help identify the environmental matrices to be monitored, the targeted treatment area, remedial action objectives, and a preliminary list of performance goals and metrics.

The *EPA Region VI Corrective Action Strategy* (EPA, 2000a) defines the CSM as a "three-dimensional 'picture' of site conditions" that "conveys what is known or suspected about a facility, releases, release mechanisms, contaminant fate and transport, exposure pathways, potential receptors, and risks." In this context, the CSM serves as the basis for conducting a risk evaluation where potential human and environmental receptors are identified, the potential for complete exposure pathways is determined, exposure point concentrations are estimated, and risk estimates are developed. From this evaluation, critical receptors and exposure pathways are identified along with chemicals of concern, and the need for remedial action is defined based on current or likely future risk potential. In this way, the CSM and risk evaluation are translated into appropriate remedial action objectives.

This section discusses, on an introductory level, some core concepts relating to DNAPL behavior and distribution in the subsurface as they pertain to in situ source zone remediation involving multiphase fluid flow.

2.1 Key Concepts Relating to DNAPLs

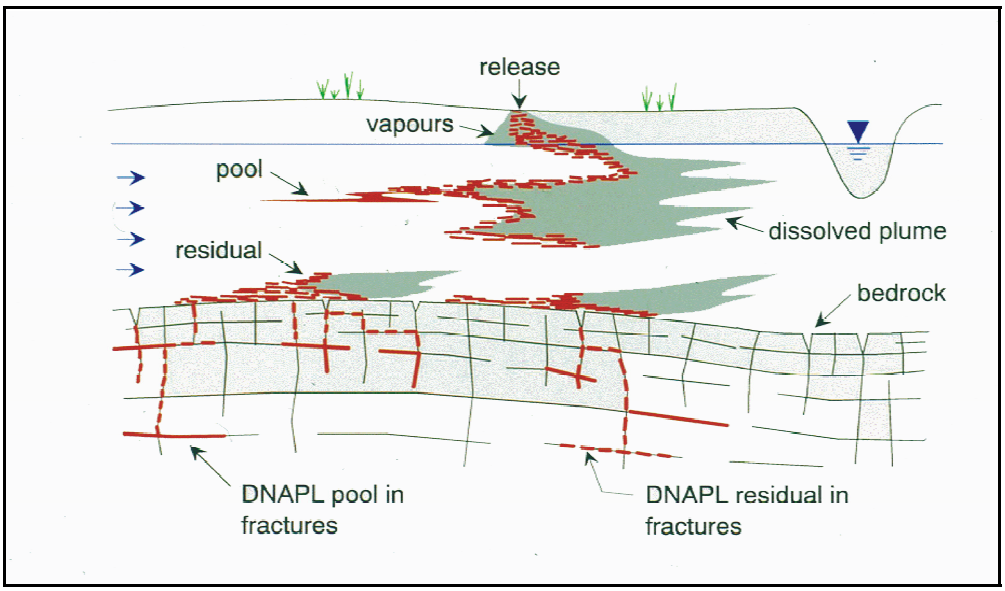
Key concepts described in this section include the physical behavior of DNAPLs, the definition of a source zone, contaminant-phase distribution, nonaqueous-phase liquid (NAPL) saturation, and how remediation technologies change the source zone architecture in order to enhance DNAPL recovery or treatment.

The area targeted for application of an in situ DNAPL remediation technology is often synonymous with the term "source zone." EPA defines the DNAPL zone as "that portion of the subsurface where immiscible liquids (free-phase or residual DNAPL) are present either above or below the water table" (EPA, 1996a). The DNAPL source zone encompasses the entire subsurface volume in which

DNAPL is present either at residual saturation or as "pools" of accumulation above confining units (Mackay and Cherry, 1989; Cohen and Mercer, 1993; Rao, et al., 2001). In addition, the DNAPL source zone includes regions that have come into contact with DNAPL that may be storing contaminant mass as a result of diffusion into the soil matrix. Figure 2-1 depicts a schematic conceptual model of a DNAPL source within the saturated zone.

2.1.1 Physical Behavior of DNAPLs in the Subsurface

DNAPLs include common chlorinated solvents, such as tetrachloroethene (PCE) and trichloroethene (TCE), as well as other hazardous substances such as creosote and coal tar (Cohen and Mercer, 1993). Generally DNAPLs are hydrophobic (not very soluble in water); however, some are soluble enough to present risks to human health or the environment. Many DNAPL compounds, like TCE, are also volatile and may cause vapor intrusion concerns.



Source: B. Kueper, pers. comm., 2004

Figure 2-1. Conceptual Model of a DNAPL Source Within the Saturated Zone

Like all fluids, DNAPLs move along paths of least resistance. When released in sufficient quantities to the subsurface soil, DNAPLs move downward, primarily due to gravity but also by infiltration, through the vadose zone and usually into the saturated zone. In addition to gravitational forces, the movement of DNAPL in the subsurface is influenced by geologic variations and whether the DNAPL is in an air-NAPL (vadose zone) or water-NAPL (saturated zone) environment. In the vadose zone, DNAPL typically is the wetting fluid so that when a fine-grain unit is encountered, it is preferentially imbibed into the small pore spaces. In the saturated zone, water generally is the wetting phase, although research has shown that many creosotes are actually the wetting phase with respect to water (Davis, E., personal communication, 2004; Powers et al., 1996). When a chlorinated solvent DNAPL encounters a fine-grain unit in this environment, it tends to collect on

the top surface of this unit and spread laterally. This accumulated solvent is often called a "pool," though the term is somewhat misleading. The accumulated DNAPL in these "pools" is often on the order of centimeters thick and occupies pores that may still be predominately filled with water. In the majority of field investigations, large, thick DNAPL "pools" are rarely encountered. If sufficient vertical accumulation and head are able to develop, the DNAPL may overcome the pore entry pressure requirements and penetrate the fine-grained material.

In the subsurface, DNAPL can also be distributed as a discontinuous mass of globules or ganglia, referred to as "residual DNAPL." Residual DNAPL is distinguished from "pools" by (1) their discontinuous and immobile nature; (2) their relatively small size; and (3) the dominance of capillary, rather than hydrostatic, forces in determining the shape and location of their free surfaces. Although residual DNAPL is immobile under normal subsurface conditions, it can act as a long-term source for continuing dissolution of contaminants into water or air flowing through the saturated and vadose zones, respectively. DNAPL pools also act as long-term sources for contaminants that partition themselves into air and/or soil.

There are many excellent books and articles that describe the physics of DNAPL subsurface behavior and migration. For more information, see Pankow and Cherry, 1996; Hunt, et al., 1988; and McWhorter and Kueper, 1996.

2.1.2 DNAPL Source Zone Architecture

Source zone architecture generally refers to the spatial distribution of DNAPL within the volume of impacted soil. More specifically, it refers to the distribution of contaminant mass among the various subsurface phases (e.g., vapor, dissolved, adsorbed, and free phase) and the hydrodynamic interactions between the DNAPL and the more permeable regions of the aquifer with which it makes contact. Source zone architecture determines the extent to which the DNAPL mass is subject to aqueous dissolution and thus, impacts the source strength, the nature of the dissolved plume, and the efficiency of remediation (Kavanaugh, et al., 2003).

Partitioning Theory

Characterization of the distribution of contaminant mass at a site using partitioning theory is useful in further understanding the source zone architecture. Contaminants introduced into the subsurface can be distributed (partitioned) among four physical phases: air, soil, water, and NAPL. Each NAPL component (i.e., each compound originally in the NAPL) is distributed among these phases according to thermodynamic equilibrium principles and mass transfer kinetic factors. Equilibrium in the system is reached when the chemical potential of each component is equal in every phase. The resulting distribution of the total contaminant mass can therefore be estimated by knowing each component's chemical phase partitioning behavior. Figure 2-2 presents a schematic depiction of contaminant mass partitioned into the four phases found within a vadose zone.

NAPL-water partitioning depends on the aqueous solubility of the specific NAPL component in question, and on the concentrations of the other components (if any) found in the NAPL. The

relationship between aqueous solubility and mole fraction of a component in the NAPL is analogous to Raoult's law for ideal gas mixtures in that the equilibrium aqueous concentration is equal to the pure-phase aqueous solubility of the component multiplied by the mole fraction of the component in the NAPL mixture.

Air-water partitioning between the aqueous and vapor phases of a NAPL component is controlled by Henry's law. The equilibrium air-water relationship is linear and is a function of the Henry's constant, which can be calculated from a component's vapor pressure, its molecular weight, and its aqueous solubility. Henry's constants for NAPL components are available in the literature.

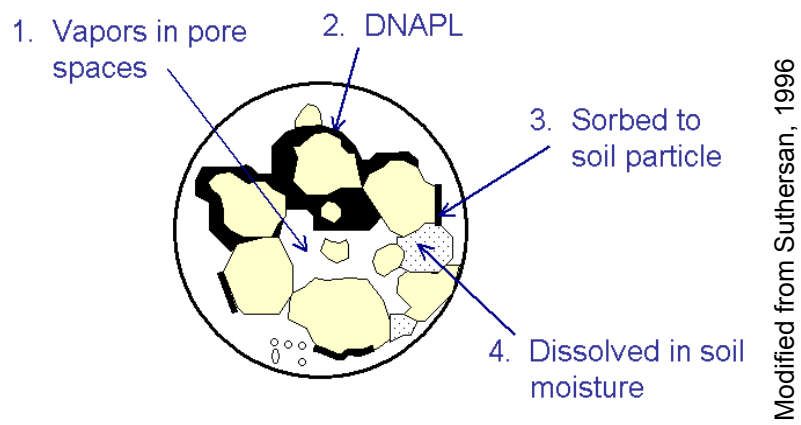


Figure 2-2. Partitioning of Contaminant in Subsurface

Soil-water partitioning is controlled by sorption to organic matter found within the sediment. In the context of most DNAPL source zones, sorption can be described by a linear function of the aqueous contaminant concentration, the mass fraction of natural organic carbon (f_{oc}), and the organic carbon to water partition coefficient (K_{oc}) for the compound in question. The mass fraction of natural organic carbon can be measured, and partitioning coefficients for specific compounds are available in the literature.

Using these partitioning relationships and the concepts of the conservation of mass and volume, the amount of each component in each of the four phases (air, soil, water, and NAPL) can be estimated, assuming equilibrium conditions have been met (Feenstra, et al., 1991). Not only is this useful for developing an understanding of how contaminant mass is distributed at a site, but it can also aid in identifying and quantifying the presence of DNAPL in soil samples. Soil-chemical data can be analyzed and interpreted using numerical tools developed to determine NAPL saturation of soil cores containing organic contaminants. These tools begin with the partitioning calculations discussed above and then proceed to solving the equations of the conservation of mass and volume, thereby obtaining an estimated value of NAPL saturation, and calculating the composition of the NAPL from the soil chemical analysis.

Saturation Concepts

Saturation is defined as the percentage of the pore space occupied by a fluid. The fluid could be a liquid or a gas, as is the case when moist soil contains both water and air within the pore spaces. For the water/air example, the water saturation (S_w) could vary between 0% (for dry soil) and 100% (for completely saturated soil). Furthermore, the liquid phase could consist of immiscible liquids, such as when both water and DNAPL occupy the soil pores together. Following the definition, the DNAPL saturation (S_{DNAPL}) is the ratio of DNAPL volume within the pore space to the total pore volume. The water saturation (S_w) is the ratio of the volume of pore water to the total pore volume. The air saturation (S_{air}) is defined similarly. The following equation reflects the sum of the three saturations:

$$S_w + S_{DNAPL} + S_{air} = 100\%$$

"Residual saturation" refers to a specific condition regarding the fluids within pore spaces that arises from the interfacial tension between fluids. Interfacial tension causes "trapping" of fluids within pore spaces such that one fluid can not be easily removed from the pores. For example, if water is used to push DNAPL from the pore spaces, some of the DNAPL becomes trapped and is very difficult to remove. This condition indicates residual saturation of the DNAPL. Depending on the type and size of the soil grains and the interfacial tension between fluids, residual DNAPL saturation values in the vadose zone can range between 10% and 20%; saturation values in the saturated zone are typically higher than those in the vadose zone and range between 10% and 50% (Cohen and Mercer, 1993).

2.1.3 Modeling the DNAPL Source Zone

The complexity of DNAPL source zones makes each impacted site unique and a well-grounded CSM incorporating the source zone can bring into focus features of the site that warrant the most attention. The site-specific nature of the DNAPL problem dictates that the performance assessment strategies and methodologies employed be highly tailored to conditions found at a particular site. Therefore, it is vital to know the general location of the DNAPL zone or zones and its interactions with the local groundwater flow regime. As is the case for conventional dissolved plume remediation, the volume and extent of the impacted area must be adequately delineated to provide a sufficient design basis for both the remedy and the performance assessment program. In practice, however, it is very difficult to precisely locate where DNAPL is present in the subsurface (ITRC, 2003a).

CSM development for a DNAPL source zone should include detailed studies of the site geology and hydrogeology. The study of the site-specific geology and hydrogeology is essential because of the role geology plays in the movement of DNAPLs. In sedimentary terrains, determining and understanding the environment of deposition affords the opportunity to build conceptualizations of the heterogeneities and structures that control the distribution of DNAPL in the subsurface. Geologic barriers and their orientation may provide clues to preferential flow pathways for DNAPL

or indicate where DNAPL may accumulate. Small changes in subsurface grain size, shape, distribution, and depositional sequences may influence where residual DNAPLs will be found.

Present and past land use at the site and surrounding areas is also critical to CSM development. If nonaqueous-phase chemicals were used or stored at a site, it is highly possible that releases occurred. Therefore, the type of chemicals that may have been used on site or are known to be used by industries associated with the site will help to focus the investigation. In addition to the types and quantities of chemicals used on the site, it is important to understand the processes and operations that used these chemicals. For example, past vapor degreasing operations typically resulted in the generation and release of low-viscosity solvents laden with oil and grease. The resulting multicomponent DNAPLs typically have physical and chemical properties that are markedly different from those of the chlorinated hydrocarbons manufactured and sold for degreasing use. On-site construction and other disturbances of the subsurface can affect DNAPL migration by creating preferential pathways and barriers to flow. The ITRC document *An Introduction to Characterizing Sites Contaminated with DNAPLs* (ITRC, 2003a) discusses these issues in more detail and provides references pertaining to DNAPL site characterization issues.

Assessment methods that can potentially be used to estimate the vertical and areal extent of a DNAPL source zone and supply data for the CSM are described in Pankow and Cherry (1996) and ITRC (2003a). These include environmental sampling, geophysical methods (such as ground-penetrating radar and vertical induction profiling), soil gas measurements, fluorescence, reactions with hydrophobic dye, and olfactory or visual evidence. Because of uncertainties inherent with using any one analytical method for detecting DNAPLs, the distribution of DNAPL is best defined by the use of "converging lines of evidence," rather than just a single measurement or observation.

Information obtained following implementation of pilot studies can be invaluable. Appendix C describes the role pilot studies and technology demonstrations play in refining the CSM and in developing a performance assessment program. For instance, if performance data collected during the pilot study indicate that DNAPLs have been mobilized as a result of treatment and have migrated beneath an assumed confining layer, the CSM and monitoring plan should be revised to account for this apparent "hole" in the stratigraphy.

2.2 Changes in DNAPL Zone Resulting from Treatment

Most aggressive technologies involve the injection of fluids, such as surfactants, cosolvents, steam, or oxidants, into the formation under engineered hydraulic gradients. These fluids not only alter the properties of the DNAPL but can also change the flow field, displacing contaminated fluids with clean fluids for a relatively short period of time. As treatment continues, changes occur in the source zone architecture that can improve removal or destruction efficiencies. Thermal technologies, for instance, are designed to add large amounts of heat to the subsurface, which (in addition to enhancing the recovery of DNAPL by affecting its vapor pressure, viscosity, and solubility) has been shown in laboratory experiments to agitate the soil microstructures and release trapped DNAPL. These changes occur primarily where advective processes dominate as a function of heterogeneity. The resultant localized changes in source zone architecture in turn change the mass flux (defined

as mass per unit area per unit time) emanating from the source. The degree of the change in mass flux is in part a function of the magnitude and nature of formation heterogeneity and the distribution of DNAPL within the formation.

It is important to recognize that the implementation of DNAPL source zone treatment technologies will likely result in physiochemical subsurface changes. As long as these changes are anticipated, the remediation project manager can judiciously plan for design and operational considerations so that these changes might benefit the remediation effort. Such subsurface changes resulting from treatment include the following.

Redistribution of DNAPL

Treatment technologies that modify DNAPL or interfacial properties or alter the subsurface structure will likely mobilize and redistribute previously immobile DNAPL. This redistribution can create a more extensive source zone. For example, the physical properties of neutral-density NAPL components can significantly vary with temperature (or other influences), and the impact of these changes on treatment design, operation, and monitoring must be considered. Consequently, monitoring and effective containment of DNAPL during remediation is of paramount importance. Knowledge of the rate and extent of this redistribution can help in the design of subsequent remedial steps.

If the remediation team does not account for mobility and potential redistribution, adverse risk consequences may result. Various source reduction techniques, such as via injection of oxidants or steam without regard to the resulting advective flow, addition of microbial substrates, or via gases formed as a result of in situ oxidation, could actually displace DNAPL as well as dissolved-phase contaminants. Finally, technologies such as thermal treatment and surfactant flooding cause physical changes that may mobilize DNAPL beyond the treatment zone. In all of these cases, it is imperative to ensure adequate perimeter monitoring and, if necessary, a means to intercept mobilized contaminants.

Increase in Vapor Pressure and Volatilization

Some thermal technologies are designed to increase subsurface temperatures to the boiling point of water, thereby increasing the rate of contaminant removal by two primary mechanisms: increased volatilization and steam stripping. Contaminant vapor pressure and the corresponding rate of contaminant extraction increase by a factor of about 30 as the subsurface is heated to boiling (Heron et al., 2000).

Once subsurface heating starts, the boiling points of various volatile organic compound (VOC)/water mixtures are reached in the following order: separate-phase NAPL in contact with water or moist soil first, dissolved VOCs next, and then uncontaminated groundwater. This phenomenon is advantageous for remediation because contaminated water tends to boil off before uncontaminated water, reducing the time and energy required to complete treatment. All boiling points increase with pressure, so higher temperatures are required to create boiling conditions with increasing depth

below the groundwater table. A phenomenon called "co-boiling", which occurs when two immiscible liquids are present, is discussed in Section 5.3.

Increase in Solubility or Dissolved-Phase Constituents

Remedial technologies designed to enhance removal of DNAPL can result in elevated concentrations of dissolved-phase contaminants during or immediately after treatment. These temporary contaminant concentration increases are commonly observed with the more aggressive source zone treatment technologies, such as thermally enhanced remediation, carbon substrate additions, and chemical oxidation. Dissolved-phase constituents are then available for further treatment via a wide range of well-established and accepted dissolved-phase remediation technologies, including permeable reactive barriers, air sparging, biostimulation, monitored natural attenuation, and bioaugmentation.

Impact on Microbial Populations

There are various DNAPL source zone treatment technologies that are designed to enhance a specific microbial group or species. Such biostimulation techniques involve the addition of carbon as an electron donor, with the goal of increasing the population of organisms capable of achieving reductive dechlorination. Alternatively, selected source reduction technologies (e.g., thermal) can produce more available organic carbon or increase kinetic rates, thereby stimulating microbial activities. Other DNAPL source zone treatment technologies, particularly in situ chemical oxidation (ISCO), create conditions (e.g., oxygen, heat) that increase and support other microbial communities.

DNAPL source reduction technologies can also negatively impact ambient microbial populations and alter the community structure by changing biochemical conditions (e.g., electron acceptors, substrate bioavailability, temperature, biotoxicants). These changes could disrupt natural attenuation processes that were in place prior to treatment.

Alteration of Subsurface Structure

Some of the more aggressive DNAPL source zone treatment technologies alter the subsurface structure either by their inherent design (e.g., forced introduction of treatment substrate into the subsurface) or through by-products, such as gas evolution during the reaction process (e.g., injection of hydrogen peroxide). Such subsurface alterations can enhance the mixing process and allow previously unavailable DNAPL to be treated. Methods used to achieve subsurface alteration/mixing include multiple injections in the same or different locations over time, injections in multiple screened intervals at one location, and high-pressure liquid or vapor injection to induce subsurface fracturing.

Preferential Flow

Geologic heterogeneities in the source can create zones of preferential flow. In addition, gases evolved during DNAPL source treatment (in particular, from thermal treatment or in situ oxidation using hydrogen peroxide) can lead to gas entrapment in porous media and a commensurate reduction in permeability along selected subsurface zones. These conditions, in turn, promote the formation of macrochannels, wherein preferential flow might occur. Such preferential flow areas can reduce the effectiveness of the source reduction delivery system. The use of mobility control agents (i.e., foams and gelants injected into the pore spaces) may mitigate the effect of preferential flow pathways and improve the delivery of remedial agents and the sweep efficiency. Pulsed operation of the system can also minimize the formation of channelized flow.

Precipitation/Clogging

An in situ source reduction technology like permanganate injection can precipitate particles by altering the existing geochemistry, and thereby affecting clays, or by yielding reaction products such as manganese dioxide nodules that can lead to plugging of the soil matrix. In addition, biotreatment or bioaugmentation techniques may promote the formation of organic biofilms that can also plug soil pores and reduce permeability. Plugging may reduce the effectiveness of future treatments. By monitoring pressure drops in the injection and extraction lines, operators can monitor and address the impacts of precipitate clogging.

Secondary Water Impact

Aggressive DNAPL source reduction technologies may alter the subsurface geochemical conditions and consequently result in deleterious impact to groundwater from contaminants apart from DNAPL constituents. If not carefully controlled, changes in subsurface redox can create conditions conducive to the formation of aldehydes, ketones, and mercaptans. In addition, technologies marked by decreasing pH conditions can potentially mobilize naturally occurring metals. Finally, source reduction technologies may generate surfactant-like compounds resulting in a "soil washing" effect that could result in contaminant displacement from soil particles. Monitoring of groundwater geochemistry during remediation will allow these secondary impacts to be measured and their impacts minimized.

VOC Off-Gassing

Some source reduction techniques may result in the generation of potentially explosive gases. Reductive dechlorination could promote conditions favoring the formation of methane, hydrogen sulfide, or ammonia. In addition, the implementation of in situ chemical oxidation may result in exothermic conditions, which in turn, may result in the stripping of VOCs from solution. Monitoring for VOC off-gassing can indicate both health and safety concerns as well as the possibility of contaminant loss via volatilization.

2.3 Addressing Rebound

"Rebound" is a term applied to contaminant concentrations measured near a source area which decrease following initiation of source treatment operations but, after the system has been shut down, increase to levels at or just below pretreatment concentrations. The phenomenon is commonly associated with vapor or groundwater extraction technologies whose contaminant mass removal rates are initially controlled by advection but reach a point during the removal process where diffusion processes dominate and mass removal rates decrease dramatically. Rebound does not necessarily indicate failure of the technology; in many cases it can be considered a measure of progress because it indicates transfer of the contaminant to air-filled pore spaces or water-bearing units that can be accessed for the application of additional treatment.

Rebound of vapor concentrations implies that either dilution or rate-limited mass transfer is occurring during soil venting. For example, if air extraction rates exceed the rate of diffusive mass transfer from within the pore water to the air-water interface and then into the flowing air stream, contaminant concentrations in the extracted air can diminish without removing all of the contaminant from the pore water. When extraction stops, the diffusion process continues, and eventually the concentration(s) within the soil pores that are most conductive to air begin to rise. If a soil gas sample is collected or extraction begins again, then the contaminant concentrations will have rebounded (USACE, 2002).

Rebound of dissolved-phase concentrations following in situ treatment can imply that treatment was not complete and that there is a nearby unremediated source of contamination. In the case of groundwater pump and treat, rebound can imply that the rate of groundwater extraction exceeds the diffusive mass transfer rate from the sorbed phase to the dissolved phase; it is essentially a function of dilution. Box 2-1 presents an example of rebound from a site in California where permanganate was used to treat a TCE source zone.

Box 2-1. Example of Rebound at a DNAPL Site in Irvine, California

In situ oxidation through injection of a permanganate solution was proposed as an alternative to vapor extraction and groundwater recovery at the BMC Olen site in Irvine, California. In situ oxidation has been "successful" at this site in terms of achieving the remedial objectives of turning off the active remediation systems and reducing the average TCE concentrations by approximately 60%. However, even after nine separate injection events were performed, concentrations of chlorinated solvents initially decreased after injection and then increased after the permanganate was consumed. Monitoring evidence showed that permanganate persisted for an average of 2.5 months, after which the dissolved TCE concentrations rapidly rebounded.

Although rebound cannot be prevented at every site, its potential occurrence can be anticipated and accounted for with an appropriate, long-term monitoring program. Thus, its impact on the progress

and outcome of the remediation can be mitigated as long as the monitoring period following system shutdown is of a sufficient duration to account for potential rebound.

There are many potential causes for rebound. First and foremost is the failure to remediate the DNAPL source generating the contamination. Factors that effect the ability to more completely remediate the source resulting in rebound include the following:

- composition of remedial fluid,
- duration of the remedial activities,
- external stresses placed on the aquifer or vadose zone changing flow during remedial activities,
- failure to fully characterize or understand the source zone (inadequate design basis),
- misapplication of the technology,
- proximity of the treatment area to other hydraulically connected source zones,
- partitioning from adjacent contaminated units with low hydraulic conductivity, and,
- heterogeneity of the aquifer and back-diffusion.

Depending on the severity of rebound, it is commonly addressed by continued application or operation of the same remedial technology, either in a pulsed mode or optimized in some manner, or application of a different technology.

2.4 Difficulty Treating and Assessing Performance at Complex DNAPL Sites

In 1994, and again in 1997, the NRC published reports that addressed the progress with and challenges for cleanup of soil and groundwater for a wide variety of contaminants as a function of hydrogeologic conditions (NRC, 1994, 1997). Both reports emphasize the difficulty of remediating DNAPL sources in the subsurface, especially in heterogeneous and complex hydrogeologic settings. Since the second report was published, there has been significant progress in treating DNAPL sources resulting from a great expansion of pilot- and full-scale treatment investigations in a variety of geologic media. However, challenges remain.

Building on the assessments in the NRC reports and incorporating results from more recent investigations, the current difficulty of DNAPL treatment under different site conditions can be summarized. In general, coarse-grained unconsolidated media are easier to treat and monitor than fine-grained or highly heterogeneous material. DNAPL contamination in clay and fractured bedrock is even more difficult. Likewise, treatment of VOC contamination within the vadose zone generally is easier than in the saturated zone for the equivalent medium. To a large extent this latter observation is the result of the great success of soil vapor extraction (SVE) for removing volatile DNAPL contaminants (less volatile contaminants are more difficult). Through summer 2000, over 17% of the Superfund Records of Decision (RODs) include SVE treatment for removal of the common chlorinated solvents from the subsurface (EPA, 2000b). Methods for the assessment of SVE performance in the vadose zone are presented in EPA guidance (EPA, 2001a).

Complex hydrogeologic settings (e.g., tight soils, fractured bedrock, karst) represent significant technical challenges and increased costs for treatment design, implementation, and performance assessment. The presence of surface and subsurface obstructions can also complicate efforts to remediate the site. In addition, some EPA documents (EPA, 1995a, 1996a) encourage the use of Technical Impracticability (TI) waivers in complex settings, creating a disincentive for addressing DNAPL contamination under these conditions. Currently, there is no definitive consensus as to when source treatment is necessary. Regardless, the fundamental technical difficulties of cost-effectively treating DNAPL sources in complex settings remain a largely unresolved problem.

Other factors that impact treatment difficulty and cost include depth of contamination and the properties of the DNAPL present. Depth is primarily a cost factor influencing all phases of the work from characterization and monitoring to treatment implementation and efficiency monitoring. Although direct-push methods can be used to collect soil and groundwater samples and often are suitable for installing treatment facilities (e.g., chemical injection wells), such methods are not appropriate at many deep sites or at locations where penetration of bedrock is required. The physiochemical properties of the DNAPL also influences the type and efficiency of the treatment method(s) employed. For instance, the relatively low volatility of wood treatment chemicals limit the types of remediation technologies that are suitable for this type of contamination.

In the more than 10 years of experience in developing and implementing innovative technologies for DNAPL source remediation, a significant fraction of treatment investigations to date has taken place within less complex settings. Therefore, our DNAPL source treatment experience is most closely associated with a relatively narrow subset of the full spectrum of possible site conditions. If our treatment and performance assessment experience is biased by the choice of remediation sites that are less complex and shallow, then how do these site conditions compare to the actual breakdown of geologic settings for DNAPL sources across the United States? In 1998, the U.S. Department of Energy (DOE) compiled information for its DNAPL sites (Early, T.O., personal communication, 2004). Approximately 25–30 sites are represented by the data, yielding the information summarized in the third column of Table 2-1.

More recently, Lebron (2004) reported the results of an extensive survey sponsored by the Chief of Naval Operations in which information from 118 locations (all but one within North America) was obtained. The Navy survey focused on sites where source treatment technology applications either had been completed or were in progress. Within the contiguous 48 states, approximately two-thirds of the sites in the survey are located east of the Mississippi River (most within Atlantic coastal states) and one-third are to the west (dominated by sites in California). Relevant site information is presented in the right-most column of Table 2-1.

The details of the data collected in the two surveys are somewhat different, but it is apparent that similarities exist in the nature of contaminants and the maximum depth of contamination observed. The DOE survey results tend to include a larger proportion of bedrock sites than those of the Navy survey, but this difference may reflect the fact that the DOE results attempted to identify all DNAPL sources on DOE sites rather than just those where technology applications are in progress or have

been completed. The perceived difficulty in treating DNAPL in bedrock could account for the lower proportion of these sites in the Navy survey.

These data provide a rough estimate of the breakdown of DNAPL site conditions both at DOE facilities and the locations included in the Navy survey. Collectively, these sites are widely distributed across the United States and located within a diverse range of physiographic provinces. Both surveys, unfortunately, focus on chlorinated solvents and not on contaminants generally found at manufactured gas plants and wood treatment facilities.

What should be obvious from this discussion is the likelihood that our experiential database for assessing DNAPL source treatment effectiveness is biased and under-represents deeper and/or more challenging hydrogeologic settings.

Table 2-1. Summary of Conditions at DNAPL Sites

Condition		DOE Complex (Early, 2004)	Navy Survey (Lebron, 2004)
Contaminants	Order of prevalence	TCE > PCE > CCl_4 > Other	Cl-ethenes > Cl-ethanes > Cl-methanes > Cl-benzene
Contaminated media	Unconsolidated sediments[1]	65%	89%
	Fractured bedrock	35%	11%
Hydrogeologic zone with DNAPL source	Vadose zone	40%	Not reported
	Saturated zone	60%	
Maximum depth of DNAPL[2]	Less than 100 ft	71%	88%
	Greater than 100 ft	29%	12%

1. Composed of approximately 25% low-permeability, 25% medium-high-permeability, and 50% heterogeneous materials.
2. Forty-three of 118 sites in Navy survey did not report the maximum depth of DNAPL.

3.0 PERFORMANCE ASSESSMENT STRATEGIES

A well-designed performance assessment program for a DNAPL source zone remediation project should be capable of cost-effectively monitoring progress toward the site-specific treatment goals. Like many aspects of site cleanup, such as setting cleanup goals or selecting a remedy, a performance monitoring program must be based on a valid conceptual model of the site and specific remediation objectives or risk reduction targets. Pilot studies, discussed in Appendix C, can be useful when the response of the subsurface to treatment is not well understood and a design basis needs to be developed. Consideration should also be given to collecting decision-quality data,

optimizing the technology, protecting nearby human and environmental receptors, and hastening the overall closure of the site.

Planning a performance assessment program should begin as soon as remedial objectives for a project are set and the approach to treating the source zone is determined. The ability to measure the performance of a remediation technology should be taken into consideration during the remedy selection process when comparing technologies. Before a performance assessment program can be developed for a project, a set of overall remedial objectives and a CSM must be agreed upon by the project team. Guidance on establishing performance objectives and metrics was covered in Section 2.

In addition to technical and hydrogeologic considerations that govern the design of a performance assessment program, there are other important factors to consider when planning a performance assessment program. Too often, especially in full-scale applications, an insufficient portion of the project's resources are devoted to assessing performance. This could be the result of budgetary constraints, inadequate planning, a lack of appreciation for performance assessment, or a lack of available technical expertise. Whatever the cause, improper planning can result in a project team lacking the capability and technical know-how to design and implement a robust performance assessment program.

3.1 Defining Performance Goals and Metrics

Performance goals can be quantitative or qualitative in nature. They should at least be measurable so that progress can be monitored objectively and transition criteria developed. Each performance goal should have its own set of performance metrics or criteria by which success can be measured and performance verified.

In keeping with the overriding goal of most state and federal regulatory programs (e.g., Resource Conservation and Recovery Act [RCRA], Comprehensive Environmental Restoration and Cleanup Liability Act [CERCLA]) to protect human health and the environment, performance goals can be specified in terms of the project's effectiveness in reducing risk to human health and the environment. Generally this approach involves setting site-specific remedial action objectives (RAOs) based on definable risk reduction targets. Within this framework, DNAPL source reduction may be considered as an early or interim remedial action as part of a phased risk reduction strategy. The accompanying performance assessment is focused on verifying attainment of interim performance goals and whether the RAOs ultimately are achieved through DNAPL source reduction, either as a stand-alone strategy or in concert with other measures.

3.1.1 Building on the Conceptual Site Model

Before realistic performance goals can be set for a DNAPL project, a valid CSM must be developed which adequately defines the geosystem and the problem at hand. Ideally, by the time a source zone remedy is being considered or has been selected, both the regulators and the remedial design team will have a fairly good understanding of the site history, contaminant distribution, and exposure

potential: the foundation for a detailed CSM. By incorporating a risk management strategy, the CSM should evolve to provide a clear vision of the desired end state for the site.

3.1.2 Phase-Specific Performance Goals

Once a decision has been made to address the DNAPL source zone, three types of performance goals may present themselves, depending on the complexity of the site (Gavaskar, 2002):

Short-term goals for DNAPL source zone remediation typically involve the mitigation of immediate risks to humans or natural resources and the prevention of further expansion of the source zone. Often this goal is addressed through some form of mass removal or containment to minimize further mobilization of a mobile DNAPL mass. Short-term goals for a source zone might include

- recovering mobile DNAPL,
- mitigating the potential for vapor intrusion, and,
- preventing further migration of DNAPL.

Intermediate-term goals target the achievement of desired cleanup levels at a response boundary or, depending on the performance assessment methodology, a series of control planes. It may take a year or several years to make a determination that the target cleanup level has been achieved at a response boundary. Long-term monitoring is required to ascertain that the cleanup levels are sustainable and are not subject to a rebound in groundwater contaminant concentrations once post-treatment equilibrium is established in the aquifer.

According to EPA, a "phased approach" to site cleanup, in which long-term risk management decisions are based on information obtained during removal or interim actions, generally accelerates risk reduction (EPA, 1997). Especially at complex DNAPL sites, where complete removal of the source in one aggressive remedial effort is typically not feasible and the levels of contamination left behind may still cause groundwater to exceed final cleanup goals for the site, there is a benefit to selecting interim remediation goals and objectives to guide the cleanup (NRC, 1994). In its recent online groundwater handbook, EPA uses the term "intermediate performance goals" to describe these interim, phase-specific goals (EPA, 2002a). Intermediate performance goals might include:

- depleting the source sufficiently to allow for natural attenuation,
- reducing dissolved-phased concentrations outside the source zone,
- reducing the mass discharge rate or flux from the source,
- reducing the DNAPL source mass or volume to the extent practicable, and,
- preventing the migration of remediation fluids beyond the treatment zone.

Long-term goals, as defined here, target the achievement of compliance with regulatory criteria applicable to all contaminated media at the site (e.g., groundwater, soil, vapor). For groundwater, achievement of regulatory criteria may lead to the discontinuation of the long-term monitoring program or plume control measures. If the target (regulation-mandated or risk-based) cleanup level is not achieved or achievable in the long-term, a secondary treatment may be required. Examples

of secondary treatments may include natural attenuation, groundwater extraction, or supplemental source treatment (like enhanced bioremediation or ISCO).

In summary, the basic premise is that a CSM is developed as a framework to evaluate risk posed by the DNAPL source to nearby receptors under current and future conditions. The results of this evaluation are used to determine the need for remedial action to address potential exposure pathways and to set specific risk-based RAOs for the remediation. Performance metrics are in turn developed and measured to evaluate the success of DNAPL source reduction in meeting these objectives. In many cases, these metrics may encompass other performance measures, such as mass removal. However, risk reduction goals provide a basis for objectivity in the assessment and site closure process.

3.1.3 Performance Metrics and Criteria

Performance metrics for DNAPL source zone remediation are response-specific parameters defined in terms of (1) the overall RAOs, (2) the particular technology being employed, (3) the location of potentially exposed receptors, and (4) the expected response of the geosystem to treatment.

There are many ways to gauge progress of a source remediation project and numerous metrics that can be applied. The process of deciding which metrics are appropriate at a given site should involve discussions among the regulators, the public, and the technical team to avoid potential misunderstandings and delays when the performance data become available and decisions are made. It requires that the expected response of the geosystem to treatment be thoroughly understood. It requires that potentially exposed populations be identified and controls put in place to protect them from risk. Results of pilot studies can be valuable in assessing what parameters to monitor in full-scale implementation.

Establishing Baseline Conditions

Provisions for measuring and evaluating preremediation conditions should be included in the predesign work planning. The resulting baseline is an essential component of measuring the performance of any remedial action. Since many performance metrics are based on measuring changes in environmental conditions as treatment ensues (operational or process criteria may not include environmental media), it is very important to establish accurate baseline conditions for these parameters prior to treatment.

Determining the Response Boundary or Control Plane

Selecting appropriate points or planes at which to measure and achieve response objectives is an important element of the overall performance assessment program. In other words, "Where should success be measured?" The response boundary should not be confused with the term "point of compliance," which EPA defines as the point where media-specific standards (e.g., maximum contaminant levels [MCLs], risk-based cleanup goals) must be achieved (EPA, 2002a). The location of the response boundary or control plane should be chosen based on the baseline configuration of

the contaminant plume and on the locations where changes in the plume are anticipated, not necessarily the point at which compliance with drinking water or other regulatory standards is required.

3.2 Developing a Strategy for Completion and Optimization

A completion strategy represents consensus among the stakeholders on what conditions or criteria must be met to satisfy short-term, intermediate, and long-term goals. In the absence of a completion strategy, the source treatment phase can be unnecessarily prolonged by disputes over whether the remedy has achieved the stated goals. A completion strategy should also incorporate system optimization plans, which the project manager can use to expedite cleanup and reduce operating costs. A completion strategy is consistent with what the DOE terms an "exit strategy" and includes many of the same elements, as described in Box 3-1.

A completion or optimization strategy is sometimes mistakenly developed only after the remedial action phase has begun and signs of failure or diminishing returns begin to emerge. Development of a strategy for system shutdown and termination (or transition to another technology) should occur early in the remedial design stage. The technical team should also have a contingency plan that allows them to change course and implement a backup remedy should performance monitoring indicate that the remediation is not progressing as expected and the system is not optimized.

Box 3-1. Elements of An Exit Strategy

According to DOE guidance, an exit strategy should consist of these four elements (DOE, 2002):

response objectives: clear statements of short-term, intermediate and long-term remedial goals and objectives. These should include operational and overall remedial objectives.

performance model: a description of the expected performance or response of the site to the remedial technology over time.

performance metrics and end points: definition of the performance metrics, including the environmental parameters, a sampling and analysis plan, and how the data will be interpreted and used to monitor progress.

contingency plan: a plan that provides general response actions to address new or previously unidentified site conditions, or poor performance of the remedial system.

The completion strategy can often be effectively documented using a decision tree or flow chart that presents decision points in implementing the exit strategy in terms of "if/then/because" options. In other words, the exit strategy should specify the metrics for evaluating cleanup progress and the steps to follow depending on the system response. Examples of these may be achieving specific

concentrations in target monitoring wells within a certain time frame, percentage declines in extracted air or groundwater contaminant concentrations, cumulative DNAPL mass removed, a specified period of time during which dissolved contaminant concentrations are static or below targeted levels at the response boundary, or similar parameters. Failure to achieve predetermined metrics that measure the expected progress should trigger contingency actions to correct the course of the remedial action or to reassess the performance goals.

The exit strategy should include a specific approach to tailoring necessary monitoring frequency, location, and analyses as site conditions change. As the remediation progresses, operating conditions will become more stable and the rate of change of most parameters will decrease. Therefore, it may be cost-effective to reduce the frequency of system efficiency monitoring over time. There are exceptions to this trend of decreasing monitoring scope with duration, however. For instance, in terms of determining when to end active treatment, the monitoring needs may significantly increase as the remediation approaches the end point in order to confirm that continuing the remediation would have diminishing returns. In addition, at sites where emerging issues (i.e., based on improving knowledge about chemical toxicity, fate, migration, or technical advances that allow refined detection of DNAPLs) expand the source zone or the exposure pathways of concern, there may be a need for provisions for increased monitoring in the event unexpected conditions are encountered.

The exit strategy also should include provisions for monitoring of response of the subsurface to the cessation of any remediation activity for some period of time (i.e., rebound monitoring). There should be contingency provisions for restart of the remediation process if some undesirable response is observed (ITRC Remedial Process Optimization Team, *Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation*, in process).

Each site-specific strategy also should be compatible with the facility-wide closure strategy to ensure consistency of assumptions, objectives, and any administrative and engineered controls. Various remediation activities (e.g., extraction from specific wells, use of a particular aboveground treatment process, or in situ treatment of a source area) may be reduced or eliminated prior to site closure or attainment of long-term goals when continuation of these activities no longer contributes significantly to progress toward the remedial objectives. The decisions as to when and how to implement these interim changes should be made in a technically sound manner based on reasonable metrics (e.g., "triggers"). Site closure is discussed in Section 3.4.

3.3 Data Quality Considerations

Performance monitoring data acquisition associated with DNAPL source zone remediation can be subject to significant sampling and analytical error, like any data collection exercise involving a highly variable and heterogeneous matrix. Because decisions concerning the effectiveness of DNAPL source zone remedies can affect public health and involve considerable risk and cost, it is imperative that the uncertainty of the data, on which such decisions are made, is understood and managed. There have been several papers published that discuss the issues of managing uncertainty (Crumbling, et al., 2001) and the representativeness of environmental data (Crumbling, 2002).

In cooperation with ITRC and other federal agencies, EPA has developed a work strategy framework coined the "Triad." The Triad approach embraces scientific and process improvements in three areas: systematic project planning, dynamic work strategies, and real-time measurement technologies. The Triad work strategy approach can be used to help teams develop performance monitoring strategies that manage decision uncertainty and increase the effectiveness and quality of DNAPL source zone remedies. The ITRC has published a technical/regulatory guideline document that describes the Triad approach in detail (ITRC, 2003c).

3.3.1 Setting Data Quality Objectives

Data quality objectives (DQOs) define what you are going to measure and how critical the quality of the data to be generated is. According to EPA, "the DQO Process is a strategic planning approach based on the Scientific Method to prepare for a data collection activity. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner" (EPA, 1996b).

Use of the DQO process ensures that the environmental data (type, quantity, and quality) used in decision making will be appropriate for the intended application, resulting in decisions that are technically and scientifically sound and defensible.

For source zone sampling activities, attaining data of high analytical quality from individual points may not be as important as in a dissolved contaminant investigation where detection levels must be very low, the tolerance for error is often more critical, and decisions about whether or not to remediate more often impact public health.

3.3.2 Use of Statistics

The use of statistical analyses of the data is an important tool in evaluating performance and managing uncertainty. Data generated from remediation sites are often full of good information but sometimes too complex to easily see system trends and may require sophisticated statistical and data modeling procedures to evaluate. For instance, assessing the degree of change in contaminant levels between pre- and post-treatment may require a modeling procedure or established methods that can account for temporal and/or spatial data correlation.

It is easy for a project manager to get lost in the world of statistics and modeling, for some of the concepts and literature in the field is quite obscure. Fortunately, there are numerous tools and guidance available to help. Appendix D contains a discussion of statistical approaches applicable to designing a performance assessment program.

3.3.3 Systematic Planning

It is critical that a systematic planning process be used to clearly layout monitoring objectives and build team consensus on how to manage the uncertainty associated with assessing performance. A

systematic project planning process should always be utilized to define site-specific performance assessment objectives and the associated sampling and analytical strategy. The team used to develop the performance objectives must be knowledgeable not only about the characteristics of the site and the remedial objectives but also about the technology being employed. Outputs of the systematic planning process should include

- consensus on the CSM and desired outcome or goal for the performance assessment,
- a preliminary performance expectation from existing information,
- a list of the various regulatory, scientific and engineering decisions that must be made in order to achieve the desired outcome,
- a list of the unknowns that stand in the way of making those decisions,
- strategies to eliminate or "manage around" those unknowns,
- explicit control over the greatest sources of uncertainty in performance data (i.e., sampling-related variables such as sample volume, sampling frequency, whether grab samples or time-integrated samples are used, etc.), and,
- an atmosphere of trust, open communication, and cooperation between parties working toward a protective, yet cost-effective resolution of the "problem".

An effective systematic planning process will result in clear communication on the performance metrics and an understanding of how different project stakeholders will be evaluating success. The systematic planning process is the foundation that allows the team to effectively modify the performance monitoring strategy as treatment is taking place as described in the Fort Lewis example below.

3.3.4 Dynamic Work Strategies and Real-Time Measurement Technologies

Work planning documents written in a dynamic or flexible mode guide the course of the project to adapt in real time as new information becomes available, allowing preliminary CSMs to be tested and evolved to maturity (i.e., sufficiently complete to support the desired level of decision confidence) in real time, saving significant time and money while supporting better resolution of uncertainties. A valuable aspect of dynamic work strategies, effective process quality control (QC) in real time, makes QC procedures more relevant and powerful than what is possible with work plans written in a static mode. Dynamic work strategies can be used for developing performance monitoring approaches that enable the technical team to decide on the location and frequency of monitoring based on meeting clearly defined project monitoring objectives.

Real-time measurement technologies make dynamic work strategies possible by gathering, interpreting, and sharing data fast enough to support real-time decisions. The range of technologies supporting real-time measurements includes field analytical instrumentation, in situ sensing systems, geophysics, on-site gas chromatography/mass spectrometry (GC/MS), rapid turnaround from traditional laboratories, and computer systems that assist project planning, and store, display, map, manipulate, and share data.

Box 3-2 describes how the Triad work strategy is being employed at the Fort Lewis Logistics Center in Washington State.

3.3.5 Benefits of Utilizing Triad Approach for DNAPL Performance Assessment

Triad's emphasis on systematic planning to manage the full range of uncertainties (i.e., to clarify project goals and concerns through open discussion and documentation) creates an atmosphere conducive to trust and cooperative negotiations among all involved parties. If the technical issues are out in the open and stakeholders are assured that resource limitations and scientific uncertainties are being fairly balanced in relation with their concerns, there is a stronger foundation for negotiating parties to communicate over the more thorny and value-laden social issues.

Box 3-2. Use of Triad Strategy for Monitoring Performance at the Fort Lewis Logistics Center Superfund Site

The Fort Lewis Logistics Center Superfund site is using a Triad work strategy for performance monitoring associated with an in situ electrical resistance heating NAPL source remediation project. An on-site GC/MS is being used to produce air and water data within 24 hours of sample collection, and project data are posted to a Web site. The on-site GC/MS allows for analysis of samples covering a large concentration range and is being used for compliance (i.e., stack emission and reinjection criteria), operational, and performance monitoring. Specific benefits of utilizing the Triad include the following:

Better control. Hydraulic, vapor, and thermal control of the treated region are maintained more effectively by interpreting groundwater concentration, temperature, and hydraulic gradient data "on-the-fly" and making adjustments in extraction and reinjection rates dynamically.

More efficient energy distribution. Dynamic sampling has enabled the team to alter system monitoring strategies to collect data supporting a decision to redirect energy input from zones that have met contract-defined temperatures and show diminishing returns of chlorinated solvent mass recovery to zones requiring additional energy input.

Quicker system shakedown. During system startup, dynamic sampling allowed rapid fine-tuning of the treatment system to ensure mass destruction was optimized and contaminant discharge criteria were being met.

Minimal contaminant migration. If temperature data indicate that heated water is leaving the treatment area, sampling frequency of the effected exterior monitoring wells is increased to ensure that contaminants are not also being lost from the site.

Other specific benefits include the following:

- flexibility in sample collection location and frequency allows for optimization of above- and belowground remedial system operations,

- uncertainty in the data being used for performance and compliance monitoring can be lowered,
- analytical approach can be flexible to allow for detection of secondary contaminants of concern,
- data reporting requirements and QC protocols can be developed to specifically meet the needs of the data use,
- systematic planning encourages the team to determine whether analyte specific data is really required or whether a less expensive surrogate contaminant method like total organic carbon (TOC) could be used,
- having the performance data available in a timely fashion allows contract requirements to be assessed while in the field and corrective actions implemented rapidly, if required, and,
- use of Triad supports the concepts of adaptive DNAPL site management (discussed in Section 3.4.2).

3.4 Keeping an Eye Toward Site Closure

The closure process is part of the life cycle of DNAPL site cleanup, which may include discovery, characterization, remedy selection, remedial action construction, operation and maintenance, and long-term monitoring.

3.4.1 What Does Site Closure Mean?

Site closure is the process of obtaining release from responsibilities under the operable regulatory driver. The operable regulations may include CERCLA, RCRA Corrective Action, state Superfund, brownfield or voluntary cleanup programs, and the Leaking Underground Storage Tank (LUST) program, to name a few.

Elements of each program may vary according to specific state and federal regulations but generally have a similar path that leads to site closure provided applicable regulatory conditions have been met. Regulatory condition elements may include setting risk-based cleanup goals, addressing source removal, post-remedial monitoring, and the determination from data collected that remedial goals have been met or that additional remediation is warranted.

3.4.2 Making Decisions about Continued Operation

The decision-making process involved in selecting the appropriate remedy or chain of remedies for a contaminated site is driven by a mix of technical, regulatory, and economic factors that is determined on a site-specific basis. These same factors must be reconsidered after the remedial system is up and running, and a decision must be made whether to cease treatment or transition to another technology or remedial approach. Objective measures of remedial performance that assess both the efficiency and effectiveness of the remedy are crucial at these transition points.

Closure with Long-Term Management

There are two possible end states for a DNAPL site: the regulatory agency issues an NFA letter or some equivalent certification of closure, or the site is placed in a long-term management program. If the groundwater impacted by a site is restored to its highest beneficial use, the site can be closed in an absolute sense. Ideally, if a source reduction or depletion action meets the final cleanup goals, the site closure process may go through a period of long-term monitoring followed by decommissioning of the sampling well locations. However, where complete groundwater restoration is not achieved following several attempts at remediation, or if waste or hazardous constituents remain on site after completing the action, long-term management requirements will likely be necessary. This is the likely scenario for sites which have completed a remedial action but where concentrations have reached asymptotic levels or residual DNAPL remains in a source area and there is no unacceptable risk.

Adaptive Site Management

Adaptive site management refers to a comprehensive, flexible approach, outlined in a recent National Research Council report (NRC, 2003), for dealing with hydrogeologically complex sites that are difficult to remediate. The goals of adaptive site management are to facilitate decision making over the long-term when the effectiveness of the remedy reaches an asymptote prior to reaching cleanup goals.

Decision making at these complex sites, which includes many DNAPL sites, does not fit easily into the linear, "Superfund-style" model where a site is characterized, a remedy is selected and implemented, cleanup goals are attained and verified, and the site is closed. A more iterative and adaptive approach to DNAPL source zone remediation may be more appropriate—one that recognizes that the performance of most in situ technologies, particularly in complex situations, is not known with a great degree of certainty and one that encourages adaptation as the remedial action progresses and new information is processed. This broad systems approach to site remediation is discussed in more detail in the NRC report *Environmental Cleanup at Navy Facilities: Adaptive Site Management* (NRC, 2003).

4.0 QUANTIFYING PERFORMANCE WITH FIELD METRICS

In most DNAPL remedial situations, the same difficulties and technological limitations that are faced when using conventional site investigation techniques to characterize a DNAPL source resurface when verifying a technology's performance or effectiveness. ITRC and others have previously discussed the difficulties in characterizing the subsurface distribution of DNAPL (Pankow and Cherry, 1996; ITRC, 2003a). For this reason, it is recommended that a "converging lines of evidence" approach be used to evaluate performance, combining several techniques.

"No single metric by itself is likely to be adequate for assessing the performance and potential benefits of source depletion technologies; thus, conjunctive use of multiple metrics should be used to evaluate performance." (Kavanaugh, et al., 2003)

This section describes various performance metrics (or measures of success) that have been used or considered to assess the effectiveness of specific in situ DNAPL source zone technologies. Each involves monitoring changes in some environmental parameter or condition in an attempt to demonstrate a reduction in contaminant mass, concentration, mobility, or toxicity. Box 4-1 highlights some of the findings from a recent survey of DNAPL projects by LeBron (2004) that provide insight into the metrics being employed in the field.

Box 4-1. Summary of Performance Metrics From Recent Survey

In 2003, the Chief of Naval Operations sponsored a project to document information about DNAPL site conditions, source treatment, and performance assessment for locations throughout the United States (Lebron, 2004). The survey collected data from 118 different treatment locations. Of these treatment projects, Lebron compiled performance assessment information on 53 DNAPL source zone technology applications that have been completed and provided a summary of the results.

In general, three types of quantifiable performance metrics were evaluated in this survey that can provide some insights into how well treatment worked: mass removal, decreases in mass flux, and observation of contaminant rebound.

Of the 20 locations that measured mass removal, more than half reported more than 90% DNAPL mass reduction; nearly 20% of these 20 locations claim to have removed 100% of the source DNAPL. The methodology used by the sites to obtain these estimates is not provided by the survey.

Approximately half of the locations in the survey where treatment applications had occurred evaluated reduction of mass flux as a measure of source treatment performance. Almost 57% of the sites using mass flux measurements report in excess of 80% reduction as a result of source treatment. In contrast, 19% of the users of this metric report only a small reduction in flux (i.e., less than 20%).

One-third of the 21 locations making measurements of post-treatment changes in contaminant rebound in groundwater observed some rebound; two-thirds did not. At present, it is not possible to determine what threshold was used by respondents to the survey used to make this determination, nor is the magnitude of the rebound known. Perhaps a follow-up survey will yield answers to these questions.

Table 4-1 provides a summary of the various methods described in this section and their relative applicability.

Table 4-1. Comparisons of Approaches for Evaluating Performance

Applicable Remedial Metric	Performance Assessment Method	Measured Parameter	Derived Parameter	Relative Complexity	Relative Accuracy	Section Reference
Adsorbed-phase reduction	Soil coring	Soil concentration	Sorbed concentration	Low to intermediate: operational metric; may require statistical analysis	Intermediate: depends on statistical use of data	4.2.1
Dissolved-phase reduction	Groundwater sampling	Aqueous concentration	• Plume extent • Change in DNAPL composition	Low: operational and remedial metric	Intermediate to high	4.2.2
Source mass extracted	Effluent sampling	Volumes and conc. of extracted fluids	Contaminant mass removed	Low: operational and remedial metric	High: depends on frequency of monitoring	4.3.1
Source mass destroyed	Groundwater sampling	Concentration of breakdown products (e.g.,chloride)	Mass of DNAPL destroyed in situ	Intermediate: intensive sampling and stoichiometric analysis required	Low: difficult to attain mass balance (e.g., other sources of chloride)	4.3.2
Source mass remaining	Soil coring	Soil concentration and visual observation	• DNAPL distribution • Sorbed mass	Intermediate: intensive sampling with geostatistical analysis required	Low to intermediate: increases with increasing density of point measurements	4.3.3
	Tracer tests	Concentration of tracers	• NAPL volume • Saturation	High: mathematical analysis and pumping / injection program required	Intermediate to high: potential limitations based on DNAPL architecture	
	Groundwater sampling	Aqueous concentration	Aqueous concentration	Intermediate: intensive sampling with numerical modeling required	Low: correlation with source mass reduction is uncertain	

Applicable Remedial Metric	Performance Assessment Method	Measured Parameter	Derived Parameter	Relative Complexity	Relative Accuracy	Section Reference
Mobility reduction	Soil coring	Soil concentration and visual observation	NAPL presence and saturation	Low to intermediate	Low: correlation with reduced mobility uncertain	4.4.1
	Product gauging	NAPL thickness	NAPL thickness	Low	Low: correlation with reduced mobility uncertain	
Toxicity reduction	Soil coring	Adsorbed concentration	DNAPL composition			4.4.2
	Groundwater sampling	Aqueous concentration	Concentrations of toxic parameters			
Mass flux/mass discharge reduction	Well transect sampling	• Aqueous conc. • Hyd. conductivity • Hyd. gradient	• Darcy flux • Mass flux • Mass discharge	Intermediate: intensive sampling with close well spacing preferred	Intermediate: increases with increasing density of point measurements	4.4.3
	Flux meter transects	• Mass of resident tracer retained on sorbent • Mass of contaminant retained on sorbent	• Darcy flux • Mass flux • Mass discharge	Intermediate: intensive sampling with close well spacing preferred	Untested in U.S. regulatory environment	
	Integral pumping tests	Concentrations-time series sampling from extraction well	• Mass discharge • Average plume conc.	High: numerical analysis required; no commercial software; pumping program required	Untested in U.S. regulatory environment	

4.1 Categories of Performance Metrics

There are three broad categories of performance metrics that capture the principal types of evaluation tools most frequently being used to measure success of DNAPL source treatment:

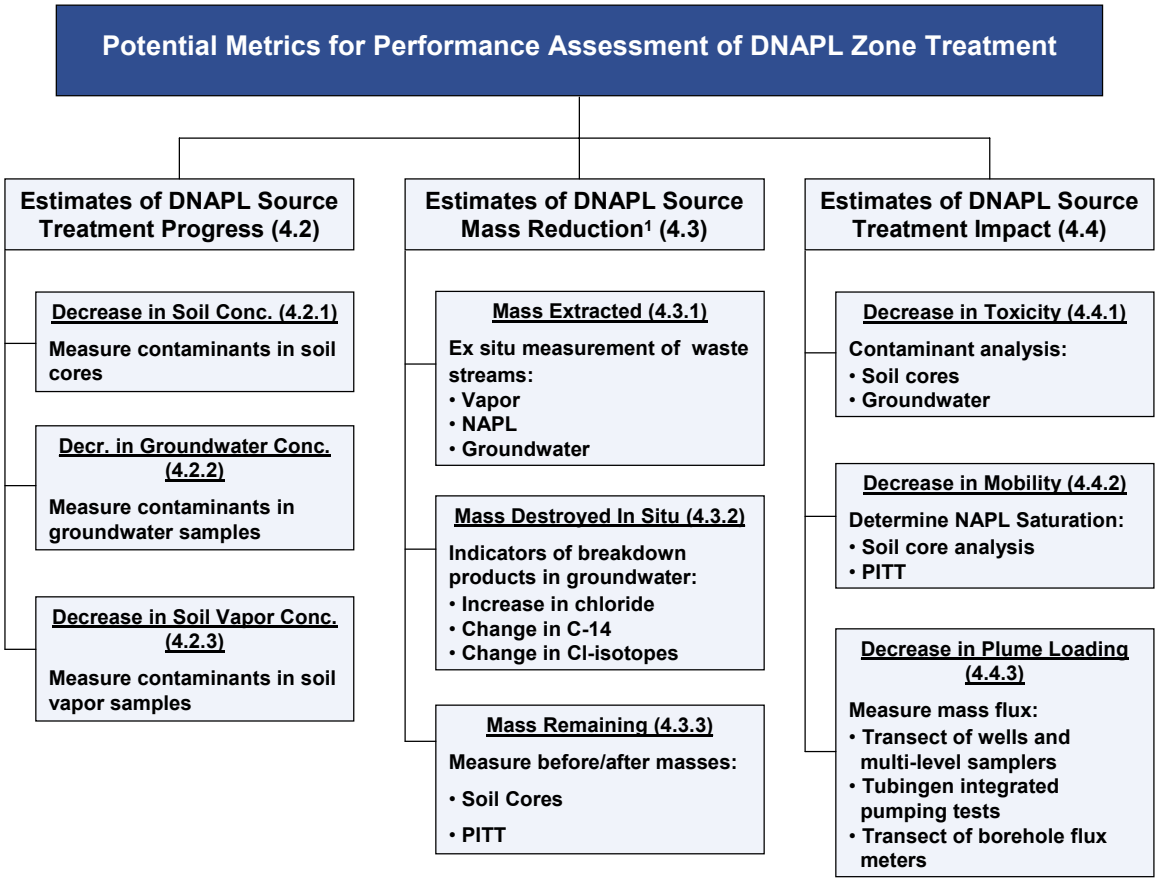
- qualitative estimates of the degree of progress towards source treatment,
- quantitative estimates of DNAPL source mass reduction, and,
- quantitative estimates of the impact of source treatment on factors such as toxicity, mobility, and plume strength.

Figure 4-1 illustrates these three classes of metrics and lists specific evaluation methods encompassed by them. Each evaluation tool is cross-referenced to a specific part of this section where more detailed information is provided. The metrics presented in Figure 4-1 are applicable to DNAPL sources in the vadose and saturated zones where soils and unconsolidated media are involved. Although the metrics could be modified for bedrock conditions, we have only limited experience in treating DNAPL sources in consolidated media and in designing appropriate performance assessment strategies. For these reasons, the performance measures outlined in Figure 4-1 are most applicable to DNAPLs in unconsolidated media.

It is important to recognize that these metrics are neither equivalent to nor interchangeable with one another. They address different types of performance measures and range from qualitative indicators of treatment progress to quantitative measures of specific impacts. Furthermore, there is little consensus within the technical community as to which metric or combination of metrics is most appropriate for evaluating the effectiveness of DNAPL source treatment. Many factors are involved in this decision. This section is designed to raise awareness of the spectrum of possible performance metrics and the primary strengths and limitations of each.

The qualitative tools, such as general decreases in soil or groundwater concentrations following treatment, typically give only an indication that progress is being made toward source cleanup without any objective way of quantifying the degree of cleanup or the long-term implications of the changes. In contrast, measures of source mass reduction and mass flux yield quantitative estimates of impacts of source treatment that frequently are required for remediation projects.

There are several methods by which DNAPL source mass can be determined, although currently it is not possible to translate the percentage of mass removed into an estimate of projected impact on plume concentrations. Mass flux measurements ideally provide insights to how source treatment is associated with decreased source loading to a plume as a function of the amount of DNAPL mass removed. Such measurements provide a snapshot of mass flux, but not necessarily an indication of long-term improvements.



1. Initial DNAPL mass estimates that rely on historical records of the amount of solvent spilled or disposed tend to be grossly in error for many sites. This information, while useful to obtain, should not be used for making estimates of DNAPL mass reduction.

Figure 4-1. Categories of Performance Metrics for DNAPL Zone Treatment

All of the quantitative metrics have associated statistical uncertainties that cannot be avoided. Steps can be taken to reduce uncertainties (e.g., more closely space soil cores or a denser network of monitoring facilities for mass flux measurements), but these steps can lead to significant increases in performance assessment costs. Performance assessment plans should be periodically reviewed and updated, if necessary, by all parties to evaluate whether new technology can improve the timeliness, cost-effectiveness, and accuracy of the assessment.

In the final analysis, four factors are necessary to guide site owners, regulators, and stakeholders in designing a performance assessment plan: (1) choice of technology for the remediation, (2) clear understanding of the CSM and technical and cost constraints imposed by site conditions on

monitoring, (3) a realistic set of performance objectives consistent with the CMS, and (4) recognition of the limitations of each of the performance assessment metrics to be applied.

4.2 Estimates of Source Treatment Progress

A remediation goal often stated in decision documents is to attain some numeric soil cleanup level or groundwater concentration at a point of compliance. The view that treatment of a DNAPL source zone was successful is often linked to a decrease in the average concentration of a contaminant in soil, groundwater, or vapor. Indeed, progress monitoring at DNAPL projects usually involves some form of sample collection and chemical analysis to evaluate changes in soil or groundwater concentration over time.

As discussed in Section 1.3.1, preventing further migration or possible exposure during remediation efforts is a primary concern expressed by regulators and the public. This concern can be addressed through monitoring groundwater or vapor contaminant concentrations at the perimeter of the treatment zone to verify that no unacceptable exposure to down-gradient receptors is occurring. Preventing contaminant migration through hydraulic control of the treatment zone is therefore an important, but sometimes overlooked, objective.

4.2.1 Decrease in Soil Concentration

Applicability and Use

Data collection methods for soil sample collection, handling, and analysis are widely known and generally accepted by regulators. The use of soil sampling for confirmation of cleanup must consider the heterogeneous distribution of contamination at a site and the uncertainties associated with sampling soils for VOCs, for instance. Soil sampling to confirm cleanup should be based on a statistical sampling design to quantify the certainty of achieving goals. Sampling design and protocols are discussed in guidance produced by the U.S. Army Corps of Engineers (USACE, 2002).

Pre- and post-treatment soil data can be analyzed in numerous ways, depending on the remediation objective and statistical approach. Discrete soil data points can be compared directly to numerical soil cleanup criteria established for the specific site or can be averaged geospatially to evaluate overall decreases in contaminant concentration to gauge performance. As discussed in Section 4.3, soil concentration data are also commonly used to derive estimates of in situ contaminant mass in order to compare the total mass *before* treatment to the mass remaining *after* treatment.

Selecting Sample Size

We can examine the difficulty in detecting a target (i.e., the DNAPL) within a site using simplified probability theory. If the DNAPL is represented by a target area A_T, within a site of area A_S, then the probability of random detection (P_D) using N attempts is found by:

$$P_D = 1 - (1 - A_T/A_S)^N$$

Using some reasonable values for both the target area and site area, we can see that our probability of finding the DNAPL is very low. It increases, of course, if more than one location is sampled. Table 4-2 shows the number of samples required to find the DNAPL for different ratios of A_T to A_S and probabilities of detection. The example illustrates that a large number of samples is required to find a target, such as a source zone, using randomly chosen locations. Better results can be obtained by selecting sampling locations based on an adequate conceptual site model which accounts for knowledge of the site's history, locations of buried utility lines and conduits, and the subsurface geology.

Table 4-2. Number of Sample Points Required to Detect Target Area

Probability of detection	Number of random samples required where:		
	$A_S/A_T = 10$	$A_S/A_T = 100$	$A_S/A_T = 1000$
98%	38	390	3,950
90%	22	230	2,400
75%	14	138	1,390
50%	7	70	700
30%	4	36	360

Source: Daniel, 1992.

Soil Sample Collection Methods

Soil sampling is most commonly performed while drilling although direct-push technologies are becoming more widely used for soil sample collection. Drilling in source zones should proceed cautiously inward from outside of the suspected source area and should be conducted with the proper precautions for protecting the integrity of capillary barriers. When drilling within the DNAPL source zone, extreme care should be taken to ensure that conduits for vertical migration are not created. If the sampling is not conducted properly, the DNAPL and/or the dissolved plume could be spread. Abandoned soil borings must be properly sealed to mitigate the potential for vertical migration. Surface casing may be used to seal off an upper contaminated zone from uncontaminated lower zones in a multilayered source zone.

Selection of the appropriate sampling devices to recover soil samples from a DNAPL zone depends mainly on the type of soil to be sampled. The objective is to choose a sampler that will maximize the recovery of soil and retain as much of the fluid in the pore spaces as possible. When sampling soil containing chlorinated solvent VOCs, for example, the manner in which a recovered core is handled and sampled can impact the extent of volatile losses. Loss of volatile compounds is not a concern when sampling semivolatile VOCs (SVOCs) like semivolatile creosote and coal tar DNAPLs. The rapid loss of volatile DNAPL components (up to three orders of magnitude) during

standard sample handling and preparation has been well documented and has given rise to the practice of performing solvent extractions in the field (Hewitt, et al., 1995). Quickly placing a portion of the soil from the sampler directly into a solvent (usually methanol) at the logging table preserves the volatile compounds in the resulting sample by lowering their partial vapor pressures. Field preservation of soil samples with solvent is highly recommended when the objective is to obtain meaningful analytical results from a DNAPL zone.

Although there are a wide variety of drilling methods, many are not appropriate for DNAPL zones, especially if the ultimate objective is to quantify NAPL saturations. For many DNAPL sites in unconsolidated sediments, drilling with a hollow-stem auger (HSA) is the preferred method, however direct-push technologies are also appropriate and may provide less-disturbed samples for VOC analyses. Direct-push methods for sampling soil are discussed in greater detail on EPA's Field Analytics Technologies Web site (http://fate.clu-in.org/direct_push/soilandsoilgassamp.asp). Segments of the borehole can be cased off to protect uncontaminated zones by driving larger-diameter surface casing to the necessary depth, and the auger itself acts as a protective casing for the sampler installed just slightly ahead of the auger bit. Also, a variety of efficient sampling systems (e.g., wireline) and sampling tools are available for use with HSA. Wash rigs and mud rotary methods may displace significant amounts of DNAPL ahead of the bit due to the delivery and recirculation of drilling fluids through the stem. Similarly, the use of air to evacuate cuttings from around the drill bit can volatilize DNAPL components in a manner equivalent to soil vapor extraction. Rotosonic drilling is an excellent method for continuous sampling and provides a large volume of core in a manner that minimizes the risk of compromising the integrity of capillary barriers. Rotosonic drilling, also known as "vibratory drilling," uses an oscillating drill head or core barrel to quickly advance through the subsurface. Drill cuttings are limited and are forced into the walls of the borehole.

Measuring Soil Contaminant Concentration

The concentration of organic compounds in soil samples can be quantified in a laboratory using a standard laboratory method (e.g., EPA Method 8260 for volatile organics) or estimated using immunoassay test kits or direct reading instruments such as the membrane interface probe (MIP) attached to various down-hole tools. Use of an on-site laboratory in conjunction with direct-push technologies should be considered when possible to provide real-time chemical analysis and improve the effectiveness of the investigation.

In addition to the total concentration of chemical constituents, DNAPL saturation estimates require that soil samples be collected for determination of f_{oc} and bulk density. As described in Section 2.1.2, the fraction of organic carbon in soil affects contaminant and surfactant sorption in the subsurface. Samples for f_{oc} should be collected from areas with little or no contamination. The soil samples should be measured for TOC. The TOC results are then converted to f_{oc} by dividing the measured TOC by the mass fraction of dry soil.

Limitations

Potential problems and challenges with using soil concentration data to verify performance include (1) the need for large numbers of samples to address site heterogeneities and temporal and spatial variability, (2) the potential for large measurement errors with some chemicals in some media (e.g., VOCs in soil), (3) the potential errors in interpolation methods used to estimate contaminant levels at locations without measurements, and (4) the fact that concentration changes may not be due to in situ treatment (e.g., changes could be due to redistribution of mass during in situ flushing or thermal technologies).

Another aspect of the difficulty of detecting DNAPLs is that soil sampling is inherently destructive. Once a sample is obtained from a location, subsequent sampling must be made in a new location that may or may not contain DNAPL. If the goal is to assess performance of a remediation technology, a direct comparison of conditions before and after treatment cannot be made.

Furthermore, soil collection methods used in the field sometimes yield lower soil concentrations because samples are sometimes combined with regard to the vertical location. Field collection methods often lead to soil from several-foot intervals being combined either intentionally or accidentally, so that the chemical analysis of the soil samples truly represents a vertically averaged and perhaps lower value.

In the saturated zone, when an upper concentration limit or threshold value is used to distinguish between DNAPL and dissolved-phase contaminant, lower soil concentrations can be misrepresented as dissolved-phase contaminant and not DNAPL. Conversely, a higher soil concentration can be misrepresented as a DNAPL source zone instead of a dissolved phase. Establishing a threshold value can be very complicated since the computation must consider the chemical properties of the DNAPL constituents, the properties of the soil, and other site-specific data, which is hard to obtain in many cases. In the absence of analytical problems, the primary reason for false positives would be inadequate information about DNAPL composition, soil organic carbon content, or the partitioning behavior of the DNAPL constituents with the soil.

Losses of DNAPL during soil collection can also significantly reduce the concentration and yield lower than actual soil concentrations. Losses can occur simply from volatilization during the sampling event. Verschueren (1983) states that half the TCE will evaporate from a 1-mg/L aqueous solution at 25°C in 19–24 minutes. Clearly, a significant amount of a DNAPL can be lost during or after the sampling if care is not exercised to prevent volatilization. Sample handling and preservation techniques recommended by EPA to minimize loss of VOCs from soil samples include on-site methanol or water preservation and the use of a headspace-free, gas-tight sampling device (Encore™ or SoilCore™).

Another consideration with respect to the soil collection method is whether the volume of soil is adequate to determine whether any DNAPL is present. Based on calculations of the "representative elementary volume" (the smallest sample volume from which derived data can be extrapolated to represent the remaining untested soils at the site) for a complex, highly heterogeneous DNAPL site,

a soil sample volume of up to 0.3 ft^3 (2.2 gal) may be required to determine the presence of DNAPL in soil. Since a typical soil sample size is on the order of 10 mg with a volume of approximately 0.003 ft^3, it is quite possible to miss DNAPL simply because the volume collected is inadequate.

For a variety of reasons, soil concentration data can easily be misinterpreted with regard to the presence or absence of DNAPL. These problems and challenges can be overcome, at least in part, by careful and integrated use of modern sampling and analyses methods, field analytical methods, innovative sensor technologies, and geostatistical modeling methods (Siegrist and Satijn, 2002). Triad work strategies can be used to assist teams with developing strategies to manage the uncertainty associated with complex DNAPL characterization efforts (ITRC, 2004).

4.2.2 Decrease in Dissolved Concentration

Techniques for monitoring groundwater concentrations are well known and will not be described in detail here. This section describes several enhancements to conventional monitoring schemes that may be applicable to DNAPL sites.

Applicability and Use

Improving groundwater quality at a DNAPL site is a commonly stated response objective. A common approach to measuring success at these sites, therefore, has been to monitor improvements in groundwater quality. This process usually involves installing a network of monitoring wells within or down-gradient from the DNAPL source area to detect changes in contaminant concentrations during or following treatment. Although theoretically this approach more closely represents the actual exposure to groundwater contamination (i.e., direct ingestion of groundwater containing VOCs) than comparisons of DNAPL mass before and after treatment, there are serious limits to relying on dissolved concentration data collected from discrete wells.

Purging Considerations

The purpose of purging is to ensure that water samples collected from a monitoring well are representative of in situ groundwater conditions that exist in the portion of the aquifer being sampled. Water in the screened portion and filter pack of a conventional well is generally in a constant state of flux as groundwater passes through the well. However, water in the well bore above the screened section is relatively isolated and becomes stagnant. Because stagnant water is subject to different physiochemical conditions than the surrounding aquifer, it is important that specific purging guidelines and techniques be followed to avoid collecting a sample biased by stagnant water. In addition, when considering changing the purging methods, it is important to evaluate if a change in analytical values results because of changing purging methods by performing a comparison of results from each method.

A nonrepresentative water sample can also result from overpumping the well. Stratification of the compounds may occur, or denser compounds may sink to the lower portions of the aquifer.

Excessive pumping during the purging of a monitoring well can dilute or increase the contaminant concentrations from what is representative of the sampling point (EPA, 2002c).

There are a number of different devices available to purge and sample a well. The device used should not change the geochemistry or physical properties of the sample. It also should not increase turbidity. Minimizing agitation of the water column helps prevent increases in turbidity, volatilization, and dissolved oxygen in the water. For these reasons, low-flow submersible or positive-displacement pumps that can control flow rates are recommended for purging and sampling. The low-flow purge-and-sample method results in a more rapid stabilization of turbidity and other field-measured parameters (e.g., pH, temperature, dissolved oxygen, oxidation-reduction potential [ORP], specific conductivity, and turbidity) and a more representative sample of conditions in the formation. Purging continues in a well until purge criteria are reached (commonly either stabilization of purge parameters or a set number of well volumes). Another advantage to a low-flow purge-and-sample technique is that the amount of purge water removed from the well is minimized, which means less water may need to be containerized, treated, stored, and disposed.

Other considerations during purging are placement of pump intake relative to the depth of water in the well and the well screen interval. Low-permeability formations that cannot support a pump will require alternative means of sampling, such as bailers. As stated above, deciding the appropriate purging technique must be based on site-specific conditions and objectives. Techniques for purging are described in greater detail in numerous technical journals and EPA guidance documents, such as *Groundwater Sampling Guidelines for Superfund and RCRA Project Managers* (EPA, 2002c).

Monitoring Well Network Design and Installation

Performance monitoring wells should be located up-gradient, within, and down-gradient of the source reduction zone and aligned parallel to the direction of groundwater flow. These wells are intended to monitor changing groundwater chemistry over time along the groundwater flow path as an estimation of DNAPL source reduction progress. Cross-gradient well locations may also be needed to define the lateral extent of treatment and provide for greater accuracy in mapping hydraulic gradients.

Selecting the depth at which to set the well intake and the proper length of the screened interval are important considerations when designing and constructing a well network. This is a challenging aspect of monitoring well design and placement; one which requires a detailed understanding of subsurface conditions (as embodied in the CSM) and an appreciation for the DQOs and specific monitoring needs of the project. Generally, screen lengths should not exceed 10 ft. Highly heterogeneous formations may warrant shorter well screens to allow sampling of discrete portions of the formation that can serve as contaminant migration pathways. Even in fairly simple geologies, the use of shorter well screens may be necessary to detect contaminants concentrated at particular depths because of its physical/chemical properties or site-specific hydrogeology. A long well screen can permit excessive amounts of uncontaminated formation water to dilute the contaminated groundwater entering the well. The use of shorter well screens reduces excessive dilution and, when

properly placed (at depths of predicted preferential flow), are more effective in monitoring discrete portions of the aquifer and the impacts of source mass depletion (EPA, 1992).

In the event of a flat groundwater gradient, it should be recognized that dissolved-phase DNAPL constituents can spread laterally in more than one direction. Greater density of monitoring may be needed to adequately define impacts and ensure protection of sensitive areas. In fact, it may be prudent to include monitoring immediately after shutdown of source treatment operations as well as extend post-treatment monitoring after shutdown to account for changing hydrogeologic patterns.

In relatively large DNAPL source areas, it may be difficult to identify an optimal location for well placement. An absence of hydraulic isolation may preclude measuring any rebound in the treated demonstration area and complicates any assessment of the technology because the mass moving into or out of the treatment area cannot be known. Numerical simulation to locate wells should be considered when there is a question about well placement.

Groundwater monitoring wells can be installed using standard drilling methods (e.g., HSA) or, where appropriate, direct-push technologies. Direct-push methods for sampling groundwater are discussed in greater detail on EPA's Field Analytics Technologies Web site (http://fate.clu-in.org/direct_push/dpp.asp). Direct-push well technology is also the subject of a guidance document being produced by the ITRC's Sampling, Characterization, and Monitoring (SCM) Team.

Multilevel Sampling

One way to enhance the conventional use of dissolved concentrations as a performance metric is to incorporate multilevel sampling into a monitoring program. Conventional groundwater monitoring is conducted using dedicated equipment to collect samples that represent an average measure from each well. In contrast, multilevel sampling systems are designed to collect depth-discrete samples over a single vertical profile of the subsurface.

A wide variety of systems and methods have been developed for this purpose, with complexity and expense of these systems generally increasing with depth. Examples of simple and inexpensive methods and systems that may be appropriate for monitoring sites with relatively shallow groundwater include direct-push technologies, closely spaced well clusters, and piezometer nests. Examples of multilevel systems that may be appropriate for assessing more complex sites with deeper groundwater contamination include the Waterloo Multilevel System™ (www.solinst.com), Continuous Multichannel Tubing™ (www.solinst.com), Westbay MP® (www.westbay.com), and Water FLUTe™ (www.flut.com) systems. In cases where wells are installed in an area where it is known with certainty that no DNAPL exists, collecting a profile of the groundwater quality with strategic placement of bailers, submersible pumps, or diffusion samplers if appropriate may provide very useful information about the groundwater quality profile that may help describe DNAPL distribution elsewhere in the aquifer.

It is important to stress that multilevel wells or wells with long screens should not be installed in areas where DNAPLs are expected as these wells can act as conduits for DNAPLs to migrate to lower portions of the aquifer. Although multilevel samplers placed within a single borehole may be appropriate for dissolved-phase measurements, it should be noted that long well screens can allow dissolved-phase contamination to migrate up or down in the aquifer, depending on the hydraulic head distribution. In order to obtain depth-specific information on DNAPL distribution within an area undergoing treatment, it may be necessary to construct a multilevel cluster of independent wells in close proximity.

Data generated by multilevel sampling systems can provide insight into the three-dimensional groundwater plume configuration before, during, and after DNAPL remediation. Particularly for heterogeneous formations where layering is suspected, the data can be used to assess the effects of source remediation on discrete vertical horizons of the dissolved-phase plume. Multilevel sampling itself is not the same as directly measuring mass flux or plume loading per se (described in Section 4.4.3); however, if the monitoring wells are properly distributed cross-gradient along the control plane (lateral extent), then data generated by a network of multilevel samplers can be used to estimate contaminant mass flux for different depths along the control plane, assuming groundwater flux is also known.

Use of Passive Diffusion Bag Samplers

Passive diffusion bag (PDB) sampling is an accurate and cost-effective alternative to standard (or low-flow) purge-and-sample techniques for collecting dissolved VOC data at monitoring wells (ITRC, 2004). The PDB sampler is a low-density polyethylene bag or diffusive-membrane capsule filled with deionized water that is sealed and mounted in a suspension device and lowered to a specified depth in a monitoring well to passively collect groundwater samples. PDB samplers rely on the free movement of groundwater from the aquifer or water-bearing zone through the well screen.

PDB samplers are relatively inexpensive and reduce or eliminate the amount of purge water associated with sampling. The samplers are easy to use and require a minimal amount of field equipment. Multiple PDB samplers can be distributed vertically within the screened interval to help locate the zone of highest concentration in the well. The membrane prevents sediments from entering the bag, so there is no interference from turbidity.

Limitations to the use of PDBs at DNAPL sites include the following:

- PDB samplers are not currently recommended for use in low-permeability formations. As a general rule, diffusion sampling should not be used in water-bearing zones with a hydraulic conductivity of less than 1×10^{-6} cm/s.

- PDB samplers integrate concentrations over time, which may be a limitation if the goal of the sampling event is to collect a representative sample at a point in time. This

characteristic may be a limitation if VOC concentrations in the aquifer are known to change over time.

- PDB samplers are useful with only a certain suite of organic compounds.

More information about PDBs can be obtained at the ITRC Diffusion Sampler Information Center Web site, which is linked from the ITRC main page (or go to diffusionsampler.itrcweb.org).

Limitations

Potential problems and challenges with using dissolved contaminant concentration as a performance metric include the high variability, both temporally and spatially, in groundwater concentrations and the fact that these changes may not be due to in situ treatment. For example, changes in dissolved concentrations could be due to rate-limited processes and dilution effects during in situ flushing or extraction technologies. These problems and challenges can be overcome, at least in part, by careful and integrated use of modern sampling and analyses methods, field analytical methods, down-hole sensor technologies, and geostatistical modeling methods (Siegrist and Satijn, 2002).

The plume's response to source zone treatment is difficult to assess and may not be immediately evident, as discussed in Section 1.5. Contaminant concentrations observed in monitoring wells near the source may decrease immediately following treatment, as desired, but may rebound to pretreatment levels after some period of equilibration. This effect may be due to the continued presence of residual DNAPL in the saturated zone and the slow release and dissolution of these contaminants into the dissolved-phase (Sale and McWhorter, 2001). Dissolved concentrations may also *increase* during treatment as the solubility of the DNAPL constituents increases. Depending on the location of the monitoring network, these trends could indicate that the technology is working properly (i.e., contaminants are being dissolved into the groundwater and captured according to plan) or that contamination is spreading beyond the monitored treatment zone. An example of how groundwater concentrations can be used to assess performance at a in situ thermal remediation project is presented in Box 4-2.

Monitoring wells located immediately adjacent to the remaining DNAPL may not reflect the overall impact of the remediation as hydraulic gradients return to near preremediation conditions. Depending on the degree of heterogeneity, groundwater flow rates, and the size of the treated area, it may take years for the groundwater to completely flush all of the regions invaded by the remedial fluids and migrate past the monitoring point. During this time, water samples obtained for post-treatment performance assessment may contain water or other fluids injected as part of the remedial process. Lower concentrations of contaminant may be measured than the new quasi–steady state condition. Because "dilution" can impact groundwater concentrations, the number or fraction of pore volumes of water added during remedial operations should be taken into account when evaluating groundwater concentrations. Groundwater concentrations in down-gradient wells could also be higher prior to equilibration due to water passing through a more highly contaminated source zone or perhaps the presence of residual remedial agents that enhance solubility.

Although it is important to monitor groundwater quality inside and outside the source area during enhanced recovery or treatment operations, it is not recommended that groundwater concentration data alone be used to assess performance because of the uncertainties described above.

Box 4-2. Bhow Changes in Groundwater Concentrations Are Used to Assess Performance of an In Situ Thermal Project at a TCE-contaminated Site in Oregon

The ICN Pharmaceuticals, Inc. (ICN) site is located in Portland, Oregon. In December 1992, ICN joined Oregon's Voluntary Cleanup Program to continue an environmental investigation initiated by the City of Portland. The presumed DNAPL zone (primarily TCE) extends approximately 120 ft to the south of the dry well with a width of about 80 ft and starting at about 20 ft below ground surface (bgs). A former dry well reportedly extends to a depth of 20 ft bgs. The water table is encountered in the silts at approximately 8 ft bgs.

The RAOs were to prevent migration of DNAPL and reduce contaminant concentrations in groundwater to levels that indicate DNAPL has been removed or treated, to the extent practicable. The selected remedial technology was to heat the subsurface using electrical resistance heating (ERH). The system was placed into operation in May 2000 and was shut down in December 2001.

Performance monitoring of contaminant concentrations in groundwater within, below, and surrounding the DNAPL zone was conducted during the ERH application. Based on groundwater monitoring data, concentration reductions up to three to four orders of magnitude have been observed in the former DNAPL zone. The highest concentrations remaining in the groundwater are on the order of 1 ppm total VOCs and represent a small portion of the originally contaminated area. Analytical results for groundwater samples collected from many site monitoring locations indicate levels of chlorinated solvents are approximately at or below drinking water MCLs. VOC concentrations in the recovered air stream generally reflected expected trends with vinyl chloride and *cis*-dichloroethene concentrations peaking first, followed by TCE concentrations.

4.2.3 Decrease in Soil Vapor Concentration

Applicability and Use

When the remediation calls for removing volatile DNAPLs from the vadose zone (using SVE), a very common method for assessing the performance is to monitor the vapor-phase concentrations of contaminants in both in the extracted vapor stream and in the vapors remaining in the subsurface. Assessment of SVE remedial effectiveness involves two phases.

The first phase is during active SVE operation. The concentration of contaminants in the SVE effluent must be monitored frequently to assess how the remediation is progressing. The concentration of contaminants in the soil vapor must also be monitored in the subsurface over the area of the soil gas plume to ensure that the remediation is addressing the entire plume. At some

point during the remediation, the concentration of contaminants in the soil vapor effluent either decreases to nondetectable or reaches an asymptotic point below which concentrations appear not to decrease. Either condition may indicate that the remediation is complete or that it has reached a point where the remediation is diffusion rate limited.

The second phase is to then turn off the SVE system and monitor the concentrations of contaminants in the soil vapor over time and over the area of the plume. If the remediation has not removed all of the DNAPL from the subsurface, there is a rebound in soil vapor concentrations. If the remediation has been successful, the soil vapor either remains at concentrations below acceptable detection levels or remains at or below concentrations set as remediation goals. It is important to remember that rebound may not be immediate depending on the geology, the contaminant, and the size and distribution of the contaminant.

Limitations

Potential problems and challenges with using vapor concentration data to estimate source treatment progress include the high variability, both temporally and spatially, in in situ vapor concentrations and the fact that concentration changes may not be due to in situ treatment (e.g., changes could be due to rate-limited processes and dilution effects). These problems can be overcome, at least in part, by employing statistically sound trend analysis and using a converging lines of evidence approach.

4.3 Estimates of Source Mass Reduction

Three types of metrics require estimating mass: mass extracted, mass destroyed, and mass remaining.

4.3.1 Mass Extracted

Source zone remediation technologies commonly use “mass removal percentage” or the fraction of DNAPL extracted as a measure of success. This approach relies on developing a fairly accurate estimate of the contaminant mass present in the ground and establishing a defensible baseline before treatment begins.

For a groundwater pumping operation, a simple estimate of mass extracted can be made by integrating the concentration history. The history is a plot of groundwater concentration versus cumulative groundwater pumped. The area under the curve represents the mass of contaminant removed. Determining the mass of DNAPL brought to the surface by an SVE is also relatively straightforward. DNAPL content and the concentrations of site contaminants in extracted water and vapor are typically measured as part of normal operational or monitoring procedures, and therefore mass removed (e.g., pounds of contaminant removed per day) is typically reported.

4.3.2 Mass Destroyed In Situ

The amount of mass destroyed in situ through oxidation or biodegradation is much more difficult to estimate and is usually based on concentrations of indicator parameters measured in groundwater.

Increase in Chloride

If chemical oxidation using potassium permanganate ($KMnO_4$) is the chosen remedy for DNAPL source remediation of chlorinated solvents, contaminant mass reduction can be estimated by using chloride (Cl^-) concentrations in groundwater samples. Chloride concentrations in groundwater should be collected during all stages of the remediation (before, during, and after). As an example, the chemical reaction between $KMnO_4$ and dissolved-phase TCE is shown as follows:

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 3Cl^- + H^+ + 2K^+$$

Based on the above stoichiometric equation, the oxidation of 1 pound (lb.) of TCE produces 0.81 lbs. of chloride. By measuring the amount of chloride generated from the oxidation process, the amount of TCE destroyed by potassium permanganate can be calculated using the following formula:

$$\text{Mass of TCE destroyed (lbs.)} = \text{Mass of chloride generated (lbs.)} \div 0.81$$

Considerable information on the hydrogeology and geology and DNAPL distribution is necessary to accurately predict mass using the above calculations. Comparing chloride concentrations before and after injections and knowing whether biodegradation is occurring allow for the determination of whether the chloride is generated by chemical oxidation or other subsurface reactions. While chloride concentrations may initially be a sensitive monitoring parameter, interpretation of Cl^- data can become ambiguous after a large amount of Cl^- has accumulated because concentration changes may be due to the movement of fluids with different Cl^- levels induced by oxidant injection and density gradients (Hunkeler and Parker, 2002).

Ratios of Carbon Isotopes

Isotopes of carbon have been used as an indicator of the oxidation of chlorinated ethenes (Hunkeler and Parker, 2002). Molecules of chlorinated solvents are composed of both light (^{12}C) and heavy (^{13}C) carbon atoms. Because there is a slight difference in the reaction rates of ^{12}C and ^{13}C, a chlorinated solvent mixture undergoing oxidation becomes enriched in ^{13}C over time. The $^{12}C/^{13}C$ ratio can be calculated and monitored to gauge the effectiveness of oxidation process. This technique has been used at a site in Florida as described in Box 4-3. (Also see Case Study 7.)

Also, some have suggested using changes in the isotopic composition of chlorine. The logic is similar to that using carbon: the Cl isotopic ratio in chlorinated VOCs differs from that in natural groundwater.

This same technology can be used to monitor the progress of reductive dechlorination of chlorinated ethenes. Molecules with the lighter isotopes (^{12}C) tend to be transformed more quickly, resulting in enrichment of ^{13}C in the residual reactant and of ^{12}C in the initial product. This technology has been used to monitor reductive dechlorination of a TCE residual source area at the Test Area North Site (Song, et al., 2002). It should be noted that although this technology can be used to monitor progress of these processes, it cannot be used by itself to generate estimates of mass of contaminant destroyed for either chemical oxidation or bioremediation.

Box 4-3. Changes in Stable Carbon Isotope Ratios Used to Demonstrate In Situ TCE Destruction at a Site in Broward County, Florida

Concentrations of TCE and chloride (Cl^-) were monitored within a distance of 1.5 m of the permanganate solution injection points utilizing multilevel sampling methods. Between February and July 2000, the concentration of TCE decreased at some of the monitoring points while it increased at others. Between July and December 2000, it decreased to relatively low concentrations at all monitoring points. The Cl^- concentration increased at depths >17 m bgs between February and July 2000, but no further increase was observed between July 2000 and December 2000 (except at the deepest monitoring point) despite a strong decrease in TCE concentrations. These data make it difficult to demonstrate TCE oxidation between July and December 2000 using Cl^- concentrations.

Carbon isotope ratios were also measured at two sampling points with the highest initial TCE concentration. While the $d^{13}C$ of TCE remained the same at the upper sampling point between February and July 2000, a strong increase in the $d^{13}C$ can be observed at the lower sampling point, clearly indicating TCE destruction by oxidation with permanganate. Between July 2000 and December 2000, when a decrease in TCE concentration was observed without an increase of Cl^-, again $d^{13}C$ values provide clear evidence for TCE oxidation. At the upper sampling point, the $d^{13}C$ increased from –27.5% to –4.4%, indicating TCE oxidation; at the lower sampling point, an increase from +32.9% to +38.5% could be observed. The Cl^- produced by TCE oxidation had migrated to greater depths, explaining the elevated Cl^- concentration at >20 m. Parker, et al. (2002) conclude that this site has only small dispersed globules of DNAPL causing chloride tracking to be less sensitive for remediation assessment. Twenty-one weeks after the last permanganate injection, the $d^{13}C$ values of TCE were close to the initial $d^{13}C$ values representative of the TCE source. The reverse trend towards the initial $d^{13}C$ value of TCE can be explained by desorption or dissolution of small amounts of TCE still present in the aquifer.

4.3.3 Mass Remaining

Estimating the mass of DNAPL remaining in the ground after treatment is important if the remedial objective is based on removing a certain fraction of the mass; however, it is a difficult undertaking.

Estimating Mass Remaining

Soil cores. Soil samples can be collected and analyzed for the DNAPL components to quantify the contaminant mass present before and after treatment. As discussed in Section 4.2.1, there are a number of different techniques to collect soil samples for chemical analysis from the DNAPL source area; each technique has its benefits and limitations. Contaminant mass remaining within a source zone is typically calculated from soil core data by multiplying the contaminant concentration in a soil sample by the density of the soil and the source zone volume (Siegrist and Satijn, 2002). Contaminant mass reduction is then estimated by comparing the estimated mass present before and after treatment. The mass calculation requires that the volume and density of the media be known and that these properties are homogeneous throughout the source zone.

Tracer tests. A partitioning interwell tracer test (PITT) can be used to better evaluate the volume and spatial distribution of DNAPL within the subsurface. Several studies have concluded that a soil coring program alone is unlikely to provide reliable estimates of the volume of DNAPL at the field-scale (Mayer and Miller, 1992; Bedient, et al., 1999). PITTs can be used as remediation performance assessment tools to determined system effectiveness by measuring the mass of DNAPL remaining in the subsurface (Meinardus, et al., 2002).

Field implementation of a PITT consists of the injection of a suite of conservative and nonconservative tracers into one or more wells and the subsequent recovery of the tracers from one or more nearby extraction wells. PITTs conducted in the saturated zone use groundwater as the carrier fluid, while air is used as the carrier for PITTs conducted in the vadose zone. The nonpartitioning (conservative) tracers pass unhindered through the DNAPL zone, while transport of the partitioning tracers is retarded by interaction with the DNAPL. After the tracer slug is injected, potable water is injected to drive the tracers across the zone of interest. The tracer responses at monitoring and extraction wells are used to estimate the average DNAPL saturation, the swept pore volume, and the total volume of DNAPL in the subsurface. The experimental and theoretical basis for the use of partitioning tracers is presented in detail in Jin (1995), Jin, et al. (1995), and Dwarakanath (1997). The execution of a PITT requires the completion of a series of tasks, including tracer selection, design simulations, implementation, and analyses.

Groundwater data. Estimates of contaminant mass remaining may also be derived by collecting groundwater data subsequent to a source treatment operation. This method is much more prone to error and uncertainty than other methods. Ideally, chemical analytical data collected from an adequate number of monitoring wells across the site on several separate occasions is available. Along with site-specific hydraulic conductivity and groundwater flow data, a numerical model is then used to duplicate the monitoring well data by assuming a location and mass of DNAPL. Other observations may be used to help locate the DNAPL zone, such as soil analytical data. If such data are not available, contaminant mass estimates from groundwater data would be rough guesses at best.

Limitations

All methods of DNAPL mass estimation have associated uncertainties, so mass reduction should be regarded as only one of several measures of performance and perhaps not even the most important. It is very difficult to estimate the mass of DNAPL in the subsurface due to the mechanics of DNAPL flow in the vadose and saturated zones. (Some claim that it is essentially impossible to find all of the DNAPL in the subsurface).

A number of issues need to be considered when verifying contaminant mass remaining. The data set needs to be of an adequate size to properly characterize site conditions, such as soil heterogeneity and extent of DNAPL contamination. Other problems when trying to quantify in situ mass (Siegrist and Satijn, 2002) can include (1) the complex distribution of DNAPL in both the horizontal and vertical dimensions, (2) the potential for errors in measurement data in certain media (e.g., VOCs in soil), (3) the potential for inaccurate interpolation when estimating levels where measurement data are not available, and (4) the possibility that subsurface conditions can change after in situ remediation has been applied and that contaminant mass may not have actually been destroyed, only mobilized away from area of treatment.

Soil concentration data. Potential problems and challenges with quantifying contaminant mass remaining using soil concentration data include all of difficulties discussed in Section 4.2 when attempting to quantify average contaminant concentrations. Removing 90% or 95% of the mass from the ground sounds good and would probably be declared a success, but the level of confidence with which statements like these can be made when based upon inaccurate initial estimates of mass is questionable.

Tracer tests. Because PITT is a relatively new and innovative technology, it is useful to be aware of its limitations and some of the consequences associated with improper tracer test design and/or implementation. Differences in media permeability can have a dramatic effect on the sweep efficiency of the tracers. Typically a "slug" of tracer, about half the swept pore volume, is used in PITTs. Because the tracer moves preferentially through the most permeable zones, much less than one pore volume goes through the low-permeabilty regions. The flow rate of the tracer moving through the low-permeability zones may be 10 or even 100 times lower than through the more permeable layers. Thus, the DNAPL mass located in the lower-permeability zones is often not detected using the PITT due to low sweep efficiency. Nelson, et al. (1999), for example, showed in an intermediate-scale flow cell that the presence of porous media heterogeneities and variable DNAPL distribution greatly reduced the accuracy of PITT in predicting DNAPL saturation. Methods to improve sweep efficiency exist for these cases, such as using viscosifiers and foam. A viscosifier has the effect of distributing the injected tracer better across heterogeneous layers, improving the sweep efficiency. Foam can also help by blocking off high-permeability zones, forcing injected tracer into lower-permeability zones.

Groundwater concentration data. Determining the DNAPL mass remaining following treatment based on groundwater concentration data is a difficult calculation to make, requiring the use of numerical modeling tools and professional judgment. Also, contaminant concentrations found in

the immediate vicinity of the DNAPL zone are commonly one to two orders of magnitude below their aqueous solubilities because the NAPL dissolution phenomena that control these aqueous concentrations depend on a number of system parameters including the following (Meinardus, et al., 2002):

- aqueous-phase velocity,
- NAPL saturation,
- NAPL composition,
- heterogeneity,
- length scale, and,
- aspect ratio (between the monitoring well and the NAPL zone).

Consequently, the use of groundwater contaminant concentrations to draw conclusions about the volume, mass, or saturation of the NAPL zone involves an ill-posed inverse problem, for which no unique solution exists even for the simplest of cases.

4.4 Estimates of Source Treatment Impact

4.4.1 Decrease in DNAPL Toxicity

For some multicomponent DNAPLs, mass reduction may not be the relevant objective; the removal of certain target components from the DNAPL mixture to reduce the overall toxicity may be more appropriate. For example, thermal or flushing technologies can generally lead to selective removal of the more soluble or more volatile components, which may be more toxic, leaving behind the less toxic components as residuals.

Performance goals for evaluating the effectiveness of treatments designed to decrease the concentration of the toxic components in a DNAPL mixture can be set to some target concentration level within the DNAPL zone for those toxic components. By targeting the removal of the more toxic components from a complex DNAPL mixture, the remaining less toxic components may meet the risk-based objectives even when the concentration of those remaining components is high. Because toxicity is difficult to measure directly, concentration levels of certain target constituents that exhibit toxic effects are monitored.

In addition to the problems and challenges associated with quantifying concentrations or mass in the subsurface, there can be questions about verifying long-term stability of the observed toxicity reduction effect. This task requires long-term testing or sufficient fundamental understanding to predict long-term effects with certainty (Siegrist and Satijn, 2002).

4.4.2 Decrease in DNAPL Mobility

Mitigating the further spread of the source by decreasing DNAPL mobility is another often-cited objective of DNAPL source remediation. The goal in such a case is to deplete the source sufficiently to reduce DNAPL to a point of relative stability. In theory, that point occurs once

residual saturation is reached (see Section 2.1.2). However, it should be noted that reaching residual saturation does not always equate to reaching a point of immobility. Immobilized DNAPL is held in place by a balance of dynamic forces which can be upset easily by minor changes in groundwater flow, tidal effects, earth pressure, and ground vibration, for example. A change in mobility is ultimately a matter of observing a change in the rate of DNAPL movement.

Measuring NAPL Saturation

Saturation is a description of the volume of DNAPL in the subsurface, and as such, is a more direct measure for assessing DNAPL source removal effectiveness than either soil or groundwater concentration. Because source removal operations inherently decrease saturation (by removing mass), this parameter can be an important one for assessing the effectiveness of such remedial actions. Although comparing NAPL saturations before and after treatment provides useful information, it should be noted that determining saturation is subject to many of the same limitations as measuring soil concentrations.

When designing an approach to measure NAPL saturation, it is important to consider factors that can influence NAPL saturation measurements such as the measurement technique used by the laboratory and biases introduced during sample collection. When collecting samples from locations with mobile NAPL, it may be very difficult to obtain a representative sample for NAPL saturation because very often NAPL drains from the sampler as the core is brought to the surface, yielding low estimates of NAPL saturation from the sample actually sent to the lab.

Laboratory Analysis of Soil Samples

Laboratory analyses of soil samples collected from the DNAPL source zone yield a measurement of the total concentration of each constituent in all phases—adsorbed, dissolved, vapor, and NAPL—detected in the soil sample. These results can then be used to calculate NAPL saturation in the subsurface. Feenstra, et al. (1991) provide the methodology for performing this calculation based on equilibrium partitioning theory. Mariner, et al. (1997) extended the calculation to multicomponent NAPL and developed a computer code for making the computations called "NAPLANAL." NAPLANAL distributes the measured total VOC concentrations in a sample among the various fluid and solid phases present. If the calculations indicate that aqueous VOC concentrations exceed solubility constraints, the NAPLANAL algorithm determines that DNAPL is present in the sample and automatically includes DNAPL as one of the partitioning phases.

For the VOC data acquired from the laboratory to be entered into NAPLANAL, the VOC concentration in the solvent extract must be converted to a concentration per soil mass (mg/kg). This step is accomplished using the jar, methanol, and soil weights recorded in the field and using the density of the soil and the solvent. A value for f_{oc}, soil bulk density, and the porosity of the soil must also be entered. Other input parameters are obtained from a database of physical and chemical constants, which is incorporated in NAPLANAL.

The NAPLANAL output includes calculations of the concentrations of VOCs in each phase and the sample NAPL saturation (volume of DNAPL per volume of pore space). If no DNAPL is present, a dilution factor is calculated to provide a measure of how much more concentrated the VOCs must be before a DNAPL would be predicted to exist in the sample (Jackson and Mariner, 1995).

Tracer Tests

Tracer tests such as PITT can also be used to estimate NAPL saturation. The application and limitations of PITTs was described in Section 4.3.3.

4.4.3 Decrease in Source Mass Flux

In many cases, the most important characteristic of the source zone from a risk perspective is the mass it is contributing to the much larger dissolved phase plume. This "source strength" (or plume load) can be defined as the mass discharge rate at steady state from a DNAPL source to the surrounding groundwater. The total mass discharge (mass per unit time) can be obtained by integrating localized mass flux across the entire source zone. Mass flux is defined here as the "rate per unit area at which solute mass in the groundwater crosses a spatial plane oriented at a right angle to the direction of groundwater flow" (Rao, et al., 2003). Figure 4-2 illustrates the complexity of mass flux in a heterogeneous subsurface and the value of mass flux and mass discharge as metrics in source remediation.

Source strength is only partly a function of the total mass present and can be strongly affected by the distribution of DNAPL in the subsurface as well as the hydrodynamic structure. Decreases in source mass may not produce correspondingly large decreases in source strength. Measuring the source strength directly can therefore provide more accurate information on the risk reduction due to source depletion and the ability of natural processes to contain the remaining mass.

Applicability and Use

The goals of removing mass from a source zone include reducing the risks of contaminant migration (via either the dissolved or vapor phase), reducing plume longevity, reducing overall remediation costs, accelerating the natural attenuation of any remaining mass, and speeding the transition to more passive technologies. Mass flux or discharge can be a meaningful metric in assessing progress towards these goals, if properly measured and calculated. Using source strength as a measure of success, shutdown of the remedial system could be considered when the mass release rate from the source to the groundwater (mass discharge) falls below the assimilative capacity or "natural attenuation capacity" of the aquifer. Natural attenuation capacity can be defined for groundwater systems as a measure of its ability to lower contaminant concentrations along aquifer flowpaths. The natural attenuation capacity of groundwater systems depends upon hydrologic (dispersion and advection) and biological (biodegradation rates) factors and can be assessed using quantitative models (USGS, 2003).

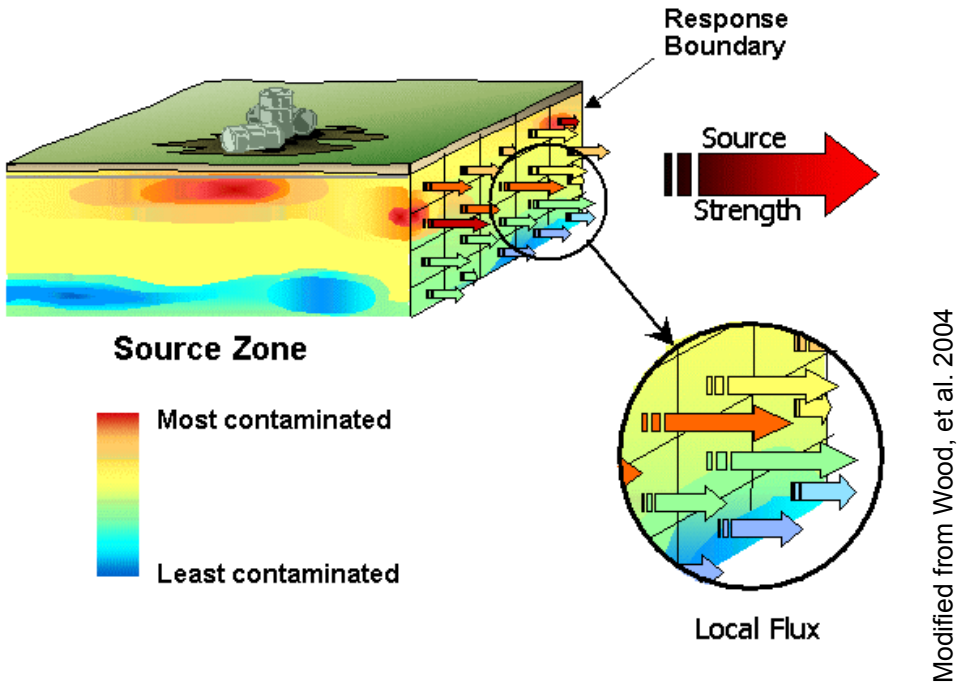


Figure 4-2. Concept of Mass Flux/Discharge and Source Strength

Measuring Mass Flux and Mass Discharge

Mass flux can be measured along one or more planes oriented perpendicular to the flow direction. Measurements near the source zone will provide an estimate of source strength. Most of the methods discussed below also allow mass flux measurements down-gradient, providing valuable data on the rates of attenuation and plume response to source treatment.

There are four methods available to estimate mass flux or mass discharge:

- measure contaminant concentrations in samples recovered during continuous groundwater extraction,
- measure contaminant concentrations and groundwater velocity during short-term pump tests ("integrated pump tests"),
- measure contaminant concentrations at multiple locations across a transect of multilevel samplers, and,
- measure contaminant concentrations and groundwater velocities at multiple locations and depths using passive borehole flux meters.

Each of these methods is described briefly in the following sections.

Continuous pumping from an extraction well. Perhaps the most direct method to estimate source strength involves capturing the entire plume using one or more extraction wells pumping at a continuous rate. By analyzing steady-state concentrations and flows, the plume load can be calculated directly. This approach can be cost-effective where there is an existing hydraulic containment system in place. The robustness of this technique also assumes that the entire plume is "captured" by the extraction well or wells. Where there is an existing plume containment system, the current contribution of the source to the existing pump and treat system can be valuable information for assessing the benefits and costs of treating sources. Extrapolating the results to unstressed source zones may be difficult, however.

Integrated pump tests. A technique known as the Tübingen integrated pump test is another method of estimating contaminant mass flux based on short-term, active pumping of wells located in a transect across the contaminant plume. This technique, developed by researchers at the University of Tübingen, Germany (Teutsch, et al., 2001; Bockelmann, et al., 2001), relies on capturing all of the contaminated groundwater flowing within the plume. An advantage of this method is that it does not require interpolation of contaminant concentrations between monitoring points as is the case with transects of multilevel monitoring wells (described below). One or several extraction wells can be used for this purpose, the number depending on the known or presumed hydrogeologic properties of the media and distribution of contaminants. The wells are pumped until the entire mass discharge at the transect location is known or assumed to be extracted, at which point the contaminant concentrations are measured in the effluent from the wells. In this case, contaminant mass discharge (M_d) is calculated as follows:

$$M_d = \sum_{i=1}^{n} Q_i C_i$$

where

M_d = contaminant mass discharge (mass/time),
Q_i = extraction rate from well I (volume/time),
C_i = contaminant concentration measured in effluent from well I (mass/volume).

For this basic method to work, one must achieve steady-state capture of the contaminant mass discharge, a goal that may be difficult to achieve in heterogeneous media and/or where plumes arise from spatially complex sources. Also, the operation of the extraction wells necessarily alters the plume itself, with potential unanticipated or undesirable impacts. Furthermore, steady-state capture of a contaminant plume can generate a very large amount of contaminated water, which would subsequently need to be treated or disposed of. For these and other reasons, Schwarz, et al. (1998) have explored the application of this approach to estimating mass discharge via shorter duration non-steady-state extraction tests. However, such tests also would be confounded by heterogeneities in flow field and source characteristics.

Multilevel sampling along transect of wells. The most common approach to measuring mass flux, at least until recently, has been the use of multilevel samplers. Multilevel sampling was discussed previously in Section 4.2.2. By collecting groundwater from numerous, closely spaced sampling points along a transect of wells intersecting the plume and aligned perpendicular to the groundwater flow direction, a geostatistical average concentration can be calculated. The development of direct-push multilevel sampling tools has allowed such high-density sampling at many sites. This approach can be useful, although the in situ heterogeneity may be so great that the resulting estimates are highly uncertain. Large numbers of analyses can be required, and it can be difficult or very expensive to obtain sufficient numbers of samples in some subsurface environments.

Passive borehole flux meter. The passive borehole flux meter, a new technology for direct in situ measurement of both cumulative subsurface and contaminant fluxes, is currently being validated through demonstrations at several contamination sites. It is a self-contained permeable unit that is inserted into a well or boring so that it intercepts groundwater flow but does not retain it. The interior composition of the meter is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and inorganic contaminants present in fluid intercepted by the unit. The sorbent matrix is also impregnated with known amounts of one or more fluid-soluble "resident tracers." These tracers are leached from the sorbent at rates proportional to the fluid flux.

Following exposure to groundwater flow for a period ranging from days to months, the meter is removed and sorbent carefully extracted to quantify the mass of all contaminants intercepted and the residual masses of all resident tracers. The contaminants' masses are used to calculate time-averaged contaminant mass fluxes, while residual resident tracers masses are used to calculate cumulative fluid flux (Environmental Security Technology Certification Program [ESTCP], 2003).

Box 4-4 describes a mass flux study conducted at Hill AFB, showing results from both borehole flux meters and integral pump tests conducted before and after remediation of a source zone. Borehole flux meters are also being used in demonstrations at the Fort Lewis Logistics Center to measure the impacts of both biological and thermal in situ treatments.

As a tool for long-term monitoring, a fence row of flux meters installed immediately down-gradient from a groundwater contaminant source can be used to characterize source strength. The spatial distribution of measured fluxes, when integrated over the fencerow, produces estimates of contaminant mass loadings to groundwater. Because water and contaminant flux measurements reflect cumulative values, reliable time-averaged fluxes can be calculated. Thus, it is possible to calculate monthly and annual contaminant mass loadings to an aquifer.

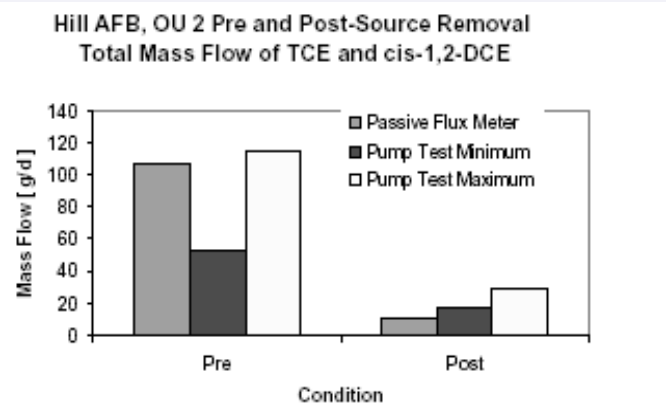
Limitations

All of these methods have limitations, and these are generally noted in the descriptions. This section discusses some of the more general limitations of mass flux measurement.

Box 4-4. Mass Flux Measurements at Hill Air Force Base, Utah

Both the borehole flux meter and integrated pump test methods were used at Hill AFB before and after source depletion (using surfactant flushing). For the flux meter tests, specially treated carbon-filled socks were deployed in monitoring wells. The socks contained granular activated carbon preequilibrated with four alcohol tracers. These tracers leach from the socks as groundwater flows through the devices, allowing calculation of the cumulative or time-averaged groundwater velocity by measurement of the tracer desorption. At the same time, the mass of TCE and other solvents that sorbed to the activated carbon was measured. From the measured mass of TCE and other solvents sorbed, the cumulative or time-averaged contaminant mass flux was determined. By suspending these flux meters at several depths in each monitoring well, the total water and contaminant mass flux could be estimated.

The integrated pump test was also used before and after treatment, using different pumping durations (Enfield, et al., in preparation). Preliminary mass flux estimates from the minimum and maximum pumping durations are shown below, along with the estimates from the flux meter testing. All of the results indicate considerable reductions in mass flux after treatment, and the comparisons suggest that the results from the two methods were at least similar.



Source: Hatfield, et al., 2003

Subsurface heterogeneity. Measuring mass flux is inherently difficult because of the heterogeneity that occurs in the subsurface, especially near a DNAPL source. DNAPL distribution is often patchy, and its presence is difficult to predict or detect. The flux from a source can be visualized as a network of stream tubes, with water in some stream tubes moving much more quickly than in smaller or more tortuous ones. Similarly, contaminant concentrations can vary greatly between stream tubes, depending on its interactions with DNAPL accumulations and distance away from DNAPL sources.

As a result, the vast majority of the contaminant flux can be in a very small proportion of the volume, and the flux can vary tremendously between sampling locations. A very dense network of

monitoring points is therefore required to ensure that most high-flux areas are sampled and that the results are representative of the actual distribution of flow velocities and concentrations. The uncertainty can be high, and it is recommended that the uncertainty be explicitly estimated when reporting flux estimates to aid in interpretation and decision making. Statistical analyses of the results from multilevel well or passive flux meter investigations should also be performed and reported because of the importance of the inherent variability.

The two active mass flux measurement techniques, continuous extraction and integrated pump test methods, attempt to overcome this limitation by capturing all of the water and analyzing the results over time to estimate steady-state flux. Careful analysis is required to compare these results to those obtained by other mass flux methods or to results at other times or locations. The results are also obtained under stressed conditions which then have to be extrapolated to flux under the existing conditions. These techniques may also be cost-prohibitive for sites without an existing infrastructure to pump and treat the extracted groundwater.

Emerging technologies. These approaches to mass flux estimation, particularly the passive flux meters and integrated pump tests, are relatively new. Development and testing are ongoing, and there is little experience to use as guidance at this point.

Regulatory uncertainty. Mass flux can be a difficult metric to use from a regulatory perspective. Mass flux can be a regulatory goal in some cases, such as flux to surface waters. However, groundwater criteria are usually based on point concentrations, and they may be difficult to modify for a specific site. The most common approach is probably to set flux criteria at a response boundary located near the source based on the capacity of the aquifer to naturally attenuate the remaining mass before the groundwater reaches a down-gradient compliance point.

5.0 TECHNOLOGY-SPECIFIC MONITORING CONSIDERATIONS

Ideally, the remedial effectiveness of all DNAPL source zone depletion technologies under consideration should be evaluated consistently using the same metrics. However, methods for monitoring remedial progress and system efficiency must address technology-specific considerations. For instance, heat-based technologies like steam injection provide unique challenges when evaluating progress, from collecting and handling hot soil and groundwater samples to selecting well construction materials that enable groundwater monitoring. Monitoring programs designed for technologies that enhance the mobility of DNAPLs, such as surfactant flushing, must account for potential mobilization of DNAPL due to decreased surface tension and lowered viscosity.

ITRC reviewed emerging and innovative technologies for DNAPL remediation in a previous publication (ITRC, 2000) and identified the lack of performance data as a barrier to using these technologies in a subsequent document (ITRC, 2002). The information in this section is intended as "suggested monitoring requirements" for planning purposes—actual monitoring varies depending on site-specific conditions and the technology being deployed.

5.1 Remedial Effectiveness and System Efficiency Monitoring

As mentioned previously, there are two types of performance monitoring: remedial effectiveness monitoring and system efficiency monitoring. By collecting performance data in accordance with a well-thought-out, systematic plan, decisions concerning continued operation or shutdown of a remedial system can be made. Planning for performance assessment and uses of performance data were discussed in Section 1.4.

"Remedial effectiveness" refers to the ability of the system to achieve remediation goals at a given site. As stated in Section 1.3, we consider effectiveness to be the degree to which a technology application achieves risk reduction goals or response objectives by reducing contaminant mass, concentration, mobility, and/or toxicity while preventing the uncontrolled mobilization or further spread of contaminants. Effectiveness monitoring is typically done after a remedial action has been completed and the project team wishes to verify that the response objectives have been met by comparing post-treatment conditions to baseline conditions. If continued operation is warranted, effectiveness monitoring may be repeated once it appears that the objectives have been met or a decision to cease active remediation is made.

"System efficiency" monitoring is intended to optimize treatment efficiency by maintaining specific design conditions within the remediation system. These conditions could include appropriate ranges of temperature, pressure, flow rate, pH, dissolved oxygen (DO), ORP, or TOC. This process involves monitoring the reaction zone, including any injection wells, treatment zone monitoring wells, and other subsurface probes. Sample protocols should be specific to the source reduction technology with special attention given to conditions favoring VOC losses (e.g., thermal treatment).

The frequency of efficiency monitoring should be a function of system operation. More frequent monitoring is required earlier in the process; less frequent efficiency monitoring is typically required as the system stabilizes at close-to-optimum conditions. Efficiency monitoring frequency may be as often as weekly to biweekly during the first few months of testing, diminishing to monthly or quarterly for the remainder of the system operation. It is also desirable to schedule monitoring to occur between active source reduction events (e.g., injections) so that the results of field measurements can be used to refine injection or extraction parameters during subsequent events. This reduction of system efficiency monitoring over time should go hand in hand with a shift of resources toward remedial effectiveness monitoring tasks such as soil confirmation sampling, groundwater sampling, or groundwater flux measurements.

5.2 Conventional Source Zone Remedies

Although conventional source zone technologies are not innovative, we include them here to allow a comparison of performance monitoring strategies.

5.2.1 DNAPL Recovery

Direct removal of DNAPL from the subsurface via pumping can be an effective means of mass removal and may be the simplest to implement, assuming that a mobile mass or pool of DNAPL has been intercepted by a well. Consequently, such actions are typically initiated soon after the problem is discovered without extensive analysis or development of performance criteria. Pumping or bailing is often continued until the efficiency of DNAPL recovery decreases over time or until a more aggressive technological approach is designed and implemented. Efficiency is therefore a function of the rate of DNAPL mass or volume recovered.

The effectiveness of direct removal is more difficult to assess and depends on the remedial goal for the project. Effectiveness can be measured by reductions in residual NAPL saturations or mobility, not just the mass of NAPL removed. In terms of reducing mobility, it is certainly beneficial to reduce the head or driving pressure atop a DNAPL pool to minimize the potential for further migration, but the effect that removing small quantities of DNAPL from a single well has on down-gradient groundwater or vapor quality remains uncertain.

It should be noted that aggressive pumping from individual wells is apt to cut off flow paths of DNAPL and reduce the ability to recover additional DNAPL. With hydraulic recovery, it is very important to enhance the DNAPL flow paths to the point of extraction and not just remove the existing DNAPL from the well as it returns to the well.

5.2.2 Soil Vapor Extraction

If the DNAPL is volatile and located in the vadose zone or in the capillary zone, SVE is often an effective remedial technology provided that the air permeability of the zone is sufficient to allow advective air flow. In this technique, vapor extraction wells are drilled near the DNAPL source areas in the vadose zone. Soil vapor is then extracted from the subsurface by applying a vacuum to the extraction wells. As the air advection through the unsaturated porous media travels towards the extraction wells, the DNAPL constituents volatilize. The volatilized DNAPL constituents migrate through the air-filled pores in the unsaturated zone by diffusion into the advective air flow and subsequently into the extraction wells, and are then removed from the subsurface. The extracted vapors are generally treated to remove the volatilized DNAPL constituents from the gas stream prior to discharge to the atmosphere.

SVE is a viable remedial technology option and is simpler and lower in cost than many other remedial options for DNAPL in vadose zone soils. Because SVE is dependant on volatilization from the DNAPL and aqueous phases, it is applicable only to compounds with sufficient vapor pressure and Henry's constants. One potential problem associated with SVE is with soils having heterogeneous distributions of air permeabilities. Because air flow in the vadose zone flow preferentially through soils with the greatest air permeabilities, those zones with lower air permeabilities have limited treatment effectiveness. As gas-phase diffusion is the controlling mechanism for the removal of volatilized DNAPL constituents from lower-air-permeability zones, particularly in layered heterogeneous systems, these zones may take significantly longer to be

treated by SVE. Once the more-volatile DNAPL constituents have been removed by SVE, adsorbed-phase compounds may take considerably longer to be removed from soils. Both diffusion and mass transfer processes are usually responsible for the asymptotic mass removal rates observed in many SVE systems.

Methods for assessing SVE performance in the vadose zone are presented in EPA guidance (EPA, 2001a) and guidance produced by the U.S. Army Corps of Engineers (USACE, 2002).

5.2.3 Air Sparging

Air sparging involves the injection of air into the saturated zone below the water table. The treatment mechanisms primarily include stripping of volatile organics and creation of oxygenated conditions favorable to aerobic biodegradation. In the case of chlorinated solvents, which are not readily aerobically biodegradable without a cometabolic substrate, the primary treatment mechanism is volatile stripping. However, air sparging can also be used to deliver alternative gas mixtures for either chemical or biological treatment. Depending on the treatment mechanisms desired, these gases can include a cometabolic substrate (such as propane), an oxidant (such as ozone), or a reductant (such as hydrogen sulfide).

Where volatile stripping is the primary air sparging treatment mechanism, SVE is typically used to remove the organic vapors from the subsurface. In cases where biodegradation or other treatment mechanisms are primary, SVE is often not included. In this case, the air sparging flow rates must by minimized to prevent excessive generation of organic vapors in soil gas or nearby receptors.

Air sparging creates a zone of partial gas saturation within the groundwater zone. This region of partial gas saturation involves various capillary-hydraulic multiphase flow mechanisms, including water displacement by air, variable fluid permeability functions with respect to fluid saturation, and capillary forces which effect both of these mechanisms. The overall effect of subsurface heterogeneity is that the injected air develops fingered flow patterns, at both the pore and stratigraphic scales. The development of fingered preferential air flow paths has a limiting effect on air sparging because some regions of the subsurface may not be effectively contacted by the injected air. This condition can result in uneven treatment of DNAPL source zones. Despite this limitation, air sparging has been found to be effective for treatment of volatile DNAPL source zones at many sites.

The successful application of air sparging for DNAPL sources zones is dependent on meeting several fundamental criteria. The air sparging well spacing and vertical intervals must be properly designed to ensure adequate overlap of the zone of influence for each well. Research has found that air sparging in coarse-grained materials leads to the smallest radius of influence because the air can readily move upward under buoyancy, while air sparging in uniform fine sands or silty fine sands creates the largest lateral radius of influence because the upward buoyant force on air flow is less dominant. In general, mild stratigraphic heterogeneity can increase the lateral radius of influence by further minimizing the dominance of upward air flow. However, substantial heterogeneity leads to the development of preferential air flow paths, which limit the treatment effectiveness.

5.3 Thermally Enhanced Remediation

Three major types of thermally enhanced remediation technologies are currently available for treatment of DNAPL sources. They differ in terms of the process used to deliver thermal energy to the subsurface. The three delivery mechanisms are direct heating by injection of steam or hot air, heating resulting from the natural resistance of the geologic medium to passage of an electrical current, and heating by conduction from electrically powered thermal wells or thermal blankets.

In situ thermal technologies can accelerate DNAPL remediation by several mechanisms. In general, for DNAPLs such as TCE or PCE located below the water table, as heating progresses, a temperature is reached at which the VOC begins to boil. Boiling occurs when the sum of the vapor pressures of VOC and water exceed the ambient pressure. The boiling points of most common VOCs are either below or just slightly above the boiling point of water (100°C at sea level pressure conditions). Deeper within the saturated zone, where the ambient pressure is greater than 1 atm, the respective boiling points of TCE-water and water are increased. However, the boiling point of a VOC DNAPL that is immersed or dissolved in water is depressed. As described by Dalton's law of partial pressure, a low-solubility VOC in contact with water boils when the vapor pressure of the VOC plus the vapor pressure of water is equal to the ambient pressure. Using TCE as an example, the boiling point of the pure phase at 1 atm pressure is 87°C. Below the water table, however, the temperature of first boiling is about 73°C. The vapor formed is about 65% TCE and 35% water by volume. Boiling continues at this temperature until all residual TCE DNAPL is vaporized; the temperature continues to rise until the boiling point of water (100°C) is reached. Continued boiling of groundwater is desirable because it creates an environment where steam stripping occurs and provides sustained treatment of contaminated groundwater. Table 5-1 lists the boiling points and co-boiling points of three common chlorinated solvent DNAPLs.

Table 5-1. Co-Boiling Points of Common Solvents

Contaminant	Boiling Point (°C)	Co-Boiling Point (°C)
PCE	121	88
TCE	87	74
Chlorobenzene	132	92

1. Davis, E., personal communication, 2004.

Davis (1997) describes these and other mechanisms in great detail. In collaboration with EPA and ITRC, the U.S. Army Corps of Engineers (USACE) is in the process of publishing a deployment guide on in situ thermal remediation (ISTR) which covers aspects of overseeing the design and operation of a thermal remediation project from a regulatory oversight perspective and covers the topic in much greater detail than can be presented here (USACE, in preparation).

5.3.1 Steam-Enhanced Extraction

Thermal remediation by steam injection is deployed under a variety of names such as steam-enhanced extraction (SEE), dynamic underground stripping (DUS), steam-enhanced recovery process, steam injection and vacuum extraction, and others (USACE, in preparation). Common to all of these processes, steam (generated in a boiler at the surface) is injected into the subsurface, migrates through permeable media within the vadose or saturated zone and directly heats the geologic media and groundwater sufficiently to vaporize or mobilize DNAPL contaminants. A network of extraction wells is used to remove vapors, mobilized NAPL, and contaminated groundwater for treatment at the surface.

There are many variations in the ways this type of thermal treatment is implemented depending on site-specific conditions and, to some extent, preferences of the vendor. For example, site-specific geology and contaminant distribution are major considerations in determining the location and completion details of steam injection and extraction wells. In addition, some vendors advocate the co-injection of air or oxygen with steam to enhance oxidative breakdown of contaminants or to provide a noncondensible gaseous phase engineered to prevent formation of a DNAPL condensation front that might lead to uncontrolled downward migration. Some processes include cycling the injection of steam with a period of extraction to enhance recovery of DNAPL from lower-permeability zones. One process, DUS, includes the combination of ERH (see the following discussion) to low-permeability units with steam injection in the more permeable zones to provide more complete cleanup.

5.3.2 Electrical Resistance Heating

DNAPL source remediation by ERH usually is deployed as either a six-phase or three-phase heating process depending on the size of the treated area and the purpose of the deployment. In either case, normal three-phase electricity is split into either three or six separate phases and directed to an array of electrodes. A summary of these two types of ERH can be found in a white paper available on one of the vendor's Web sites (TRS, 2003). One of the primary advantages of ERH is that relatively uniform heating of the subsurface can be achieved irrespective of the lithologies encountered. Therefore, fine-grain units are able to be heated directly to facilitate volatilization and transport of VOCs to more permeable units to enhance recovery (USACE, in preparation).

ERH can be employed in both the vadose and saturated zones. Typically, vapor recovery wells are installed throughout the depth interval that is treated. However, the high buoyancy of steam causes it to rise to the top of the water table very rapidly. Thus, in practice, most vapor recovery occurs in the vadose zone. Vapors generated by heating are recovered by these wells and directed to an ex situ treatment system.

Vapors formed by heating within the saturated zone rise buoyantly and, under ideal conditions, migrate into the vadose zone where they are captured by the vapor recovery system. However, there are several examples of field deployments of ERH where adequate thermal monitoring was performed to show that the heating process resulted in lateral displacement of contaminated fluids

outside of the treatment zone due to the impact of lithologic changes. Apparently, lower-permeability units can interfere with the vertical rise of hot water and vapor to cause this effect. Some ERH systems are now being designed to anticipate this potential problem and provide more assurance of hydraulic control during heating.

5.3.3 Thermal Conduction Heating

Thermal conduction heating, known commercially as in situ thermal desorption (ISTD), uses both conducive heating and vacuum to remediate soils contaminated with a wide range of organic compounds. Heat is applied to the soil with an array of vertical or horizontal heaters containing a heating element (typically an electrically powered resistance heater) operating at temperatures of approximately 1,400–1,500°F. Heat flows through the soil from the heating elements primarily by thermal conduction. In their vertical configuration, these heaters are termed "thermal wells."

As the soil is heated, organic contaminants in the soil are vaporized and/or destroyed by a number of mechanisms, including evaporation, steam distillation, boiling, oxidation, and pyrolysis (chemical decomposition in the absence of oxygen). The vaporized water and contaminants, as well as some volatilized inorganic compounds, are drawn counter-current to the heat flow into the vacuum extraction wells (termed "heater-vacuum" wells).

The conductive heating process is very uniform in its vertical and horizontal sweep because the energy input into the soil by thermal wells is uniform over each heater's length. In addition, thermal conductivity values do not vary much over a wide range of soil types, leading to a highly predictable rate of heat front propagation around each heater. As neighboring heat fronts overlap, the entire treatment zone will reach the target temperature provided that heat losses to the atmosphere or due to water influx (rainfall percolation or groundwater recharge) are not excessive (USACE, in preparation). For many VOCs, a temperature of 100°C has been demonstrated to be sufficient to achieve significant mass removal (>99.9%) from many types of soil, mainly through in situ steam distillation (LaChance, et al., 2004). For the treatment of less volatile organics, such as PCBs, PAHs, and dioxins (with higher boiling points), a temperature of 325°C has been demonstrated to be a suitable target temperature to accomplish >99.9% removal from sandy, silty, and clayey sites (Stegemeier and Vinegar, 2002; Bierschenk, et al., 2004; Baker and Kuhlman, 2002). It should be noted that the presence of even small amounts of liquid water will limit temperatures obtainable in the subsurface to100°C, the boiling point of water.

5.3.4 Key Monitoring Parameters

Monitoring for thermal projects should be performed both in the subsurface and at key locations throughout the treatment train, including the steam injection/extraction wellheads, electrodes, unit process inlet/outlet piping, stack discharges, and groundwater monitoring wells. When groundwater extraction is employed as part of the thermal remediation, samples of extracted groundwater should also be analyzed for the purposes of calculating the amount of contaminants recovered and to help determine when the point of diminishing returns is being reached. Table 5-2 outlines some of the

key monitoring parameters applicable to thermally enhanced remediation. More detailed information on monitoring is presented in the ISTR design manual (USACE, in preparation).

Temperature

Subsurface temperature monitoring is part of the system built and operated by the thermal remediation vendor. The remediation contract should stipulate that the data is shared with those doing the oversight at an agreed on frequency. In discussions with the technology vendor, the number of thermocouples to be used and the frequency of temperature measurement should also be agreed on. It is common for subsurface temperature data to be collected daily during operations of in situ thermal remediation systems.

The vendor will likely have minimum monitoring requirements that they need for operation of the system, but those overseeing the remediation may desire to have a greater degree of monitoring built into the system. Commonly, thermocouple strings are placed in between injection and extraction wells and at extraction wells in steam injection systems, or at various locations between electrodes or heating elements in ERH and conductive heating systems, respectively. Thermocouple strings are also generally colocated with monitoring wells, both inside and outside of the treatment area. Generally a 5- to 10-ft vertical spacing of thermocouples is used on thermocouple strings.

To prevent downward contaminant migration during heating, a “hot floor” can be established. The area beneath the treatment interval is heated first to establish a hot barrier beneath the remediation area so that in the event that downward migration occurs during remediation, the contaminant contacts this hot floor region and quickly transitions to vapor and is recovered by the vapor recovery wells. If a hot floor is desired, thermocouples should also be installed below the treatment area to ensure that the hot floor is established. The more heterogeneous the subsurface system, the more thermocouple strings should be employed.

Electrical resistive tomography (ERT) can be used to measure changes in electrical resistivity of the subsurface, which can be caused by changes in the composition of the fluids in the pore spaces as well as changes in temperature. ERT has been used only for steam injection; it is not likely to provide effective monitoring for ERH or conductive heating processes. The main resistivity changes that normally occur in steam injection remediations lower the saturation of the pore spaces by formation of a steam zone. When ERT is used to monitor steam movement in a steam injection system, thermocouples should also be installed. The use of ERT does not substitute for thermocouples.

Temperature may also be a better indicator of loss of hydraulic control during thermal remediation than water level measurements or contaminant concentrations. Perimeter monitoring wells used for monitoring groundwater or vapor should also have thermocouple strings installed to monitor temperature at various depths. Temperature increases at a certain depth indicates flow of heated water from the treatment zone. Knowing where water is leaving the treatment zone allows adjustments to be made to improve hydraulic control.

Table 5-2. Performance Monitoring Parameters for Thermally Enhanced Remediation

Location / Media		Parameter	Purpose
GENERAL			
Treatment zone (before, during, and after treatment)	Thermocouples	Temperature	Heating progress and completeness
	Soil	Contaminant concentration	Remedial performance/progress
	Groundwater	Contaminant concentration	Remedial performance/progress
	Vapor	Contaminant concentration	Remedial performance/progress
Perimeter monitoring	Groundwater	Water levels and contaminant concentration	Migration control
	Vapor	Subsurface pressure	Migration control
	Thermocouples	Temperature	Migration control
Extraction and treatment system	Extracted fluids (water, vapor, and DNAPLs)	Temperature, pressure, and flow rate	Mass and energy balance, cooling, vacuum confirmation, mass and energy balance
		Contaminant concentration	Remedial performance
FOR STEAM-ENHANCED EXTRACTION ONLY			
Injection well head	Steam, liquid, and vapor lines	Temperature, pressure, and flow rate	Steam injection confirmation, injection safety and process control, energy balance, and site balancing
Steam system	Steam header	Temperature, pressure, and flow rate	Safety and process control, mass and energy balance
FOR ELECTRICAL RESISTANCE HEATING ONLY			
Electrical heating system	Electrodes	Power, current draw, and voltage	Energy balance and site balancing
		Water flow rate	Power delivery maintenance
FOR THERMAL CONDUCTION HEATING ONLY			
Electrical heating system	Thermal well circuits	Power, current draw, and voltage	Heat delivery, confirmation, and energy balance

Sources: Heron, SteamTech; Baker, TerraTherm; Beyke, Thermal Remediation Services.

Vapor Concentration

Soil gas or extracted vapor monitoring can provide valuable qualitative information regarding the progress towards meeting remediation objectives at sites with VOC contamination. Similar to SVE system behavior, concentrations in extracted vapors will approach an asymptote at some level above zero where increases in the rate of energy input (in the form of heat) fail to result in higher mass removal rates. For a well-designed, well-operated, and optimized extraction system, this condition indicates that a point of diminishing returns has been reached and that further reductions in DNAPL mass using enhanced recovery methods may not be feasible. However, there are many variables involved in advective-phase mass transfer that together may result in asymptotic behavior (EPA, 2001a), and vapor concentrations alone are not sufficient indicators of performance.

Accurate tracking of vapor concentrations over time to determine whether an asymptotic rate of recovery has been reached or whether to shut down the system and collect confirmation samples relies on proper vapor and subsurface temperature monitoring to ensure that the subsurface temperatures required to generate the observed vapor-phase concentrations are being maintained.

Soil Concentration

Soil concentration data can be obtained during installation of the remediation system as well as follow system shutdown. The benefits of soil sampling during system installation is that it can provide additional characterization information on the extent of contamination, as well as provide a baseline of contaminant concentrations in soil before remediation begins. In most cases, soil sampling performed for characterization purposes was not completed at the same frequency as drilling done to install the system, so considerable additional information can be obtained. After completing the remediation, the frequency of soil sampling may not need to be as great as before the remediation, but some paired soil cores should be obtained, and sampling should be done at locations where there is some question as to the effectiveness of treatment (i.e., those areas that were difficult to heat completely). Interim soil sampling can also be used to help judge the progress of the remediation.

Groundwater Monitoring

If groundwater extraction is being employed, samples of the extracted fluids should also be collected and submitted for laboratory analysis to gauge the progress of the remediation. Groundwater concentrations are used to calculate the mass recovered and to help determine when the point of diminishing returns is being reached.

Monitoring wells could also be used for water level measurements, especially for ERH and conductive heating projects at sites with high permeability. Manual measurements of water level can be very difficult when the temperatures approach boiling. Thus, the use of pressure transducers that are installed in the wells permanently and read automatically should be evaluated.

Subsurface Pressure

Subsurface pressure is another parameter that can be measured during in situ thermal remediation to ensure control of the vapors that are generated during the remediation. Piezometers are often used to measure subsurface pressure during in situ thermal remediation projects. These measuring points can be included within and around the perimeter of the treatment area and can be colocated with monitoring wells. The exterior monitoring points must be close enough to the treatment area so that subsurface pressure can be expected at that monitoring point.

5.4 Surfactant/Cosolvent Flushing

5.4.1 Technology Description

Surfactant/cosolvent flushing describes an approach to enhanced DNAPL removal involving the injection, and subsequent extraction, of chemicals to solubilize and/or mobilize DNAPLs. The chemicals are injected into a system of wells designed to "sweep" the DNAPL zone within the aquifer. The solubilized or mobilized DNAPL is removed through strategically placed extraction wells. The produced liquids are then treated and either disposed or returned to the subsurface. The chemicals used are typically aqueous surfactant solutions or cosolvents (e.g., alcohols). In the former case, the process is referred as "surfactant-enhanced aquifer remediation" (SEAR), while in the latter, it is referred to as "cosolvent flooding." Both chemical solutions lower the interfacial tension between DNAPL and the aqueous phase and increase the apparent solubility of DNAPL constituents. Both surfactant and cosolvent flooding have been applied at full scale in the field. Surfactant/cosolvent technology is described in greater detail in a technical and regulatory guidance document developed by the ITRC DNAPLs Team (ITRC, 2003b).

Media heterogeneity is one of the greatest impediments to subsurface remediation using current flushing technologies. The practical efficiency of these technologies varies greatly depending on the ability of the aqueous phase to contact the resident DNAPL. In heterogeneous geologic systems with complex DNAPL architectures, the majority of flushing solution flows through the most permeable layers of the aquifer. These sections may or may not be the most contaminated. Because of media and DNAPL distribution heterogeneities, numerous pore volumes of flushing solution are needed to ensure that at least one pore volume of flushing solution moves through lower-permeability regions. The system can be designed, though, to have a better sweep efficiency that addresses this issue.

For more detail, refer to the Navy's SEAR Design Manual (NAVFAC, 2002) and Implementation Manual (NAVFAC, 2003) and the ITRC document on surfactant/cosolvent flushing (ITRC, 2003b).

5.4.2 Key Monitoring Parameters

Table 5-3 lists suggested performance monitoring parameters for surfactant/cosolvent flushing. Key parameters to monitor are discussed below.

Surfactant/Cosolvent Contaminant Analysis

A key to the successful application of this technology is ensuring that the surfactant/cosolvent is doing what it was designed to do. In some cases when using surfactants as the remedial agent, small fluctuations in electrolyte concentrations can have profound effects on the performance of the technology because the phase behavior is usually dependent on the electrolyte concentration. In addition, cost and time savings can be realized by monitoring concentrations of contaminants of concern (COCs) in recovered fluids and evaluating when the remediation goals have been met at the site. Thus, it is important to monitor both remedial agent and contaminant concentrations during a surfactant or cosolvent flood. The frequency and locations of that monitoring are dependent on the subsurface conditions encountered at the site.

Table 5-3. Performance Monitoring Parameters for Surfactant/Cosolvent Flushing

Location/Media	Parameter	Purpose
Mixed injectate, extraction wells, and monitoring points	Temperature, pH, specific conductance, electrolyte conc.	Fluid chemistry
Extraction wells and monitoring points	DNAPL volume, dissolved contaminant concentration	Remedial progress
All pumping locations	Pumping flow rates	Fluid flow properties
Injection, extraction, and wastewater processing fluid lines	Pressure	Fluid flow properties
Injection and extraction wells and monitoring points	Water levels	Aquifer properties
All monitoring points	Free-phase DNAPL levels	Aquifer properties

Source: Modified from NAVFAC, 2003.

Groundwater Quality

One of the criteria for determining the success of surfactant/cosolvent flushing is a significant reduction in aqueous contaminant concentrations in the injection, recovery, and monitoring wells after the chemical flood. Before the surfactant/cosolvent flood, baseline groundwater samples should be collected to determine the preflood aqueous contaminant levels. Typically, these samples are collected immediately before the surfactant flood, during the prestabilization pumping period (before the surfactant water flood).

Post-treatment groundwater sampling should be carried out after the groundwater system has reequilibrated. To assess any rebound of contaminant concentration, post-sampling events can be conducted quarterly, semiannually, or annually, depending on the magnitude of groundwater flow across the zone of interest.

Additional groundwater samples can also be collected from selected wells outside the treatment zone before and after treatment to verify that DNAPL and surfactant did not migrate out of the well field due to the surfactant/cosolvent flood. These sentinel wells should be screened to monitor the aquifers above and below the treatment zone. Care should be exercised when installing wells below the treatment zone, especially when penetrating thick clay, to avoid providing an additional DNAPL migration pathway.

Injection/Extraction Flow Rate

The injection and recovery flow rates should be monitored closely during the flood. Accurate flow rate measurement is crucial for estimating the recovered DNAPL and surfactant/cosolvent mass as previously described. In addition, unbalanced injection and extraction rates result in poor sweep efficiency and mounding of the water table. Significant fluctuation of the water table can stress the hydraulic control system and potentially lead to insufficient hydraulic capture.

5.5 In Situ Chemical Oxidation

5.5.1 Technology Description

Remediation of contaminant source areas using ISCO involves injecting oxidants and other amendments as required directly into the source zone. Three of the most common chemical oxidants used for ISCO are permanganate (either sodium or potassium permanganate), hydrogen peroxide, and ozone. Permanganate is an oxidizing agent with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups, or hydroxyl groups. Under normal subsurface pH and temperature conditions, the carbon-carbon double bond of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion. There are two forms of permanganate, $KMnO_4$ and $NaMnO_4$. Hydrogen peroxide involves free radical generation and direct oxidation. However, to achieve the desired contaminant reductions in a reasonable time, a metal catalyst is required. Iron is most commonly used, and, when mixed with hydrogen peroxide, the catalyst is known as Fenton's reagent. Ozone (O_3) is one of the strongest oxidants available for ISCO. Ozone can oxidize organic contaminants in two ways, either with direct oxidation by ozone or by the generation of free radical intermediates. The hydroxyl radicals are nonselective oxidizers, which rapidly attack organic contaminants (typically in less than 10 seconds) and break down their carbon-to-carbon bonds (ITRC, 2001).

Another oxidant, sodium persulfate, is also being applied at some sites. Persulfate requires activation by either heat or catalysis by chelated metals. The oxidants, ozone, persulfate, and peroxide create free radicals that react with the contaminant, breaking chemical bonds and producing innocuous substances such as carbon dioxide, water, and chloride (ITRC, 2000). The permanganate ion (MnO_4^-) reacts through electron transfer without the formation of free radicals. Each oxidant has different chemical and physical characteristics and therefore behaves differently in the subsurface. The rate of reaction between the oxidant and soil matrix varies, which affects the transport and distribution of the oxidant in the subsurface. For example, peroxide reacts more

rapidly than MnO_4^- and therefore presents greater challenges for oxidant distribution and the ability to reach the DNAPL.

Treatability studies using soil and groundwater samples from the site may be necessary prior to implementing an ISCO technology. There are different objectives of the bench-scale treatability study. Because natural oxidant demand affects the efficiency of ISCO, one objective should be to determine the oxidant demand of the native soil in order to estimate/design the oxidant concentration and loading need for the full-scale.

Oxidant injection rates are functionally dependent on subsurface conditions, such as hydraulic conductivity. High hydraulic conductivity is desirable for oxidant distribution and, therefore, important to the success of delivering the oxidants to the targeted DNAPL zones. Oxidant distribution can also be attempted in subsurface systems with low hydraulic conductivity and/or high anisotropy using close injection well spacing. ISCO technology is described in greater detail in a technical and regulatory guidance document developed by the ITRC's ISCO Team (ITRC, 2001).

5.5.2 Key Monitoring Parameters

The overall monitoring program for ISCO projects must provide information that is compatible with the agreed-upon regulatory framework and should include elements of both efficiency monitoring and effectiveness monitoring.

Efficiency monitoring is done as a quality control measure before, during, and immediately after the injection operation and consists primarily of the following elements:

- confirmation of oxidant injection concentrations, volumes, and flow rates,
- measurement of oxidant concentrations in groundwater or soil gas samples distributed across the site, and,
- measurement of oxidant persistence.

While ISCO monitoring is done in real time during the oxidant injection process, effectiveness monitoring is done primarily during and after the injection operations, although preinjection data must be gathered to establish a baseline. Depending on the oxidant chemical applied at a site, there can be certain oxidant-specific monitoring parameters that should be included. Despite these differences, all applications of ISCO in DNAPL source zones share the same fundamental performance assessment strategies and performance metrics described in Sections 3 and 4. ISCO technology-specific performance assessment considerations relate to the fact that ISCO is:

- a contaminant mass destruction technology,
- nonselective and attacks both target and nontarget oxidizable matter,
- very sensitive to the distribution and persistence of oxidant chemical delivered to the subsurface, and,

- is a relatively rapid treatment technology, where geochemical changes are highly transient, with some exceptions (e.g., permanganate can persist for months after injection, and the geochemical change of MnO_2 formation may be long-lived).

Since ISCO is a mass destruction technology, contaminant mass is not actually removed from the subsurface as observed in other treatment technologies (i.e., surfactant flooding technology). This fact means that assessment of mass treatment obtained is more difficult and must rely on pre- and post-treatment subsurface evaluations. For this reason, on many ISCO projects, an accurate estimate of source mass reduction (as described in Section 4.3) may not be practical. Therefore, ISCO performance assessment commonly focuses more on estimates of source treatment progress (Section 4.2). Table 5-4 outlines some of the key monitoring parameters applicable to ISCO.

Table 5-4. Performance Monitoring Parameters for In Situ Chemical Oxidation

Location/Media	Parameter	Purpose
Groundwater in monitoring wells down-gradient of injection wells (pre- and post-injection)	Contaminant concentrations	Remedial progress and effectiveness
	Oxidant	Estimate oxidant persistence and radial influence
Soil within source zone (pre- and post-injection)	Contaminant concentrations	Remedial effectiveness
Injection wells (during injection)	Injection flow rate	Determined based on hydraulic conductivity of aquifer system
Recovered oxidant from extraction wells associated with recirculation system, if installed	Extraction flow rate	Fluid flow properties
Groundwater in monitoring wells, down-gradient of injection wells (pre-, during, and post-injection)	Field parameters (DO, pH, temperature, specific conductance, redox)	Evaluate system efficiency
	Tracers (e.g., bromide or potassium)	Observe travel times and distribution of oxidant
	Metals (e.g., iron, manganese, aluminum, arsenic, lead, chromium, magnesium)	Evaluate potential for formation clogging
	Water quality parameters (sulfate, chloride, calcium, nitrate, alkalinity)	

Source: ITRC, 2001

With some oxidants, unintentional contaminant mass redistribution and/or transport can occur, such as with improper application of Fenton's reagent or ozone. Under this condition, significant heat

and/or oxygen gas can be generated that may volatilize and strip contaminants into the vapor phase where they can be lost to the unsaturated zone and atmosphere. Transfer of contaminants can also occur in the gas phase with ozone. Monitoring for these conditions is important to ensure that these potentially adverse effects do not occur or are managed. With the application of Fenton's reagent (especially at higher H_2O_2 concentrations), adequate performance monitoring must be done to ensure that contaminants are destroyed rather than transferred to the atmosphere.

Because ISCO is nonselective, key monitoring parameters include both organic and inorganic constituents. Furthermore, monitoring in multiple media, including soil, groundwater, and potentially vapor phases, can be critical. Analysis for organic contaminants in both soil and groundwater is important for in situ oxidation, since only a small percentage of the mass of DNAPL constituents are present in the aqueous phase. Furthermore, mass transfer of DNAPL of adsorbed-phase material into groundwater during treatment can result in little change in dissolved concentrations, potentially despite effective treatment of a large mass of DNAPL constituents. For these reasons, analysis of groundwater alone at ISCO sites provides limited information on the overall level of DNAPL mass reduction achieved. However, in cases where the objectives of ISCO treatment are solely to reduce dissolved organic concentrations, groundwater monitoring alone may be adequate.

Groundwater Quality

Groundwater analytical data obtained during the in situ oxidation process can be highly dynamic and frequently shows transient increases and decreases in contaminant levels. Since the reaction kinetics with TOC are generally faster than the reaction kinetics with contaminants, contaminants can be released from soils during the initial stages of treatment. A common observation is that dissolved organic contaminant levels increase for a short period, followed by a permanent decrease as the contaminant mass is degraded (ITRC, 2001). This pattern reinforces the importance of a comprehensive performance assessment program.

Since ISCO groundwater data are generally dynamic during the treatment process, data collected while oxidant is still present and conditions are highly nonequilibrium can be confounding. In many cases, real-time groundwater quality monitoring has greatest value to ensure that the oxidation process is not displacing contaminants or creating other safety concerns. Groundwater quality data collected for assessing the final performance of DNAPL source treatment should be obtained after all oxidant reactions are complete and site conditions have returned to equilibrium conditions to account for rebound (refer to Section 2.3 on addressing rebound). Depending on the oxidant applied, the time required to reach equilibrium conditions following oxidant injection can vary from one week to several months and, in some cases, up to one year. There are various parameters (e.g., rebound, oxidant persistence, ORP) that can be monitored to make this determination, which are dependent on each oxidant (ITRC, 2001).

If contamination exists after treatment at levels above established criteria, then additional oxidation may be needed. Sometimes, post-oxidation ground water monitoring is planned to occur at specific, arbitrary intervals. However, contingencies should be established prior to beginning a treatment that

allow for additional injections based on the monitoring data. In most cases, multiple applications of the oxidant will be needed. Thus, the performance assessment program should be developed to accommodate multiple applications of the oxidant.

Analysis of dissolved metals in groundwater is also important since certain pH and redox-sensitive metals can become mobile under conditions that may exist during or as a result of an ISCO application. Most metals are more soluble in low-pH environments, which occurs during Fenton's-type reactions. Redox-sensitive metals are more mobile in an oxidized state and can include chromium, uranium, vanadium, selenium, lead, and molybdenum. At a particular site, they may be in a chemically reduced, insoluble state, and therefore undetectable in groundwater. However, because they are more soluble under oxidizing conditions, these metals can be mobilized by in situ oxidation. Sites where this can be a potential problem can include sites where either naturally occurring metals concentrations in soils are elevated, historical metals contamination was attenuated by naturally occurring chemical reductions processes, or metals were codisposed with organic contaminants.

In most cases, field and laboratory data have shown that the metals liberated by oxidation are readily attenuated back to background conditions. However, this may not always be the case. To minimize the possible risk of mobilizing metals at a site where ISCO is in use, several approaches can be implemented for site screening. Soil laboratory data of total metals content can indicate if the site contains sufficient metals to be problematic. More detailed evaluation can be performed by conducting laboratory treatability tests using samples of soil and groundwater from the site. In these bench-scale tests, aquifer materials are subjected to oxidation, and the solution water is analyzed for metals content before and after treatment. If metals are liberated into the aqueous solution, this solution can then be contacted with site soils to determine the ability of the soils to attenuate the metals to background conditions. At the field scale, metals analysis of groundwater samples is important to verify that metals mobilization is not occurring.

5.6 Enhanced In Situ Bioremediation

In situ bioremediation (ISB) of DNAPL source zones is an emerging area of inquiry and has been demonstrated in the field at only a few chlorinated solvent sites. Mass removal rates attainable by ISB are generally thought to be significantly lower than rates attainable by other, more aggressive source zone reduction technologies. ISB is, therefore, often considered in conjunction with other technologies as a "polishing step" or follow-on remedy after the DNAPL source zone has been depleted. Nevertheless, many field studies are under way to further evaluate the effectiveness of enhanced ISB in treating DNAPL source zones directly. ITRC has created a new work group to follow the progress of this technology regarding its applicability to DNAPLs.

5.6.1 Technology Description

Remediation of contaminant source areas containing halogenated, solvent DNAPL sorbed to soil or pooled as separate phase in groundwater using in situ anaerobic reductive dechlorination, a form of enhanced ISB, involves injecting electron donor amendment directly into the source zone. For

source area treatment to be effective, the soluble amendment must make the DNAPL bioavailable by enhancing the dissolution of the DNAPL. A common amendment used to enhance the dissolution of DNAPL is sodium lactate. For chlorinated solvent DNAPL reductive dechlorination, the anaerobic bacteria degrade the solvents to carbon dioxide, water, and chloride. This technology is described in greater detail in a technical and regulatory guidance document developed by ITRC's In Situ Bioremediation Team (ITRC, 1998).

5.6.2 Key Monitoring Parameters

Assessing ISB effectiveness is different than for most other DNAPL remediation technologies because of the way the technology is implemented. Whereas most of the aggressive DNAPL remediation technologies discussed in this document are deployed as one-time, short-duration remedial actions (weeks to months), ISB in DNAPL source zones is typically applied somewhat continuously over a longer time frame (several years).

Groundwater Quality

The most common metric used to assess ISB performance is groundwater concentrations. As described in Section 4.2.2, this metric alone is not generally recommended for assessing the performance of a DNAPL remediation. However, the only parameter measured for most DNAPL performance assessments that use groundwater concentration as a metric is the contaminants that are being remediated. In contrast, for ISB, several groups of parameters can be monitored through groundwater sampling throughout the operation of an ISB system to assess performance. These include contaminants and degradation products (e.g., PCE, TCE, cis-dichloroethylene [DCE], trans-DCE, vinyl chloride, ethene, chloride), redox-sensitive parameters (e.g., ORP, DO, ferrous iron, nitrate, sulfate, methane, dissolved hydrogen), electron donor parameters (e.g., chemical oxygen demand, total organic carbon/dissolved organic carbon, speciated electron donors, and volatile fatty acids), biological activity indicators (e.g., carbon dioxide and alkalinity), biological nutrients (e.g., phosphate and ammonia), and water quality parameters (e.g., temperature, pH, specific conductance). This approach essentially provides a multiple lines of evidence approach to monitoring the performance of ISB that is analogous to using more than one performance assessment metric described in Section 3 for assessing the performance of other DNAPL remediation technologies.

Table 5-5 presents performance monitoring parameters for ISB of chlorinated solvents. Since the media for all parameters is groundwater, the second column lists the parameter type rather than the media.

Table 5-5. Performance Monitoring Parameters for In Situ Bioremediation of CVOCs

Parameter	Type or Category	Purpose
PCE, TCE, cis-DCE, trans-DCE, vinyl chloride	Contaminants and degradation products	Required to monitor the extent of dechlorination
Ethene and ethane	Degradation products	Ultimate end product of reductive dechlorination of chloroethenes; required to monitor the extent of dechlorination
Chloride	Degradation product	May be useful for monitoring the extent of dechlorination
ORP, dissolved oxygen, ferrous iron, manganese II, nitrate, sulfate, and methane	Redox-sensitive parameters	Required to assess suitability of conditions for reductive dechlorination
Dissolved hydrogen	Redox-sensitive parameters	May be useful in assessing the suitability of conditions for reductive dechlorination
Chemical oxygen demand, total organic carbon/dissolved organic carbon	Electron donor parameters	Surrogate measures of available electron donor in the subsurface; may be useful for assessing the extent of electron donor distribution in the subsurface
Volatile fatty acids and speciated electron donors (e.g., lactate)	Electron donor parameters	Actual measures of available electron donor in the subsurface (parameters will vary depending on the amendment used); may be useful for assessing the extent of electron donor distribution in the subsurface
Carbon dioxide and alkalinity	Biological activity indicators	Indicators of microbial respiration; may be useful for evaluating areas of increased biological activity
Ammonia and phosphate	Biological nutrients	May be useful for assessing potential nutrient limitations
pH, temperature, specific conductance, and turbidity	Water quality parameters	May be useful for evaluating the suitability of conditions for reductive dechlorination
Microbial community and molecular parameter	Microbial parameters	Assess the presence of particular functionality, genetic information, or community structure
Stable carbon isotopes	Contaminants and degradation products	Can be useful to monitor the extent of dechlorination

6.0 OTHER ISSUES

This section addresses health and safety, regulatory issues, and stakeholder concerns that pertain to performance assessment.

6.1 Health and Safety

Hazards associated with monitoring performance that involve collecting samples while a remedial system is operating should be addressed in the job hazard analysis section of the site-specific health and safety plan. In general, the same hazards that impact workers involved in site operations apply to sampling technicians. The following subsections point out some general warnings and provide examples of some of the potential health and safety concerns associated with the treatment technologies discussed in this document.

6.1.1 Sampling Hot Media

With thermal treatment approaches, it is important to take precautions to prevent possible injury when collecting samples of hot media. To minimize these risks, confirmation sampling of groundwater or soil can be delayed until after the subsurface temperature has cooled to safer levels. Depending on the thermal properties of the soil and the velocity of groundwater through the treatment zone, this process could take from a couple weeks to several months or longer. For progress monitoring or intermediate sampling while the subsurface is still hot, the thermal remediation vendors have developed safe methods to obtain valid hot groundwater and soil samples, some of which are presented below.

Sampling Hot Groundwater

Collecting groundwater samples that are more than 90°C can obviously be very hazardous without taking special precautions. If monitoring wells are not properly sealed or vented, flash boiling can result. Box 6-1 shows what can happen if pressure is allowed to build up in the subsurface to the point where flash boiling is a problem. Safe sampling protocols have been developed, including constructing monitoring wells with stainless steel sampling ports to facilitate sample collection and cooling prior to transfer to a sample vial.

Sampling Hot Soil

In addition to issues related to loss of volatile compounds, handling of hot soil also presents a danger to the field technicians collecting samples of the soil. Methods employed at Cape Canaveral LC34 should help to minimize the loss of volatiles as well as prevent injury (Gaberell, et al., 2002).

Box 6-1. NASA Launch Complex 34: "Geyser"

Photo showing a "geyser" at LC34 in the ERH demonstration plot because the monitoring wells were not vented. When the cap was removed during active heating, the pressure dropped, and flash boiling occurred.

Source: Laymon Grey, Florida State University.

6.1.2 Handling and Working near Hazardous Chemical Agents

Hydrogen peroxide and potassium permanganate, oxidants used in the ISCO technology, and alcohols, used for cosolvent flushing, are relatively safe chemicals with respect to toxicity. However, dangers associated with the handling of any oxidizing chemicals or flammable liquids are present with these chemicals. In general, oxidizing chemicals are either potentially flammable or explosive when mixed with combustible chemicals. Oxidizing chemicals not only react violently with combustible materials, but also release oxygen gas during decomposition, which could help fuel a fire or explosion. Ethanol, a commonly used cosolvent, is classified as a flammable liquid and must be handled carefully. Personnel who lack experience and skill with these chemicals may be prone to mishandling of the chemicals and therefore should be supervised closely or assigned to other tasks.

Additional health and safety concerns related to performance monitoring at DNAPL remediation projects include the following:

- vapor monitoring and respirator use,
- electrical hazards,
- sampling extracted fluids, and,
- shipping samples of DNAPL.

6.2 Decision Support: Forecasting Performance

As mentioned, one of the uses of performance assessment results is the potential to allow predictions of future performance of these technologies at other sites and to develop *performance standards*. Performance standards would allow knowledge of a technology's performance at one site to be used

to support decisions about its performance at another. This section discusses some numerical tools being developed that may help decision makers forecast plume response and remediation time frame.

6.2.1 Predicting Plume Response

Currently, there are a limited number of tools available that predict or monitor plume development and attenuation in terms of organic mass flux reduction after source zone treatment or that facilitate a cost-benefit analysis of potential treatment technologies. Unfortunately, they can be inappropriately or inconsistently applied or not validated with good data from the field. Efforts are under way (under ESTCP funding) to develop methods for measuring mass flux that do not require pumping, unlike the plume capture methodology used in Europe. These techniques will be capable of measuring flux both pre- and post-remediation to evaluate the benefits of the remedial efforts. Research is also in progress to develop and evaluate a suite of tools that can be used by site managers to predict the change in mass flux resulting from a partial source removal action. These tools will be useful to predict flux reduction in terms of remedial effort expended and could be extended to produce cost-benefit curves needed to make environmental decisions. The reader is referred to the ESTCP Web site for more information about these projects (www.estcp.org).

Data from selected source zone remediation field tests are being used to evaluate the measurement techniques and the ability of selected numerical simulators to realistically forecast the performance of a remedial activity. These source zone models will provide input to dissolved-plume models that predict the natural or enhanced attenuation expected within the plume. Laboratory studies are expected to supplement ongoing field data collection efforts attempting to assess the relationship between mass removal and resultant contaminant flux from the source area for a broad range of hydrogeological conditions.

6.2.2 Estimating Remediation Time Frames

Current methods to estimate remediation time frames and NAPL source zone dissipation are summarized below.

Method 1: C vs. T Extrapolation

If a well screened in a NAPL zone has a long enough concentration vs. time record, any decreasing trends in the data (if present) can be extrapolated to estimate the time when the well will reach a certain concentration. This calculation can be done on a spreadsheet or using specially designed source dissipation software packages (e.g., the SourceDK software, Farhat, et al., 2003). Statistical information, such as the 95% level of confidence, can also be calculated using this method. Alternatively, a concentration vs. time rate constant can be calculated using the methods outlined in Newell, et al. (2002) and the rate constant used to estimate the rate of source dissipation.

Method 2: Simple Box Model

A simple box model that considers a mass of NAPL in a source zone and the mass flux of dissolved constituents leaving the source zone has been applied to estimate source dissipation patterns (e.g., Wiedemeier, et al., 1999). The key assumption is that the concentration vs. time pattern can be described as a first-order decay process. With this assumption, the source decay rate constant in the box (k_s) can be estimated and used to predict concentration values as a function of time (C_t).

$$k_s = (Q \times C_{gwo})/M_o$$

$$C_t = C_{gwo} \exp(-k_s \times t)$$

where

k_s = source decay rate constant (per time),
C_{gwo} = concentration of dissolved constituent in groundwater at time 0 (mass/volume),
Q = specific discharge through the box (volume/time),
M_o = mass in the box at time = 0 (mass),
C_t = concentration of dissolved constituent in groundwater at time t (mass/volume),
t = time (time).

Software packages that include this type of source dissipation box model include the BIOSCREEN model (Newell, et al., 1996), the BIOCHLOR model (Aziz, et al., 2000) , and the SourceDK model (Farhat, et al., 2003). The authors of the SourceDK software state that their tool can be used as a planning tool for developing order-of-magnitude estimates of remediation time frame, although at most sites, the uncertainty in the estimate is large.

Method 3: Process-Based Models

Available process-type models are based on mass transfer equations for various configurations of NAPL in the subsurface. Wiedemeier, et al. (1999) summarize key process-based models for NAPL systems. Examples of process-based models in public domain software are described below.

The Natural Attenuation Software (NAS) (Chapelle, et al., 2003) uses a numerical model, SEAM 3D, to estimate the time required for dissolution of a NAPL zone before a dissolved-phase concentration goal is achieved. This model follows the work of Imhoff, et al. (1993), where the driving force for NAPL dissolution is the difference between the actual aqueous-phase concentration and the aqueous-phase concentration in equilibrium with the NAPL. NAS calculates the length of time required to meet cleanup goals ("time of remediation") given various values of plume load. Site characterization data, entered by the user, is used to calculate the natural attenuation capacity of various contaminants at a particular site. Using this estimate of the natural attenuation capacity and contaminant source data, the user may chose to evaluate the effects of source reduction or complete removal in terms of meeting a user-specified contaminant concentration at a specific point of compliance. Like most numerical modeling tools, NAS requires the input of detailed site

information about hydrogeology, redox conditions, and the distribution of contaminants. For highly heterogeneous systems, the program may introduce unacceptable errors which may warrant more detailed, site-specific modeling. NAS is available for download at Virginia Tech's Web site (http://www.cee.vt.edu/NAS/).

Other process models in public domain software packages include two models in the SourceDK software (Farhat, et al., 2003): a dissolved-only plumes source decay algorithm from Wiedemeier, et al. (1999) and a source decay model for NAPL-affected source zones, originally developed by Powers, et al. (1994) and modified in Wiedemeier, et al. (1999). SourceDK is available at the Groundwater Services, Inc. Web site (http://www.gsi-net.com/Software/SourceDK.htm) for download.

6.3 Regulatory Concerns

The concerns of the various regulatory agencies that require and oversee the remediation of DNAPL sites are to a great extent the reason for the development of this document. At the present time, there are generally clear regulatory guidelines for the remediation of contaminated groundwater and soil, but these guidelines are often not appropriate to issues unique to DNAPLs. They therefore cannot clearly guide the regulator in assessing the performance of a remediation approach targeting DNAPL source zones.

When assessing the performance of a DNAPL remedy, regulators must have confidence that the proper tools and proper metrics are selected to successfully evaluate the remedial technology performance. This document attempts to provide guidance for assessing the performance of the remediation. Regulator must develop remedial goals and determine what constitutes successful remediation performance. These goals will likely be site and contaminant specific. The case studies in Appendix B of this report demonstrate several strategies that regulators have used to assess performance of various DNAPL remediation technologies.

Other issues that regulators must consider when reviewing, planning, or overseeing a DNAPL source zone remediation include, but are not limited to ensuring proper sampling techniques so the performance can be accurately assessed, stakeholder issues, and public acceptance of the remediation. Some of these concerns are described in more detail below.

Concerns over Drilling in a Source Area

Soil borings. Due to the large number of soil samples that may be needed to assess a remedial performance, regulators need to ensure that drilling will not mobilize the DNAPLs. Regulators also need to ensure that plugging/ abandoning of drill holes with impermeable materials will not decrease the conductivity of the formation enough to prevent the flow of remedial fluids or create channels that will redirect portions of the flow to prevent them from reaching the DNAPL. Regulators must also ensure that the plugging material will not react unfavorably with the DNAPL specific to the site.

Baseline soil sampling should be completed as the system as installed, if possible, to minimize the need for backfilling boreholes. Soil cores that are not collected as part of the injection or extraction well installation should be backfilled with a grout that is compatible with the type of remediation being implemented. For instance, if thermal remediation is to be done, cement grout with 40% silica flour has been used.

Monitoring wells. Regulators must ensure that the performance assessment wells

- do not create preferential flow pathways for DNAPL or contaminated groundwater,
- do not block the flow of remedial fluids or DNAPLs that are being recovered,
- do not change the subsurface flow regime, and,
- do sample areas that are representative of actual groundwater and subsurface conditions to accurately assess remedial performance.

Regulators must oversee the well planning process to ensure that the correct types of wells are incorporated into the design. For example, if wells contain multilevel samplers, they must be constructed and used correctly to avoid creating preferential pathways for contaminant flow. Well construction must also take into account the DNAPL present at the site to ensure that the well materials and grout do not interact with it. Sampling equipment must also be compatible with the DNAPL.

Concerns over Sampling Methods and Techniques Appropriate to the Remedial Technology

The sampling technique, analytical procedures, and the detection limits chosen must be appropriate to measure against the performance assessment goals and objectives. The sampling locations must be selected to be representative of the desired zone and/or depth being assessed.

Regulator must ensure that the sampling method used to assess the remedial performance will work as intended. For example, accurate sampling of volatile organic DNAPL-contaminated soil and groundwater may require special techniques when the media remain hot following a thermal remediation process. Specialized sampling techniques may also be required where injection of surfactants is necessary in the remediation effort. In this case, there may be significant foaming of any materials pumped out of the ground. Accurate analysis of these residuals must be accomplished to assist regulators in the determination of the success of the remediation.

Concerns Related to Statistical Evaluation of the Data

Regulators must ensure that the statistical methods or models used to evaluate the data are appropriate for the type and amount of data collected. Based on the limited type of data that may be available from the site, certain statistical methods may not apply. For example, when performing trend analysis, regulators must ensure that sufficient rounds of sampling and appropriate seasonal data are available. When this is not the case, application of certain statistical methods may produce erroneous results.

Concerns over Potential Mobilization of DNAPLs

Regulators must ensure that DNAPL is not migrating beyond the treatment zone, particularly off site or to areas that were previously uncontaminated. Additionally, performance measurement may be complicated by the fact that the contamination has been moved rather than removed by the remedial technology. Thus, sampling of the original zone of contamination may show reduced levels of DNAPLs, when in fact, contamination may have simply migrated to a different zone.

Concerns Related to Other Regulatory Agencies

Regulators must ensure that the remediation efforts meet other regulatory requirements. These can include underground injection control regulations, air standards, discharge permits, and RCRA hazardous waste treatment requirements, among others.

Public Concerns over Injected Remedial Fluids

While public concerns regarding the performance assessment are not directly part of a regulator's concerns, regulators must be prepared to answer the public's questions and allay fears. These concerns include both the actual hazards that may be directly posed by the remediation and general anxiety sometimes expressed by the public. Stakeholder concerns and public involvement in measuring success at DNAPL sites are addressed in Section 6.4.

6.4 Stakeholder/Public Involvement

Public stakeholders may be persons who own property on or near a contaminated site, or they may be persons concerned about air emissions or groundwater conditions. They may be members of an environmental group such as the Sierra Club or Natural Resources Defense Fund. They may be members of a Department of Defense (DoD) Restoration Advisory Board (RAB) or of a DOE Community Advisory Board (CAB). Whether a tribal, public, or community stakeholder, all stakeholders are generally interested in similar outcomes—limiting or eliminating risk for public health and the environment and future liability.

This document does not suggest that removing DNAPL source areas is required; it is intended simply to describe the state-of-the-art and science with respect to measuring the effectiveness and efficiency of available treatment systems. Regardless of the remedial approach selected, the primary concern for stakeholders should be the most complete characterization of the extent and nature of DNAPL contaminants in the subsurface.. This process must begin with a complete and thorough operational site history, as this first step is the foundation to identifying the location of contaminants and potential receptors along the plume.

The delineation of the plume is also critical in assessing the performance of the chosen remedial technology. For example, a remediation technology may be deemed effective in terms of facilitating the transfer of contaminant mass into the dissolved phase where it can be recovered or treated in situ. It may be viewed as having performed very poorly in terms of efficiency, however.

The scientific and engineering background required to comprehend the complexity of DNAPL source zone remediation are not trivial; hence, many of these concepts are not easily conveyed or understood by a nontechnical audience. Conveying even the most basic concepts dealing with DNAPL source zone delineation and remediation can be a daunting task for the regulator, the property holder, and/or the remediation contractor. Most of the time, the public simply wants to know that the "stuff has been cleaned up." To offer this reassurance, however, there must be some form of tribal, public, or community stakeholder oversight to ensure that the remediation system selected will behave as promised and not exacerbate the situation, meaning that the stakeholders need either instruction in the basic concepts of contaminant delineation and remediation or the services of an independent consultant to review the contractor documents and the regulators' response to proposed work plans and investigation reports. Technical assistance for stakeholders is available through most federal agencies, though time limits on the years this assistance is provided may be limited.

Public involvement requirements differ by state. Arizona, for instance, has extensive state statutes that spell out very clearly the steps required to inform stakeholders about a proposed remedial solution. Applicable state and federal law (mostly RCRA and CERCLA) have requirements for stakeholder involvement, but these generally require a minimum number of public meetings or hearings.

Remediation of DNAPL source areas has proved a daunting task in many cases that has lasted far longer than represented to many stakeholders. The use of newer and better investigative technologies has identified more sources and new remediation technologies offer some hope for solving removal problems at the source. Another benefit of the new technologies available for the remediation of DNAPL is the reduction in the likelihood that a TI waiver is granted without consideration of source control, since TI waivers require NAPL removal to the extent practicable. Such waivers are perceived by many stakeholders as having the potential of leaving them "holding the bag" of future liability and exposure to unnecessary risks. The downside of new technology is that it has meant longer decision-making periods as regulators, insurers, and stakeholders wait for case studies and proof of both effectiveness and efficiency.

All stakeholders benefit by becoming as educated as possible in the many concepts and technologies available for both DNAPL identification and remediation. ITRC documents and online training sessions are a great resource for this need. The challenge for property owners, contractors, and consultants is to aid in the communication of these concepts and systems so that the process does not become bogged down, either because stakeholders do not understand the system being proposed or because they do not believe the nature and extent of the contamination has been fully delineated.

Doing one's homework in advance of presenting to the public is important, as is having a fall-back plan should the proposed remediation fail. Fully explaining how the remediation technology and performance monitoring will get the community to the goals for the site and how steps will be taken along the way to change course will all be valuable in keeping progress from being disrupted.

As this document has pointed out, identification and treatment of DNAPL zones is "a work in progress." Communication that is early, often, truthful, and conveyed and understood in layman's terms goes a long way toward keeping a project on track, even if there are missteps along the way. Going beyond the communication requirement of RCRA or CERCLA and offering primers in DNAPL terminology and system descriptions will probably be beneficial.

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APPENDIX A

List of Acronyms

Appendix A. List of Acronyms

ACL	alternate cleanup level
ANOVA	Analysis of Variance
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ASTM	American Society for Testing and Materials
bgs	below ground surface
CERCLA	Comprehensive Environmental Restoration and Cleanup Liability Act
cfm	cubic feet per minute
COC	contaminant of concern
COD	chemical oxygen demand
CSM	conceptual site model
CVOC	chlorinated volatile organic compound
DCE	dichloroethylene or dichloroethene
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
DPT	direct-push technology
DQO	data quality objective
DUS	dynamic underground stripping
EPA	U.S. Environmental Protection Agency
ERH	electrical resistance heating
ERT	electrical resistance tomography
ESTCP	Environmental Security Technology Certification Program
ft	feet or foot
GC	gas chromatograph
GPR	ground penetrating radar
H_2O_2	hydrogen peroxide
HPO	hydrous pyrolysis/oxidation
HSA	hollow-stem auger
INEEL	Idaho National Engineering and Environmental Laboratory
ISCO	in situ chemical oxidation
ISTD	in situ thermal desorption (or destruction)
ISTR	in situ thermal remediation
ITRC	Interstate Technology & Regulatory Council
LUST	leaking underground storage tank
LNAPL	light, nonaqueous-phase liquid
mm	millimeter
MCL	maximum contaminant level
MIP	membrane interface probe
MNA	monitored natural attenuation
MS	mass spectrometry
MSL	mean sea level
MTBE	methyl tertiary butyl ether

NAPL	nonaqueous-phase liquid
NAS	Natural Attenuation Software
NFA	no further action
NRC	National Research Council
O&M	operation and maintenance
ORP	oxidation reduction potential
OST	Office of Science and Technology
PAH	polynuclear aromatic hydrocarbon
PCBs	polychlorinated biphenyls
PCE	tetrachlorethylene (perchloroethene)
PCU	power control unit
PDB	passive diffusion bag
PID	photoionization detector
PITT	partitioning interwell tracer test
PMA	photo-acoustic multigas analyzer
ppm	parts per million
PVC	polyvinyl chloride
QC	quality control
RAO	remedial action objectives
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RPO	remedial process optimization
SEAR	surfactant-enhanced aquifer remediation
SEE	steam-enhanced extraction
SERDP	Strategic Environmental Research and Development Program
SVE	soil vapor extraction
SVOC	semivolatile organic compound
SWMU	solid waste management unit
TAN	Test Area North
TCA	trichloroethane
TCE	trichloroethene (trichloroethylene)
TI	technical impracticability
TMP	temperature monitoring point
TOC	total organic carbon
TPH	total petroleum hydrocarbon
USACE	U.S. Army Corps of Engineers
VC	vinyl chloride
VOC	volatile organic compound

APPENDIX B

Case Studies

Appendix B. Case Studies

The following case studies are intended to highlight performance assessment approaches used at some recent DNAPL source treatment projects. Cost data are included where it was reasonably available; however, costs for performance assessment are typically not provided as detailed expenses.

In half the instances, the information contained in the case studies was provided by the site operator or technology vendor. In the other half, the state regulator or a researcher overseeing the project provided details. The case studies have not been independently reviewed by third parties.

The case studies are organized by technology. Table B-1 below provides a summary of the case study sites and directs the reader to the appropriate page.

Table B-1. Summary of Case Studies

Case Study	Technology	Geology	Contaminant	Page
Maska Dry Cleaning Site	SVE and Air Sparging	Glacio-lacustrine sand and silty sand	PCE	B-3
Cape Canaveral LC34	ERH, SEE, and ISCO	Surficial fill and silty sands	TCE and DCE	B-8
Young-Rainey STAR Center	SEE and ERH	Surficial fill and silty sands	TCE, toluene, and other solvents	B-18
Air Force Plant 4, Building 181	ERH	Surficial fill and silty, clayey sand and gravel	PCE and degradation products	B-23
Paducah Gaseous Diffusion Plant, Bldg C-400	ERH	Sand and gravel overlying interbedded sand/silt/clay	TCE and technetium	B-31
NSB Kings Bay, Site 11	ISCO (hydrogen peroxide)	Surficial fill and silty sands	PCE, TCE, and DCE	B-36
Broward County Site	ISCO (permanganate)	Medium sands	TCE, TCA, and DCE	B-40
INEEL Test Area North	Enhanced ISB	Fractured basalt	PCE, TCE, radionuclides	B-47

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CASE STUDY 1. MASKA DRY CLEANING SITE
BRADFORD, VERMONT

TECHNOLOGY:	Soil vapor extraction and air sparging
SCALE:	Full
GEOLOGY:	Glacio-lacustrine sand and silty sand
CONTAMINANTS:	PCE

Background. The site is located on a glacio-lacustrine terrace on the west side of the Connecticut River in Bradford, Vermont. The site was used for manufacturing of clothing by two different companies from the early 1970s through 1998. During the manufacturing, the clothing was dry cleaned on site. During the operation of the facilities, dry cleaning chemicals were released on site by both companies. The facilities had on-site septic, and the wastewater from the solvent recovery still was piped directly to a subsurface leach field. Chemical analyses of water from this machinery indicated that the water being disposed of on site had tetrachloroethene (PCE) in it at concentrations well above solubility. Still bottoms were washed out in facility sinks connected to the septic system. Floor drains in the facility buildings were also connected to on-site leachfields. One company that occupied the facility reportedly used PCE to clean the floors. The waste from this operation was disposed of in the floor drains. PCE was also sprayed on knitting machines to keep them clean.

The buildings were concrete slab-on-grade construction. Dry-cleaning machinery was located on the concrete slab; however, for vibration protection, a square area where the dry cleaner was located had been cut completely to the subsurface and an antivibration cork liner installed along the concrete. When the dry cleaners were operated, there were boilovers and releases of PCE. The released PCE would drip through the antivibration pad to the subsurface. There were also reportedly releases of PCE when it was carried in buckets from aboveground storage tanks to the dry cleaning machinery and PCE saturated clothing was taken out of the dry cleaning machinery.

The operations at this facility lead to on-site releases of significant quantities of PCE as unused chemical, used chemical (used both as a dry cleaning solvent and as a solvent to clean floors and machinery), and dissolved in wastewater. Very strong indications that PCE exists as DNAPL in the subsurface were found in both the unsaturated and the saturated zones.

Conceptual Site Model. Very high concentrations of PCE were found in the vadose zone soils below the location of the dry cleaners and in a subsurface leachfield area and associated with a cesspool into which the floor drains from one facility discharged. Based on known releases of PCE as DNAPL to the vadose zone, it is believed that this PCE resulted in the formation of a large PCE vapor plume migrating outwards from the source areas and contacting the top of the water table. Discrete interval sampling of the top of the water table showed that the PCE was partitioning/dissolving from the vapor plume to the groundwater causing a dissolved PCE plume in the upper portion of the groundwater. Infiltrating recharge waters dissolved some of the vadose zone DNAPL PCE to carry PCE in them to the saturated zone.

While no pooled PCE DNAPL was found during the site investigations, very high concentrations of PCE in groundwater and the knowledge that PCE DNAPL was disposed on site provides sufficient evidence that DNAPL exists in the subsurface below the water table at the site. The sands

at the site are underlain by a fine silty layer ridge, the top of which is below the manufacturing facility. It appears that DNAPL released on site traveled vertically downwards through the vadose zone to the saturated zone and downwards through the saturated zone (leaving behind residual-phase DNAPL) until it encountered the fine silt ridge. This appears to have acted as a low-permeability barrier that directed the DNAPL to have flow downwards along the subsurface slope of the ridge. The DNAPL apparently flowed on top of this low-permeability layer to below the Connecticut River located east of the facility.

The DNAPL does not appear to have migrated any further east of the site as the releases of DNAPL stopped, and there was no longer a driving force to move the DNAPL. The majority of the DNAPL in the saturated zone probably now exists as residual-phase ganglia or in small lenses controlled by the stratigraphy. The PCE dissolved in groundwater as the groundwaters move by the DNAPL discharges to the Connecticut River. The PCE is not present in the river in measurable concentrations due to the flow of the river compared to the contaminant transport flux to the river.

The soil vapor plume was causing a dissolved PCE plume to grow and caused a potential indoor health risk in one house due to apparent infiltration into the basement through a stone foundation. The groundwater plume negatively affected property values and severely limited development in the industrial park where this facility is located. The large PCE plume and presence of DNAPL has also prevented the use of groundwater on potential residential properties along the Connecticut River.

Performance Objective. When determining the appropriate remedy for this site, the State of Vermont determined that a full removal of all DNAPL would not be possible considering the geology and the available technology. The primary goals of the remediation were to prevent risk to human health and the environment, to prevent DNAPL or the dissolved PCE plume from spreading, and to permanently reduce the size of the dissolved and vapor plumes. The regulators required that the soil vapor plume be remediated and required the size of the residual source of DNAPL in the vadose and saturated zones to be reduced enough to remediate the vapor plume in the vadose zone and to allow the dissolved plume to become smaller. No specific amount of PCE or DNAPL to be removed from the subsurface was defined.

The remediation also targeted the removal of DNAPL from the shallow portion of the aquifer and the vadose zone (see above description of the geology and location of contamination). The DNAPL at 90 ft bgs appears to be immobile, and the aqueous-phase plume emanating from this DNAPL is discharging into the Connecticut River (where, as described above, it does not adversely affect water quality in the river) and will not likely spread significantly laterally. The depth of the DNAPL in the deeper portions of the plume where it has apparently migrated would preclude the simple remedial technology used at this site, and the DNAPL does not need to be remediated as it is immobile and will not cause risk to human health and the environment (institutional controls will prevent well drilling into this plume).

The State of Vermont decided that the performance of the remediation could be assessed by the long-term observable effect on the plume. The plume needed to be shrunk and prevented from expanding once the active remedial system was turned off. The vapor plume had to be removed from the subsurface and not rebound after ceasing active remediation.

Technology Description. The primary remedial action at this site was a combination of SVE (to address the DNAPL and soil vapor plume) in the vadose zone, air sparging coupled with SVE (to remove a portion of the DNAPL source) in the saturated zone, and excavation of contaminated soils in and near the leachfield (associated with washing floors with PCE). Deed restrictions were placed on the areas where contamination will remain after remediation. A low-tech subsurface heating system was installed in an area of likely DNAPL increased the amount of PCE that could be stripped from the subsurface by the sparging system.

Performance Monitoring and Verification. The environmental consultant for the responsible parties, in coordination with the Vermont regulators, determined that a simple and inexpensive method of performance monitoring and verification would be adequate to assess the effect of the remediation. The parties determined that measuring groundwater, soil gas, and soil quality would indirectly indicate whether the DNAPL had been sufficiently remediated for the site to meet remedial goals. The performance assessment was a combination of the following activities.

Groundwater Quality Monitoring. Reducing the size of the dissolved PCE plume was one the primary goals of the remediation; therefore, periodic groundwater quality monitoring was initiated to evaluate the performance of the remediation. Active remediation was considered complete when the areal extent of groundwater contamination was reduced to a size that would not likely pose a threat to human health or to the environment and would be less of a deterrent on potential development in the area. This condition was considered an indication that some of the short-term goals of the remediation had been met. To ensure that contaminant concentrations do not rebound and that the plume does not expand past the post-remediation boundaries, long-term groundwater quality monitoring is continuing.

Soil Vapor Monitoring. As soil vapor and vadose zone DNAPL had been a significant issue at this site, it was necessary to demonstrate that contaminants were no longer present in soil vapor at concentrations high enough to support expanding the dissolved PCE plume or soil vapor plume or become a risk to indoor air in potential future residential development. As the contaminant at the site is volatile, the lack of vapor-phase contamination in the areas where DNAPL was suspected following remediation strongly indicates that the remediation removed the bulk of the DNAPL and PCE from the vadose zone.

Soil Quality. Soil quality above and below the water table has been attempted to be used to indicate the effect of the remediation on the DNAPL. However, due to the residual nature of the DNAPL and the lack of knowledge of exactly where DNAPL exists as residual phase or in small lenses, soil sampling has not served to prove that remediation was successful. While soil samples do indicate a likely reduction in the presence of PCE in soil, there is no way to ensure that a soil sample was collected from the correct location due to the nature of DNAPL distribution. The indirect method of assessing the long-term effect on the groundwater and soil vapor plumes provided a better method of assessing whether the remediation reached the goals.

Contaminant Removal and Removal Rates. Monitoring of contaminant removal rates provided an indication of whether or not the remedial systems were removing significant concentrations of PCE from the subsurface. Once the extraction of PCE became asymptotic, it likely indicated that the remediation had removed much of the readily available contaminant in the source zone and was limited to removing contamination at the rate of diffusion from the sorbed contaminant to the

extraction system. This by itself, however, was not a good indication that the remediation was complete. Because the amount of DNAPL and dissolved PCE released on-site was not known, an estimate of the percentage of contaminant removed from the subsurface could not be determined. The remediation was not designed to remove all of the contamination at the site. Instead, it was designed to remove enough DNAPL from the vadose zone to halt the production of a significant soil vapor plume; and to remove enough DNAPL from the shallow source zone to reduce the size of the PCE plume. Therefore, while tracking the amounts of contaminant removed was useful to indicate the progress of the remediation, it did not help make final decisions regarding how long the remedial system would need to operate.

Costs. Costs to assess performance of SVE on soil vapor plume and groundwater plume averaged $25,000 per quarter during active remediation. These costs are expected to decrease significantly as the number of sampling points decreases and the frequency of sampling decreases. Confirmatory soil sampling and analysis will no longer be a cost once the effects of the remediation are confirmed.

Lessons Learned. While the long-term effectiveness of the remediation is still being assessed, we have learned that a low-tech, low-cost remediation can be effective at a DNAPL site. In this case, a low-tech SVE/air sparge system coupled with limited subsurface heating appears to have removed the majority of residual-phase DNAPL from the vadose zone and enough DNAPL from the source area to reduce the size of the PCE plume. The remediation did not attempt to remove all DNAPL from the subsurface or completely restore groundwater quality but is protective of human health and the environment (with the placement of institutional controls). It prevents the plume from expanding, removes the great majority of DNAPL mass in the vadose zone (therefore preventing problems associated with a large soil vapor plume), and prevents people from coming into contact with the contaminated groundwater through institutional controls and monitoring.

Soil sampling was found to be helpful in understanding the effect of the remedial activities but by itself could not fully show the effects of the remediation. It turned out that a "weight of evidence" of the effectiveness of the remediation of the soil vapor and aqueous-phase plume provided strong indications that the DNAPL at the site was remediated enough to meet the remedial goals. We also determined, however, that if the remedial goal was to remove all DNAPL, this remedial approach would likely not be an effective remediation technique.

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CASE STUDY 2. CAPE CANAVERAL LC34
CAPE CANAVERAL AIR STATION, FLORIDA

TECHNOLOGY:	Electrical resistance heating, steam enhanced extraction, and ISCO
SCALE:	Demonstration
GEOLOGY:	Surficial fill and silty sands
CONTAMINANTS:	TCE, DCE

NASA's Launch Complex 34 (LC34) at Cape Canaveral Florida was the site of side-by-side testing of three DNAPL source remediation technologies between 1999 and 2001 in a project jointly sponsored by NASA, DOE, EPA, and DoD (Navy and Air Force). Technologies tested included in situ chemical oxidation (ISCO), electrical resistance heating (ERH), and steam enhanced extraction (SEE).

Background. LC34 was used as a launch site for Saturn rockets 1960–1968. Historical records suggest that large amounts of TCE were used at the site to flush rocket engines during testing on the launch pad and to degrease engine parts in the Engineering Support Building (ESB) located nearby. The demonstrations were conducted adjacent to the ESB where preliminary field characterization activities indicated the presence of an extensive region of subsurface DNAPL contamination. Spent TCE was discharged from the ESB directly to the ground surface in the region of known contamination and into floor drains connected by clay tile passing through the contaminated region to a nearby septic system. It is believed that the joints in the clay tile pipe leaked.

The federal agencies identified above formed the Interagency DNAPL Consortium (IDC) to test three innovative DNAPL source zone treatment technologies. The primary objective of the demonstrations was to evaluate the technologies for cost and performance in treating DNAPL contamination under very similar site conditions. In addition, each demonstration was designed to reveal lessons learned that could be integrated into future applications of the technologies to improve their performance and reduce costs. All vendors submitted designs to maintain hydraulic control of their respective test plots. However, the ISCO design called for recirculation of oxidant solution, which would require an injection permit. Significant delays and added cost were anticipated in resolving this issue and the IDC and its technical advisory group ultimately decided that the vendor should be permitted to proceed without provisions for recirculation.

The technology testing region near the ESB was subdivided into three demonstration plots. Each rectangular plot was 50 x 75 ft in surface dimensions and extended to a depth of 45 ft. A 15-ft buffer separated adjacent plots. A portion of the footprint for each plot underlay the ESB to evaluate the ability of the technologies to remove contamination underneath a structure, as shown in Figure B2-1.

The shallow subsurface lithology at the site is comprised of a fine, sandy Upper Sand Unit (USU; approximately 20–25 ft thick) underlain by a silty/clayey sand Middle Fine Grained Unit (MFGU; approximately 5–10 ft thick) and a coarse, sandy Lower Sand Unit (LSU; approximately 10–15 ft thick). A thin, clay-rich, Lower Clay Unit (LCU) underlies the Lower Sand Unit and occurs at a depth of approximately 45 ft bgs. Overall, the approximate total amount of TCE contamination observed in the vicinity of the test plots is distributed among the major lithologic units as follows: USU 5%, MFGU 26%, and LSU 69%.

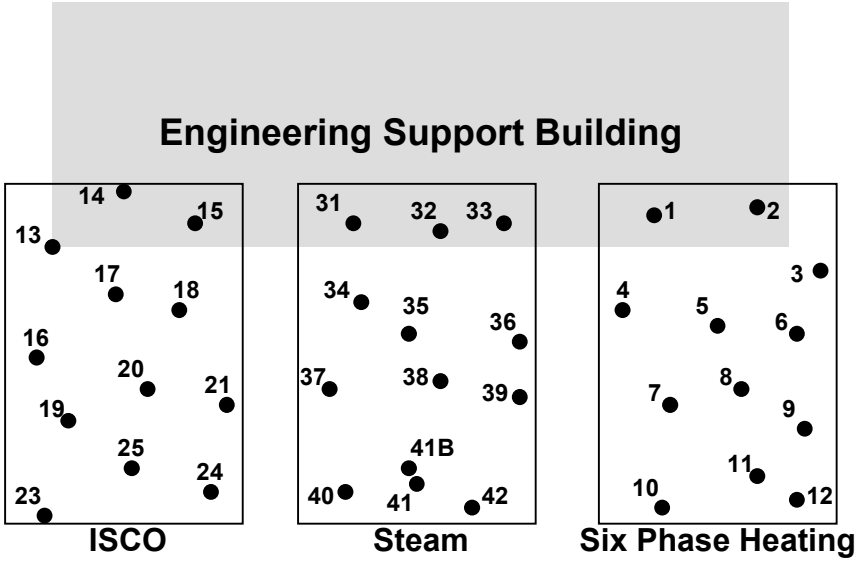

Figure B2-1. Schematic map of the LC34 site and the three DNAPL source treatment cells. Approximate locations of soil borings are noted.

In Situ Chemical Oxidation. In situ chemical oxidation using potassium permanganate ($KMnO_4$) was one of the first two demonstrations deployed; oxidant injection began in September 1999. There were three phases of injection (September–October, 1999; November, 1999; March–April, 2000) that involved a total of over 800,000 gal of oxidant solution (average concentration approximately 2%), a volume approximately three times the pore volume of the demonstration plot. On a volumetric basis, nearly 90% of the injection occurred during Phases 1 and 3 and overall, the LSU received more than half of the $KMnO_4$ solution. Oxidant solution was injected through multiple soil lances that were advanced in 2-ft increments to a depth of 45 ft near the LSU–LCU contact. The demonstration design and operation did not include any provision to ensure hydraulic control and a comparison of the amount of fluid injected vs. pore volume as well as evaluation of monitoring data from a network of wells and soil cores from locations surrounding the plot following the demonstration illustrate that significant fluid displacement occurred.

Electrical Resistance Heating. Electrical resistance heating was deployed as a combination of both three- and six-phase heating during the late summer of 1999. The original electrodes were completed in both the lower part of the LSU and the MFGU, although electrodes were added to the USU midway through the demonstration to improve heating in this zone and avoid vapor condensation. The vacuum vapor extraction system was deployed in the vadose zone at a depth of about 3–5 ft bgs. Heating began in August 1999 and continued until late September when the first of a series of hurricanes and tropical storms impacted LC34 necessitating a shutdown of power. These storms resulted in a rise of the water table in the test plot to the ground surface rendering the vapor recover system inoperative and caused damage to some of the equipment. In addition, lateral migration of shallow groundwater during this time carried high concentrations of dissolved TCE to a nearby drainage ditch where it discharged to the surface. The vapor recovery system was redesigned, a storm water diversion modification was implemented, and heating was resumed in mid-December. In spring, 2000 there was another shutdown lasting 48 days. Active heating continued until final shutdown in mid-July, 2000.

As a result of the hurricanes and tropical storms occurring early in the demonstration, an unknown quantity of TCE was transported laterally beyond the plot boundaries in a northwesterly direction. Four to five months after the weather-related transport, a large zone of dead grass developed to the northwest of the ERH plot, and the presence of a plume of hot, shallow groundwater was observed underlying this same region. The location and timing of the plume is consistent with displacement of hot water from the plot due to active oxidant injection in the ISCO plot. In an apparently unrelated observation, significant perturbations also were noted in the vertical temperature profile at a monitoring location about 15 ft beyond the eastern perimeter of the plot. The temperature data indicated that contaminated hot water was migrating laterally outward from the plot both at the surface of the water table and the top of the LSU. This effect was observed throughout the demonstration and probably was related to thermally driven flow caused by the ERH process as modified by site lithologic features.

Steam Enhanced Extraction. The SEE demonstration began in July, 2001 and continued until December, 2001. For this demonstration steam was injected in two wells located in the central part of the plot and steam/groundwater extraction wells were located along the perimeter of the plot. The objective of this arrangement was to ensure hydraulic control, a goal that was confirmed by careful monitoring of subsurface temperatures throughout and surrounding the plot. One outcome of this design was the fact that as much as 200,000– 400,000 gal. of groundwater from outside the treatment plot was captured by the extraction wells. The amount of TCE associated with this water probably amounted to several hundreds of kilograms.

The design of this demonstration incorporated steam and co–air injection. The purpose of the air was to create a noncondensible gas phase in the subsurface to help mitigate the potential for formation of a condensation front of TCE that might lead to uncontrolled downward migration.

Performance Objectives. The primary objective of each demonstration was to estimate the amount of TCE removed from the plots, with a general performance criterion for the vendors of at least 90% removal of TCE DNAPL. Secondary performance objectives include the following:

- verify that TCE did not migrate to surrounding regions due to the demonstrations,
- evaluate aquifer quality before and after the demonstrations,
- verify that the demonstrations do not impact one another or determine the extent of the interaction, and,
- verify operating requirements and costs of the technologies.

Although the eventual target for the LC34 aquifer is to achieve Florida state–mandated groundwater cleanup goals (3 μg/L of TCE, 70 μg/L of cis-1,2-DCE, and 1 μg/L of vinyl chloride), a more feasible and economically viable goal of 90% reduction of TCE DNAPL mass was agreed upon as the primary objective for the demonstration projects. The ultimate end state goal for the site is to meet MCLs in groundwater, but if concentrations can be brought down to within 100 times the MCLs, then state regulators have indicated they would be satisfied and, in accordance with the Florida DEP's Natural Attenuation Default Source Concentrations, may allow active source zone remediation to be shut down as long as natural attenuation processes are occurring.

Performance Monitoring and Verification. The primary objective of performance assessment for all three technologies tested was to estimate the percent reduction in mass of TCE, with a goal of

>90% mass removal. Predemonstration characterization to determine the mass of TCE present in the three demonstration plots was accomplished by taking a series of continuous soil cores from the surface to the depth of the Lower Clay Unit. Specific core locations for each demonstration plot were determined by an unaligned systematic sampling design (Battelle, 2003) in which a 3- x 4-ft coarse grid subdivided the cell into 12 equal area elements. A 4- x 4-ft fine-mesh grid was overlaid on each coarse grid element, and a core location was selected from among the grid nodes of the fine mesh by using a table of random numbers.

Soil cores were collected by a direct-push rig and were obtained with split spoon samplers in 2-ft increments and preserved in the field with methanol prior to transport to a laboratory for analysis. Following completion of each demonstration, a second set of cores was obtained from locations selected, as before, by the unaligned systematic sampling design and analyzed to determine the mass of TCE remaining after treatment. The average lateral separation of the paired before/after core locations was approximately 4.5 ft.

Post-treatment soil cores obtained from the ERH and SEE demonstration plots were at elevated temperatures (up to 90°C). Special procedures were devised and tested to ensure that no significant loss of TCE occurred due to evaporation. In general, 2-ft segments of core were obtained in split spoon samplers, the ends capped, and the entire assembly cooled in an ice bath until near-ambient temperatures were reached. Subsequent handling, preservation, and analysis procedures were identical to those used for all other soil core samples. The effectiveness of this method was verified by spiking several hot test cores with a known amount of surrogate volatile tracer and confirming that complete recovery was achievable.

In addition to the statistically based sampling program, one set of duplicate soil cores was obtained from each plot before and after treatment to determine the magnitude of variation in TCE concentrations from what were intended to be nearly identical locations. Figure B2-2 illustrates several examples of duplicate core results. For the pair SB-210/SB-210B, the profiles are very similar and the total mass of TCE measured in each core agrees to within approximately 4%. For the other two pairs of cores shown, there is good to fair agreement of the general trends of the depth profiles, but there are specific zones where significant differences in TCE concentrations exist between the members of each pair. These differences tend to occur near the bottom of the profiles (near the top of the Lower Clay Unit), where DNAPL might be expected to be locally pooled. Comparison of paired cores SB-41/SB-41B and SB-217/SB-317 reveals total TCE masses that differ by a factor of up to four times for the duplicates. These comparisons are important because they confirm that significant heterogeneities in the lateral and horizontal distribution of DNAPL can exist over short distances.

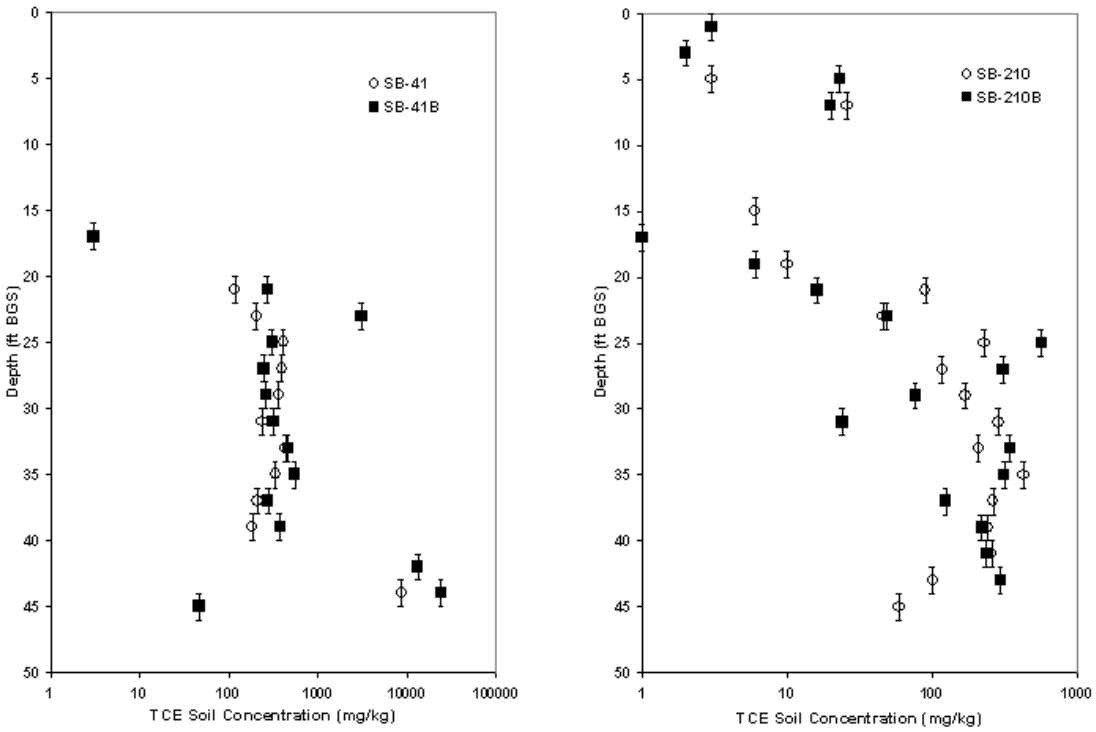

Figure B2-2. Concentration depth profiles for TCE in soils for two pairs of duplicate cores. In each case, the paired core holes are located within 3 ft of one another.

The TCE concentration data for the cores at LC34 were converted to total effective mass of TCE in each plot by two different methods (Buxton and Gavaskar, 2002). One approach was to estimate TCE mass by 3-D contouring of TCE concentration results using the EarthVision™ software package, which linearly interpolates among TCE concentration data in soil. The TCE mass was calculated using the contoured isoconcentration shell volumes. The second approach employed geostatistical analysis (kriging) that takes into consideration the spatial variability between neighboring TCE soil concentration data. In principle, this method captures the type of variability illustrated in Figure B2-2.

Table B2-1 presents the results of both methodologies for each of the three demonstration plots before and after treatment. An initial observation indicates reasonable agreement between the two methods of mass estimation. One benefit of the kriging method is that estimates of the uncertainty of mass are obtained and one can specify the confidence level desired for the uncertainty; greater confidence requires a wider range of uncertainty. For the work at LC34, an 80% confidence interval was selected for data evaluation, which leads to an uncertainty of ±25% in the mass estimates. From a performance assessment perspective, the ability to accurately define the magnitude of DNAPL mass reduction or the amount of remaining TCE mass is limited by these statistical uncertainties. Of course, one can reduce the level of uncertainty by collecting more soil core data, but there is a trade-off in terms of increased cost of drilling, sampling, and analysis.

In general, it appears that all three technologies were capable of removing a large fraction of the total mass of TCE (and DNAPL) estimated to be present in the plots prior to implementing the demonstrations. Only ERH met the performance criterion of 90% mass reduction of TCE DNAPL

established for the tests, however. TCE concentrations in groundwater for each of the plots were variable (especially vertically) both before and after the demonstrations. Predemonstration values tended to be well in excess of 1 mg/L and ranged as high as the solubility limit for TCE (1100 mg/L). Post-demonstration groundwater samples on average indicated improvement in terms of TCE concentration but still were near the solubility limit in a few places.

Table B2-1. Mass estimates of TCE in treatment cells at LC34 obtained from soil core data

Estimation method	TCE mass estimates (kg)		
	ISCO	SEE	ERH
PRETREATMENT			
EarthVision™ contouring	6,100	10,400	11,300
Kriging (80% confidence interval)	6,200 - 9,200	7,500 – 15,700	11,100 – 14,200
POST-TREATMENT			
EarthVision™ contouring	1,100	1,500	1,100
Kriging (80% confidence interval)	1,500 - 2,300	1,000 - 1,500	1,300 – 2,500

Source: Buxton and Gavaskar, 2002

One must determine the importance of estimating the amount of DNAPL mass reduction as a metric for performance assessment. For the reasons already mentioned, uncertainties with making this estimate from core data are inevitable. However, all methods of DNAPL mass estimation have associated uncertainties suggesting that mass reduction should be regarded as only one of several measures of performance and perhaps not even the most important. From the perspective of technology design, only ISCO requires a pre-deployment estimate of DNAPL mass in order to estimate the amount of oxidant that will be required. For both thermal technologies, the amount of energy required to heat the subsurface to about 100°C far exceeds the energy needed to vaporize and mobilize the DNAPL. Knowing the amount of DNAPL present in the source (and the rate at which it will vaporize and enter the vapor recovery system) may be important for designing the vapor treatment system.

DNAPL Migration. As part of performance assessment activities and in an effort to ascertain if DNAPL migration accompanied any of the demonstrations, a comparison of TCE soil and groundwater concentrations was conducted in pre- and post-demonstration samples obtained from regions surrounding the demonstration plots. A number of monitoring wells peripheral to the ISCO plot showed sharp increases in dissolved concentrations of TCE during and following the demonstration. In general, it is believed that these increases occurred as a result of displacement of highly contaminated groundwater from within the plot during permanganate solution injection. However, one monitoring site located approximately 25 ft from the SW corner of the ISCO plot revealed evidence from soil cores of apparent large increases in TCE in several places within the soil profile following the demonstration. One potential conclusion is that the steep hydraulic gradients associated with permanganate injection may have caused some migration and redistribution of DNAPL in this area, but one cannot dismiss the possibility that the before and after soil core results simply reflect natural variations in DNAPL distribution over relatively short lateral distances (e.g.

Figure 2). None of the pre/post treatment soil cores from other areas surrounding the ISCO plot that were monitored showed similar effects.

It has been noted already that lateral migration of hot water (and dissolved TCE) occurred in association with the ERH demonstration. Strong evidence of localized DNAPL migration related to this technology exists. In a cluster of monitoring wells located about 15 ft from the eastern perimeter of the ERH plot the presence of DNAPL was confirmed in the bottom of wells completed in the MFGU and LSU following the ERH demonstration. No DNAPL was present in these wells prior to the demonstration. In addition, comparison of pre- and post-demonstration soil cores from this same location suggest possible increases in the amount of DNAPL in the MFGU and the upper part of the LSU following the demonstration. It is suspected that DNAPL was mobilized in this region as a result of the ERH demonstration. The source of the mobile DNAPL may have been due to local redistribution or may have originated from within the ERH plot by mechanisms already discussed.

Because the demonstration plots were located within a much larger area of DNAPL contamination it is impossible to estimate how much DNAPL might have been transferred from within the plots to the surrounding area; this region was not sampled nearly as extensively as that within the plots, so relevant data are not available. However, the poor mass balance for the ERH demonstration and other associated observations suggest that contaminant migration to regions external to the treatment plot, perhaps including DNAPL mobilization, probably occurred for this technology. One of the lessons learned from these results is the need to reevaluate the engineering design and operation of aggressive DNAPL treatment technologies to prevent or minimize DNAPL migration outside of the zone of influence of the technology.

Costs. The estimated cost of treatment using each of the technologies is presented in Table B2-2. Actual costs for other sites will depend upon site-specific conditions (depth and nature of contamination; contaminated medium, etc.), improvements in engineering design and implementation, and anticipated improvements in cost-effectiveness due to scale-up. Constraints placed on the vendors by the IDC (e.g. site logistics, treatment plot size, requirement to maintain hydraulic control, etc.) resulted in applying some design strategies differently than would be employed for a typical deployment leading to increased costs.

Table B2-2. Cost Estimates for TCE Treatment

Cost basis	Cost (dollars)		
	ISCO	SEE	ERH
Per pound of TCE removed	$109	$61	$29
Per cubic yard treated	187	192	104

Consequently, the costs presented in Table B2-2 are not representative of what would be encountered had these technologies been deployed for full-scale cleanup of a site comparable to LC34. The fact that these were demonstrations of limited scale and with special conditions imposed by the IDC and NASA, account for the relatively high unit costs. Some vendors of these

technologies cite typical unit costs well below these figures, but generally they do not include the same range of constraints encountered for the demonstrations at LC34.

The cost of conducting the performance assessment for each of the demonstrations is not trivial. For each of the three technologies used at LC34, performance assessment cost approximately $500,000 to $650,000. However, the IDC requested more extensive performance evaluation activities at LC34 than might be necessary at many sites, possibly accounting for some of the cost.

Lessons Learned

- A comprehensive and accurate site conceptual model is essential for successfully designing and implementing DNAPL source remediation. In addition, understanding how a specific technology will respond to different components of the site model (e.g., lithologic heterogeneities) is of key importance,
- Although DNAPL mass removal was significant in each of the demonstrations (84%–97%), reduction in groundwater concentrations of TCE did not drop dramatically. Part of the reason for this was residual DNAPL remaining after treatment, but another cause was the fact that the treatment plots were located within a much larger area of contamination and post-treatment reinvasion of contamination could occur,
- The location of the three test plots in close proximity to one another and the lack or imperfect achievement of hydraulic control observed for two of the demonstrations (ISCO and ERH) resulted in impacts on a region outside of the test plot areas,
- Soil and groundwater sampling in post-treatment thermal plots must deal with hot samples. Special precautions are required to avoid VOC losses due to inappropriate handling procedures.

<u>ISCO</u>

- Hydraulic control during oxidant injection is essential to avoid displacement of contaminated groundwater and possibly DNAPL,
- Due to the strong purple color associated with MnO_4- and the brownish color related to the MnO_2 reaction products with TCE, collection and visual examination of soil cores proved to be the most effective means of performance monitoring for determining the extent of oxidant distribution,
- The amount of DNAPL to be treated is strongly related to the amount of $KMnO_4$ required and is a significant cost driver for the remediation. Treatment by ISCO of sites highly contaminated with DNAPL might not be a cost-effective alternative.

<u>SEE</u>

- The demonstration design involved steam/air injection to the central part of the test plot with vapor/groundwater extraction along the perimeter in order to maintain hydraulic control. This resulted in the extraction and treatment of a large quantity of contaminated groundwater coming from outside of the treatment plot (perhaps 200,000 to 400,000 gal of water). The preferred and most cost-effective design for SEE probably would have included steam injection on the perimeter that drives contaminants to extraction wells located in the central part of the plot.

- There was considerable debate (and some controversy) during the demonstration design phase of the efficacy of co-air injection. The potential benefits and problems of this design feature need to be evaluated carefully before implementation.

ERH

- The design and implementation of electrodes needs to be carefully considered so that they work effectively,
- Lithologic variations within the treated region can have an important impact on groundwater/vapor flow dynamics and lateral fluid migration outside of the plot can occur if the conceptual model is not properly integrated into the design to ensure hydraulic control,
- The vapor recovery system needs to be designed to maintain effective control of contaminants. Vapor recovery limited to the vadose zone may not be sufficient. Furthermore, at some sites it may be necessary to design for significant fluctuations in water table levels during treatment with the ability of adjusting the water table elevation,
- TCE mass balance calculations reveal that less than 50% of the TCE mass assumed to have been removed from the source zone was actually captured by the aboveground recovery systems. Lateral migration outside of the treatment plot is suspected as an important cause, but other explanations cannot be ruled out.

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CASE STUDY 3. YOUNG-RAINEY STAR CENTER
LARGO, FLORIDA

TECHNOLOGY:	Steam-enhanced extraction with electrical resistance heating
SCALE:	Full
GEOLOGY:	Surficial fill and silty sands
CONTAMINANTS:	TCE, toluene, vinyl chloride, methylene chloride, DCE, PCE, o-xylene

Background. The Young-Rainey Science, Technology and Research (STAR) Center is a former U.S. Department of Energy (DOE) facility located in Largo, Florida. DNAPLs have been found in the subsurface at the Northeast Site. These DNAPLs serve as a source of dissolved-phase contamination and must be reduced to acceptable levels before remediation of the dissolved-phase can be completed. The principal contaminants of concern (COCs) present in soil and groundwater are trichloroethene (TCE), and toluene, which both occur as free product. Other COCs present are vinyl chloride, methylene chloride, cis-1,2dichloroethene, tetrachloroethene (PCE), and o-xylene.

Characterization activities indicated two distinct areas of DNAPLs: a smaller area (approximately 10,000 sq ft) in the northern portion of the site (Area A) and a larger area (approximately 39,000 sq ft) in the southern portion of the site (Area B). Characterization activities also determined that DNAPLs were present as deep as 6 ft into the confining clay unit located below the surficial sediments (approximately 36 ft bgs). It is roughly estimated that total DNAPL mass is 16,000 lbs. This case study covers the recently completed Area A remediation.

The remediation design used a combination of steam-enhanced extraction (SEE) and electrical resistance heating (ERH) of soil and groundwater. A combination of SEE and ERH was chosen because of the unique challenges presented at this site including low-permeability soils and the presence of a complex mixture of NAPLs. ERH was applied in the lower, less-permeable, clay-rich Hawthorn, and both SEE and ERH were used in the upper, more-permeable sandy aquifer.

Performance Objectives. The primary remediation objective was to remove NAPLs from the subsurface and attain concentration-based cleanup goals for soil and groundwater as shown in Table B3-1. The groundwater goals are equivalent to 1% of the compound's respective aqueous solubility. No groundwater sample could exceed the goal by more than 50%. Additional performance objectives included the following:

- Dissolved concentration should remain below the cleanup goals for at least 24 weeks following cessation of operations (see TableB3- 1).
- A minimum operating temperature of 84°C will be maintained at all times during operation.
- Hydraulic control will be maintained in the remediation area to ensure that cleanup goals are not exceeded outside these areas.

Table B3-1. Cleanup Goals for Remediation at Area A

Contaminant	Groundwater (µg/L)[1]	Soil (µg/kg)[2]
Trichloroethene	11,000	20,400
cis-1,2-Dichloroethene	50,000	71,000
Methylene chloride	20,000	227,000
Toluene	5,500	15,000
Florida Petroleum Range Organics (FL-PRO)	50,000	2,500,000

1. No groundwater sample can exceed the cleanup goal by more than 50%.
2. There must be a 90% certainty that 90% of the site was at or below the cleanup goals and no soil sample can exceed the goal by more than 100%.

Performance Monitoring and Verification. The progress of remediation was evaluated using several lines of evidence, namely by measuring the NAPL content in extracted fluids, the total petroleum hydrocarbon content in extracted water, the temperature distribution, and interim soil and groundwater sampling.

Soil. Two interim soil sampling rounds were conducted during operation using a Geoprobe rig to provide detailed chemical information in support of the remedial progress. Samples were collected from areas selected based on the process and subsurface monitoring. Problematic areas, such as areas of the upper sands that were not heating at the desired rate due to low permeability or "cold spots" identified by the thermal monitoring, were also sampled. In addition, areas that received satisfactory treatment based on the operational parameters were sampled for verification. A total of 25 soil samples were collected and analyzed by EPA Method 8021. Since the sampling was done while the site was still hot, the steam and electrical heating systems were turned off at least 24 hours prior to drilling and sampling. The subsurface temperatures within 20 ft of the drilling locations were tested and verified to be below 100°C prior to drilling. Also, the temperature of the asphalt cap in a 10-ft radius of the penetration holes was measured and verified to be safely below 80°C to ensure that there was no steam present at the location of the penetration.

Post-operation soil sampling was conducted after cessation of operation to test the remedial performance based on soil COC concentrations. A Geoprobe was used to collect hot soil cores from the surficial sediments into stainless steel core tubes. Cores were capped immediately and cooled by placing them on ice. After cooling, the core tubes were opened, and a sample was collected using a syringe-type sampler. Analytical parameters were VOCs (by EPA Method 8021) and TPH (by Florida Petroleum Range Organics [FL-PRO]). Locations of the boreholes were selected solely at the discretion of DOE and its technical contractor.

Figure B3-1 is a contour plot presenting the results of soil sampling for TCE only.

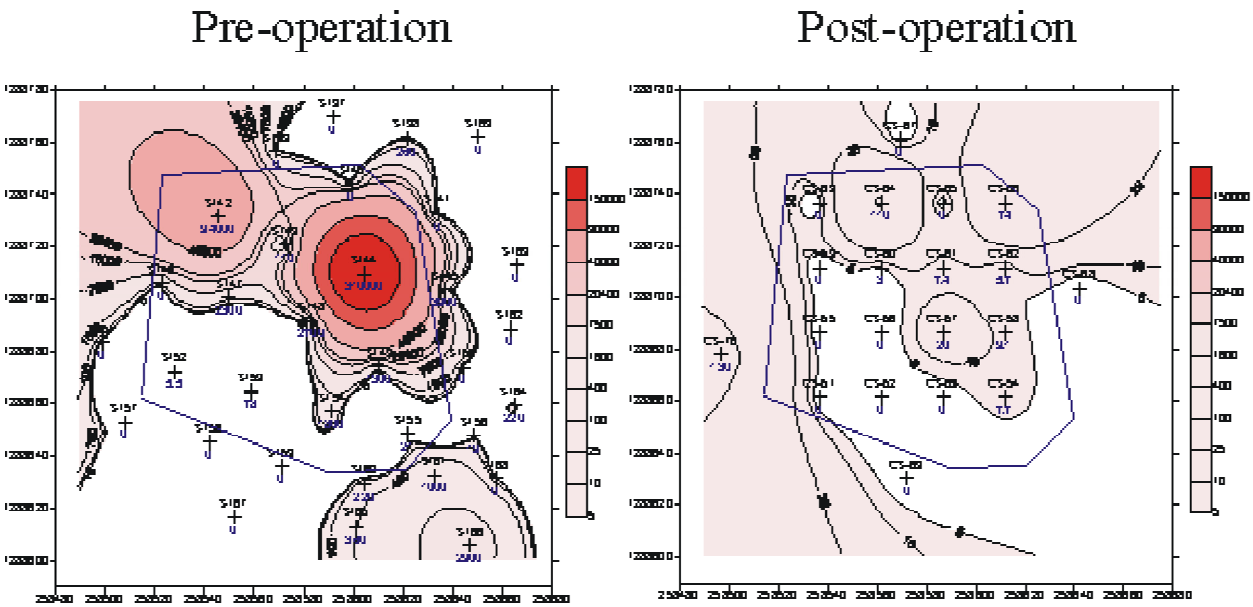

Figure B3-1. Comparison of soil concentration contours pre- and post-operation for TCE (µg/kg).

Groundwater. For remediation of Area A, groundwater samples were collected and analyzed for numerous parameters from three extraction wells located within the DNAPL remediation areas and from eight monitoring wells located outside the remediation area. Monitoring wells located outside the remediation area were used to monitor for contaminant mobilization. Groundwater samples were collected and analyzed for numerous parameters from the prescribed wells at least every two weeks during the operational phase of the remediation.

To prevent loss of contaminants, hot sampling techniques were used to collect samples during confirmatory sampling. Hot groundwater samples were collected by placing Teflon tubing down the well to the middle of the screened interval and purging at the surface with a peristaltic pump. The Teflon tubing ran first to a stainless steel coil submerged in an ice chest, then connected to the silicone pump tubing, and then to a flow cell containing instrumentation used to measure groundwater parameters to determine when stability was reached during purging. Groundwater samples were then collected using the pipette method, which consisted of stopping the pump, removing the tubing from the well, then allowing groundwater to flow from the bottom of the tubing into the sample bottle.

Groundwater was sampled at four weeks after remediation was complete, at 12 weeks after the remediation was complete, and again at 24 weeks after remediation was complete. The purpose of this sampling event was to check for any rebound effects and to confirm that remediation was complete. A soil sampling event was also performed at randomly selected locations to confirm that the source of the NAPLs had been removed.

Groundwater results show that all groundwater concentrations for the COCs were much lower than the remediation goals; therefore the post-operational data was compared with the criteria for complete site restoration. Overall, 42 of 48 (88%) of the groundwater samples collected were below the Maximum Contaminant Level (MCL) for all COCs.

In addition to the monitoring mentioned above, samples were collected of storm water runoff after rainfall events and surface water from the East Pond (a storm water retention pond located east of Area A) and analyzed as a best management practice. These samples were collected prior to and during DNAPL remediation activities to monitor for potential effects of contaminant runoff. The results of these analyses showed no impact.

Mass Removed. Table B3-2 lists the estimated contaminant mass before and after NAPL remediation.

Table B3-2. Comparison of Before and After Contaminant Mass by Compound[1]

Contaminant	Pretreatment mass (lbs)	Post-treatment mass (lbs)
Trichloroethene	1,010	0.14
cis-1,2-Dichloroethene	130	0.19
Methylene chloride	300	0.03
Toluene	800	0.89
FL-PRO	2,960	1,160

1. Mass estimates calculated based on average soil and dissolved concentrations projected over entire treatment cell.

Operational. Progression of the steam and electrical heating was monitored using two somewhat complimentary techniques: direct temperature monitoring (thermocouples) and Electrical Resistance Tomography (ERT). Thermocouples were used to monitor in-ground temperature at least once per day. Because of the high dissolved solids content of the groundwater at this site (which prevented resistivity effects caused by temperature and saturation changes from being distinguished from those caused by changes in groundwater chemistry), ERT was not effective at this site, and its use was abandoned.

Process water and vapor sampling and the monitoring of numerous parameters of the overall well-field, subsurface, and liquids from extraction wells were conducted to estimate the completeness of remediation. In particular, extracted fluids were monitored to determine whether they were free of mobile NAPLs, and equilibrium calculations were performed using vapor concentrations to determine whether levels in pore water were approaching cleanup goals.

Costs. The total project subcontract cost was approximately $3,800,000. This cost included all aspects of the project from design, permitting, drilling, construction, operations, sampling, waste disposal, demobilization, and reporting.

Lessons Learned.

- Need to add air stripper to vapor/water train to address higher than expected levels of methylene chloride.

- Temperature reached targets sooner than expected, suggesting that the combined use of the two technologies (i.e. ERH and Steam Enhanced Extraction) appears to be more efficient than either technology used alone.

- System was operated through February 15, 2003, two weeks longer than planned, to address the unexpected discovery of residual resinous materials in one area of the treatment zone.

- Based on initial discussions with the electrical power company, it appeared adequate power would be readily available. However, this was not the case and an additional high-voltage power line had to be constructed.

- During the interim soil sampling, it was determined that one area was not being heated, and additional steam injection points were added in order to heat the entire target area.

- The actual objective of the remediation that was done at this site was to remove mobile NAPL. The soil and groundwater cleanup standards were set based on this goal; these concentrations were thought to demonstrate that no NAPL remained.

- The post-treatment soil sampling showed that all soil concentrations were significantly lower than the soil cleanup standards.

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CASE STUDY 4. AIR FORCE PLANT 4, BUILDING 181
FORT WORTH, TEXAS

TECHNOLOGY:	Electrical resistance heating (three-phase heating)
SCALE:	Full
GEOLOGY:	Surficial fill and silty, clayey sand and gravel
CONTAMINANTS:	TCE, PCE, 1,2-DCE, vinyl chloride

Background. The Air Force Plant 4 complex (AFP4) is located in Fort Worth, Texas. The 602-acre facility is an active military aircraft manufacturing facility. U.S. Air Force fighter jets, including the F-16 and Joint Strike fighter, are manufactured here. The origin of the TCE source material is believed to be degreaser tanks in Building 181. The estimated TCE release was approximately 20,000 gal. The degreaser tanks were removed from service in 1991.

At AFP4, Tertiary Age Terrace Alluvium is exposed at ground surface or lies beneath fill material that is generally composed of the same Terrace Alluvium. Regionally, these sediments are characterized as heterogeneous or interbedded gravel, sand, silt, and clay mixtures. Drilling logs from Building 181 record the presence of silty clay deposits (with some sand and gravel) that range in thickness from 15 to 35 ft.

Beneath the Terrace Alluvium lie weathered and competent bedrock consisting of Cretaceous Age Goodland Limestone Formation and Walnut Clay Formation, undifferentiated at the site. Regionally, the Goodland Formation is a white, fossiliferous, micritic limestone, and the Walnut Formation is a marl or marly limestone that contains fossilized oyster reefs. Together, these formations comprise the Fredericksburg Group, which functions as an aquitard overlying the Paluxy Formation of the Trinity Group aquifers. Drilling logs from Building 181 record the presence of weathered limestone layers at 15–20 ft bgs in the western portion of the site, and at 30–35 ft bgs in the eastern portion of the site. The logs consistently record the presence of competent bedrock at 30–35 ft bgs beneath the entire site.

Residual DNAPL was identified in the vadose zone (Terrace Alluvium and overlying fill soil under Building 181) which consists of heterogeneous interbedded clay, silt, and poorly to moderately sorted sand and gravel extending to approximately 35 ft bgs. The shallow aquifer is encountered at 27–35 ft bgs and has a thickness of approximately 5 ft with a hydraulic conductivity of 4.6×10^{-3} to 4.7×10^{-2} cm/sec. Pumping rates range from less than 0.4 to 2.8 gallon per minute. Bedrock (Goodland Limestone of the Walnut Formation) is encountered at 15–20 ft bgs in the western portion of the site and at 30–35 ft bgs in the eastern portion of the site.

Accurate information is not available on the total amount of TCE that spilled or leaked from the tanks or how much TCE was in the unsaturated zone. The maximum concentration of TCE in soil and groundwater were reported at 2,770 mg/kg, and 285 mg/L, respectively. Based on the maximum solubility of TCE in groundwater and the one percent rule of thumb, a DNAPL source area was assumed. The TCE DNAPL is believed to be the source of the Eastern Parking Lot (EPL) groundwater plume at the site. It was conceptualized that the DNAPL migrated through the vadose zone, through the unconsolidated saturated zone, and then along the bedrock upper surface to a

former paleochannel. The full-scale treatment area was approximately ½ acre, with a treatment volume of approximately 20,000 cubic yards.

Selection of the ERH technology for the full-scale remediation (source removal) was based on the findings of the previous ERH pilot-scale test conducted at the site in May 2001. The pilot test area was inside the subsequent full-scale remediation footprint. The pilot test area was believed to contain approximately 220–440 lbs of VOCs. Tracer tests were used to estimate the mass of VOCs in the pilot test area. The high degree of variation common in tracer tests is the reason for the large range in the approximate mass estimate.

Tracer test results also indicated more DNAPL in the F-218 test area (790–1,580 lbs) than within the Building 181 pilot test cell. It should be noted that tracer tests are not geared for determining the mass of pooled DNAPL; rather, they are performed to determine the mass of nonpooled, residual product. These results would be biased low if DNAPL was pooled, which could explain this apparent inconsistency (based on groundwater concentrations and the location of prior spills, it would appear more likely that a greater volume of DNAPL would be present under the formerly leaking tanks within Building 181). Because the pilot test cell volumes were small (56–73 cubic yards swept), extrapolation of these data to the much larger contaminant plume of interest is problematic, especially moving in the down-gradient direction from the F-218 test area (i.e., out into the parking lot east of Building 181).

Performance Objectives. The primary RAOs were to reduce residual-phase DNAPL in soil and remove free-phase DNAPL to the extent practicable. The groundwater RAO was to prevent groundwater that has contamination above MCLs from leaving the property boundaries. Specific targets for both soil and groundwater are presented in Table B4-1.

Table B4-1. Soil and Groundwater Cleanup Targets for Air Force Plant 4, Building 181 Site

Performance Criteria	Performance Objectives	Methods of Measuring Performance
Subsurface temperatures in the treatment volume	Boiling point of TCE	Temperature monitoring point measurements
Soil -TCE remediation goal	<11.5 mg/kg[1]	Pre- and post-application subsurface soil sampling
Groundwater -TCE remediation goal	<10 mg/L[1]	Pre-application, interim and post-application groundwater sampling

1. These performance objectives are equivalent to the ROD-based remedial action objectives for the soil and groundwater media and represent a >99% reduction in TCE concentrations from the highest previous detections in the enlarged ERH application volume. The ROD-based remedial action objectives were calculated using a 95% upper confidence limit (UCL) statistical analysis.

The intent was to reduce the TCE concentration in soils to <11.5 mg/kg, which, based on leaching modeling, is the allowable soil concentration to prevent underlying groundwater concentrations from exceeding the respective RAOs.

ERH System Installation. To implement the full-scale ERH remediation at the site, a network of 74 ERH electrodes was installed. In conjunction with electrode construction, an SVE network was established. While many SVE wells were colocated in vertical or angled electrode boreholes, some SVE wells were independently located.

The ERH power control unit (PCU), which conditions electrical energy for optimum subsurface heating, was equipped with numerous automatic shut-off components to prevent unwanted exposure to hazardous voltages. Emergency stop buttons were located both remotely and locally in the event a personnel or equipment hazard was identified. The SVE piping was installed to manifold the SVE wells together into a common inlet at the steam condenser.

ERH System Operations. Electrical voltage and current readings were measured routinely throughout the full-scale ERH remediation to ensure optimum system performance while maintaining safe working conditions. Vacuum pressure and vapor flow rate readings were also routinely collected from each SVE well and from various header pipes supporting some or all SVE network wells. The data were used to assess the performance of the vacuum blower and SVE network, and, in conjunction with laboratory analytical results for influent vapor samples, to calculate the mass of TCE removed from the subsurface over time. The data were also used to determine which system adjustments were needed to optimize steam extraction on a weekly basis.

Soil vacuum pressure readings were routinely collected from each temperature monitoring point (TMP). The data were used to assess the cumulative affect of the vacuum blower and SVE network on surrounding soils at various depths. In conjunction with SVE vacuum pressure and vapor flow rate readings, the data were also used to determine which system adjustments were needed to optimize steam extraction on a weekly basis.

As part of the routine system measurements, recovered steam and vapor were measured at their respective locations downstream of the condenser skid. The condensate was pumped through a turbine-type totalizer (water meter) before it was sent to the equalization tank inside the SVE building. The operator would record the date, time, and totalizer reading so that the time-averaged flow rate of condensate could be calculated. If no condensation occurs in the piping network before the condenser, then the condensate flow rate is equal to the steam recovery flow rate.

Indoor air-quality measurements were collected to ensure occupational health and safety and to detect any accidental releases of vapors from the subsurface or collection piping. For this long-term monitoring the photoacoustic multigas analyzer (PMA) was placed indoors and collected air samples for analysis, via tubing, from a location near the center of the heating array. Discrete measurements were collected at times, but most measurements were collected on an automatic 5-minute cycle, 24 hours per day throughout the duration of the remediation. No TCE or other VOC detections occurred at a detection limit of 1 part per million volume (ppmv).

The PCU and the PMA were controlled locally (when personnel were present) through a computer installed for each unit. When personnel were not present, the PCU and PMA were controlled through a remote computer. The PMA was dynamically linked to the PCU (and thus, the heating array) via interlock. If the PMA were to detect TCE above 5 ppmv, the PCU would then shut down the heating array.

Performance Monitoring and Verification. For the purpose of monitoring groundwater TCE concentrations before, during, and after ERH system operation, a network of 12 monitoring wells was established. This network consisted of five preexisting monitoring wells and seven new monitoring wells installed during the ERH system construction. Three monitoring wells were to the east of the ERH treatment area and served as down-gradient wells.

Groundwater samples were periodically collected from the network of 12 monitoring wells and laboratory analytical results were used to track the progress of groundwater remediation. Prior to each sampling event, the ERH system was deactivated a minimum of 12 hours. Water level measurements were collected at each monitoring well, after which a disposable bailer was lowered into the well to obtain a water sample. Using a peristaltic pump, the water sample was then pumped through a stainless steel coil submerged in ice to cool the water prior to filling sample bottles.

During ERH system installation and after ERH system demobilization, hollow-stem auger (HSA) drilling was used to collect split-spoon soil samples from various site locations (including monitoring wells, TMPs, and soil borings). The laboratory analytical results from soil samples were used to characterize and delineate the extent of initial soil contamination, as well as to record the extent of soil remediation throughout the site at the conclusion of ERH system operation. Screening of soil for VOC content was conducted for each depth interval using a photoionization detector (PID). Preremediation soil intervals with the highest VOC content based on PID screening were collected in EnCore™ containers. Post-remediation soil samples were collected from the same depths from boreholes drilled adjacent to the initial sample locations.

For the purpose of monitoring soil temperature and pressure conditions during ERH system operations, a network of 14 TMPs was established. This network consisted of four TMPs that were installed during the pilot-scale test and ten TMPs that were installed during the construction of the full-scale ERH system. Each TMP was constructed to include two components: a series of electrical thermocouples connected to a data acquisition computer for recording soil temperature at various depths and a series of pressure piezometers to be monitored manually for recording soil vacuum pressure at various depths.

Many of the measurements described above were used for diagnostics, electrical and vapor extraction optimization, and general health and safety. Portions of the system measurements previously described were used to calculate parameters to evaluate the performance and the ultimate success of the remediation. The methods used for sampling and sample analysis are defined in detail in the remediation work plan. Table B4-2 shows the performance metrics and the associated measurements that were used to evaluate them.

Table B4-2. Performance Measures and Metrics

Performance Metric	Performance Objectives	Measurements Required	Method
Input power	To evaluate efficiency of power input and heating potential.	Power rate (voltage x current)	Direct reading in PCU.
Subsurface temperature[1]	To evaluate the effect of the input power on subsurface temperature.	Temperature	Direct temperature reading through TMPs and thermocouples.
Vacuum propagation	To determine if the steam extraction system is effectively capturing contaminated steam.	Vacuum pressure	Direct pressure reading through TMPs with hand-held instrument.
TCE mass removed	To quantify the actual mass of contamination removed.	Vapor phase concentration	SUMMA canister sample from process header.
		Temperature	Direct reading from thermocouple placed in process header.
		Vacuum pressure	Direct reading, hand held instrument from process header.
		Differential pressure	Direct reading, hand held instrument from process header.
		Condensate concentration	Water sample collected from tap downstream from condenser.
		Condensate flow rate	Calculation from condensate discharge totalizer readings.
Soil vapor results	To evaluate the ERH application's effectiveness of lowering soil vapor concentrations of TCE.	In situ concentration	Conversion of direct PID measurement from soil vapor extraction wells and vapor monitoring points.
Soil results [1]	To evaluate the ERH application's effectiveness of lowering soil concentrations of TCE.	TCE soil concentration	Laboratory analysis of samples collected from boreholes.
Groundwater results [1]	To evaluate the ERH application's effectiveness of lowering groundwater concentrations of TCE.	TCE groundwater concentration	Laboratory analysis of samples collected from monitoring wells.

1. One of the three primary performance metrics for evaluation remediation success.

Remediation Results. A calculated total of 1,417 lbs. of TCE was removed from the subsurface in Building 181 via the ERH remediation system. The total TCE mass removed from the subsurface is the sum of the mass that was removed via vapor and via steam (condensate). The mass removed via vapor was calculated on the basis of the vapor flow rate and the vapor-phase concentration. The mass removed via condensate was calculated on the basis of the dissolved-phase concentration and

the condensate discharge rate. Of the 1,417 lbs. that was documented removed from the subsurface, only about 0.5 lb. was removed via condensate. It should be noted that these results do not account for any reduction in mass due to biodegradation effects.

The shutdown criteria consisted of monitoring the TCE concentrations in the vapor stream until asymptotic conditions were achieved. The vendor recommended system shutdown and then confirmatory soil and groundwater sampling was performed. Groundwater monitoring was also performed during operations.

Roughly 150 soil vapor samples were collected both before and after heating to evaluate the ERH remediation effects on TCE soil vapor concentration. Samples were collected from various types of wells, including SVE wells and vapor monitoring wells. The wells were purged for 3–5 minutes with a portable pump prior to sample collection and analysis with a PID. The results indicate that both the concentration and extent of the vapor plume decreased. Specific observations include the following:

- The mean TCE concentration in vapor was reduced by 93% (1,049 to 73.4 ppm),
- There was a marked reduction in the area of vapor plume >100 ppm, and,
- The maximum result decreased from >5,200 to 1,358 ppm.

Figure B4-1 shows the before (left) and after (right) TCE soil vapor plumes. The data collected for the pre-ERH application soil vapor survey was collected during March 2002. The data for the post-application survey was collected in early February 2003.

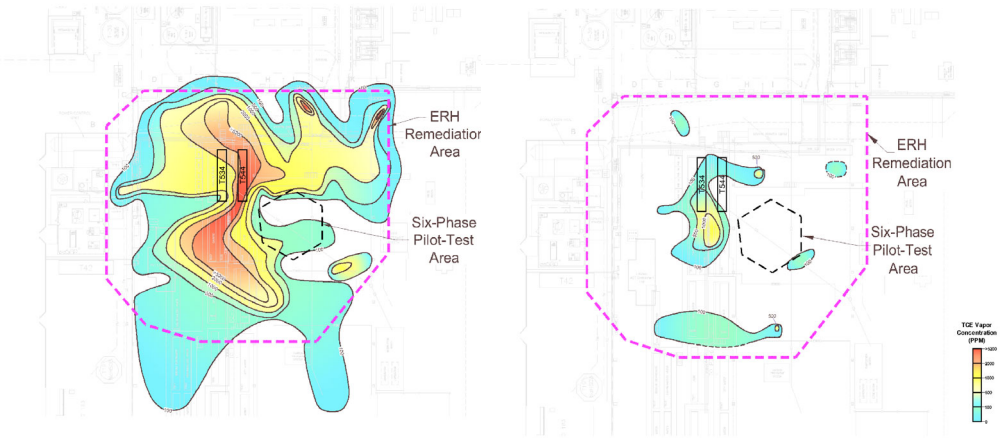

Figure B4-1. Before (left) and after (right) TCE soil vapor plumes vear Building 181

Following the full-scale ERH remediation, soil samples were collected from four soil borings and from the borings associated with several TMP locations by the methods outlined previously. The results of the post-ERH application were compared to the pre-ERH results specific observations for this comparison include the following:

- The mean TCE concentration was reduced by 90% (1.76 to 0.184 mg/kg),
- The 95% UCL TCE concentration reduced by 97% (8.4 to 0.29 mg/kg), and,
- All post-ERH results were below RAO of 11.5 mg/kg TCE.

Figure B4-2 illustrates the comparison of the pre- and post-application data across various depth intervals. Fifty-two samples were collected pre-ERH, whereas only 48 were collected post-ERH due to auger refusal in one of the post-ERH boreholes. A preapplication average concentration of TCE for each depth interval is compared to the post-application average concentration of TCE for the same interval.

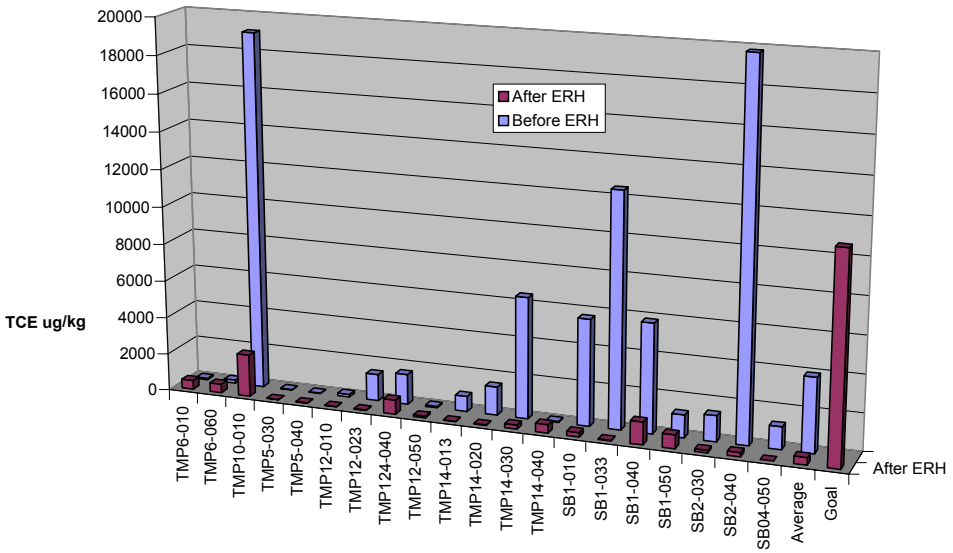

Figure B4-2. TCE concentrations in soil before and after full-scale ERH remediation

Groundwater samples were collected from the 12 ERH monitoring wells before, during, and after heating. Overall, results for groundwater reveal the following:

- The mean TCE concentration was reduced by 87% (33.2 to 4.3 mg/L),
- The 95% UCL TCE concentration was reduced by 85% (47.2 to 7.3 mg/L),
- The post-application mean and 95% UCL TCE concentration in groundwater were less than the 10 mg/L RAO, and,
- A 353% increase in average chloride concentrations was noted.

Total organic compounds (TOCs) are important because they represent a reservoir of electron donor compounds to support continued reductive dehalogenation of chlorinated hydrocarbons. The final TOC levels should be adequate to support the reduction of the residual TCE in the groundwater.

The probability is high that the ERH pilot test area will become recontaminated following the remediation because the pilot test was located on the periphery of a large TCE DNAPL source area. Nothing was done to prevent or reduce recontamination of the pilot test area before the samples were obtained.

Lessons Learned. The following are a few observations from the project manager:

- Power input rate**.** The actual power input rate was lower than the calculated rate; therefore, operating days to achieve the energy input needed to complete the project are greater than plan. Several factors including malfunction of system components, the

electrical curtailment program, water addition drip locations, and the electrode array design specifications led to the reduced power input.

- Groundwater well screen intervals**.** The well screen in wells used to assess the performance should intercept the bedrock/ alluvium interface and possibly extend some distance into the limestone bedrock..

- Heating distribution**.** Despite all attempts, targeted heating was not successful in the vicinity of MW-10. It is unclear why TCE concentrations dropped significantly in MW-9 in late July and increased significantly in August.

- Building logistics**.** Because the AFP 4 is an active operating facility and remediation cannot significantly interfere with the manufacturing process, the logistical issues (e.g., remediation at night) were magnified from the pilot test.

- Soil analytical methodology**.** The distilled-water-preserved backup soil sample analyses provided lower contaminant levels than the original methanol-extracted soil sample.

- Soil evaluation methodology**.** The Encore™ sampling methodology provided limited information in remediation effectiveness, however, the heating effects of the technology on soil gas concentrations has been adjusted.

- **ERH treatment interval**. The heating electrode should be placed as close to the contaminant as possible.

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CASE STUDY 5. PADUCAH GASEOUS DIFFUSION PLANT, BLDG C-400
PADUCAH, KENTUCKY

TECHNOLOGY:	Electrical resistance heating (six-phase heating)
SCALE:	Prototype demonstration
GEOLOGY:	Sand and gravel, overlying inter-bedded sand/silt/clay
CONTAMINANTS:	Chlorinated solvents (primarily TCE), Technetium

Background. The DOE's Gaseous Diffusion Plant in Paducah, Kentucky completed a prototype demonstration project to evaluate the performance of Electrical Resistance Heating (using Six-Phase Heating for the demonstration). Soils and groundwater are impacted by TCE and low levels of other solvents, to a depth of approximately 100 ft, near and beneath an existing facility designated Building C-400 (see Figure B5-1).

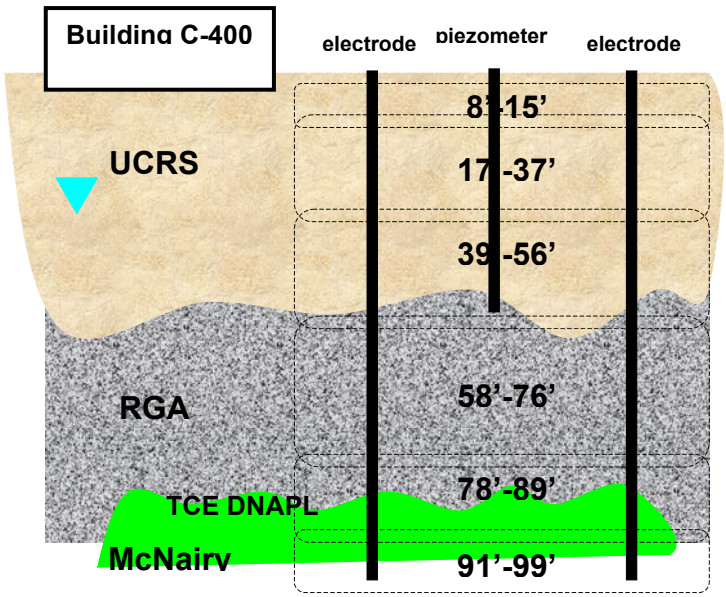

Figure B5-1. Vertical Profile of Treatment Area

Groundwater is encountered approximately 50 ft bgs. The silt-sand overlying soils (the so-called Upper Continental Recharge System, or UCRS) extend to approximately 56 ft bgs, and the gravelly Regional Gravel Aquifer (RGA) extends from about 56 to about 100 ft bgs, to the contact with the low-permeability McNairy formation. TCE is present as residual DNAPL throughout the unsaturated and saturated zones and is present in places within the upper McNairy. DNAPL is also believed to be present as pools at the McNairy interface in some areas.

Six electrodes were installed in an area of approximately 30 ft in diameter, and VOCs were removed by vapor extraction and carbon absorption. Treatment continued for almost 7 months (175 days of active heating, over a period extending from February to September, 2003). The estimated heated treatment area was 43 ft in diameter. The treatment area was near the suspected source of TCE (an aboveground storage tank and associated piping), within an identified "source area" that covers approximately 200,000 sq ft.

Performance Objectives. The overall objective for the project was to demonstrate the implementability and cost-effectiveness of the ERH technology for treating the unsaturated and saturated zones of the overlying soils, and the groundwater of the RGA. The performance criteria and objectives established for the project are listed in Table B5-1.

Table B5-1. Performance Objectives and Methods at Paducah GDP

Performance Criteria	Objective	Measurement Method
Vadose zone	75% mass removal	Pre- and Post-Test soil cores: 9 cores, sampled each 2-ft interval
Groundwater	<1% TCE solubility (11 mg/L)	Monitoring well samples: 2 wells, 6 sampling depths

The following metrics were also used to evaluate the process efficiency:

- Uniform temperature gradients throughout the test cell,
- TCE removal rates as a function of operational time and energy consumption,
- Constructability of the ERH system in the C-400 Building area,
- Construction and operation costs as a function of TCE mass removed or destroyed,
- No negative effects of the ERH system on adjacent utilities and facilities.

A review panel was convened to evaluate the technology performance and the performance assessment methods. The panel questioned the objective of 75% reduction in mass of TCE in the soils for three reasons: mass reduction is not a typical regulatory objective, mass reduction is difficult to measure adequately given typical source characterization data, and there was no clear linkage to overall RAOs for the site. The panel considered the second goal, reducing average concentrations in groundwater to below 1% of aqueous solubility, to be a reasonable objective, particularly if post-treatment rebound and recontamination were monitored.

The process efficiency criteria were deemed reasonable as well. However, the panel did note that the cost evaluation should include total life-cycle cost assessments for this and other source treatment or containment options. If treatment does in fact leave residual groundwater concentrations near 1% of solubility, that is still 2000 times higher than the MCL value for TCE. Although the RAO for TCE at this site is unknown at the present time, it is likely that it will (may?) be lower than the 1% criterion. Consequently, further treatment and/or containment probably will be needed after thermal treatment, and these costs can impact remedy selection and performance goals for full-scale source management.

Technology Performance. The percent mass removal from the soil was based on nine borings obtained before and after treatment, with sampling of each 2-foot interval to the maximum depth to which soil could be sampled (56 ft bgs). Based on the average soil concentrations, the performance exceeded the goal of 75% mass removal. The average soil concentrations decreased by 98%, from an average of approximately 125 mg/kg before treatment to 2.5 mg/kg after treatment. As might be expected, the variability was very large. Averages from the nine pretest cores (generally 28 samples each, over a total depth of 56 ft) varied 1.3–464 mg/kg. Averages of the post-test soil cores varied 0.1–6.5 mg/kg.

A crude estimate is that the initial mass of TCE in the UCRS was about 1,250 lbs., and the final mass was only 25 lbs. These estimates are based on average concentrations of 125 mg/kg TCE initially and 2.5 mg/kg afterwards, a treated volume of 80,000 cu. ft., and a density of 125 lbs./cu. ft. of soil. No estimates of the TCE mass or mass removal in the RGA could be made because soil cores could not be advanced into this gravelly matrix.

The average groundwater concentrations from the two multilevel wells within the treatment zone did reach the target criteria of 11 mg/L TCE, with an average reduction of approximately 99%. Similar results were observed at all six depths sampled, with initial concentrations ranging 500–1,000 mg/L TCE in most samples and final levels 1–10 mg/L.

The target temperatures were reached at most depths, except in the lowest intervals (95 and 105 ft bgs) as shown in Figure B5-2. This inability to establish a so-called "hot floor" raises some concerns regarding the potential for removal or containment of DNAPLs at the base of the impacted aquifer. However, modifications to the final design should allow heating the lowest depths as well.

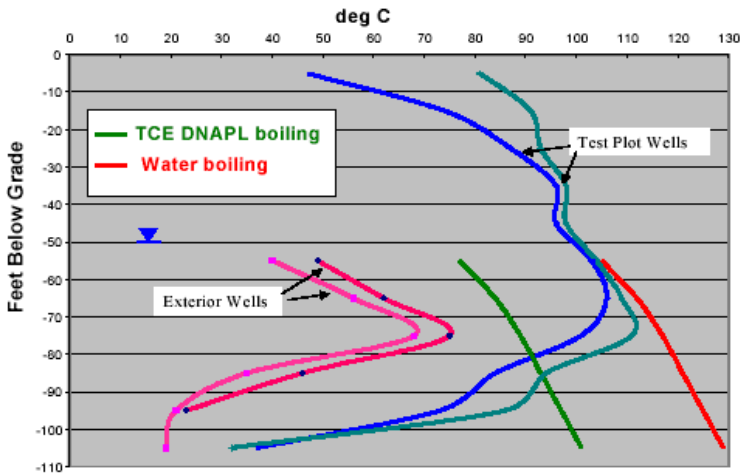

Figure B5-2. Temperature vs. Depth (5/1/03)

No adverse effects on the adjacent facilities were observed. Pneumatic control of the generated vapors was achieved, and monitoring of both vapors did not show any evidence of enhanced migration or escape of VOCs from the treatment area. Unfortunately, hydraulic control was not a goal of the demonstration, complicating any evaluation of the performance. Groundwater temperatures increased, and TCE concentrations decreased, in both of the control wells that were located outside the treatment area.

Lessons Learned. The project demonstrated the capabilities and robustness of the technology. The test was conducted in a deep, highly permeable aquifer, with difficulties ranging from power shutdowns to electrode failures. Nevertheless, the results showed ERH effectively heated vadose and saturated zones, to a maximum depth of up to 100 ft bgs. TCE concentrations were consistently reduced by 99% or more, in groundwater with concentrations of up to 1,000 mg/kg, over a 50-ft depth, with a groundwater velocity of approximately 1 ft per day in the RGA.

The project revealed some other important lessons for future demonstrations and source treatment projects:

- Simplify the electrode design. The electrodes were originally designed to heat at six different depth intervals. However, the steel shot backfill was too heavy over such a great depth, leading to collapse and shorting of the entire electrode lengths. Future projects should learn from these design difficulties.

- Link performance assessment criteria to RAOs. The goals for treatment should be clearly linked to the Remedial Action Objectives for the site. For example, it is not clear whether 99% reductions in concentration, to values that still exceed MCLs by three orders of magnitude, will be acceptable. The impacts of such performance at full scale on the overall site risks, plume size, plume longevity, or total remediation costs have not yet been established.

- Identify termination criteria. In this test, as in many other source treatment projects, the end point was not clear. As a result, there was continuing debate about when active treatment could be stopped. Termination criteria should be established beforehand, and data should be evaluated continually during the project, to determine when these endpoints have been achieved.

- Hydraulic isolation is valuable for demonstrations. The lack of hydraulic isolation precluded effectively measuring rebound in the treated source area and complicates any assessment of technology performance. It also made it impossible to accurately measure changes in mass flux during and after treatment.

- Continually update the CSM. The CSM suggested DNAPL was pooled at the base of the RGA, but the demonstration results indicated this was not the case. The distribution of DNAPL throughout the vadose and saturated zones was shown to significantly affect the design and costs of the full-scale deployment..

- Avoid DNAPL migration during installation. The evidence suggests that DNAPL migrated into deeper layers during installation of the electrodes. This apparent movement of DNAPL along the electrode conduit complicated assessment of the treatment and possible movement of DNAPL into the low-permeability layer beneath the RGA..

- Phase deployment, especially at large sites. The prototype demonstrated that the initial design and operations needed considerable modification. This experience is probably typical, as designs are optimized to specific site conditions. For a costly technology, phasing deployment allows both cost-efficient operation and the flexibility to respond to new site-specific information.

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CASE STUDY 6. NSB KINGS BAY, SITE 11
KINGS BAY, GEORGIA

TECHNOLOGY:	Chemical oxidation (hydrogen peroxide)
SCALE:	Full
GEOLOGY:	Surficial fill and silty sands
CONTAMINANTS:	PCE, TCE, DCE

Background. The Naval Submarine Base at Kings Bay, Georgia is located in southeast corner of Georgia, where the St. Mary's River discharges into the Atlantic Ocean. This Base supports the Navy's submarine-launched ballistic missile program. It is the only East Coast Naval base capable of supporting the Trident II (D-5) missile.

NSB occupies approximately 16,000 acres in Camden County, Georgia. Site 11 on the NSB was the site of an old Camden County Landfill that was incorporated by the NSB in 1979. This site is a 25-acre municipal landfill that operated between 1974 and 1980. The landfill is a Solid Waste Management Unit subject to corrective action as part of a RCRA Part B Permit. The remedial investigation identified chlorinated volatile organic compounds (CVOCs), specifically, tetrachloroethene (PCE), and its degradation constituents TCE, cis-1,2-dichloroethene (DCE), and vinyl chloride (VC) in groundwater emanating from the landfill towards a residential subdivision approximately 500 ft away. Over 600 homes are located in the subdivision and many use groundwater for irrigation purposes.

Groundwater extraction wells with an air stripping treatment system were installed in 1992 to prevent migration of contaminants into the subdivision. While this measure effectively halted the migration on the plume, it was not reducing the contamination. The source of PCE contamination was identified on the perimeter of the landfill with concentrations of over 9,000 µg/L. Natural attenuation of the groundwater was found to be highly efficient but there was not enough distance prior to reaching the subdivision to complete the process due to the relatively high source area concentrations. ISCO was selected to reduce the source of contamination so that the natural attenuation processes could efficiently treat the residual concentrations.

Three phases of chemical oxidation treatment were conducted during August 1998 through April 2000. During the entire treatment program, approximately 35,000 gal of 50% hydrogen peroxide and an equivalent amount of ferrous iron catalyst were delivered to the subsurface. Phase I chemical oxidation treatment was performed from August 1998 through February 1999. Because of a concentration increase was measured following the Phase I treatment, a cone penetration testing program was conducted in April 1999 to confirm and delineate the horizontal extent of dissolved groundwater contamination. Phase II chemical oxidation treatment was performed from May 1999 to July 1999 on areas east and west of the Phase I area of concern. Because of a concentration rebound following the Phase II treatment, a Geoprobe investigation was conducted in August 1999 to investigate and locate the potential new source of PCE. Excavation of the suspected source area was conducted in September 1999. Phase III chemical oxidation treatment was performed from January 2000 to April 2000 on the delineated source area. Based on the analytical results from the post-injection sampling event on May 30, 2000, a source area of PCE contamination appeared to remain beneath the injectors.

Source Area Delineation. An focused source area delineation effort was conducted in two phases from November 6, 2000 through January 12, 2001 to delineate the horizontal and vertical extent of the potential source area PCE contamination (and its degradation products) beneath the Phase III chemical oxidation treatment injectors. Source Area Delineation No. 1 was completed in November 2000 using a membrane interface probe (MIP)/DPT rig. Groundwater samples were collected from each boring using the DPT rig with peristaltic sampling pump and analyzed by the on-site mobile laboratory. Based on the groundwater sample analytical results collected during this initial effort, the vertical interval of contamination in the source area was determined to be 44–48 ft bgs); however, additional groundwater collection sampling and analysis was determined to be necessary to delineate the horizontal extent of contamination.

Source Area Delineation No. 2 was completed in January 2001. Groundwater samples were collected on a 25-ft grid, with samples collected from each of nine borings at depths of 36–40, 40–44, 44–48, and 48–52 ft bgs and analyzed for USEPA SW-846 Method 8021B. This delineation effort, along with the initial effort, provided sufficient data to determine the horizontal extent of contamination and the area requiring remediation.

Final Fenton's Reagent Chemical Oxidation Injection. Based on the source area delineation data, a Fenton's reagent chemical oxidation treatment zone was targeted in the depth interval from approximately 40–50 ft bgs. A total of 20 new injectors were installed to a depth of 48 ft bgs with a screen interval 45–48 ft bgs. The Fenton's reagent chemical oxidation injection program was performed in two phases: a primary injection and a polishing phase. Typical injection rates ranged 0.4–1.5 gpm, and the total volume of fluids injected at the site was approximately 23,585 gal (approximately 12,220 gal of catalyst and 11,365 gal of 50% hydrogen peroxide). At no time during the injection was the concentration of hydrogen peroxide injected greater than 25%. Groundwater samples were collected for field analytical tests on a daily basis during the injection program. The field parameters collected were pH, total iron, chloride, alkalinity, hydrogen peroxide, and photoionization detector headspace. These analytical parameters were used as screening tools to assist with the injection program.

Performance Objectives. The ultimate goal or RAO at the landfill is to treat groundwater within the contaminated plume to concentration levels below the MCLs established by the Georgia Environmental Pollution Department. Modeling results indicate that source area reduction of CACs to a cleanup objective of 100 µg/L for each compound would be sufficient for natural attenuation to achieve compliance levels in the groundwater plume prior to leaving the base boundaries and reaching off-site monitoring points.

Table B6-1. Cleanup Levels for Groundwater at NSB Kings Bay

Contaminant	MCL (µg/L)	Cleanup Objective (µg/L)
PCE	5	100
TCE	5	100
DCE	2	100

Performance Monitoring and Verification. ISCO was used to treat groundwater contaminated with high concentrations of tetrachloroethene (PCE) at the landfill. As a result of the ISCO treatment, levels of total chlorinated hydrocarbons in the most contaminated areas were reduced from nearly 200,000 µg/L in 1999 to 120 µg/L in 2002. Furthermore, in the three years since source treatment began, the off-site plume has decreased to below MCLs, and the on-site plume is approaching those same levels. This effort has allowed the Navy to accelerate the estimated time for cleanup of the site and turn off the existing pump-and-treat system. The residual on-site contamination will be addressed by natural attenuation.

The ISCO treatment achieved over 98% reduction in mean dissolved chlorinated hydrocarbon concentration. Concentrations of PCE measured at >9,000 µg/L were reduced to <9 µg/L. Figure B6-1 shows the PCE trend between November 1998 and August 1999.

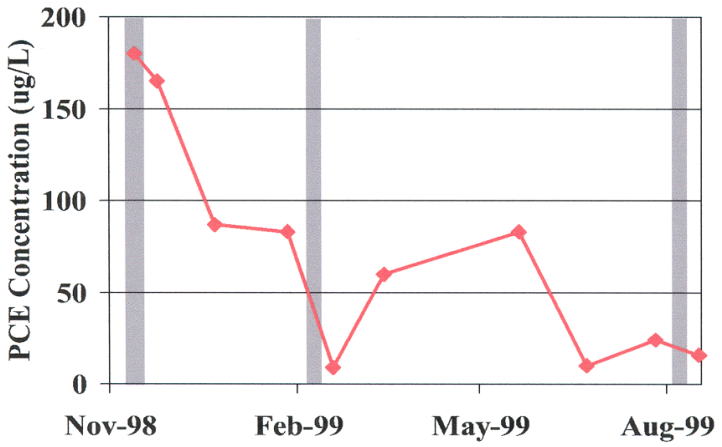

Figure B6-1. Kings Bay Phase I-III Results Showing Dissolved PCE Concentrations

Costs. The total first year cost for implementation of Phase I and II ISCO and UV oxidation treatment is estimated at $1,050,000. This cost estimate includes an implementation cost of $900,000. Additional annual costs include $65,000 for operations and maintenance, $40,000 for monitoring, and $15,000 for reporting. Phase III chemical oxidation treatment is estimated at $282,000. It is expected that long-term monitoring cost will be substantially diminished at this site, as the time for residual concentrations to meet MCLs through MNA is predicted to be complete within less than five years. Net present value of project life cycle cost savings are expected to exceed $3.3 million.

Summary. ISCO has been effectively implemented for source reduction at NSB Kings Bay. At NSB King Bay, 23 injectors were installed and over 12,000 gal of hydrogen peroxide was injected over 24 days during two treatment events. Source area CVOC concentrations were reduced by an average of 98%. The most contaminated well experienced a reduction from >9,000 µg/L total CVOCs (including 8,500 µg/L PCE) to 65 µg/L (>99% reduction), with little or no rebound 13 months after treatment, when total CVOCs measured 85 µg/L. As a result, the State of Georgia approved MNA as a final remedy for the down-gradient plume and terminated a long-term pump-and-treat program.

Lessons Learned

- Additional ISCO treatments were required because highly contaminated source areas within the landfill were not initially well understood. The remediation was successful once the source of the contamination was finally well defined both vertically and horizontally.

- The geology (coastal plain deposits) the site was sufficiently permeable that injection of the reagents into the aquifer was capable of contacting and destroying the contaminants.

- A remedy utilizing a combination of ISCO and MNA posed some early concerns regarding how quickly the microbial community would rebound from the treatment process. This was determined to be a relatively short period of time. Within six weeks of treatment, the source areas that had been saturated with dissolved oxygen returned to anoxic conditions indicative of anaerobic microbial activity.

- The success of the chemical oxidation of the source area precluded the need to install new recovery wells and a new expensive off-gas treatment system (UV oxidations) to ensure containment of the plume.

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CASE STUDY 7. BROWARD COUNTY SITE
FORT LAUDERDALE, FLORIDA

TECHNOLOGY:	Chemical oxidation (permanganate)
SCALE:	Full
GEOLOGY:	Medium sands
CONTAMINANTS:	TCE, TCA, DCE

Background. Inadvertent releases of small volumes of TCE and TCA occurred in the mid-1990s along an outside wall of an industrial building used to manage waste solvents in Broward County, Florida. The site is underlain by medium-grained sand with a shallow water table (< 3 ft bgs). TCE and TCA contaminated soil and groundwater was discovered in April 1997 at which time solvent use was discontinued and more extensive groundwater investigations were initiated. Initial direct-push sampling in 1997 was followed by installation and sampling of a network of conventional 2-inch-diameter monitoring wells with 5- or 10-ft-long screens to delineate the extent of contamination (Parker et al., 2002).

Following a failed attempt to remediate the source zone by injecting a Fenton's-type reagent in 1998 and early 1999, a detailed site characterization was done in February 2000 to facilitate the design of the permanganate solution injections for remediation of the DNAPL source zone. Two continuous cores were collected from ground surface to direct-push refusal depth of 75 ft bgs. Detailed sampling of these cores for DNAPL detection using the Sudan IV dye method and analyses by gas chromatography showed no DNAPL occurrences and highest TCE values at 50% TCE solubility. Detailed depth discrete groundwater sampling was also done using multilevel monitoring systems (bundle wells) similar to those described by Cherry, et al.(1983). The highest TCE value measured in the bundle wells prior to treatment was 625,500 µg/L, and the highest TCE value found previously by Geoprobe sampling was 940,000 µg/L. These values are only slightly below the aqueous solubility for pure-phase TCE (1,100,000–1,400,000 µg/L). Concentrations of TCA were an order of magnitude below TCE.

The persistence of high TCE concentrations beneath the TCE release area and the occurrence of highest TCE values deep in the sand aquifer (55–65 ft bgs) indicate that the TCE contamination is caused by DNAPL; however, the DNAPL is probably distributed sparsely as small globules that constitute extremely low residual saturations. Figure B7-1 illustrates the conceptual model for the TCE contamination and also shows typical pretreatment TCE results obtained from two bundle wells. DNAPL occurs in the source zone as dispersed globules representing the vertical trail of downward DNAPL migration. Apparently, the DNAPL descended vertically until it entered a thin (8-inch) coarse sand layer at 57 ft bgs. The larger permeability of the coarse sands likely caused the DNAPL to spread laterally with minimal DNAPL penetrating below this zone. All of the highest TCE and TCA concentrations found prior to permanganate treatment occurred within a near circular area with a radius of 10–15 ft.

Passive Approach for KMO_4 Treatment. The remediation approach used at the Broward County site is destruction of the TCE mass in the DNAPL source zone by $KMnO_4$ injections while minimizing the displacement of contaminated groundwater away from the source zone. These dual objectives were pursued through injection episodes in which many discrete zones of near-saturation

$KMnO_4$ solution were created at multiple depths in direct-push holes in the targeted zone. At the end of an injection episode, the pressure pulses in the aquifer quickly dissipate. However, density-driven advection combined with fingering and diffusion causes the $KMnO_4$ solution to spread, which achieves the coverage in the targeted volume. In the DNAPL source zone the injection point was driven to 60 ft bgs using a direct-push rig.

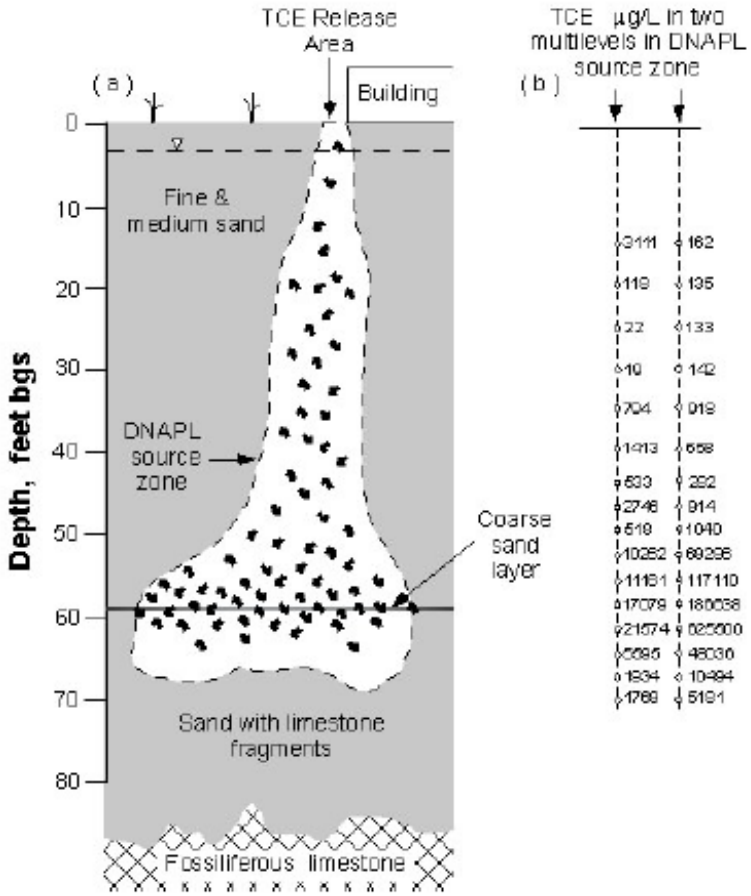

Figure B7-1. Nature of the DNAPL source zone: a) geology and conceptualization of DNAPL occurrence, and b) TCE concentrations in two multilevel systems in the source zone prior to $KMnO_4$ treatment.

The remediation of the Broward County site was done using the "inject-and-leave" approach in three episodes, all in 2000. In the three episodes, a total of 2,791 lbs. of $KMnO_4$ dissolved in 9,166 gal of water at a concentration of 40 g/L was injected into a total of 21 holes. Each episode was followed by two sampling events of the detailed network of multilevel systems for measurement of $KMnO_4$, VOCs, and chloride concentrations for tracking remediation progress.

Performance Objectives. The primary goal of the permanganate remediation was to oxidize the TCE mass in the DNAPL source zone so that the source for the plume no longer existed, allowing the plume to attenuate by natural processes. In accordance with the Florida DEP's Natural Attenuation Default Source Concentrations, state regulators may allow cessation of active source zone remediation as long as dissolved concentrations are brought to within 100 times the MCLs and that natural attenuation processes are occurring. A secondary objectives was to minimize the

displacement of groundwater with high TCE concentrations away from the source zone. The effectiveness of the $KMnO_4$ treatment was demonstrated based on a before-and-after comparison of TCE and TCA concentrations in the detailed network of multilevel systems and conventional wells.

Performance Monitoring and Verification. Figure B7-2 shows that, before $KMnO_4$ treatment, all seven of the monitoring locations situated inside the 10,000-µg/L contour (referred to as the DNAPL source zone) had TCE values >16,000 µg/L and as high as 625,500 µg/L. When the comprehensive post-treatment monitoring occurred three months after the last injection episode, only two of these seven locations showed high values, but at concentrations <35,000 µg/L. Figure B7- 2 also shows two locations just outside of the 10,000-µg/L contour that had moderately high TCE values (3,560 and 7,650 µg/L) before treatment.

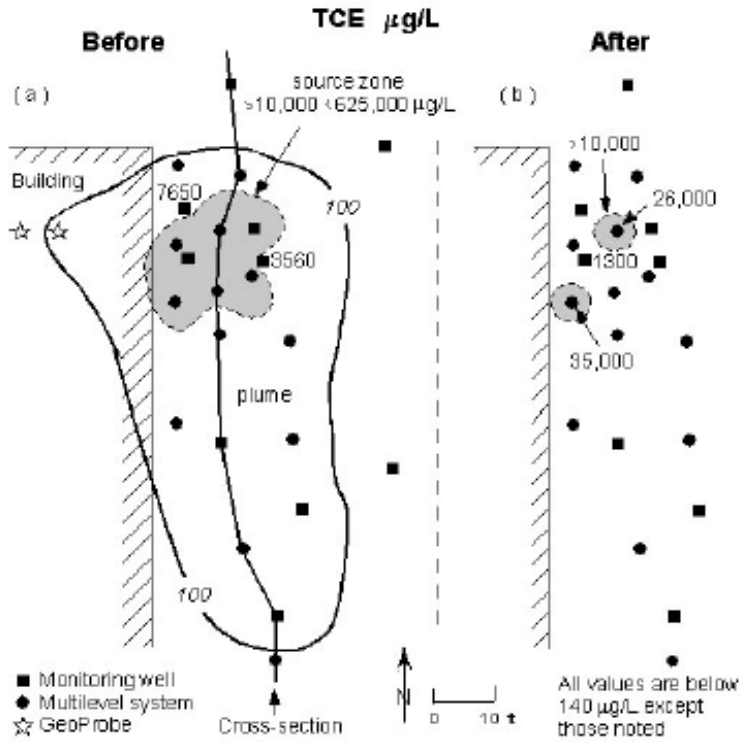

Figure B7-2. Plan view of maximum TCE concentrations found at each monitoring location prior to $KMnO_4$ injections and 3 months after.

After $KMnO_4$ treatment, TCE values at these two locations were below 50 µg/L. Of the five inside the initial 10,000-µg/L contour area that declined below 10,000 µg/L after treatment, three dropped below 150 µg/L, and the other two dropped to 1,300 and 670 µg/L. Therefore, this plan view comparison of the maximum before-and-after TCE values at monitoring locations shows clearly that the volume of aquifer with high TCE values diminished greatly after $KMnO_4$ treatment.

Figure B7-3 shows the large decline in TCE contamination in cross-sectional view through the middle of the $KMnO_4$ treatment zone three months after the last injection. (Refer to Figure B7-1 for the cross-section location.) The cross-sectional area >100 µg/L declined markedly to 10% of the before-treatment area, and the area >10,000 µg/L declined to 3% of the before-treatment area.

Evidence for the TCE destruction is also established by the number of sampling points above specified concentrations shown on the cross section. Figure B7-3 shows that 20 sampling points had TCE in the 100–1,000 µg/L range before treatment; only four had such values after. Before treatment, 10 sampling points had TCE values >10,000 µg/L, but after, only two were >10,000 µg/L. Other vertical sections positioned across the former source area displayed similar large decreases in areas and number of sampling points above specified values.

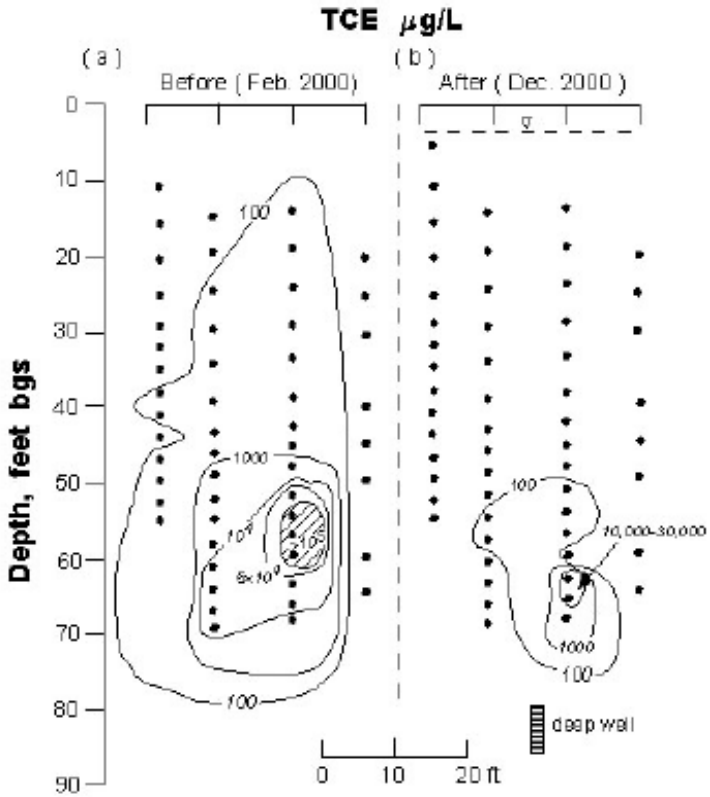

Figure B7-3. Comparison of TCE concentrations one month before and three months after $KMnO_4$ treatment observed along cross section through DNAPL source zone.

Measurements of the stable carbon isotope ($^{12}C/^{13}C$) ratio of TCE in groundwater before and after $KMnO_4$ treatment provided confirmation of TCE mass destruction. Large increases in ^{13}C relative to ^{12}C attributable only to oxidation were observed in the treatment zone (Hunkeler and Parker, 2002).

An issue that must be resolved when assessing treatment effectiveness is the role of displacement of contaminated water away from the injection points. Depending on sampling locations observed, post-injection declines might reflect the displacement of contaminated water rather than actual TCE mass destruction. The before-and-after monitoring results at the site are not attributable to displacement because monitoring at all locations in the plume declined after the injections. If contaminated water had been displaced from the source zone into the plume, increases in TCE at one or more plume locations would be expected. Negligible displacement was ensured given the design of the injections. Another concern inherent in remediation performance assessment is the potential

for rebound of contaminant concentrations in the treated zone as a result of persistent residual DNAPL dissolution. The comprehensive post-injection sampling described above was done three months after the last injection. Additional sampling of selected multilevel points was done three months later. These sampling events comprised several points in each of eight bundle wells within the former source area. Three of the bundle wells showed no increase, and in the fourth, one point at 60 ft bgs increased from 34,500 to 50,400 µg/L. This small increase is consistent with the temporal variability expected from slight groundwater gradient changes causing shifts of the position of the highest concentration zone. The expected rebound would be much larger if appreciable DNAPL mass remained in this zone.

Discussion. Success of the passive method involving episodic injections of small volumes of dense $KMnO_4$ solution at multiple discrete depths depends on post-injection spreading and sinking of the solution. Density-driven advection combined with fingering and diffusion must cause invasion of the $KMnO_4$ between injection points. Evidence of this invasion derives from the large decrease in volume of the TCE contaminated zone, described above, and from comprehensive sampling of the bundle wells for $KMnO_4$ at various times following each injection episode. As expected, immediately after each injection episode, $KMnO_4$ appeared in only a few sampling points because the volume input at each injection point was small. At later sampling times, nearly all sampling points in the target zone (i.e. inside the initial 10,000-µg/L contour) showed $KMnO_4$ on one or more occasions. These occurrences were only temporary because the $KMnO_4$ is continually moving, mixing and being consumed by oxidation of TCE and reaction with natural aquifer components.

The distribution of monitoring points that existed prior to the $KMnO_4$ injection and during the comprehensive post-treatment sampling left uncertainty about the maximum depth of initial TCE occurrence and deep TCE treatment. Therefore, near the end of this study a deep monitoring well was installed using Rotosonic core drilling. This hole was drilled at the location where deepest TCE would most likely be found if present. Figure B7-3 shows this well situated in the depth range of 81.3–86.3 ft bgs, which is directly below the zone of highest TCE in the 55–65 ft depth zone. This well showed no significant TCE (12 µg/L). Resampling in February 2002 confirmed the absence of TCE in this well (<1 µg/L). These results indicate that the TCE source zone did not extend to this depth or that the sinking of $KMnO_4$ below the deepest injection depth (60 ft bgs) destroyed any deep TCE.

The oxidation of TCE results in release of chloride ions (Cl^-) from the TCE to the groundwater. The stoichiometry for this oxidation reaction specifies that for each mole of TCE oxidized, three moles of Cl^- are produced. The preinjection Cl^- values in the source zone ranged 20–60 mg/L. The maximum post-treatment Cl^- values were in the range of 150–260 mg/L in the zone where the pretreatment TCE values were generally 100–300 mg/L. The stoichiometric view for Cl^- production presented above considered only the dissolved-phase TCE in the source zone. It is likely that DNAPL residual also existed prior to treatment in the source zone, as dispersed globules spaced sufficiently far apart to prevent TCE concentrations from approaching TCE solubility even at the small spatial scale used for groundwater monitoring. $KMnO_4$ treatment oxidized dissolved-phase TCE, and as the dissolved-phase TCE was destroyed, it was replenished by DNAPL dissolution. Therefore, one should expect that Cl^- would accumulate in the treatment zone to cause a concentration rise above the concentrations expected when only the initial aqueous TCE distribution is considered. No such Cl^- accumulation is indicated by the post-treatment Cl^- distribution. However, the $KMnO_4$ treatment system at the Broward County site is an open system, with an outlet

at the bottom. Density-driven sinking of the $KMnO_4$ solution after each injection episode must cause downward transport of Cl^- by the sinking $KMnO_4$ solution. Therefore, some of the Cl^- was probably transported below the maximum depth of Cl^- monitoring (i.e., below 70 ft bgs).

The three episodes of $KMnO_4$ injection caused a large reduction in the volume of groundwater with TCE concentrations >100 µg/L and >10,000 µg/L. These results indicate that it is reasonable to expect that an additional injection episode will bring the destruction of the DNAPL source zone to completion. The selection of three injection episodes for the initial phase of this project was arbitrary. The total initial TCE mass in the source was unknown and therefore there was no basis for specifying the number of injections and total mass needed to achieve complete remediation. It was intended that three injection episodes would be sufficient to establish a trend that would serve as a basis for judging prospects for complete remediation. The trend from the three injections indicates that very little DNAPL remains in the source zone and that it exists in a very small volume, exemplified by the small areas within the >10,000 µg/L-contour (Figures B7-2 and -3). Although not expected, the $KMnO_4$ treatments reduced the concentrations and volume of TCA contaminated aquifer similar to the TCE reductions.

Lessons Learned.

- Isotope analysis made it possible to demonstrate TCE oxidation at locations where Cl^- concentration did not yield unequivocal evidence for TCE oxidation, possibly due to migration of Cl^-.

- By injecting small volumes of near-saturation $KMnO_4$ solution at several depths, an initial condition of many small, stacked $KMnO_4$ zones with large vertical gaps in between was created. However, during the few weeks following each injection episode, these many small $KMnO_4$ zones spread out and descended under the influence of density and diffusion to achieve complete coverage within the source zone.

- Use of this passive, "inject-and-leave" approach resulted in no observable displacement of high-concentration TCE water outward from the source zone into the surrounding plume.

References

Hunkeler, D., and B.L. Parker. 2002. "Monitoring In Situ Oxidation of TCE by Permanganate Using Carbon Isotopes." In A.R. Gavaskar and A.S.C. Chen (eds.), *Treating Dense Nonaqueous Phase Liquids (DNAPLs)*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, Columbus, Ohio.

Parker, B.L., J.A. Cherry, and T.A. Al. 2002. "Passive Permanganate Remediation of a Solvent DNAPL Source Zone." In A.R. Gavaskar and A.S.C. Chen (eds.), *Treating Dense Nonaqueous Phase Liquids (DNAPLs)*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, Columbus, Ohio.

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CASE STUDY 8. INEEL, TEST AREA NORTH
IDAHO FALLS, IDAHO

TECHNOLOGY:	Enhanced in situ bioremediation (anaerobic reductive dechlorination)
SCALE:	Full
GEOLOGY:	Deep-fractured basalt aquifer
CONTAMINANTS:	PCE, TCE, radionuclides

Background. The historical injection of liquid wastes and concentrated sludges into the Snake River Plain Aquifer using Well TSF-05 has resulted in a nearly 1.9-mi-long TCE, PCE, and tritium plume in groundwater at the TAN facility of the Idaho National Engineering and Environmental Laboratory (INEEL). The depth to water at TAN is approximately 200 ft. The aquifer and most of the unsaturated zone are comprised primarily of layered basalt flows, intercalated with sedimentary interbeds deposited during periods of volcanic quiescence. Groundwater flow in the aquifer is controlled by the highly transmissive zones that occur at the contacts between individual basalt flows, and to a lesser extent, by fractured zones within flow interiors. The scale of the basalt geology dictates that preferential flow can be very important at spatial scales less than approximately 100 m (330 ft), after which a transition to continuum behavior occurs and the aquifer can be thought of essentially as a macro-porous medium.

The distribution of TCE at TAN exemplifies the fringe and core hypothesis for the anatomy of chlorinated solvent plumes by Cherry (1997). A very large, low-concentration fringe surrounds and emanates from a much smaller, high concentration core (gray shaded area in Figure B8-1). Within the core is a very small residual source area that continues to contaminate fresh groundwater flowing through from up-gradient. The transition from the scale of the residual source, where preferential flow is significant, to the scale of the fringe, where sufficient vertical communication has been present along the flow path to create a relatively well-mixed, predictable groundwater plume.

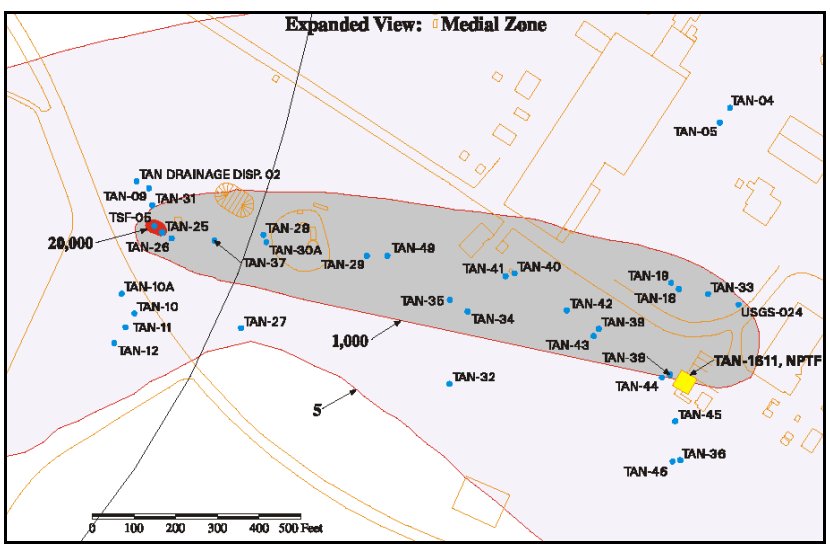


Figure B8-1. Medial zone of TCE plume at TAN

The residual source of contamination in the aquifer near TSF-05 is believed to be composed primarily of the sludge that was injected into the well over 15–20 years. The pore water of the

sludge probably contains large amounts of TCE, with PCE and tritium also present in significant amounts. Given the organic content of the sludge, sorbed PCE and TCE are also likely to be present. TCE concentrations as high as 300,000 µg/L have been measured in groundwater from well TSF-05. Some of the sludge has been shown to have TCE concentrations as high as 3%. The sludge therefore represents a long-term source of contamination to the aquifer.

It has also significantly affected the properties of the aquifer in the area. The effective porosity near TSF-05 has been estimated to be about 0.05%, and the transmissivity is about an order of magnitude lower than nearby wells. Both gamma logs measuring radionuclides associated with the sludge and tracer tests measuring effective porosity yield an estimated radius for the sludge distribution of about 100 ft.

The 1995 ROD identifies the primary RAO for TAN, which is to restore the contaminated aquifer groundwater by 2095 (100 years from the date of the ROD) by reducing all contaminants of concern to below MCLs and a 1×10^{-4} total cumulative carcinogenic risk-based level for future residential groundwater use and for noncarcinogens, until the cumulative hazard index is less than 1. The ROD selected pump and treat as the default remedy for the residual DNAPL source area, but because this approach was unlikely to restore the site in a meaningful time frame, it also identified five alternative technologies to be evaluated for their potential to enhance or replace the default remedy. One of the technologies identified was enhanced in situ bioremediation (ISB).

As described in Section 5.6, the most common performance metric used to assess ISB performance is groundwater concentrations. Although this metric alone is not generally recommended for assessing the performance of a DNAPL remediation, the monitoring of several groups of parameters (contaminants and degradation products, redox-sensitive parameters, electron donor parameters, biological activity indicators, biological nutrients, and water quality parameters) can essentially provide a multiple lines of evidence approach to monitoring the performance of ISB that is analogous to using more than one metric described in Section 3 for assessing the performance of other DNAPL remediation technologies.

Field activities for enhanced ISB began in November 1998 with the shutdown of the interim pump-and-treat facility that was operating in the hotspot and the initiation of the first phase of ISB field operations. The primary performance objective of the field operation was to determine whether anaerobic reductive dechlorination of TCE in the residual DNAPL source area could be enhanced through the addition of an electron donor (sodium lactate). Initially, baseline sampling and a conservative tracer test were performed, followed by initiation of weekly lactate injections into the original disposal well and biweekly groundwater monitoring for the parameter sets described above.

Seven months after sodium lactate injections began, significant dechlorination activity was stimulated to distances of >40 m from the injection well. For example, TCE concentrations in well TSF-05 decreased to <10 µg/L, with increases in ethene of up to 2,500 µg/L. Dechlorination was strongly correlated with elevated electron donor concentrations and the establishment of strongly reducing conditions. In particular, dechlorination of TCE to cis-DCE coincided with sulfate reduction, while dechlorination of cis-DCE to vinyl chloride and ethene was observed only in the presence of methanogenesis. Electron donor concentrations [as chemical oxygen demand (COD)] of >4,000 mg/L and >5,800 mg/L were observed in wells TAN-25 and TAN-26 (refer to Figure B8-2 for well locations). By the end of the field evaluation, methane concentrations in these wells were

20,000 µg/L and 17,000 µg/L, while TCE concentrations had dropped to 68 µg/L and nondetect. Figures B8-3a, -3b, and -3c show the temporal correlation between electron donor arrival, the onset of methanogenic conditions, and complete dechlorination of TCE to ethene for well TAN-26. After nine months, lactate injections were discontinued to evaluate anaerobic reductive dechlorination performance when propionate and acetate (lactate fermentation products) were the primary electron donors in the system. The cessation of lactate injections marked the end of the field evaluation and the beginning of optimization activities at TAN.

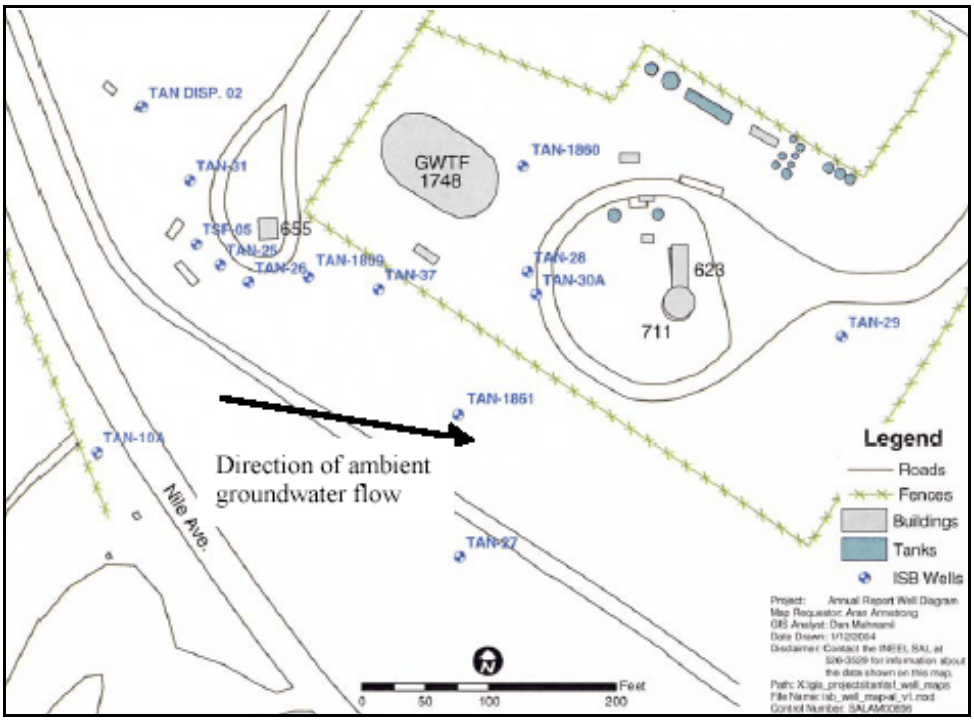


Figure B8-2. TAN ISB treatment cell map

A significant outcome of the field evaluation work was the strong evidence indicating that the injected sodium lactate solution significantly enhanced the bioavailability of TCE in the residual DNAPL source area, thereby accelerating degradation of the source. This effect was evidenced by the near 21-fold increase in TCE concentrations that corresponded to arrival of lactate in well TAN-26, followed by complete dechlorination of this newly bioavailable TCE to ethene (Figure B8-3c). Two mechanisms have been described by other investigators that contribute to the enhanced mass transfer effect (Carr, et al., 2000). A third mechanism, which may be the most significant, is the interaction between the electron donor itself and the nonaqueous TCE. The electron donor solution enhances dissolution of the TCE and mixes it with the electron donor, making the TCE highly bioavailable (patent pending). Based on the field data from the FE and subsequent laboratory experiments, it was hypothesized that reduced interfacial tension between the nonaqueous TCE and the aqueous phase was responsible for this effect.

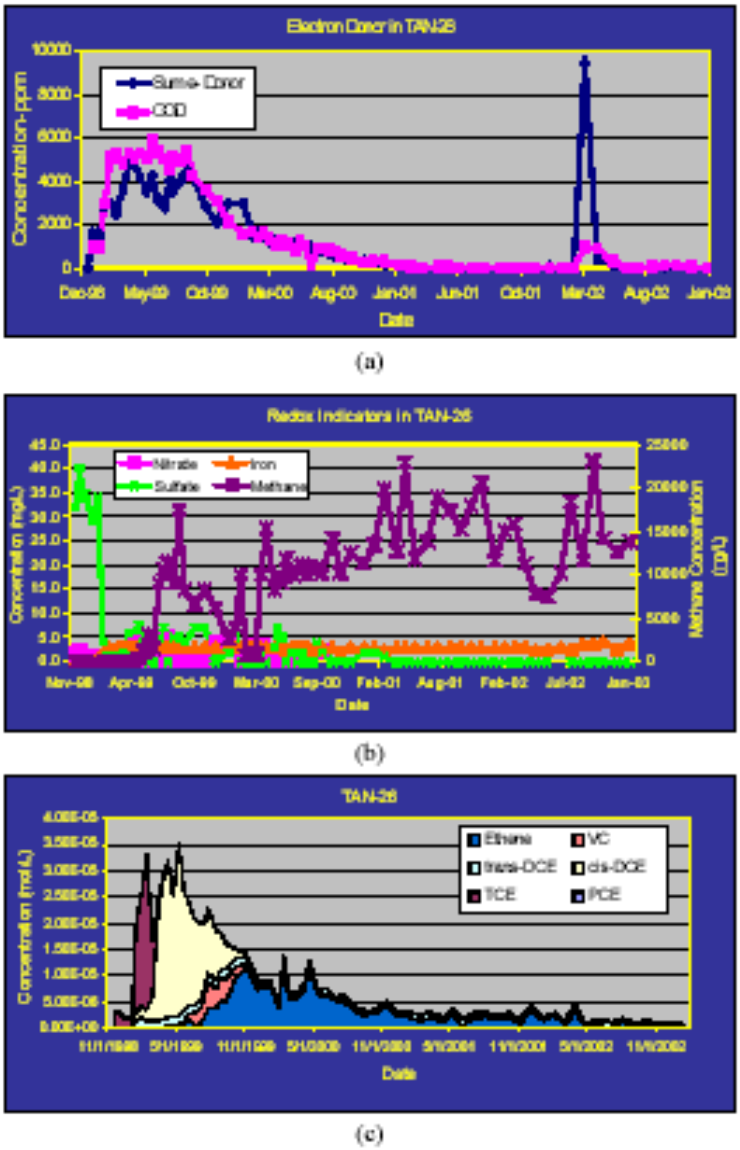
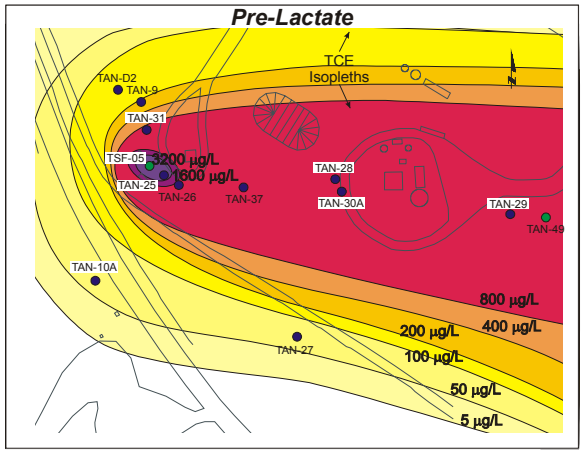


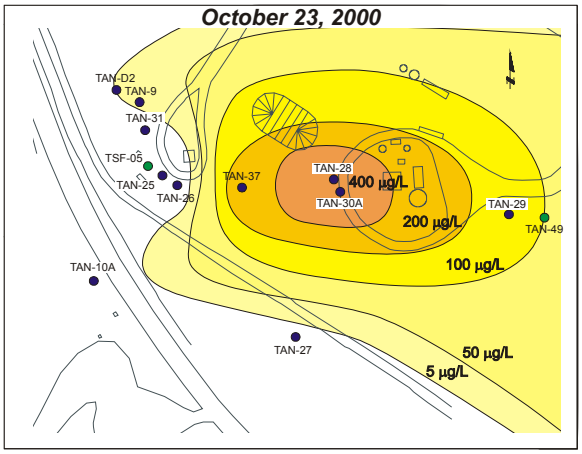
Figure B8-3. Electron donor (a), redox conditions (b), and VOCs (c) for a TAN ISB monitoring well

ISB has been demonstrated to be a much more effective technology for treatment of residual source areas than previously believed. Figure B8-4a shows the pre-lactate TCE concentrations in the residual source area, and Figure B8-4b shows the TCE concentrations after 21 months of lactate injections. Based on these substantial concentration reductions within and immediately down-gradient of the DNAPL residual source area, coupled with the evidence for accelerated degradation of the residual DNAPL source, an amended ROD was signed by the State of Idaho and EPA Region 10 to replace pump and treat with bioremediation for restoration of the TCE source area at TAN. Operations conducted since the conclusion of the field evaluation have been focused on optimization (the current phase of operations) and long-term implementation of ISB as defined by the objectives described below.



(a)

Figure B8-4. Pre-lactate TCE concentrations (a) and TCE concentrations after 21 months of lactate injection.



(b)

Figure B8-4b. TCE concentrations after 21 months of lactate injection

Performance Objectives. Two stages of operations remain for the TAN ISB hotspot remedy—optimization activities and long-term operations. The primary performance objective for ISB optimization activities, which is the current phase of ISB operations, is to distribute electron donor throughout the entire residual source area to eliminate VOC migration beyond the ISB treatment cell. The performance metric for this objective, as it was for the ISB field evaluation, is changes in groundwater concentration. However, in this case, a group of four key wells will serve as sentinel monitoring locations. Wells TAN-28 and TAN-30A will be used to determine when contaminant migration from the residual source has been eliminated in the down-gradient direction, and wells TAN-1860 and TAN-1861 will be used to determine when contaminant migration from the residual source has been eliminated in the cross-gradient direction. Each of these well pairs will serve to indicate when the area of active biological treatment encompasses the entire residual source area.

Once down- and cross-gradient migration has been eliminated, then the ISB remedy will move into its final phase, long-term operations. The primary performance objective of ISB long-term operations is to maintain the sufficiently large biologically active zone for a period of time such that the residual source material is degraded to a point where natural attenuation processes will address the residual levels of groundwater contamination.

Performance Monitoring and Verification. The performance objective for ISB optimization activities is to distribute electron donor throughout the entire residual DNAPL source area to completely eliminate contaminant migration to down-gradient wells. During the field evaluation, a relatively constant supply of lactate was provided through weekly injections. During initial optimization activities, however, the presence of propionate and acetate combined with the absence of lactate resulted in increased dechlorination efficiency as evidenced by conversion of all accumulated cis-DCE to ethene throughout the residual source area. Therefore, the primary operational change during optimization activities was to inject larger pulses of lactate less frequently, approximately every six to eight weeks, to increase periods when propionate was the primary electron donor. This has resulted in significant progress towards meeting the performance objective.

Electron donor distribution has improved during optimization activities, both in terms of distribution of electron donor to wells not previously impacted, and in terms of higher observed donor concentrations. For example, neither lactate nor its fermentation products (propionate and acetate) were detected in well TAN-D2 (Figure B8-2) during the field evaluation. However, during optimization activities, propionate (84 mg/L) and acetate (58 mg/L) both were observed eight days following a sodium lactate injection. Also, the maximum electron donor concentration (as COD) in well TAN-31 during the FE was 1,700 mg/L. During optimization activities, COD in TAN-31 was measured at a concentration of 4,000 mg/L eight days after an injection.

Although substantial progress toward the performance objective for optimization activities has been made, the objective has not yet been achieved. To achieve this objective, a second injection well, TAN-1859, was incorporated into ISB operations in December 2003. Although the ISB remedy has not yet moved into long-term operations, progress toward this objective can still be measured by monitoring chloroethene and ethene groundwater concentrations in ISB wells. During optimization activities, the same pattern of enhanced TCE dissolution in response to sodium lactate injections, followed by complete dechlorination of the newly bioavailable TCE to ethene that was observed in the field evaluation still persisted. During optimization activities, TCE concentrations in well TSF-05 have routinely increased from nondetect to 500–1000 µg/L in response to lactate injections, but then have been subsequently reduced below detection by 4–5 weeks after injections.

The most important and direct evidence for residual source destruction involves well TAN-D2, which is approximately 115 ft cross- and up-gradient of the TSF-05 injection well (see Figure B8-2). To understand these observations, the fate and transport of trans-DCE in the TAN system needs to be understood. When TCE is biodegraded via reductive dechlorination, greater than 99% of the TCE is transformed to cis-DCE rather than trans-DCE. Thus, it is unlikely that any trans-DCE observed at TAN is generated biologically. However, significant concentrations of trans-DCE (up to 500 µg/L) have been observed near TSF-05 during ISB operations. This suggests two things—trans-DCE is present as an original contaminant in the injected sludge and diffuses into groundwater, and trans-DCE is recalcitrant to reductive dechlorination in the TAN system. Because of these things, trans-DCE acts as a semiconservative tracer for residual source material at TAN. It should be noted that the MCL for trans-DCE is 100 µg/L and that concentrations are an order of magnitude below that at the down-gradient edge of the ISB treatment cell (Well TAN-29).

From 11/98 to 3/03, limited reductive dechlorination was occurring at TAN-D2, as evidenced by the small amount of ethene production (up to 50 µg/L), however, it was not sufficient to completely degrade all of the TCE diffusing from the residual source near TAN-D2. During the course of ISB optimization activities, an injection strategy employing relatively infrequent, large volume injections was adopted. These injections contacted a portion of residual source material near TAN-D2 that had not been contacted before. Coincident with the electron donor arrival and trans-DCE increase, redox conditions became methanogenic at TAN-D2 as evidenced by the reduction of sulfate to 0 mg/L and the presence of ferrous iron and methane. Concurrent with the redox changes, TCE concentrations declined to nondetect.

Currently, the only VOC at TAN-D2 remaining above the detection limit is trans-DCE (approximately 20 µg/L). The importance of the trans-DCE trend at TAN-D2 cannot be overstated. Since trans-DCE acts as a tracer for residual source material, the dramatic increase observed in response to the larger injections indicates that additional source material was contacted by these

larger-volume injections. The fact that trans-DCE is now significantly declined, combined with the facts that no TCE rebound has occurred and ethene production at TAN-D2 has ceased, suggests that this source material has been degraded. In addition, the recent smaller volume injections have resulted in sulfate concentrations rebounding to near background levels and ferrous iron and methane concentrations decreasing. This event indicates that redox conditions at TAN-D2 are beginning to be influenced by up-gradient, uncontaminated water. The fact that neither trans-DCE or TCE has rebounded coincident with the onset of less-reducing conditions at TAN-D2 is convincing evidence that the residual source material that was present near TAN-D2 is now completely degraded as a result of ISB operations.

Overall, significant progress towards the performance objective for both optimization activities and long-term operations has been made at TAN. Additional optimization activities are needed to distribute electron donor throughout the entire residual DNAPL source area to completely eliminate flux to down-gradient wells, evaluate alternative electron donors that may decrease long-term costs, and study microbial competition to determine whether the system can be optimized to favor the organisms of interest.

Lessons Learned

- Enhanced in situ bioremediation can be very effective even in complex source areas,
- Toxicity of chlorinated solvents to bacterial communities, once thought to be a problem for ISB of DNAPLS, may not be an issue. In fact, dechlorinating bacteria may have an ecological niche in these high concentration areas,
- Reductive dechlorination is strongly correlated both to electron donor distribution and redox conditions, and,
- Dechlorination efficiency can be controlled in the field by the electron donor addition strategy and type.

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APPENDIX C

Role of Pilot Tests and Technology Demonstrations

Appendix C. Role of Pilot Tests and Technology Demonstrations

Pilot studies are primarily conducted to gather information needed to design a full-scale remedial system. Treatability studies and technology demonstrations may also be conducted during the remedy selection process to compare the cost and performance of alternate technologies. Because they are designed to provide answers to specific questions about a technology's suitability at a site, pilot studies and technology demonstrations are typically instrumented and monitored more extensively than full-scale deployments. As such, these technology implementations afford opportunities to obtain performance data not typically collected in full-scale remedial operations (although this information comes at a cost). Careful design and implementation of a robust performance assessment program is therefore essential to evaluating the pilot or demonstration and when selecting final performance metrics for a scaled-up implementation.

The selection of the type of DNAPL remediation technology is dependent on the remedial objectives to be achieved by the remedial action. The link between the performance objectives for the demonstration and the criteria for selecting, deploying, and terminating a full-scale DNAPL source reduction technology should be clear. This section describes the objectives of a performance review that might be conducted to demonstrate the efficacy of a DNAPL source zone reduction technology in the unsaturated and saturated zones and to assist in the decision making required under state and federal programs.

Demonstrating the Feasibility of a Technology

Pilot-scale work and field demonstrations are designed to answer fundamental questions about a technology's performance under certain site conditions. They provide an opportunity to apply knowledge to other sites and possibly predict performance. Because pilot studies are often highly instrumented, they may provide data on the technology's impact to the source zone and the dissolved plume, which can be used to calibrate predictive models.

How does a particular option fare with respect to conventional methods of treatment? A pilot study can be designed to demonstrate whether a technology is feasible, and if not, what the limiting factors might be. Data obtained from a well-documented and instrumented site can be useful when identifying and choosing an appropriate remedy at another site. Laboratory bench-scale and pilot-scale treatability tests are often performed prior to a full-scale remediation to evaluate the effectiveness of a technology and develop specific design parameters for a full-scale remediation system. The pilot-scale test is typically conducted in the field presumably under identical conditions as the full-scale remediation. There are limitations to both tests. For example, a bench-scale test is generally performed in a laboratory in a microcosm designed to simulate real site conditions and therefore can produce results which may or may not reflect the performance of the technology in the field.

Determining Realistic Performance Objectives and Criteria

RAOs for a full-scale DNAPL source reduction need to take into account how the specific treatment technology impacts the three-dimensional source strength and architecture. To evaluate treatability study performance relative to achievement of full-scale RAOs, the relationship between source

treatment, mass reduction, mass flux (distribution of flux and associated mass discharge), and plume response needs to be understood. In addition, the time scale of the response must be understood to estimate cost and performance.

Improving the Conceptual Site Model

The DNAPL architecture and the hydrostratigraphy in the area where the pilot study is performed must be defined adequately enough to understand how site-specific characteristics may impact the technology performance assessment. Soil stratigraphy data collected during the pilot study well installation can provide key information on subsurface features (e.g., confining layers, stratigraphic interfaces) that might influence the migration and distribution of DNAPL and augment the CSM. For instance, some estimate of the mass and distribution of DNAPL, as well as the uncertainty and potential error of that estimate, should be determined pre- and post-treatment to validate and test the CSM.

There will always be uncertainties in a site-specific CSM. However, these uncertainties can be managed through the remediation design if they are adequately characterized prior to the design process. It is not unusual that a pilot will demonstrate that the design and operations need modification to be implemented at full scale. Phased deployment can allow cost-efficiencies both in testing and optimizing the modified operational design and in responding to new site-specific information.

Selecting the Pilot Study Location

The ideal location for a pilot test would be a small lobe of contamination that extends cross-gradient from the main contaminated region. Obviously, such "ideal" pilot-test locations are rare. In general, the pilot test should be located in a representative portion of the site, using knowledge about the site geology and DNAPL distribution, so that lessons learned from the pilot can be applied sitewide. Alternately, the project team may elect to locate the pilot study in a section of the site that is considered to be more challenging than average so that success achieved under more difficult conditions might extend to the remaining source material.

During a pilot test that is located adjacent to a more contaminated region, the act of remediation creates concentration gradients and advective flows of vapors and groundwater that cause an inward contaminant flux from the surrounding regions. Contaminant flux from concentration gradients is regulated by diffusion. Advective flows into the pilot test volume can result from vapor extraction activities in the vadose zone or the removal of groundwater as steam during thermal treatments. For example. Additionally, if there is a natural groundwater gradient from surrounding contaminated regions into the pilot study area, fresh contamination will enter the area throughout the study. These contaminant flux sources have several impacts:

- the remediation of the pilot test region proceeds more slowly and requires greater energy density than a full-scale remediation would require,
- the continual influx of contamination may limit the percentage reduction that can be achieved in a pilot test,

- groundwater concentrations may rebound after the pilot test is complete due to groundwater mixing and diffusion if monitoring wells are not placed near the center of the pilot test region, and,
- soil is typically not prone to the same mechanisms that cause rebound to occur in groundwater concentrations; however, treatment-induced redistribution of DNAPL could cause post-treatment soil concentrations to increase in some regions of the treated zone and influence post-sampling results in a manner suggestive of rebound. Soil samples can be collected from locations that are closer to the edge of the pilot test treatment region, in locations where monitoring wells would not be recommended.

Addressing Scale-Up Issues

Designing a full-scale remediation based on a pilot-scale demonstration requires understanding the limitations of the pilot-scale data and identifying which problems can be accounted for and overcome in the full-scale design. Information essential for the design that should be collected during the pilot study includes the following:

- effectiveness of treatment delivery,
- DNAPL removal rates as a function of operational time and energy consumption,
- constructability of the source reduction system,
- effectiveness of the design in controlling DNAPL migration,
- construction and operation costs as a function of DNAPL mass removed or destroyed,
- effects of the source reduction system on adjacent utilities and facilities, and,
- potential for operations to impact vulnerable receptors.

It is especially important to address the following issues before designing a full-scale system:

Potential Impacts to Groundwater. Field demonstration work plans should include groundwater monitoring at treatment completion as well as over a predetermined period. The work plan should address ongoing measures of removal, contaminant rebound, recontamination of the test area after treatment, and methods to improve performance during full-scale treatment. In addition, an adequate number of sampling events must be determined to effectively characterize starting conditions, including allowance for any natural variability in groundwater concentrations.

Formation of Treatment By-Products. The pilot study should be adequately designed and monitored to provide information on potential treatment by-products. For example, the potential for forming toxic intermediates in situ during subsurface oxidative processes should be addressed. Also, the possibility of steam venting at the surface or induced pressure gradients causing uncontrolled migration of vapors should be considered. Hydraulic control of surfactant or cosolvents and the impact of residual chemicals and their breakdown products should be considered for in situ flushing treatments.

Effectiveness and Efficiency of Treatment. The pilot study should provide information on how effective the technology is in dealing with heterogeneity in the treatment volume, recovering DNAPL, and reducing the mass flux emanating from the treated source. Data from the study should allow remediation effectiveness and efficiency to be evaluated at the deepest treatment interval and at any key stratigraphic interfaces. It should be noted that if a pilot study is conducted within a

larger DNAPL zone, it may be very difficult to assess performance with respect to the longevity of reductions in DNAPL source strength.

Transition criteria. The criteria for shutoff of the source reduction system must have a clear technical basis (e.g., technically supportable asymptote-based goals based on predicted subsurface contaminant concentrations or ex situ operational data). The transition to the next step (unit process) in the treatment train should be planned in advance and critical parameters and decision points identified prior to performing the pilot test, if possible.

Constructability. The pilot study should be adequately designed to assess the constructability of the DNAPL source reduction technology. In addition, the DNAPL source reduction system should not negatively impact adjacent utilities and facilities, including no observed vapor transport into nearby engineered structures.

Assessing Costs

An examination of cost with respect to DNAPL mass removal is of questionable value for comparing the costs of alternate mass removal technologies unless the mass removal rates are normalized by an accurate estimate of the mass originally in place. The cost assessment should be designed to both determine operation costs as a function of DNAPL mass removed or destroyed and assess the cost-effectiveness of the DNAPL source reduction technology. It should be noted that costs for pilot studies are strongly affected by site scale.

The cost-effectiveness of a technology is also influenced by the long-term operational costs for plume management and/or containment, including long-term groundwater monitoring costs, plus any secondary treatment technology costs for plume management. Final cost comparisons should therefore include total costs to achieve RAOs even if a technology is being considered for partial source depletion only (i.e., the impacts on subsequent technologies in a treatment train should be considered, and total costs of alternate treatment trains should be compared).

The following information is needed for the full-scale cost estimate:

- Operating costs. The pilot study should be used to determine the full-scale treatment technology duration and the time-dependent operating costs as estimated by the pilot demonstration.

- Mass capture and performance of adjunct treatment technologies**.** The demonstration should provide data needed to estimate adjunct treatment process requirements (e.g., off-gas treatment) and select the most cost-effective technology. For example, granular activated carbon treatment may be expensive for long-term projects; therefore, it would be prudent to identify and cost alternate off-gas treatment processes.

- Vertical DNAPL profiles**.** The design should be successful at reducing the DNAPL source at the deepest portions of the source. The full-scale design must ensure source recovery at all targeted depths.

- Contaminant residuals**.** The long-term impacts of remaining contaminant mass on source strength should be included in long-term projections of groundwater plume migration and longevity.

APPENDIX D

Statistical Approaches to Evaluating Performance

Appendix D. Statistical Approaches to Evaluating Performance

The use of statistical analyses of the data is an important tool in evaluating performance. Accurate measurement of performance is critical to making project decisions. For example, deciding whether to expand a pilot test to full scale or how long to operate a remediation system. DNAPL remediation technologies, some of which are summarized in Section 4, are biologically, chemically, and physically complex engineered systems. Data generated from remediation sites are often full of good information but sometimes too complex to easily see system trends and may require sophisticated statistical and data modeling procedures to evaluate. For instance, assessing the degree of change in contaminant levels between pre- and post-treatment may require a modeling procedure or established methods that can account for temporal and/or spatial data correlation.

It is easy for a project manager to get lost in the world of statistics and modeling, for some of the concepts and literature in the field is quite obscure. Fortunately, there are tools and reports to help. The EPA has published a series of guidance documents to assist managers in making defensible decisions, some of which are listed below:

- *Guidance on Choosing a Sampling Design for Environmental Data Collection* (QA/G-5S). EPA/240/R-02/005. www.epa.gov/quality/qs-docs/g5s-final.pdf,
- *Guidance for the Data Quality Objectives Process* (QA/G-4). EPA/600/R-96/055. www.epa.gov/quality/qs-docs/g4-final.pdf,
- *Decision Error Feasibility Trials (DEFT) Software* (QA/G-4D). EPA/240/B-01/007. www.epa.gov/quality/qs-docs/g4d-final.pdf,
- *Guidance for the Data Quality Objectives Process for Hazardous Waste Site Investigations* (QA/G-4HW). EPA/600/R-00/007. www.epa.gov/quality/qs-docs/g4hw-final.pdf,
- *Guidance for Data Quality Assessment: Practical Methods for Data Analysis* (QA/G-9) EPA/R-96/-84 (QA00 Update). www.epa.gov/quality/qs-docs/g9-final.pdf,
- *Data Quality Evaluation Statistical Toolbox (DataQUEST)* (QA/G-9D). www.epa.gov/quality/qa_links.html#software.

In addition, comprehensive descriptions of most statistical methods, with tutorials, can be found in the recently published *Contemporary Statistical Models for the Plant and Soil Sciences* (Schabenberger, 2001).

Sampling Design

The sampling program and the statistical model must be designed in a manner that meets the specific goal. The question is, which should be selected first: the statistical model to be used for the data analyses or the sampling program? It would be prudent to plan this process in advance so that the appropriate data set (spatial and temporal) is collected to meet the data analysis requirements. Because the appropriate statistical model to be used will depend upon the nature and form of the data being collected (e.g., seasonality, data distribution), the sampling program should be designed initially using some assumptions about the data, with an agreement to review the data as it is being collected and to modify that plan, if necessary.

Most statistical methods require a minimum round of samples and a particular sampling methodology (e.g., random sampling, systematic grid sampling, or cluster sampling). Additionally, some statistical methods require a "repeated-measures" sampling design, which may involve the repeated collection of samples from the same location and depth.

The objectives or goals of a particular technology evaluation may be set to determine the following:

- the approximate reduction in contaminant concentrations that occurs in groundwater within the treatment zone as a result of using a particular remediation technology, or,
- the mass removal over the course of treatment, or,
- the decrease in mass discharge,
- whether the mean concentration after treatment is significantly different from the mean concentration before treatment.

The two main approaches to solving these challenges involve the use of statistical or approximation models and of integrated physics-based models with statistical representations of the subsurface with site data. In either process, the optimal estimate of the subsurface condition is desired. The data needs and level of effort to produce the estimates vary widely and fitting the analysis with the needs of the project is strongly advised.

Some models may require a comprehensive exploratory data analysis before the formal model is fit to any contaminant data. This analysis may include the construction of time-trend data plots for each well-depth interval combination (to assess the degree of consistency in the treatment effect), temporal and spatial variance analyses (to assess variance stability assumption across different wells and sampling time frames), and the need for any data transformation(s). Additionally, a decision must be made regarding the treatment of the nondetects. In many cases, a zero concentration may be a very useful piece of information, as it can bound the extent of impacts and thus help limit overextrapolation exhibited by some of the predictive methods, such as kriging. Some statistical methods may require a degree of detectable contaminant levels, however minimal that is. Nondetect data may be deleted or some percentage of the detection limit may be used.

To assist the project manager who lacks extensive statistical training with sampling plan design, free public domain software called *Visual Sampling Plan 2.0* is available. It implements eight commonly used statistical methods in Excel® spreadsheets and a Microsoft Windows package, specifically, the One-Sample t-Test, Two-Sample t-Test, Wilcoxon Signed Rank Test, One-Sample Proportion Test, Two-Sample Proportion Test, Wilcoxon Rank Sum Test, MARSSIM Sign Test, and MARSSIM WRS Test. See www.hanford.gov/dqo for details, users guides, software, and tutorials. The software is limited to two-dimensional analysis.

Data Analysis Procedures

- Analysis of variance (ANOVA). This is the analysis of variance procedure, a collection of statistical models and procedures for comparing means (Maxwell and Delaney, 1990). Comparing background wells to compliance wells can be accomplished using this method. The one-way ANOVA test is used when one factor (such as the presence of DNAPL) is responsible for the differences in the data

populations, whereas the two-way ANOVA test is used when the differences are due to two factors, such as DNAPL saturation and geology. These can be parametric or non-parametric procedures.

- Tolerance and prediction intervals. Comparing background wells to response boundary or compliance wells can also be accomplished using this method. The tolerance interval is obtained from the data in the background wells. Then, the data collected from the nonbackground wells are used to assess whether they fall within the tolerance interval. If not, a conclusion that the nonbackground wells are affected is reached. This test is best used when the geology is fairly homogeneous and the data (raw or log-transformed) are normally distributed.

- Control charts. These are constructed primarily from nonimpacted-well data. They can be used to detect when the concentration in a well goes "out of control," indicating probable contamination. The Shewart-CUSUM control chart is well-suited for this application (Gilbert, 1987).

Geostatistical Estimation Techniques

Geostatistical methods comprise a collection of techniques to solve estimation problems when georeferenced spatial variables are involved. This includes estimating the mass of DNAPL or volume of dissolved plume, for example. Spatial dependence of variables is expressed in terms of a variogram.

Many geostatistical methods are employed at hazardous waste sites. There are variance-based geostatistical methods, concentration-based geostatistical methods, as well as others. A commonly used method of estimating mass and volumes of DNAPL is kriging, a linear geostatistical interpolation method. A good reference on geostatistical methods is available for download at the U.S. Army Corps of Engineers Web site (USACE, 1997). The method used when kriging chemical data is affected by the sampling program, specifically preferential sampling (bias sampling) of the high-concentration areas.

There is a significant growth in the use of mixed models, brought on by an increased appreciation of the importance of modeling variation in complex systems. These can be classified into three main groups: mixed-linear models, generalized linear models, and nonlinear mixed models. Mixed models broaden the statistical inference, recover all the relevant information in the data, handle correlation structures in the data, and handle nonhomogeneous variances. The mixed-linear model is a good example for modeling data with both spatially and temporally dependent error structures. It can be used to estimate and test the statistical significance of the treatment effect, while at the same time adjusting any spatial and/or temporal effects. The mixed-linear model is described in detail in Milliken and Johnson (2001) and Littell, et al. (1996). The commonly used statistical software package called SAS/STAT® implements all three of the main types of mixed models.

Trend Analysis

In addition, the statistical analysis may include a nonparametric test for trend. The Mann-Kendall test is a good example of the nonparametric test for trend. This test is a useful technique for

analyzing the data since missing values are allowed and the data do not have to fit any particular distribution. Also, nondetect and trace concentrations can be used. These data can be used because the Mann-Kendall test uses only the relative magnitudes of the data rather than their measured values. A detailed description of the Mann-Kendall test can be found in *Statistical Methods for Environmental Pollution Monitoring* (Gilbert, 1987). Other trend analyses are potentially applicable to data analyses involving DNAPL source remediation.

Integrated Physical-Geostatistical Methods

The methods described above rely on historical data and professional judgment. Physical-geostatistical methods, in contrast, integrate the physics of the remediation (through simulation models), the uncertainty (through geostatistics), the spatial-temporal data (using a Kalman filter to estimate the confidence interval of the plume fringe), and the best locations and time to sample (to reduce uncertainty in the estimate of residual DNAPL). They are also used to develop optimal long-term monitoring plans for assessing the performance of a remedial action, for example, or natural attenuation monitoring. Physical-geostatistical methods are more complex to implement but provide very valuable information based on physical models and site data.

These are some of the many options the site managers have at their disposal to conduct a statistical evaluation of the data. Table D-1 lists some statistical and probabilistic methods for analyzing environmental data and their use in performance assessment.

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Table D-1. Examples of Statistical and Probabilistic Methods for Analyzing Concentration Data from Non-Natural Sources

Statistical Method	Description/Example Use	Comments
Analysis of variations (ANOVA)	Compare background well to compliance well(s) concentration "populations." Typically compare the population means. Grouped into parametric or non-parametric procedures.	One-way ANOVA applied when one factor (i.e., DNAPL source) is responsible for inter-population differences. Two-way ANOVA appropriate when DNAPL and geology account for differences in populations. When data in background wells collected different time period than the non-background data, important to correct for seasonal components.
Tolerance and prediction intervals	Compare background well to compliance well(s) concentration "populations." Tolerance interval constructed for background well(s). If any results from the compliance/remediation well concentration are outside of tolerance, conclude well is contaminated. Prediction interval is constructed using the mean and standard deviation of the background data. Evidence of well contamination is concluded if a mean falls outside the prediction interval. Called "prediction" as samples collected for tests are usually in the future.	Best when either the raw or log-transformed data are normally distributed. Most appropriate when the hydrogeologic system is relatively homogeneous.
Fixed standards comparison	Compare well concentrations to a fixed standard, such as an alternative concentration limit (ACL). Grouped into parametric or nonparametric procedures. Can use confidence or tolerance intervals.	If the lower limit of the confidence interval in a nonbackground well exceeds the MCL/ACL, contamination is concluded.

Statistical Method	Description/Example Use	Comments
Single-well assessments	Used to evaluate trends in a single well via Shewhart-CUSUM control charts. Used to assess changes in concentrations in a well due to unnatural causes, such as probable contamination.	Best for uncontaminated wells, where eight seasonally corrected concentration measurements are available in a single year. Raw or log-transformed data are normally distributed.
Mann-Kendall test	Used to evaluate trend. Useful since missing values are allowed and data need not conform to any particular distribution.	The relative magnitudes of data are used rather than their measured value. Therefore, trace or less than detection limit can be used.
Mixed models	Three main groups: mixed linear models, generalized linear models, and nonlinear mixed models. Mixed models broaden the statistical inference, recover all the relevant information in the data, handle correlation structures in the data, and handle nonhomogeneous variances.	The mixed-linear model is a good example for modeling data with both spatially and temporally dependent error structures. It can be used to estimate and test the statistical significance of the treatment effect, while at the same time adjusting any spatial and/or temporal effects.
Geostatistical methods	Methods which estimate georeferenced, spatially distributed data. Kriging is a geostatistical interpolation method. Can be used to estimate concentration where data do not exist, the volume of plume or DNAPL mass, or the location of samples collection to reduce the variance of the estimation error in the above.	Various types of kriging exist, such as ordinary, nonstationary (when the contaminant is moving), co-kriging (when two or more variables provide information for the estimate), quantile kriging, and nonlinear geostatistics. Performance is highly dependent of variability of the concentration data and preferential sampling of high concentration areas.
Integrated physical and stochastic estimation	Integrated approach uses geostatistics, flow and transport models to simulate distributions of contaminants in space and time. Uses Kalman filters and other algorithms to optimize well locations for plume finding and sample timing for optimal plume monitoring.	Requires (even a rudimentary) subsurface flow and transport simulator. Requires estimation of geostatistical variogram for stochastic simulation.

APPENDIX E

Responses to Comments

Appendix E. Responses to Comments

NOTE: Responses to comments are in bold. Specific pages and line numbers mentioned in the comments refer to a review draft of this document. In many instances those references do not correspond to the published version.

Tom Sale - Colorado State University

1. My hat is off to you and your ITRC colleagues. This is a very good document. Specifically: 1) the material is relevant and topical, 2) the document is well organized and clearly written, and 3) the document maintains objective perspectives on a series of difficult topics. My primary suggestion is that you consider expanding the executive summary. As is the document is far more than a quick read. Most people that pick up the document will not have the time to get through it. Consider writing a 5 to 8 page executive summary that hits the high points of each section. Those seeing topics critical to their interests will be inspired to dig deeper. One option would be to use a frequently asked questions format per API Bulletin 18.

We concur. The Executive Summary has been lengthened.

2. Recently, there has been recognition that sorbed and dissolved phases in relatively stagnant portions of source zones can sustain concentrations at plume heads for extended periods. With this the EPA Expert Panel Source Zone Report and the soon to be released NRC Report recognize the source as the areas in which DNAPL or an alternate high concentration release initially occurred. As an example one could imagine fractured clay in which most of the DNAPL has been depleted by diffusion into stagnant zones. Contaminants in stagnant zones (sorbed and dissolved contaminants) can express themselves via back diffusion. (See the source zone definition in the recently released EPA Expert Panel document http://www.epa.gov/ada/pubs/reports.html).

We will revise Section 2.3 on rebound to incorporate the concepts of stagnant zones and potential back diffusion. Based on other comments, Section 2.1.2 on matrix diffusion and discussion of fractured bedrock has been eliminated from the document. The definition of a DNAPL source zone has been revised to coincide with the EPA Expert Panel report.

3. Figure 1.2 was originally developed by Bernie Kueper at Queen University. You should give him credit.

Dr. Kueper has been contacted and has agreed to let us use the figure.

4. Page 14, Line 4. It might appropriate to add that rigorous definition of the amount of DNAPL is difficult.

We agree that it is difficult to define the location of DNAPL source zones; and we say so.

5. Section 2.2, 2nd paragraph, first sentence, not all changes in source zone architecture will improve removal or destruction efficiencies, consider rephrasing this.

The sentence has been rephrased to read "... changes *may* occur in the source zone ..."

6. Page 17, Line 7, you might want to note that increased temp can increase NAPL mobility (primarily a concern with coal tar and creosote).

We concur and addressed this issue under *Redistribution of DNAPL*.

7. Page 20, in the bullets, consider adding back diffusion from stagnant zones as a cause of rebound

This has been addressed in comment 3.

8. Page 21, 3rd full paragraph, consider adding surface obstructions as a factor effecting treatment difficulty (e.g. working under process unit in refineries is different than working in an open field)

We have added a reference to surface and subsurface obstructions.

9. Section 3.1.2 – It seems that eliminating any complete exposure pathways should be the first short-term goal.

We consider "controlling immediate risk" to be the same as "eliminating any complete exposure pathways."

10. Section 3.2.1 – Is DNAPL removal really the primary goal, Why not reducing contaminant loading to the environment, there are more than a few situations where DNAPL removal is not the primary goal, consider rewording.

We have deleted the first paragraph and the bulleted list.

11. Typically, developing rigorous estimates of contaminant mass in place is not practical. Be careful in this section with leaving the impression that it is typically a doable thing.

We agree and have made a few modifications as appropriate.

12. Section 3.6.2 2nd paragraph, text describing the rarity of closure in the "absolute sense", should be included to managing expectations; to my knowledge no DNAPL site has been cleaned up to MCLs. Text supporting this position can be found in the recent EPA expert panel report (http://www.epa.gov/ada/pubs/reports.html).

We concur and the paragraph has been modified.

13. Table 4-1 Source mass remaining & Mobility reduction: (a) the combination of two topic confuses me, perhaps some punctuation or an "and" would help; (b) why aren't soil cores listed as a performance method? ©) PITTs only work in the swept volume and don't work in thick NAPL zones due to mass transfer limitations, I'm surprised that the relative accuracy is intermediate to high. I suspect more than a few people who have used PITTs would debate this.

(a) We have separated into two topics or metrics; (b) we have included soil coring as a method of estimating mass; ©) the relative accuracy of PITTs has been changed.

14. Table 4-1 Mass flux / mass discharge. Listing the relative accuracy as Intermediate to High seem premature. It seems to me that our understanding of this topic is evolving rapidly and that you are getting a bit ahead of the science.

With a sufficiently high number of discrete measurements, mass flux can be determined accurately; however, to address your concern, we have lowered the rating to "Intermediate." The two other methods are untested in the United States and are therefore not given a rating.

15. Figure 4-1. Under "Decrease in Mobility" you might want to include reduced NAPL thickness in wells and reduced formation transmissivity to NAPL (e.g. bail down or low flow pumping tests)

We have modified Table 4-1 to include measuring NAPL thickness in wells.

16. Page 56, Monitoring well network design and installation. It seems that you should discuss appropriate length of screens here; this is a challenging topic that should be mentioned.

We have added a discussion of well intake placement.

17. Box 4-1, a series of email circulated about this site that contaminants had been driven off site via formation and subsequent condensation of steam under a capillary barrier. If this is true some mention of the issue might be warranted.

The intent of the highlight box was to provide a short summary or example of the use of groundwater data to assess performance.

18. Page 62 top, It might be worth mentioning technology inefficiencies that may exist due to natural oxidant demand (e.g reduced iron or sulfur compounds).

We have made changes to reflect this phenomenon.

19. Page 69, Applicability and Use, 1st paragraph, Last sentence, The statement that Mass flux is often the most…… seems unfounded, In many instances it is debatable as to whether it can be reliably measured, consider a less aggressive position.

We have revised the text to be less assertive.

20. Page 71, Top. It seems that the equation should be written as a summation.

We concur and have revised the equation.

21. Page 76, Line 5. I'm confused by the text string "Effectiveness monitoring." Is this a header or is there missing text?

We have added text describing effectiveness monitoring.

22. Page 78, last bullet at bottom. I'm aware of no references that support the statement, include a reference if you know of one. Also, there is a double period at the end.

We have provided references supporting this statement.

23. Page 84. An interesting attribute of Surfactant/Cosolvent Flushing is that is has never been selected as full-scale remedy for a site (perhaps recent work at HILL AFB, OU2 is an exception) despite upward to 50 demonstrations. Consider mentioning this.

It is not our intention to discuss the pros and cons of individual technologies.

24. Page 99, end of page. The position that TI Waivers are a "get out of jail free card" should be removed. This presents a seriously flawed misrepresentation of the process.

We have revised the language and omitted this phrase.

25. 7.0 References – If you get a chance you should check that the cited references are in this section, I think a few may be missing.

We have reviewed the entire document and have made numerous corrections pertaining to the references. Thank you.

26. Appendix B – Case Studies. It would be nice if all of the case studies included costs.

We have provided costs where reasonably obtainable, however in many cases costs for performance assessment were impossible to separate from overall remediation costs.

27. In my PDF printout many of the figures are difficult to read. If possible improve figure resolution.

We have attempted to improve the resolution and readability of many of the figures.

28. Page B-4. The representation that DNAPL traveled 500 feet seems highly unlikely, if this position is speculative it should be removed.

We have removed the statement.

29. Page B-26, 2nd to last bullet. What is UCL?

Upper confidence limit.

30. Page B-34, 3rd Paragraph. Typo, What is 9,000 Fg/L?

This was a typographical error which has been corrected.

Michael Kavanaugh - Malcolm Pirnie

31. The performance assessment (PA) document contains information and performance claims that have not been independently reviewed. Presenting such information without qualifying language creates the appearance of endorsement where none may be intended. Section 1.1 of the document contains an appropriate caveat as reiterated below.

"This document describes a number of performance assessment approaches and methodologies, including a discussion of their applicability and limitations. Source zone treatment technologies are, in many cases, still under development and there are no guarantees with any of the current technologies that DNAPL will be completely removed. Likewise, none of the performance assessment technologies described in this document can completely remove all the uncertainty associated with the measuring success."

Language that is consistent with this caveat should be included with discussions of performance assessment techniques that are not obtained from peer reviewed sources. Examples of discussions where such language is needed are presented below under specific comments.

We have attempted to provide accurate, objective information for our targeted audience. Although we agree that such qualifying language is needed at the beginning of the document and perhaps at the beginning of Sections 4 and 5, we don't think it's necessary to repeat this for every innovative monitoring technology.

32. The PA document contains background information that, while critical to the design and implementation of a successful source remediation program, is better addressed by presenting short descriptions and references to more complete discussions in the

published literature. Examples are presented below under specific comments.

We concur and have provided numerous additional references to the published literature. We do, however, feel it is important to provide the reader with sufficient background matter in a document such as this.

33. Section 2.1.2, Page 9. The definition of source architecture is vague. Also, this section does not present the concept of DNAPL distribution in low-K vs. high-K zones, which is the primary limitation of DNAPL architecture on flushing technologies.

We have attempted to clarify the meaning of source zone architecture and the affect that proximity of DNAPLs to more permeable zones has on remedial effectiveness.

34. Page 13. The suggestion that bacteriophages are used as particulate tracers in groundwater needs a peer-reviewed reference.

We have removed this reference.

35. Section 2.1.3: Source Zone Delineation. This section is unnecessary. The concepts are better addressed by reference to published literature such as the referenced ITRC document and Pankow and Cherry's Dense Chlorinated Solvents.

We have revised this section to focus on CSM development instead of source zone delineation. It has been renamed and reduced in length, and additional references have been added.

36. Section 2.2: Changes in DNAPL Source Zone Architecture Resulting from Treatment. This section presents eight potential impacts to the DNAPL source zone that may occur due to application of an aggressive source removal technology. The fact that the relative importance of each impact is technology specific is lost without relating each impact back to the technology.

We use specific technologies as examples throughout the section.

37. Page 15. The meaning of "magnitude and style of heterogeneity" is not clear.

We have deleted the phrase.

38. Page 17. The paragraph under Preferential Flow refers to "mobility control (as practiced in the petroleum industry)." Most readers will not know what this is.

We concur and have revised the sentence to read: "The use of mobility control agents (i.e., foams and gelants injected into the pore spaces) may mitigate the effect of preferential flow pathways and improve sweep efficiency."

39. Section 3.1.4 Assessing Costs, Page 27. The discussion on total restoration costs begins with the phrase "It may be prudent that..." A more appropriate introduction would be "It is essential that…"

We concur. Also, Section 3.1 on the role of pilot studies has been moved to Appendix C.

40. Section 3.4: Statistical Approach to Evaluating Performance and Section 3.5: Data Quality Considerations. Both of these sections contain information critical to performing source area characterization and remediation. However, for the purposes of the PA document the discussion could be better addressed by referring the reader to published literature.

We concur. Section 3.4 has been moved to Appendix D. Discussion of the Triad has been revised to focus on performance assessment.

41. The TRIAD discussion contains too much information on what TRIAD is and too little on what its benefits are for performance assessment.

Comment accepted. See revised text for Section 3.4.

42. Section 4.2.1: Decrease in Soil Concentration, Page 52. In Table 4-2 the ratio of Target Area (AT) to Site Area (AS) should not be greater than one.

We have made corrections to the Table 4-2.

*43. Section 4.2.2 Decrease in Dissolved Concentration, Page 54: in order to be consistent with Section 4.4.3, the last sentence under Multi-level sampling should read (changes in bold) "Multi-level sampling itself is not the same as **plume loading measurement** per se (described in section 4.**4**.3); however, if the monitoring wells are **properly** distributed cross-gradient along the control plane (lateral extent), then data generated by a network of multi-level samplers can be used to estimate contaminant **plume load** for different depths along the control plane."*

The suggested language has been added/revised.

44. Page 55, Second paragraph. The reference to the difficulty of monitoring large DNAPL source areas is a good place to incorporate elements of the TRIAD approach or adaptive site management, which were introduced in Section 3. Ending the discussion with a reference to numerical simulation is weak.

Comment accepted. The paragraph has been strengthened.

45. Section 4.3.3, Mass Remaining, Box 4-3. The discussion indicates that based on post-treatment soil sampling 75 to 90% of the TCE and 84 to 97% of the DNAPL were removed from each cell. However, at LC34 some of the DNAPL was mobilized into adjacent cells rather than being removed or destroyed in place. Box 4-3 should indicate what portion of the DNAPL or TCE was mobilized.

We have made the following modification to Box 4-3 (insert in last paragraph after the 2nd sentence): "There is evidence that both the ISCO and ERH demonstrations may have resulted in some mobilization of DNAPL in several regions peripheral to the demonstration plots (see Case Study 2 in Appendix B for more details)."

46. Page 63. Provide published references to efforts to make PITT technology more cost-effective so that the reader can evaluate the likelihood of implementation.

We have removed reference to the "Quick-PITT" system or other efforts to reduce costs of PITT.

47. Page 65: Delete the last sentence of Section 4.3.3. This sentence contradicts the previous statements that there are serious limitations to estimating mass remaining in-situ.

We do not agree that the sentence contradicts previous statements about the limitations of in situ mass estimations. Specifically, it states that the use of groundwater concentrations to estimate "volume, mass, or saturation of the NAPL zone" is nearly impossible.

48. Section 4.4.2 Decrease in DNAPL Mobility. The discussion on NAPLANAL is largely a repetition of the discussion in Section 2.1.2, and therefore is redundant.

We concur. The material in Section 2.1.2 has been moved to Section 4.4.

49. Section 4.4.3 Decrease in source mass flux, Page 69. Given the state of development, it may not be correct to describe either passive borehole flux meters or integrated pump tests as a "method available to estimate mass flux". It would be better to separate these two out as "emerging technologies" as identified toward the end of the section.

We agree that the passive flux meter is still in the research and development/demonstration stage and should not be touted as "available for use." However, based on an analysis of the literature, the integrated pump method espoused by Teutsch has been around since the mid-1990s and has been used quite often in Europe. It may not be cost-effective, especially when there is no readily available place to treat the water, but it has gone beyond the label of "emerging." The text has been revised.

50. Page 69. Paragraph under: "Continuous extraction from well transects" should indicate the basis for cost-effectiveness. For example, the cost-effectiveness derives from the use of existing wells and the assumption that the system achieves 100% plume capture.

We concur. This would be an expensive proposal if meant to start from scratch (without a preexisting network of monitoring wells in place). The paragraph has been revised.

51. Page 70. Paragraph under multi-level samplers should give an example of subsurface environments in which multi-level sampling is difficult or expensive, such as in fractured systems.

We agree that any kind of sampling within fractured bedrock is difficult and expensive, but we have decided not to address bedrock in this document.

52. Page 73: The suggestion that integrated pump tests can be used to overcome heterogeneity is correct. However, it should be noted that one of the limitations may be excessive cost of this technique.

We concur.

53. Section 4.5 Summary of Performance Metrics from a Recent Survey. The PA document uses the terms "surprisingly", and "incredibly" to preface the presentation of the Lebron survey results. It is difficult to know how much validity to place on the survey results. Therefore, the discussion of the Lebron survey should be dropped from the PA document. The PA document should reference the results of peer-reviewed performance assessments, or strongly qualify the other assessments of DNAPL source removal.

We agree that some of the results in the Lebron survey are difficult to interpret, but we are not sure that the survey results should be removed altogether. The words "surprisingly" and "incredibly" have been removed and text has been added that explains why these specific results are questionable. This information has also been moved to Box 4-1.

54. Section 5.0 Suggested Technology-Specific Monitoring Tools. Discussions on technology-specific monitoring would be more useful to decision makers if the discussions were framed in terms of the decision-making process. What decisions are supported by collection of the performance assessment data?

Section 1.4 discusses the importance of collecting performance data and the various decisions that can be supported. We refer the reader to that section.

55. Section 5.2 Conventional Source Zone Remedies. These technologies are well known or better described in the published literature. A table would suffice to present relevant information needed for the reader.

We feel that the two pages describing conventional technologies are useful in placing the more innovative techniques into perspective.

56. Section 5.3 Thermally Enhanced Remediation. This section should reference EPA, 2003a.

Section 5.3 has been revised (insert at end of pg 78 as part of last para.) "In addition, EPA (2003a) provides a detailed discussion of thermal remediation methods including the science behind the methods, engineering considerations, and case studies. Treatment of chlorinated solvents, wood treatment chemicals, and PCBs are included in this report."

57. Appendix B: Case Studies. The case studies should clearly distinguish between DNAPL removal from the unsaturated zone and the saturated zone. Appendix B should (also) include a statement indicating that the case studies were provided by the site operators or technology vendors and have not been independently reviewed by third parties.

Information about the DNAPL distribution and zones targeted for removal/treatment is contained in each case study. For the most part, DNAPL existed in the saturated zone. We have added a qualifying statement to Appendix B about the lack of any independent review. A point of contact is identified for those seeking more detailed information.

58. Case Study 2 (Cape Canaveral LC-34). The case study neglects to discuss the mobilization of DNAPL to adjacent remediation cells as a result of the technology demonstrations. It is very difficult to assess the performance without knowing how much DNAPL was mobilized. In fact, the case study is a demonstration of one of he limitations of aggressive DNAPL removal technologies.

Case Study 2 has been modified.

Carmen Lebron - Naval Facilities Engineering Service Center

59. Page 18 bottom: Title "Secondary Water Impact" is split from the paragraph pertaining to it. Perhaps formatting can be altered so that they're both together.

We have fixed the formatting error.

60. Page 22. The reference for the report which is now finalized is: Assessing the Feasibility of DNAPL Source Zone Remediation: Review of Case Studies (NFESC report No. CR-04-002-ENV, dated May, 2004).

We have corrected the citation.

61. Page 22. I would change "from 92 different DNAPL sites" to "118 locations." The reason why I'm suggesting this change is because even though we had 92 sites, there were sites that had multiple locations, so in reality we have sets of data for 118 locations. Since later in the document we refer to 118 locations, it's probably better to be consistent.

We have made the suggested change.

62. Page 23 Table 2-1: You need to close the parenthesis for "Early, 2004." Also, in table footnote no. 2, please change 118 sites to 118 locations.

We have made these changes.

63. Page 25, second paragraph: Replace 9% with 11%. Also, replace "any" in the last sentence (have completed any technology application) with "their" (it'll now read "13 bedrock locations included in this survey have completed their technology application).

Based on other comments, we have deleted all references to fractured rock in this document.

64. Page 32, bottom: There are 2 periods ending the sentence titled "Operating Costs." I don't know if you meant to have it this way for formatting reasons or whether one of the periods should be deleted.

We have fixed this error.

65. Page 37, bottom: There are 2 periods ending the sentence titled "Analysis of variance." I don't know if you meant to have it this way for formatting reasons or whether one of the periods should be deleted.

We have fixed this error.

66. Page 38, top: There are 2 periods ending the sentence titled "Tolerance and prediction of intervals." I don't know if you meant to have it this way for formatting reasons or whether one of the periods should be deleted.

We have fixed this error.

67. Page 38, top: There are 2 periods ending the sentence titled "Control Charts."

We have fixed this error.

68. Page 65, 3rd paragraph: There's a comma separating the first and second sentences. Either place a period or lower case "this" in the second portion of the statement.

We have fixed this error.

69. Page 71, 1st paragraph: Second sentence states "Also, the operation of the extraction wells necessarily alters the plume…" What does "necessarily" mean in this context?

Alteration of the plume is an intended consequence or result of pumping.

70. Page 74, 5th paragraph: In referring to the "Lebron survey" the date should be 2004, not 2003.

We have changed the date to 2004. The contents of Section 4.5 have been incorporated into a new Box 4-1.

71. Page 78, 4th paragraph: There are 2 periods ending the third bullet starting with "As subsurface temperatures rise, the rates of...." I don't know if you meant to have it this way for formatting reasons or whether one of the periods should be deleted.

We have corrected this mistake.

72. Page 83, 3rd paragraph: Seems like there's some text missing after "Box 5-1 shows"

Reference to Box 5-1 has been deleted

73. Page 98, 5th paragraph: "Whether tribal, public or …" seems like is missing a partial thought.

We concur and have revised the sentence.

74. Page 100 last sentence: I suggest combining last 2 sentences into 1 reading "Going beyond the communication requirement of RCRA or CERCLA and offering primers in DNAPL terminology and system descriptions will probably be beneficial."

We concur.

State of Oregon

75. Clearly there was substantial work put into the preparation of the document. The report does a nice job of providing multiple references regarding DNAPLs. It does not give a project manager with any DNAPL experience much new information or actual "how to" guidance. What was good in the report was the reinforcement of the importance of the Conceptual Site Model and planning ahead for performance assessment and exit strategies.

Comment accepted. We agree that CSM development and planning are two cornerstones of a robust performance monitoring program.

76. The report is extremely general in scope, unnecessarily lengthy and repetitive, and does not constructively educate those already generally familiar with DNAPL attributes.

Remedial project managers of all skill levels are faced with DNAPL issues at some point in their careers and will benefit from some repetition of important concepts. We disagree that the document is too general to be useful. We have reduced its length somewhat by removing discussions of material not directly related to performance.

77. The report is not unique in its content or presentation, and only reproduces information compiled from already existing sources; it does pull together the information coupled with available resources regarding monitoring techniques (although one needs to read to 2 sections of material that doesn't directly pertain to monitoring strategies before getting to sections 3 and 4 that are more helpful toward available techniques for monitoring);

Although the document does contain information that is available elsewhere, we disagree with the reviewer's statement that the document is not unique. We are unaware of any other document on this topic that targets the regulatory community.

78. The report does not contain wrong information per se, but it does not provide much new or particularly useful guidance which could be effectively used by DEQ project managers at DNAPL sites.

See response to Comment 77.

79. Even though the existing information is not wrong – where the report provides brief guidance on topics such as preferred drilling methods and sampling methods, it could be misleading because it is not complete. Unless it pertains directly to monitoring strategies, it should not be included but referenced to other guidance documents. An example is a preference for hollow stem auger drilling or use of push probe technology on page 56. Many sites need to use air rotary or other techniques based on the geology.

We do not recommend the introduction of air while sampling for VOCs; therefore, the use of air rotary techniques should be avoided. Because air rotary drilling is most appropriate for drilling in rock, we have removed this reference in Section 4.2.1.

80. The report focuses (at length) upon aggressive DNAPL source reduction technologies (i.e. cosolvent; thermal; chem-ox) that dramatically change and increase the potential for DNAPL mobility.

This emphasis is somewhat skewed and Section 5.2 (DNAPL recovery) needs to be enhanced with descriptions of alternate, yet proven approaches (e.g. hydraulic DNAPL recovery by dual phase pumping or water flooding) for DNAPL source reduction. For example, enhanced bioremediation is one less aggressive technology discussed and it is more oriented toward dissolved plume reduction than DNAPL source depletion;

This document was not intended to exhaustively list and discuss the applicability of all available DNAPL treatment technologies for a site or promote any specific treatment technology. The reader is informed at the beginning to assume that a treatment technology appropriate for the specific site and contaminants in question has already been selected.

81. There is little detail provided in the report that certain technologies and/or performance assessment strategies are unique to specific types of DNAPL (e.g. air sparging for heavy DNAPL PCE does not work for creosote DNAPL);

See response to Comment 80.

82. There is little to no discussion about the range of specific gravity DNAPL and the implication of neutral-density NAPL components. This is an important omission because neutral-density NAPL fractions can vary with temperature (or other influences), and this factor creates remedial design and operational problems; and,

We concur. Text has been added to Section 2.2 to address neutral-density NAPLs.

83. The report includes very abbreviated case studies, but the specific lessons or objectives associated with these individual cases are not clearly conveyed.

We have attempted to provide a broad array of case examples and to present them in a concise manner. The reader is advised to contact the project contact listed for more detailed information.

84. Page iii Second Paragraph: Include Water Flooding as a source reduction technology.

See response to Comment 80.

85. Page 6: To monitor potential impacts beyond the treatment zone: Mention that some source removal actions may increase mobility or produce toxic, mobile by-products.

This issue is addressed in the paragraph already and will not be revised.

86. Section 1.4.2, Page 8. A skill set is mentioned, but no information on what that skill set should be. This is an example of where the report is general such that it is not helpful. Naturally, people with the appropriate skills should be providing the input to make decisions on project. So, one would expect if you are working on a DNAPL remediation, you will have a person with DNAPL expertise, and if you are designing a system, you will have the appropriate type of engineer and hydrogeologist designing the system. Statements like this are not helpful and make the document longer than it needs to be.

We merely wanted to reiterate the importance of having experienced people on board during the planning phases of the performance assessment. We do not agree that this statement is not helpful.

87. Page 8, Key Concepts Relating to DNAPLs: I think this should be a referenced section instead of presenting the properties and distribution of NAPL in the subsurface here. This document should only focus on the monitoring strategies and although this information is important, it is presented more thoroughly in other references.

Section 2.1 has been shortened, however, we contend that a brief discussion of the subsurface behavior of DNAPLs and source zone architecture is critical to developing a conceptual model of the site and planning a performance program.

88. Page 12: Where did the 8% and 22% come from – these numbers need to be referenced. Also the "between 1 and 5 percent" should be referenced.

We have provided a reference to Cohen and Mercer, 1993, and changed the reported ranges of residual saturation.

89. Page 18. Preferential Flow: "use of Mobility control (as practiced by the petroleum industry)" - provide a reference for this. Or describe what mobility control is, so that PMs can implement it at their sites.

See response to Comment 38.

90. Page 21: The information provided on this page is already well understood and does not add to the understanding of monitoring strategies. Much of this type of information could be eliminated from the document so that it focused more directly on monitoring strategies and techniques.

See response to previous comments.

91. Page 26: Short-term goals: I think it is misleading to state that short-tem goals target the "maximum achievable DNAPL mass removal within economic restraints" Many sites are driven by risk and thus, the short-term goal may be to reduce the mobility of the DNAPL which is not the same as maximum removal or even "removal to the extent feasible" as the required removal amount to reduce mobility and eliminate risk may be less than what is feasible to remove.

We agree. "Mass removal to the extent feasible" should be an intermediate goal.

92. Page 32. First bullet. Eliminate the extra period.

All double periods have been eliminated.

93. Page 33. Second bullet. Vertical DNAPL Profiles: The design may not need to be successful at reducing the source at the deepest portions of the source. One needs to understand the Conceptual Site Model and therefore, understand where the pathways exist to receptors. For example, if DNAPL is discharging into a river, it may be the shallow source material that remediation should focus on and DNAPL that has migrated deeper may not have a potential receptor and removal of it may not reduce risk.

This discussion has been moved to Appendix C. Many states require source treatment, or at least a demonstration that it is not feasible, irrespective of risk. Nonetheless, the bullet has been revised to read "...must ensure source recovery at all targeted depths."

94. Page 39: Second Paragraph: Table 3-1 reference should be Table 3-2.

We have moved the statistics section to Appendix D and corrected the table number.

95. Page 47. Section 4.0 Eliminate space before first period.

The space has been eliminated.

96. Page 57: Last Paragraph. Eliminate the word "poorly". If you are planning to measure flux, then placing wells across the flux plane is not poor design.

We have replaced the word "poorly" with "properly."

97. Page 59. (Sale et. al., 2001) is not included in the reference section – add to reference section.

We have added this reference (Sale and McWhorter, 2001).

98. Page 76. Section 5.1 Effectiveness and Efficiency has already been discussed and this section does not even discuss efficiency monitoring – if it is meant to be more specific towards monitoring for effectiveness and efficiency.

We have revised this section to specifically highlight remedial effectiveness monitoring and system efficiency monitoring.

99. Page 76. Conventional Source Zone Remedies. You should already know what remedy you are planning on implementing when you are designing your monitoring strategy - thus this section does not need to go into detail on the remediation technology – but only on the monitoring strategies appropriate for each technology.

We agree that the focus should be on the monitoring strategy, but felt that it would be confusing to introduce such strategies without first giving a short technology description.

100. Page 76. DNAPL Recovery. It is a mistake to suggest to folks that it is ok to just proactively remove DNAPL from individual wells without a recovery plan. This is apt to cut off flow paths of DNAPL and reduce your ability to recover NAPL. With hydraulic recovery, it is very important to enhance the DNAPL flow paths to your well and not just remove the existing NAPL from the well as it returns to the well. Effectiveness may also be measured in reduction in residual NAPL saturations – or mobility – not just the mass of NAPL removed.

We agree that implementation of a DNAPL recovery system, particularly an automated pumping system, is not a simple matter. We have incorporated your comments.

State of Nebraska

101. From an outsider, layman's point of view, the title did not immediately evoke the main ideas and/or provide an encapsulated summary of what this document should be used for. Suggest replacing the word "Monitoring" perhaps with Rating and/or Measuring, add "and Progress" after the word "Performance," and replace "Remedies" with something like Remedial Action Projects. The resulting document title would read something like this: Strategies for Measuring the Performance and Progress on DNAPL Source Zone Remedial Action Projects.

We do not concur. The document title has not been changed.

102. Box 1-1, page 4: The terms listed should be put into some sort of order, either (1) alphabetical or (2) most important/used to least important/used, (3) simple to more complex, or (4) general to specific. Add a note at the top of the box to indicate the ordering so readers can follow the logic and be able to better retain the information and be more organized in the future when referring back to the concepts.

We have placed the terms in alphabetical order. No note is necessary.

103. Introducing/spelling out Acronyms: I believe that acronyms should be introduced (i.e., spelled out) when they first appear in the document text/illustrations. PCE is first used on page 6 but not spelled out/properly introduced until page 9. NAPL is first used on page 8 without spelling out. ROD is used on page 21 and not spelled out or listed in Appendix A. Both ft and bgs are first used in Box 2-4 on page 22 without being properly introduced or spelled out. DOE is first used on page 22 and not spelled out. BTEX is first used and not spelled out on page 24. AFB, RAO, RCRA , and CERCLA are first used on page 25 is not spelled out, perhaps intentionally and while AFB is included in Appendix A, the other three are not. Additionally, RAO is later spelled out on page 29. MCL and ARAR are first used on page 28 without being spelled out and ARAR is not included in Appendix A. RA first used on page 34 without being spelled out and not included in Appendix A. GC/MS is first used on page 43 and not spelled out and while GC is included in Appendix A, MS is not. TOC is first used on page 44 without being spelled out and then later spelled out on page 53. LUST is first used on page 45 and not spelled out or included in Appendix A. MIP is first used on page 55 without being spelled out and it not included in Appendix A. VC is first used in Box 4-1 on page 59 without being spelled out and is not included in Appendix A. ERH is spelled out for the first time on page 79 but used earlier twice (in Box 4-3 on page 64 and also on page 78). ERT is first used with out being spelled out on page 82. ORP and PA are first used on page 90 without being spelled out and are not included in Appendix A. ISCO is introduced/spelled out a second time on page 85 after being first spelled out on page 64. ESTCP is used on page 94 and it's not spelled out nor is it in Appendix A. Other acronyms that are not listed in Appendix A include but are not necessarily limited to CSM, ISB, ORP, PDB, and RPO.

We appreciate the reviewer's suggestions and have incorporated most of them.

104. Sub-section 1.4.2, Scoping a performance assessment program, page 8: This section is likely to attract a lot of interest and needs some clarification. Consider adding some additional information to provide a more detailed account of what "skill set and technical expertise" are needed to design and implement a performance assessment program.

We have decided to limit the discussion in Section 1.4.2 to timing and budgetary considerations.

105. Figure 2-1, page 9: I am unable to differentiate between the two DNAPL zone/areas labeled "Pool" and "Residual" in the figure. If it's possible, please be sure that the labeled areas are not "questionable" areas that may fit both descriptions or if it may fit both, label it "Pool/Residual."

The resolution of the figure is not detailed enough to allow one to distinguish between residual and pooled DNAPL, differences which are observed at the micro-scale level. We trust that the reader is able to interpret the information presented in the figure using the accompanying text and references to the literature which describe DNAPL behavior in detail.

106. Sub-section 2.1.1, first paragraph, second sentence, page 9: The sentence reads "Although DNAPLs are hydrophobic (not very soluble in water), some components are soluble enough to present risks to human health or the environment." (1) Perhaps the sentence should be reworded to say "generally" or "mostly" or "typically" hydrophobic because it becomes evident, as you read on, that they are not totally hydrophobic. (2) Also, perhaps the word "components" should be replaced with "types" or use both terms "components/types". (3) Additionally, the meaning of "components"

should be introduced to the reader here instead of waiting until it's used in sub-section 2.1.2 on the next page, although the amplification on page 10 is not a complete explanation.

We concur and have modified Section 2.1.1.

107. Sub-section 2.1.1, second paragraph, second sentence, page 9: The sentence reads "When released in sufficient quantities to the subsurface soil, DNAPLs will move downward, primarily due to gravity, through the vadose zone and usually into the saturated zone." It's hard to believe that infiltration from precipitation and run-off does not also share the primary role in downward mobility. Consider the following alternative "... move downward, primarily due to gravity and infiltration (where applicable), through the vadose zone and gravity within the saturated zone."

We have included infiltration as another possible cause of downward movement through the vadose zone, but have otherwise left the sentence as is.

108. Sub-section 2.1.3, page 14, second paragraph, second sentence: The sentence reads "As is the case for conventional plume remediation, the volume and extent of the problem must be adequately delineated to provide a sufficient design basis for both the remedy and for the performance assessment program." Consider replacing the term "problem" with "area of contamination" or "impacted area" or some other appropriate terminology.

We concur and have revised the sentence as the reviewer suggests.

109. Hyphenated terms like In-Situ and Soil-Gas: I think it's appropriate to use the hyphenation for both of these terms throughout the document. It's not used at all for "in situ" and soil-gas appears both with and without hyphenation. Regardless of how it's done, the document needs to be checked for consistency. Please check for others, for example three-dimensional needs hyphenation on page 29 and site-specific appears both ways throughout the document.

Thanks for pointing out some inconsistencies. The term "in situ"is now consistently used (without hyphenation or italics). "Soil gas" does not require hyphenation, in our opinion.

110. Section 2.2, sub-section Alteration of subsurface structure, last sentence, page 18: The sentence states "Methods used to achieve subsurface alteration/mixing include multiple injections in the same of different locations, multiple screened intervals ..." I appears that the word "of" should actually be "or." There are other instances of missing words or inappropriate/extra word usage, for example, on page 29 under sub-section 3.2.1, the third sentence of the second paragraph states "A valid and representative program for measuring for RAO achievement ..." -- the second "for" is redundant. Then on page 34, under sub-section 3.3.2, the third sentence of the third paragraph states "... percentage declines in extracted air or groundwater water contaminant concentrations, cumulative DNAPL mass removed, ..." -- there should not be a need to use "groundwater" and "water" together, in the sentence, delete one of the two (whichever is most appropriate). Also, on page 55, under the Purging considerations, the first sentence of text reads "The purpose of purging is to ensure that water samples collected from a monitoring well are representative of in situ groundwater conditions the portion of the aquifer being sampled." -- It appears that a word is missing (perhaps "in" or "for") after the word "conditions."

We have made these changes as suggested.

111. Section 2.2, sub-section Preferential flow, sixth sentence, page 18: The sentence reads "The use of mobility control (as practiced by petroleum industry) mitigates the effect of preferential flow pathways and improves sweep efficiency." Perhaps a little bit more should be said to explain what is meant by the use of mobility controls for those of use who are unfamiliar with those practices.

See response to Comment 38.

112. Box 2-3, page 20: Suggest moving Box 2-3 before the preceding paragraph because (1) both the text and referencing the box will have a better flow and (2) that paragraph of text serves as a good summary to the sub-section and would be more effective if merged with the two brief paragraphs of text following the box.

We concur.

113. Section 2.4, third paragraph, second sentence, page 21: The sentence reads "Many of these barriers have not been adequately addressed by the scientific community and regulatory agencies." Does this have to be said and what's the point of this statement? It may be viewed as a potential "put-down" by some regulators. If you intend to keep this statement, it may be necessary to add text (perhaps a follow-on support sentence or two) to explain what is meant by this sentence.

We have removed the sentence.

114. Section 2.4, fourth paragraph, first sentence, page 21: The sentence reads "Other factors that impact treatment difficulty and cost include depth of contamination and the type of DNAPL present (e.g., chlorinated solvents or wood treatment chemicals)." Within the parentheses, it may be more appropriate to briefly say that the characteristics vary and some DNAPLs are more persistent than others before listing the two examples. In other words, it was not immediately obvious to this reader what the main point was for listing the two examples.

We have clarified the meaning of the sentence.

115. Box 2-4, third sentence of first paragraph and the last sentence of the second paragraph, page 22: These two sentences very long are unclear and may need to be broken down into two sentences each and perhaps made simpler to understand for readers that do not have extensive geology/hydrogeology expertise. For example, terms like "thrust sheet" and "dip" may have to be clarified by adding a brief description in parentheses immediately after each term. Also, why abbreviate only a couple words like "approx." and "deg"? Suggest spelling out those two words, it does not save any space or serve any useful purpose to abbreviate just two words.

Box 2-4, along with other references to fractured bedrock and karst, has been eliminated from the document.

116. Table 2-1, page 23: There are a few minor things needing adjustments: (1) the is a right parenthesis missing after "Early, 2004" in the heading of the third column, (2) consider adding "Maximum" to the bottom entry in the first column so it reads "Maximum Depth of DNAPL Contamination," (3) what does the "N/A" term actually represent (third item listed in fourth column)? -- it may be better to replace it with "Not Reported" or "Not Determined", and (4) the second footnote (i.e., footnote #2) appears to apply to all the sites (i.e., both the DOE and Navy sites) and thus the superscript "2" should be moved from its present location above the 88% in the fourth column, to the a position right after "Maximum Depth of DNAPL Contamination," in the first column.

We have made the changes as suggested.

117. Sub-section 2.4.2, EPA's fractured rock database, page 23: Suggest adding the words "contaminants in" before the word fractured so the sub-title reads "EPA's contaminants in fractured rock database".

We have removed any discussion of fractured bedrock from this document.

118. Sub-section 2.4.2, first sentence of the first paragraph, page 23: The sentence reads "Although DOE's experience with treating DNAPL contamination in bedrock is not extensive, EPA's Technology Innovation Office has developed a database ..." What is the value of having that open statement that "Although DOE's experience with treating DNAPL contamination in bedrock is not extensive"? Suggest deleting that first segment of the sentence.

See response to comment 117.

119. Box 3-1, page 27: The example presented in this box is very general and does not provide much additional information/value beyond the discussion it is intended to support, therefore, consider strengthening the example. Also, move Box 3-1 before the paragraph that currently precedes it because Box 3-1 is referenced in and presents an example related to intermediate performance goals and yet it is presently positioned within/after the discussion on long-term goals.

We have eliminated Box 3-1.

120. Sub-section 3.2.3, second sentence of second bulleted statement following the second paragraph of text, page 30: The sentence reads "The practical pilot test limit is a reduction in the range of 95 - 99%." Should the reader have to except this fact without indicating where it originated? Suggest adding a reference or lead-in statement like: "According to ..., the practical pilot test limit is a reduction ..."

We have removed the statement.

121. Sub-section 3.2.5, first paragraph, first sentence, page 32: The sentence reads "An examination of cost with respect to DNAPL mass removal is of dubious value for comparing the costs of alternate mass removal technologies unless ..." The word "dubious" is of questionable tone and distracting/awkward as used; suggest replacing the word "dubious" with "questionable" or "doubtful" or restructure the sentence.

We have replaced the word "dubious" with "questionable" and moved the discussion of pilot studies to Appendix C.

122. Sub-section 3.2.5, end of the first bulleted statement within the third paragraph, page 32: There are two periods at the end of the sentence. There are a few reoccurrences of double periods elsewhere in the document (often at the end of bulleted statements), as in sub-section 3.4.3 for example; please check for and correct them.

We have corrected this error throughout the document.

123. Box 3-2, page 44: The example on use of the Triad Strategy presented in Box 3-2 starts out great but end up being very anticlimactic in the last sentence which presents one very weak specific benefit. Suggest strengthening this example with more significant benefits if possible.

We concur. The text has been revised.

124. Sub-section 4.2.2, under the Multi-level sampling sub-heading, second paragraph, third sentence, page 55: The sentence lists examples of complex, multilevel systems that may be appropriate for sites with deeper groundwater. What is the value of simply name-dropping these systems? Suggest some brief descriptions of each of these systems be included within the text to aid unfamiliar readers.

We do not concur. The reader is encouraged to visit the referenced internet sites for more detailed information.

125. Sub-section 4.2.2, under the Use of passive diffusion bag (PDB) samplers , second and fourth bulleted statements in the third paragraph, page 58: The first statement indicates "PDB samplers integrate concentrations over time, which may be a limitation if the goal of the sampling event is to collect a representative sample at a point in time and the aquifer is know to show VOC concentrations that change over time. The second statement indicates "Because concentrations of groundwater collected from PDBs represent localized concentrations while traditional techniques represent average concentrations, groundwater collecting from wells located adjacent to DNAPL source zone may provide a bias result due to fluctuation of the groundwater movement. Please consider rewording to make the point being made more clear/direct to the reader.

Comment accepted. We have reworded the bulleted section.

126. Sub-section 4.4.1, page 67: The text under this sub-section is a bit gappy. Suggest moving the third and fourth paragraphs up to join/merge with the second paragraph without changing the text.

We concur. The suggested changes have been made.

127. Figure 4-2, page 69: There are two large arrows with "Contaminant Flux (J,)" -- there are two concerns: (1) it is difficult to determine if the symbol after the letter J is a comma or period or some other extraneous character and (2) the letter/variable "J" should be explained/introduced.

We have improved the readability of the figure and eliminated undefined variables.

128. Figure 4-3, page 71: The following observations/concerns are offered: (1) consider labeling the flow lines, (2) is it likely and/or useful to have so many injection and/or multilevel monitoring wells that are way off of the two ends of the source material, in order words, the drawing seems to illustrate that there are too many wells, and (3) would it be useful to add a footnote that indicates that tracers are used to help determine when the appropriate time would be for collecting samples from the multilevel wells.

We have deleted the figure.

129. Sub-section 5.3.3, first paragraph, third sentence, page 79: The sentence reads "A summary of these two types of ERH can be found in a white paper available on one of the vendor's websites (TRS, 2003)." What is a "white" paper?

A white paper is a term used to describe a short publication and is often used to introduce technology innovations or products.

130. Sub-section 5.3.4, third paragraph, third sentence, page 80: The sentence reads "In addition, thermal conductivity values vary over a very narrow range over a wide range of soil types, leading to a highly predictable rate of heat-front propagation around each heater." This sentence is confusing, please consider rewording.

We concur and have revised the sentence to read "...values do not vary much over a wide range of soil types."

131. Table 5-2, page 84: Please consider adding a column or additional notes elsewhere in the table to present the reasons/purpose for each parameter like was done in Table 5-1.

Comment accepted. The table has been modified as suggested.

132. Table 5-3, page 89: Please consider adding a column or additional notes elsewhere in the table to present the reasons/purpose for each parameter like was done in Table 5-1.

Comment accepted. The table has been modified as suggested.

133. Section 6.1, both sentences of what appears to be the second paragraph, page 92: The sentences of concern read "General warning about technologies associated with PA activities." and "Standard monitoring requirements." These two fragmented phrases are not complete sentences, however, this review realizes that these two entries may simply be place holders/reminders to add text at a later point in time.

The reviewer is correct. The placeholders have been revised.

134. Sub-section 6.1.1, last sentence of text under the Sampling hot groundwater sub-heading, page 92: The text of concern reads "Box 6-2 Appendix C describes procedures used for sampling hot groundwater at a site located at the Charleston Naval Complex where ERH was employed." There is no Box 6-2 in the document and the reviewer was unable to find any of the information, including Appendix C, in the document.

The reference to Box 6-2 and hot sampling procedures has been deleted.

135. Sub-section 6.1.3, the first and fifth bulleted statements, page 93: The first bulleted statement is simply a restatement of the sub-heading and of the discussion presented in the previous sub-section (i.e., 6.1.2 Handling and working near chemical oxidants), yet sub-section 6.1.3 is suppose to present "additional health and safety concerns" beyond those presented in the previous sub-sections. Then the wording of the fifth bulleted statement appears to be incomplete, consider adding terminology to identify whatever it is that is hazardous to get into direct contact with.

We concur. The subsection has been consolidated with the previous subsection.

136. Section 6.3, fourth sub-heading page 97: Consider rewording the sub-heading in italics, it sounds awkward as is: "Concern over potential for mobilization potential off site migration of DNAPLs."

The heading has been reworded.

137. Section 6.4, first paragraph, first two sentences, page 98: The sentences of concern read "In the context of DoD and DOE, the term "community" takes on a different meaning than what most might think. Their use of the term "community" means appointed or elected public officials." These statements are not likely to be totally defensible and may be considered inflammatory or taken as a "pot shot" or otherwise condescending remark designed to insult the intelligence of DoD/DOE environmental and/or administrative personnel. It's very possible that the meaning of the term "community" as presented in these statements may have been "taken out of context." Please consider deleting these two sentences since they do not add any conceptual value to the rest of the section and may undermine the bigger picture and intent of the other material presented in that section.

We concur and have removed these sentences.

138. Section 6.4, pages 98 and 99: This section is gappy and have many short paragraphs that can be merged with success. Please consider merging the first short paragraphs to form one. Next, consider merging the fifth, sixth, and seventh paragraphs. There are others, for example, merging the tenth and eleventh paragraphs would appear to be appropriate. There are also a couple paragraphs who's first sentence begin with the word "And" and that structure can likely be improved and/or that is an indication that the paragraph involved can be merged with the preceding paragraph.

Extensive reworking of Section 6.4 has been completed.

139. Section 6.4, eleventh paragraph, second half of the last sentence, page 99: The portion of the sentence of concern reads "... though time limits on the years this assistance is provided may prove too limited." It is not clear what point is being made here, please clarify.

See response to Comment 138.

140. Somewhere appropriate, perhaps late in Section 5.0 or at the end of Section 6.0: Please consider adding some text and a summary table to introduce the eight case studies presented in Appendix B. The table should identify each study by site name, the major contaminants of concern, what the strengths are or lessons learned are for each study, and any unique or otherwise significant ideas provided by the case study.

We have modified the table of contents and created a more useful Table B-1 as you suggest.

141. Appendix C, missing items/text: They were likely intentionally not provided for this review but it should be noted that the following items were not included: (1) ITRC Fact Sheet, (2) ITRC Product List, and (3) User Survey.

We have added these items to the final version.

Commonwealth of Kentucky

142. My overall assessment is that this is a very well written document. I believe that it will serve as a valuable resource for others like myself that are grappling with the issue of how to best implement and subsequently evaluate the success or failure of DNAPL remediation technologies.

Thank you for the feedback. It is our hope that the document will be useful and serve as a good foundation to help regulators begin to think about many of the important issues in performance assessment.

143. One of my job duties is to oversee groundwater cleanup at the Paducah Gaseous Diffusion Plant located in Paducah, Kentucky – the subject of Case Study #5. The Department of Energy has proposed to install an ERH system that will be designed to remove VOCs (primarily TCE) from the unsaturated, vadose, and saturated zones. I plan to rely upon the information provided in this ITRC document to assist me in my efforts to insure that this project is implemented in the most complete, technically sound, and cost effective manner possible.

Again thank you for the feedback. This is exactly how we hoped that the document could be used. Please let us know more about the Paducah project as it progresses.

144. Section 3.2.4, Page 32, 2nd Paragraph: The text presented in parenthesis in the first sentence should be reworded. The phrase "a

technically supportable asymptote-based goals…" does not make sense.

We agree that this phrase is not as clear as it could be and we will reword this section. We believe that it is an important concept to recognize that contaminant concentrations alone in the subsurface may not necessarily be the only or even the best measure in every situation. Every remediation alternative will eventually reach a point of "diminishing returns" and it is no longer beneficial or cost effective to operate the remediation system. At this point either another remedial option could be employed or it may not be possible or cost effective to remove any further source material. It is important to recognize when a given technology is no longer yielding significant returns, not that this point would necessarily be the acceptable end point for the remediation.

145. Section 3.6.2, Page 46, 3rd Paragraph: The last sentence of this paragraph is somewhat confusing. Why would long-term management requirements be required when there is no unacceptable risk remaining following cleanup? Perhaps some clarification is in order.

Since it is unlikely that all DNAPL can be removed, once the remediation reaches asymptotic levels and assuming that there are no unacceptable exposures then long term management would be necessary to insure that conditions do not change and that risk assumptions remain valid. This sentence will be clarified to indicate that we are referring to instituting long-term management to monitor any residual DNAPL remaining. Obviously if there is still a risk posed by the residual DNAPL, additional measures including possibly institutional controls would be necessary in addition to long-term management.

146. Section 4.2.2, Page 58, 3rd Paragraph, 3rd Bullet: The sentence appears to refer to groundwater flow as being less permeable than an aquifer. This sentence should be reworded.

This is an important limitation of passive diffusion bag (PDB) samplers; it is crucial to ensure that the PDB is not less permeable than the surrounding aquifer materials to obtain representative samples because of the potential for inadequate exchange.

147. Section 4.3.3, Page 64, "Tracer tests": The last sentence states, "PITTs can be used as remediation performance assessment tools to determined system effectiveness…" It appears that the word "determined" should be changed to "determine."

We agree the word should be "determine."

148. Section 5.2.2, Page 77, 1st Paragraph: The second to last sentence should be revised. Perhaps the last portion of the sentence referring to volatilized DNAPL constituents should read, "and are then removed from the subsurface."

We concur.

State of Vermont

149. Page 1, ¶ 1: This states that DNAPLs are organic liquids. While this is generally the case, there are potentially other DNAPLs, ie Mercury. Please consider removing the word "organic"

We concur and have removed the word "organic."

150. Page 11, last sentence of ¶ continued from previous page: Consider changing "World Wide Web" to "internet". I think this term has broader usage the world wide web.

We have made the suggested change.

151. Page 30, 2nd ¶ of 3.3.1: Please consider the following change from one sentence to two sentences: "In this context, the CSM serves as the basis for conducting a risk evaluation where potential human and environmental receptors are identified,. t The potential for complete exposure pathways is determined, exposure point concentrations are estimated, and risk estimates are developed."

We concur and have changed the text.

152. Page 43, Other Programs: The paragraph references "No Further Action" letters. Not all states use this terminology (ie: we in VT don't use this). While this is not really that important as most people reading this know what is intended, it might be a little better to say: "No Further Action (NFA) or equivalent.."

We concur.

153. Page 48, last ¶, first sentence: This uses the term "rather casual". It might be better to remove these words so it reads: "… range from rather casual, qualitative indicators of…"

We have made the suggested revision.

154. Page 50, Measuring soil concentration: Please check you analytical references: Method 8015B measures a small suite of volatile and semi-volatile chemicals . I would prefer to use 8260 for volatiles (as referenced in the paragraph) and Method 8270 for semi-volatiles.

We concur. We have removed references to specific methods.

155. Page 51, last sentence on ¶ that continues from previous page: I think you could remove: "…however some regions/states do not require field preservation using solvents." We are introducing an excellent sampling method and probably do not need discuss whether or not it is required.

We concur. The phrase has been deleted.

156. Page 51, near the end of the first full ¶: I would argue the statement: "For most DNAPL sites in unconsolidated sediments, drilling with a hollow stem auger (HSA) is the preferred method." Direct push is many investigators preferred investigation method in unconsolidated materials where the geology will allow it. This method provides much less disturbed samples for sampling for VOCs.

We concur and have added direct-push technologies to the preferred list.

157. Page 55, 3rd ¶: I suggest making the following change: "Nonetheless, it is may be prudent to have at least …"

We concur.

158. Page 56, Use of passive diffusion bag (PDB) samplers: I think you should add some language to the first paragraph of this section that the suite of chemicals that can be monitored with this technology is limited.

We have made the suggested change.

159. Page 74, last sentence in ¶ continued from the previous page: I would use the term "karst" instead of "karstic". (I have never seen

this term and it isn't in my geologic dictionary. Karst is probably the correct word.)

Comment accepted.

160. Page 86, Table 5.3: The method column is empty for most of the parameters.

We have revised Table 5-3.

161. Page 87, 5.6.2: This section states that ISB is a long term remedial process and that other remedial processes are "typically implemented as a one-time, short-duration remedial action". SVE generally takes quite a while and other technologies such as heating can also take a long time. I would suggest removing or revising this sentence.

We agree that SVE takes longer, but we think the sentence is clear enough as written.

162. Page 90, section 6.1, 2nd ¶: This paragraph appears incomplete. I am assuming you have been waiting for a contributor to supply this information.

Section 6.1 has been completed.

163. Page 92, top of page. The ¶ at the top of the page appears incomplete and does not appear to flow from the previous page.

The paragraph has been rewritten.

164. Page 94, Public concerns over injected remedial fluids: This paragraph uses the term public outrage. I am not sure that outrage is the correct word here. The "outrage perceived" could be clarified.

We concur. Section 6.4 has been reworked.

Scott Huling - EPA Office of Research & Development

165. It is recommended that Section 5.5, In Situ Chemical Oxidation, be revised with more specific information regarding the various oxidants. Currently, the text does not address the significant differences in reactions and in in situ field behavior of the different forms of chemical oxidants (e.g., Fenton's reagent, permanganate, and ozone). These oxidants are similar in some respects but can be quite different in others. For example, in Section 5.5.1, it was stated that the injected oxidants create free radicals, however, permanganate oxidation occurs through nonradical electron transfer. Additionally, the gas phase can be important with Fenton's reagent and with ozone, but not necessarily with permanganate. DNAPL redistribution may occur due to elevated pressure, heat, and steam resulting from inappropriately high concentrations of H_2O_2 with Fenton's reagent. It is recommended that this section be revised to reflect differences between the oxidants and the monitoring requirements.

We have revised Section 5.5 to address differences between oxidants; however, only general differences are presented. The ITRC 2001 Chemical oxidation document is referenced for additional detail.

166. Although a good attempt was made in defining the terms and phrases used in the document, and in consistent usage, there are some inconsistencies and discrepancies in the terms used. These are discussed further in the Specific Comment for Section 5.1. It is recommended that complete consistency be maintained, so as to not confuse the reader with additional jargon.

Revisions to text to address inconsistencies have been made.

167. The comments given here generally relate to technical issues within the document. While the review was being conducted, editorial items were noted, such as incorrect word usage or punctuation. These were marked on a hard copy of the document (available as a pdf file). The locations of these items are indicated on the document by a marked "x" in the right-hand margin or by an explanatory note. Some of these items include improper word selection that could confuse the technical issue at hand, and which might not be caught or noted by other reviewers or editors.

We have made many of these suggested editorial changes.

168. Section 1.2.2 Organization. It is mentioned that the document is divided into eight major sections, yet only seven are listed.

We have made the change.

169. Section 2.1.1 Physical behavior of DNAPLs in the subsurface. Pg. 10, last paragraph - Two references are cited (Hunt, Sitar and Udell, 1989; and McWhorter and Kueper, 1996) that are not listed in Section 7, References.

We have added these references to Section 7.

170. Section 2.1.3 Source zone delineation. Pg. 15, first text paragraph - It is recommended that the phrase "hard rock terrains" be replaced by "igneous and metamorphic rock terrains". "Hard rock" is a colloquial term that might be misunderstood by some nongeologist readers who might interpret "hard rock" as rock that is hard (e.g., unweathered rock) as opposed to soft (e.g., weathered rock), rather than differentiating igneous and metamorphic rock from sedimentary rock.

Based on other comments, we have deleted all discussions pertaining to contamination in bedrock.

171. Section 2.1.3 Source zone delineation. Pg. 14, 1st full paragraph - The citation "(EPA, 1992)" is given. There are two 1992 EPA citations in the Reference section. The citation here should be "1992a".

We have made the change.

172. Section 2.3 Addressing Rebound. The definition of rebound, as given below from the document, indicates that rebound implies that concentrations will be higher after treatment than before treatment. "Rebound is a term applied to observed increases in contaminant concentrations as compared to preremediation levels following cessation of active remediation." A common usage of "rebound" is to indicate the increase in concentrations after they have been lowered during the active phase of treatment. Rebounding concentrations may be higher than pretreatment concentrations, but "rebound" can also apply to concentrations at or below the pretreatment concentrations. This latter, common, usage of "rebound" is used later in the document, on page 59: "Contaminant concentrations observed in monitoring wells near the source may decrease immediately following treatment, as desired, but may rebound to pretreatment levels after some period of equilibration."

We have revised the definition of rebound in the first instance under Section 2.3.

173. Section 3.1.3 Performance criteria and metrics. Last paragraph - The phrase "groundwater plume anatomy" is somewhat

uncommon. Perhaps it could be changed to "groundwater plume dimensions" or "groundwater plume architecture."

We have incorporated the suggested revision into Section 3.1.3.

174. Section 3.2.3 Selecting the pilot study location. 2nd bullet - It is mentioned that the practical pilot test limit is a reduction in the range of 95-99%. The discussions in the document to this point have been much more general, and emphasize uncertainties, so it appears a little abrupt and inconsistent to include an actual quantification at this point. It might also raise questions for the reader as to whether their pilot studies need to achieve a 95-99% reduction to be judged successful (Case Study 2 specified a goal of at least 90%). This sentence could be deleted.

We have deleted the sentence.

175. Section 3.4.2 Sampling Design. Results using the equation given in this section do not appear to match the results given in Table 3-1. For example, using $P_D = 1 - (1-A_T/A_S)^N$ with $A_T = 1$, $A_S = 10$, (i.e., $A_S/A_T = 10$), $N = 16$ gives $P_D = 1 - (1-1/10)^{16}$ or $P_D = 0.82$ (or 82%, not the 98% as listed in Table 3-1). It is recommended that the equation and the results in Table 3-1 be verified, to ensure that they are consistent.

The equation gives the probability of using N-borings randomly located to find the target A_T within a site A_S. The original table gives the probability for uniformly located borings. These values are lower, as the reviewer suggested. They were calculated by the referenced author using a Monte-Carlo simulation (not an equation). A revised set of values has been generated and the table has been revised. We have moved the content of Section 3.4 to Appendix D.

176. Section 3.4.6 Integrated physical-geostatistical methods. The last paragraph refers to Table 3-1, but should refer to Table 3-2.

We have made the change. The statistics section has been moved to Appendix D.

177. Section 4.2.2 Decrease in dissolved concentration. Pg. 57, last paragraph - It is not clear why the word "poorly" appears in the following sentence: "Multi-level sampling itself is not the same as flux measurement per se (described in section 4.3.3); however, if the monitoring wells are poorly distributed cross-gradient along the control plane (lateral extent), then data generated by a network of multilevel samplers can be used to estimate contaminant flux for different depths along the control plane." It may require additional explanation to indicate why a poor distribution of wells would allow a contaminant flux estimate to be made. Use of the word "properly" would appear more appropriate in this sentence.

We concur and have made the correction to the typographical error.

178. Section 4.2.2 Decrease in dissolved concentration. Pg. 58, last paragraph - The word "levels" in the following sentence is ambiguous: "Potential problems and challenges with this type of goal and verification approach include:1) the high variability, both temporally and spatially, in groundwater levels,..." The word "levels" could refer to ground-water elevations as wells as to concentrations. It is recommended that "concentrations" be used, if that is what is meant.

We have substituted the word "concentration" for "levels."

179. Section 4.2.2 Decrease in dissolved concentration. Pg. 59, 2nd to last and last paragraph - There is mention of the fact that ground water taken from monitoring wells may contain water injected as part of the treatment process, and this may lower contaminant concentrations. This is a good point, and perhaps could be strengthened by an additional sentence explicitly mentioning that "dilution" can impact the ground-water concentrations and that the number or fraction of pore volumes of water added should be taken into account when examining these ground-water concentrations.

We concur and have added a sentence suggesting that dilution can impact the assessment of dissolved concentration data.

180. Section 5.1 Remedial Effectiveness vs. System Efficiency. The terms and discussion in this section appear somewhat contradictory to the terms and discussion in sections 1.3.1 and 1.3.2. Most significantly, the heading "Effectiveness monitoring" is apparently used for two paragraphs of what sounds like it should be referring to efficiency monitoring, not effectiveness monitoring (as described in sections 1.3.1 and 1.3.2). It might even be that the words "Effectiveness monitoring" were meant to start off a paragraph or two that were somehow omitted, rather than to be used as a heading. Also, these paragraphs use the phrase "system process monitoring," whereas, sections 1.3.1 and 1.3.2 use "system efficiency." The phrase "process monitoring" is used in a few other places in the document (primarily in section 5.5.2). This phrase appears to be equivalent to the phrase "efficiency monitoring". As stated in the beginning of the document, "performance monitoring" encompasses both "effectiveness" monitoring and "efficiency" monitoring. It is recommended that the entire document be consistent in what terms are used, and their definitions, e.g., efficiency monitoring, performance monitoring, effectiveness monitoring, and process monitoring. The addition of a definition of "process monitoring" to Box 1-1 might help lessen these discrepancies. The term "progress monitoring" is used in section 4.2, first paragraph, and in section 6.1.1, first paragraph. This is an example of the use of yet another phrase.

We have attempted to rectify all of these inconsistencies throughout the document by using the terms "effectiveness" and "efficiency" monitoring where appropriate.

181. Section 5.3.6 Key monitoring parameters. Pg. 83, Dissolved concentrations - At the end of the first paragraph, the words "Box 5-1" are given. This is incomplete and there is no Box 5-1.

We have deleted that reference.

182. Section 5.5.1 Technology Description. Pg. 86 paragraph 1 - It was reported that the oxidant creates free radicals that react with the contaminants. However, the oxidants can react with some contaminants directly. Additionally, the permanganate ion (MnO_4^-) reacts through electron transfer without the formation of free radicals. It is recommended that the wording in this section be revised to reflect these observations.

We have revised the text accordingly.

183. Section 5.5.1 Technology Description Pg. 86 paragraph 1, last sentence - It is recommended that the last sentence of the paragraph be replaced with the following sentences. "Each oxidant has different chemical and physical characteristics and therefore behaves differently in the subsurface. The rate of reaction between the oxidant and aquifer material varies which effects the transport and distribution of the oxidant in the subsurface. For example, H_2O_2 reacts more rapidly than MnO_4^- and therefore presents greater challenges for oxidant distribution."

We concur and have made the suggested change.

184. Section 5.5.1 Technology Description. Pg. 86 paragraph 2, 1st sentence - It is recommended to change "are necessary" to "may be useful".

We concur.

185. Section 5.5.1 Technology Description. Pg. 86 paragraph 2, 2nd - 4th sentences - It is recommended to replace the 2nd - 4th sentences with the following. "There are different objectives of the bench-scale treatability study. One objective is to determine the soil oxidant demand which can be used to conduct a preliminary feasibility study, and to estimate/design the oxidant concentration and loading. Oxidant injection rates are functionally dependent on subsurface conditions, such as hydraulic conductivity. High hydraulic conductivity is desirable for oxidant distribution, and therefore, to the success of delivering the oxidants to the targeted DNAPL zones. Adequate oxidant distribution can also be accomplished in subsurface systems with low hydraulic conductivity using close injection well spacing."

We have made the suggested revisions.

186. Section 5.5.2 Key Monitoring Parameters. Pg. 86, last paragraph, 4th bullet - While many of the reactions and geochemical changes in ISCO are rapid or transient, there are some exceptions. Permanganate can persist for months in some cases, and the geochemical change of MnO_2 formation may be long-lived.

We concur and have changed the text.

187. Section 5.5.2 Groundwater Quality. Pg. 87, 1st paragraph - The statement that "Since ISCO is a mass destruction technology, no mass removal is involved." is incorrect. Unintentional contaminant mass removal and/or transport can occur with improper application of Fenton's reagent. Under this condition, significant heat and $O_2(g)$ can be generated that may volatilize and strip contaminants into the vapor phase where they can be lost to the unsaturated zone and atmosphere. Transfer of contaminants can also occur in the gas phase with ozone. It is recommended that this section be revised to reflect these observations, especially, as significant monitoring may be required to ensure that these adverse effects do not occur. With the application of Fenton's reagent (especially at higher H_2O_2 concentrations), adequate performance monitoring must be done to ensure that contaminants are destroyed rather than transferred to the atmosphere.

We concur and have changed the text.

188. Section 5.5.2 Groundwater Quality. Pg. 87, 3rd paragraph - It was reported that the reaction kinetics with TOC are generally faster than with the contaminants, and contaminants can be released from the soils. This observation is not necessarily true. Oxidant reaction kinetics with some contaminants can be very rapid. In general, the TOC (organic matter) oxidation and contaminant release concept is currently a hypothesis and it is unclear whether it has been proven. It is recommended that a reference be provided to support this observation or that it be deleted from the text of the report. There are many chemical and physical processes occurring during and/or shortly after oxidant injection which would effect the fate and transport of contaminants in ground water. It is difficult to differentiate between these various fate and transport mechanisms, including desorption due to TOC oxidation.

We have provided a reference.

189. Section 5.5.2 Groundwater Quality. Pg. 87, 4th paragraph - It is agreed that real-time ground water quality monitoring has value, but it is important to note which parameters and for what reason. For example, real time ground water concentrations of the oxidant can be used to determine the radial influence of the oxidant injection. Or, ground water concentrations of VOCs in nearby sentry wells can be used to assess whether the plume is expanding via displacement of contaminated ground water. However, monitoring VOC's during oxidation or shortly thereafter can be confounding due to nonequilibrium, as reported.

190. It was reported that post-oxidation final performance should be determined after all oxidant reactions are complete and site conditions have returned to equilibrium. It was also reported that this could take 1 week to several months. The time frame to reestablish equilibrium conditions is relatively uncertain. There does not appear to be a well established guideline regarding when to analyze for contaminants and how much time it takes for equilibrium to be established. There are various parameters that could be monitored to make this determination, but these will vary from site to site and will depend on each oxidant. Non-equilibrium (eg., rebound, oxidant persistence, ORP) can take well over 1 year. Non-equilibrium conditions are likely to be much more significant with Fenton systems than with other oxidant forms simply due to the extreme conditions associated with the heat and $O_2(g)$ released. Some Fenton vendors will monitor for VOCs soon after oxidant injection (7 days) so a determination can be made whether additional applications of the oxidant are needed. In this case, it is assumed that if contaminants exist, then additional oxidation is needed immediately. However, for long term performance evaluation, this is not acceptable. Sometimes, post-oxidation ground water monitoring will occur at specific, arbitrary intervals. However, there are contingencies involving the detection of contaminants and obligatory ground water quality monitoring.

In most cases, multiple applications of the oxidant will be needed. The post-oxidation performance evaluation monitoring program should be developed to accommodate multiple applications of the oxidant.

We agree with your statements and have modified the paragraph accordingly.

191. Section 5.5.2 Groundwater Quality. Pg. 87, last paragraph - pH and redox sensitive metals can be mobilized under Fenton conditions. There is a wide range of metals that can be mobilized under acidic conditions. It is recommended that this issue be discussed.

We have modified the text to include mobilization of pH-sensitive metals.

192. Section 5.5.2 Groundwater Quality. Pg. 87, last sentence - It is recommended that the last sentence be replaced with the following. "Sites where this can be a potential problem can include sites where either, (1) naturally occurring metals concentrations in soils are elevated, (2) historical metals contamination was attenuated by naturally occurring chemical reductions processes, or (3) sites where metals were co-disposed with organic contaminants."

We have replaced the referenced sentence.

193. Section 5.5.2. Table 5-3. This table for performance monitoring of ISCO has ground water as the only media to be monitored. However, soil samples can also be useful to assess treatment performance of ISCO. In fact, the document recognized the limitation of relying solely on ground-water samples for performance assessment in section 4.2.2 ("Although it is important to monitor groundwater quality inside and outside the source area during enhanced recovery or treatment operations, it is not recommended that groundwater concentration data alone be used to assess performance because of the uncertainties").

We have modified Table 5-3 to include soil sampling.

194. Section 6.1 Health and Safety. Pg. 92, 2nd paragraph - This paragraph is incomplete.

We have completed the paragraph.

195. Section 6.1.1 Sampling hot media, sampling hot groundwater. The document mentions "Box 6-2 Appendix C". There does not appear to be a Box 6-2 in the document.

We have deleted reference to Box 6-2 in Appendix C.

196. Section 6.4 Stakeholder/Public Involvement. Pg. 100, 2nd to last paragraph - This paragraph includes the sentence: "Fully explaining how both remediation monitoring and performance monitoring get the community to the goals for the site,..." The difference between "remediation monitoring" and "performance monitoring" is unclear (See the Specific Comment for section 5.1).

We have clarified the meaning of the sentence.

197. Section 7.0 References. It is recommended that the format of the citations be standardized. Currently some citations have the authors' initials before their last names, and other citations have the initials after the last name. In at least one case, the entire first name is given. Other aspects, such as punctuation, should also be standardized.

We have gone through the references to ensure consistency.

198. Section 7.0 References. The references in this section were not reviewed for correctness, to verify that all references cited in the text were included, or to determine if any references were included that were not cited in the text. It is recommended that an editor conduct this review.

We have gone through the document to check the accuracy of all references and citations.

199. Appendix A. List of Acronyms. The correct name for ASTM is "American Society for Testing and Materials" (with the "and"), although the official name is now simply "ASTM International". Also, the first occurrence of "VOA" should be "VOC" (and put in correct alphabetical order).

We have made the changes.

200. Appendix B. Case Studies, p. B-1. Table B-1, cited on this page, was not found in the document. It is recommended that the remedial technology be listed on page B-1 in the Table of Contents, along with the name of the site. Perhaps the table of contents could be made into a table that includes this information, and maybe the additional information found in the box at the beginning of each case study (this would help the reader who is interested in a particular technology to quickly find a relevant case study).

We have modified the table of contents and created a more useful Table B-1 as you suggest.

201. Case Study 1. Pg. B-5, first full paragraph - A "Figure 1" is mentioned; however, there is no figure. Pg. B-5, third paragraph - "Figures 2-5" are mentioned; however, there are no figures.

We have deleted references to figures in Case Study 1.

202. Case Study 2. Pg. B-12, Figure 3 - It is difficult to read the details of this figure, as the font is very small. It is an interesting and useful figure, and increasing the readability is recommended. It would also be very useful if the lithologic units could be marked in the figure. Also, the case study uses "Steam" and "SEE" interchangeably, and "ERH" and "SPH" interchangeably. Although these terms and abbreviations are explained elsewhere in the document, for even greater clarity, it is recommended that just one term be used consistently for each remedial technology.

We have enlarged the figure to make the text legible and have made consistent use of the terms SEE and ERH in the case study and throughout the document.

203. Case Study 6. This case study does not include any information about monitoring for temperature increases due to the high H_2O_2 concentrations used, nor about the vapor monitoring results. Pg. B-34, 3rd paragraph - The PCE concentration is given as 9,000 "Fg/l". The units need to be corrected. Figure 1 - This figure only provides concentration data to August 1999; however, additional site characterization, oxidant injection, and/or monitoring occurred through 2002. It is recommended that the figure be replaced by one that provides the complete history of the concentrations at the site.

Discussion of temperature increases and vapor monitoring is not critical to the case study. The units have been corrected to read "µg/L." The information in the figure has not been updated, however.

204. Case Study 7. Pg. B-40, last paragraph - The text says to "Refer to Figure 1" for the cross-section location. This apparently should be "Refer to Figure 2".

We have made the change.

Eva Davis - EPA Office of Research & Development

205. In general, I find that the document is well-written, however, I feel that the document spends too many pages on ancillary information, and lacks detailed information on performance assessment itself, at least for thermal remediation technologies. I note that the core of the document in approximately 100 pages long, while only about 13 pages are contained in Chapter 5, which is on Suggested Technology-Specific Monitoring Tools. Only about two pages of this chapter are devoted to assessing the performance of thermal remediation technologies. I believe the document could be made more useful by reducing its overall length, while increasing the information contained on performance assessment itself. My detailed comments, including some suggestions on where cuts could be made and suggestions on performance assessment for thermal remediation to be included, are below.

We have tried to reduce the overall length of the document where applicable. Your suggestions on deleting or reducing some text have been applied throughout the document. See responses below in detail.

206. On page 7, it states that performance based contracts reduce the financial risk of source zone treatment by making the vendor responsible for meeting performance objectives. Actually, what happens is that the financial risk is transferred to the vendor, which has the effect of driving up the overall costs of a fixed price contract. The degree to which costs will increase will depend on the complexity of the site, how well the site has been characterized, and how stringent the performance standards are. The vendor has to include contingency funds to cover the unknowns that are always going to be a part of these types of projects. If the remediation turns out to be relatively straightforward, the vendor makes a handsome profit, but whoever paid the bill has paid more than they perhaps would have with a contract that shares the risks of the unknowns in the subsurface. As an example, consider the fact that it cannot be determined accurately with the amount of characterization that is done at most sites how much of the contaminant is in the treatment area. However, the amount of contaminants brought to the ground during the remediation will significantly affect the costs of the vendor to treat the contaminants.

We concur and have revised the text and added the following sentence: "The contracted vendor will likely increase the price as appropriate for the level of risk that is being assumed."

207. On page 7, what is meant by demonstrating "whether feasibility is obtainable"?

The paragraph has been revised to clarify its meaning. It has been moved to Appendix C.

208. On page 9 it states that in the saturated zone water is generally the wetting phase. Although this may generally be true for chlorinated solvents, recent research has shown that many creosotes are actually the wetting phase with respect to water. I found creosote to be the wetting phase when I have observed it in the field and in my laboratory. This observation was also made by Powers et al. (Powers, S. E., W. H. Anckner, and T. F. Seacord, Wettability of NAPL-contaminated sands, Journal of Environmental Engineering, 122(10):889-896, 1996.) This has important implications in terms of their movement in the subsurface.

We have revised the text to clarify the difference in wetting behavior.

209. A reference or references should be provided on page 11 for calculating partitioning of a chemical between phases in the subsurface.

We have added a reference to the 1991 article by Feenstra, et al. describing a method for calculating partitioning between phases.

210. Page 1 states that the focus of this document is on unconsolidated sediments, however, pages 12 and 13 contain a full page of discussion on matrix diffusion, a phenomenon that occurs in fractured rock. I would suggest that, in order to shorten the length of the overall document and maintain its focus, that this section be deleted.

We concur. As stated in Response 2, discussions of fractured rock and matrix diffusion have been eliminated from the document.

211. Page 1 states that this document is intended for readers who are familiar with the term DNAPL and its physical characteristics, however, section 2.0 contains almost 10 pages on DNAPL flow in the subsurface. Perhaps in the interest of focusing the document on performance assessment, readers that are not familiar with the flow of DNAPL in the subsurface should be referred to an appropriate document and this section could be deleted.

Comment understood; however, we are going to keep the background discussion intact so readers understand the complex parameters that change as a result of treatment and that could be monitored.

212. On page 16, it states that thermal technologies affect a DNAPL's bioavailability. I would disagree that this is an important effect of thermal technologies on DNAPLs in the subsurface, or even that it has been proven that thermal remediation has this effect. For VOC and SVOC DNAPLs, vaporization is the most important effect that the commonly used thermal remediation technologies have on DNAPLs.

We concur and have removed the reference to bioavailability.

213. Page 17 discusses steam stripping. My experience has been that many people in the remediation area are not aware of this physical phenomenon which occurs when two immiscible liquids are present. I would recommend that the co-boiling point of several common DNAPL contaminants be included in this section as an example. For instance, the boiling points of TCE, PCE, and chlorobenzene are 87°C, 121°C, and 132°C, respectively, and the co-boiling point of TCE DNAPL in the presence of water is 74°C, PCE is 88°C, and chlorobenzene is 92°C.

Comment accepted. This level of detail is not appropriate for this section. We have expanded on this topic in Section 5.3 and added a table of co-boiling points with a reference to personal communication with Eva Davis, 2004.

214. Page 1 states that the focus of this document is on unconsolidated sediments, however, page 23 and 24 discusses EPA's fractured rock database. In order to keep the document more focused, I suggest that this section be deleted.

We concur. As stated in Response 2, discussions of fractured rock and matrix diffusion have been eliminated from the document.

215. Page 34 states that monitoring needs decline as the remediation continues. However, in terms of determining when to end active treatment, the monitoring needs may significantly increase as the remediation approaches the end point, in order to confirm that continuing the remediation would have diminishing returns.

We concur and have provide some examples of when monitoring needs may increase over time. This issue is also addressed in our response to Comment 224.

216. Page 35 states that data from remediation sites is sometimes too complex to easily see trends and may require sophisticated statistical and data modeling to evaluate. I am concerned that most environmental data is not suitable for statistical evaluation, and statistical assessments may actually misrepresent the data because in fact the data does not fit any statistical model. I suggest deleting (or at least reducing) the discussion of statistics, and just referencing other appropriate sources of information. A little information without providing enough information for a full understanding may be dangerous and lead to attempts to apply statistics incorrectly and the derivation of erroneous results. Deletion or reduction of this section will also help to focus the document on the topic of performance assessment. Also, my experience with well designed and operated thermal remediations is that the reductions in concentrations are obvious.

As written, the document does not advocate any particular statistical approach and primarily suggests topics for "further reading" as the reviewer recommends. However, to focus the document we have moved the entire statistics section to Appendix D.

217. Section 3.5.2: This section discusses the Triad approach, and I am currently on the team for the Ft. Lewis site where the Triad approach is being used during a remediation. However, I had trouble following how this section is applicable to remedial projects (versus site characterization processes). To make this information more useful, I would recommend focusing it more on how it is used to aid in performance monitoring.

Comment accepted. Section 3.5 (Data Quality Considerations) has been revised.

218. Table 4-1(page 48) states that the relative accuracy of source mass extracted is low. I believe this statement is only true for percent of source mass extracted. In general terms, measuring the amount of contaminant extracted is likely to be significantly more accurate than estimates of mass in place before or after remediation.

Comment accepted. We have revised Table 4-1 to state that the relative accuracy of source mass extracted is intermediate to high.

219. Page 51 states that three factors are necessary to guide the development of a performance assessment plan. I think the choice of technology for the remediation is an equally important factor in development of the performance assessment plan, and this should be added to the list.

The last paragraph of Section 4.1 has been revised to add a fourth factor.

220. Page 52 discusses problems with VOC losses during soil sampling. It should be pointed out that this applies to chlorinated solvent VOCs, but not to the semi-volatile creosote and coal tar DNAPLs. The sampling technique discussed is not appropriate for SVOCs.

The sentence has been revised to clarify the issue regarding loss of VOCs and SVOCs.

221. Why would "poorly" distributed cross-gradient monitoring wells allow estimates of contaminant flux along the control plane (see the last sentence on page 57)?

The text now reads "properly distributed."

222. Section 4.4.2: Although I agree that it would be great to know NAPL saturation in the subsurface to have an indication whether the NAPL is mobile or not, it should be pointed out that when mobile NAPL is present in the subsurface, it may drain from the sampler as the core is brought to the surface, yielding low (perhaps significantly low) estimates of NAPL saturation and mobility.

We concur. Text has been added to Section 4.4.2.

223. Section 4.4.3 describes several pumping techniques for estimating mass flux. All of these techniques that involve pumping will have the same limitations that are caused by the pumping, which include difficulties with extrapolating the results to unstressed source zones, and alteration of the plume. It should be made clear that these limitations apply to not just one method but to all the pumping methods.

Two of the four techniques involve pumping. We have made sure that both techniques are included when describing this limitation.

224. Page 76 states that more frequent monitoring is required earlier in the process, while less monitoring is required when the system stabilizes. It should also be pointed out that more frequent monitoring may be needed as you approach the end of the remediation and are looking for diminishing returns to determine when to turn the system off.

We addressed this issue in our response to Comment 215. Additional text has been added to Section 5.1 to clarify.

225. Section 5.3: Mechanisms that are important in thermal remediation are: 1) vaporization; 2) viscosity reduction; 3) solubilization, and in the case of steam injection, 4) displacement. I suggest the EPA Issue Paper "How Heat Can Enhance Thermal Remediation" for more information on these mechanisms (Davis, E. L., How heat can enhance in-situ soil and aquifer remediation: Important chemical properties and guidance on choosing the appropriate technique, Ground Water Issue Paper, US Environmental Protection Agency, EPA/540/S-97/502, April 1997). Steam generated in situ by ERH or conductive heating does not "sweep DNAPLs out of low-permeability soil lenses" but vaporizes compounds which have sufficiently high vapor pressures. Biological activity or chemical reactions depend on many factors; these are secondary factors at best and not primary means of treating DNAPLs via thermal remediation. More information on chemical processes during thermal remediation is given in comment #232. It should be pointed out that the USACE thermal remediation manual is not meant to be guidance for designing thermal remediation systems, but only provides information for those doing oversight.

Based on this and other comments about maintaining a consistent level of detail when describing the technologies, we have deleted the bulleted list. The reader is referred to the USACE guidance and the Davis paper (1997) for detailed discussion of mechanisms.

226. Section 5.3.3: Collecting vapors only in the vadose zone is not a good design for ERH systems unless only the vadose zone is to be treated. In ERH systems being designed today, vapors are collected over the depth of the zone being treated. In many of these systems, particularly where groundwater flow rates are high, groundwater extraction is also employed.

We agree that vapor extraction wells are installed over the entire treatment depth, but in practice, most vapor recovery occurs in the vadose zone. The text has been revised to clarify.

227. Section 5.3.3: It should be made clear that steam distillation and steam stripping, which are described in the third paragraph of this section, are not particular to ERH systems but occur regardless of how the heat is applied to the subsurface.

We have moved the paragraph to Section 5.3 so that it applies more generally to all thermally enhanced technologies.

228. Section 5.3.4: Thermal conduction heating is known commercially as in situ thermal desorption, not destruction.

We have made the change.

229. Section 5.3.4: Heating is not necessarily uniform or "inevitable" using thermal conductive heating. Heating near the soil surface has been found to be particularly difficult for this process. Also, temperatures will not go above 100°C when water is present (all of the energy will go to vaporize the water).

We concur. The subsection has been revised to reflect your concerns.

230. Section 5.3.4: It should be pointed out that temperatures above 100°C can only be achieved in the vadose zone or where groundwater influx is controlled by pumping. The temperature will not go above 100°C while there is water present.

We have addressed this concern in response to Comment 229.

231. Section 5.3.4: The last paragraph of this section appears to be out of place as design parameters and well spacing is not discussed for any of the other thermal technologies.

The last paragraph in section 5.3.4 has been deleted.

232. Section 5.3.5: Additional information is now becoming available from research funded by EPA under a cooperative agreement with Georgia Tech University. These carefully designed and controlled experiments show much less transformation of TCE than was found in the work done by Lawrence Livermore National Labs. A presentation on this research was made at the Battelle-Monterey conference in May 2004, and the draft report will be going out for peer review soon. In fact, a review of the literature on TCE hydrolysis or oxidation shows considerable variation in the reported

transformation rates. The conclusion I have at this point is that transformations in the subsurface under the conditions of thermal remediation have not been fully documented. I recommend that this section be deleted. Thermal remediation methods are excellent for extracting VOCs and SVOCs from the subsurface, but it is not clear how important transformation processes are under the conditions of typical thermal remediations.

We concur. The subsection has been deleted.

233. Table 5-1: For a regulatory person or site owner overseeing the remediation of a site using thermal remediation, the most important performance measures are temperature in the subsurface, water levels and vapor pressures in the subsurface to ensure hydraulic and pneumatic control, and the extraction rate of contaminants to allow calculation of mass removed. Also, for compliance purposes, vapor and water discharges from the treatment systems should be monitored. The other things listed in the table, such as injection rates or power and current draw, I consider things that the thermal technology vendor should be monitoring for their operation of the system, but not data that is used for performance assessment by regulators or others providing oversight. I'm used to having this data shared to some degree with those overseeing the process, but I question whether it should be included in this table. I see it as being outside of the purpose of this document. I would like to see the document provide more discussion on frequency of monitoring and where the subsurface monitoring should be done.

We disagree. Power density is considered by practitioners of ERH and ISTD to be one of the most important parameters for evaluating the efficiency and effectiveness of thermal treatment.

234. Subsurface temperature monitoring is part of the system built and operated by the thermal remediation vendor, but the contract should stipulate that the data is shared with those doing the oversight at an agreed on frequency. In discussions with the technology vendor, the number of thermocouples to be used and the frequency of temperature measurement should also be agreed on. The vendor will likely have a minimum monitoring that they need for operation of the system, but those overseeing the remediation may desire to have a greater degree of monitoring built into the system. Commonly, thermocouple strings are placed in between injection and extraction wells and at extraction wells in steam injection systems, or at various locations between electrodes or heating elements in ERH and conductive heating systems, respectively. Thermocouple strings are also generally co-located with monitoring wells, both inside and outside of the treatment area. Generally a 5 to 10 foot vertical spacing of thermocouples is used on thermocouple strings. If a hot floor is desired, thermocouples should be installed below the treatment area also to ensure that the hot floor is established. The more heterogeneous the subsurface system is, the more thermocouple strings should be employed. Also, it is likely that more thermocouple strings will be required in a steam injection system than in a ERH or conductive heating system. When ERT is used to monitor steam movement in a steam injection system, thermocouples should also be installed. The use of ERT does not substitute for thermocouples. The target temperature will be dependent on the contaminants to be treated and the technology used. For VOCs, the target temperature is generally 100°C, or the co-boiling temperature of contaminant to be recovered. The objective should be to heat the entire target area to this temperature, not to achieve this temperature on average in the treatment area. If cold spots remain, contaminant vapors may be transported to the cold area and condense, particularly if the vacuum extraction system is not strong enough.

We concur and have added text describing the placement of thermocouples and achieving a "hot floor." We have also provided a new table that lists co-boiling points of common solvents, as suggested in Comment 213.

235. Under "General" in Table 5-1, vacuum pressure in the subsurface is another parameter that should be measured during thermal remediation to ensure control of the vapors that are generated. Vapor measuring points should be included within and around the perimeter of the treatment area. They can be co-located with monitoring wells. The exterior monitoring points must be close enough to the treatment area so that vacuum can be expected at that monitoring point. I like to see vacuum measurements made once a week during a remediation.

We concur and have added a new subsection entitled "Subsurface pressure."

236. Under "General", soil sampling should be included. Normally, soil samples are obtained during installation of the remediation system, and then confirmation samples are obtained after the remediation has been completed. The benefits of soil sampling during system installation is that it can provide additional characterization information on the extent of contamination, as well as providing baseline soil concentrations. In most cases, the soil sampling done for characterization purposes was not at the same frequency that drilling will be done to install the system, so considerable additional information can be obtained. After completion of the remediation, the frequency of soil sampling may not need to be a great as before the remediation, but some paired soil cores should be obtained, and sampling should be done at locations where there is some question as to the effectiveness of treatment, ie, those areas that were difficult to heat completely. Interim soil sampling has also sometimes been used to help judge the progress of the remediation.

We have revised Table 5-2 to reflect the reviewer's suggestions and also added a new subsection on soil and groundwater sampling.

237. Under thermal conduction heating in Table 5-1, the line for "Thermocouples" can be deleted as subsurface temperatures are covered under the "General" heading.

We concur. The line has been deleted from the table.

238. If the treatment area extends below the water table, monitoring wells should be both within and outside of the treatment area. Baseline groundwater samples should be obtained before the remediation begins. If desired, some samples may be obtained during the remediation to gauge the progress of the remediation. Monitoring wells should also be used for water level measurements, especially for ERH and conductive heating projects at sites with high permeability. Manual measurements of water level can be very difficult when the temperatures approach boiling. Thus, the use of pressure transducers that are installed in the wells permanently and read automatically should be evaluated. It has been found at the Ft Lewis ERH site that temperature is the better indicator of loss of hydraulic control. Exterior monitoring wells also have thermocouple strings, and temperature increases at some depths at these monitoring wells indicates flow of heated water from the treatment zone. Knowing where water is leaving the treatment area allows adjustments to be made to improve hydraulic control. Also, samples are obtained on a regular basis from the exterior wells that show temperature increases to ensure that contaminants are not also being carried out of the treatment area.

We agree and have added a subsection on groundwater monitoring.

239. Page 82 mentions ERT, but I don't believe that this acronym has been used previously in this document, nor has the process been described. ERT does not measure temperature, but changes in electrical resistivity of the subsurface, which can be caused by changes in the composition of the fluids in the pore spaces as well as

changes in temperature. ERT has only been used for steam injection; it is not likely to provide effective monitoring for ERH or conductive heating processes. The main resistivity changes that normally occur in steam injection remediations lower the saturation of the pore spaces by formation of a steam zone.

We have added a description of ERT to the subsection on temperature monitoring.

240. Page 82: A hot floor is measured beneath the target zone, not necessarily at the perimeter of the target zone.

Comment accepted. The discussion in Section 5.3.6 has been revised.

241. The middle of page 83 contains an incomplete sentence that consists of, "Box 5-1 shows". The document does not contain a Box 5-1.

We have deleted the reference to Box 5-1.

242. Section 5.3.6: When groundwater extraction is employed as part of the thermal remediation, groundwater samples should also be analyzed for the purposes of calculating the amount of contaminants recovered and to help determine when the point of diminishing returns is being reached.

We concur. Section 5.3.6 has been modified to include monitoring extracted fluids.

243. In Section 6.1, the second paragraph consists of two incomplete sentences.

We have corrected the error.

244. Section 6.1.1: It is true that sampling hot liquids and soils can be dangerous if you do not know how to do the sampling. Thermal remediation vendors have developed safe methods to obtain valid hot groundwater and soil samples. If final groundwater and soil samples are to be obtained by those overseeing the remediation rather than the vendor, they should consult with the vendor about safe sampling methods. Another good source of hot soil sampling information is the paper by Gaberell that is referenced.

We concur and have revised the text somewhat.

245. Although it is true that flash boiling of groundwater can occur during thermal remediation, explosive conditions do not occur.

We concur and have removed reference to explosive conditions.

246. Section 6.3: As mentioned in Comment #28, I recommend that soil sampling for baseline data be done as the system as installed, thus the need for backfilling the boreholes is a moot point. If soil sampling is done for characterization that is not part of the system installation, the boreholes should be backfilled with a grout that can withstand thermal remediation temperatures if thermal remediation is to be done. Normally, cement grout with 40 percent silica flour is used for this purpose. This is especially important if steam injection is to be used.

We concur and have added a sentence on grout compatibility.

247. Page 97: See comment #216 above in relation to statistical methods to evaluate the data.

Discussion of statistical methods has been moved to Appendix D.

248. Page 99: TI Waivers require NAPL removal to the extent practicable.

Comment accepted.

249. Appendix B, Case Study 2: The case study states that verifying that TCE did not migrate to surrounding regions was one of the performance objectives, and that constraints placed on the vendors included the requirement to maintain hydraulic control. However, it also states that the demonstration design for the ISCO portion did not include any provision to ensure hydraulic control, although approximately 3 pore volumes of water/oxidant were injected. This becomes very confusing. The case study also states that indications were that lateral migration did occur during the ERH demonstration. However, nothing is provided on what these indications were, and monitoring methods for determining whether or not migration occurred is not discussed. Clarification should be provided as to what monitoring was done for each of these demonstrations, including to determine if hydraulic control was maintained, what evidence there was of contaminant movement out of the treatment area, and at what time the migration occurred. It is my understanding that baseline characterization of all three plots was done before any of the demonstrations. Thus, displacement of TCE by the ISCO demonstration could have effected concentrations in the other two cells. Also, it appears that some relocation of contaminants occurred due to the hurricanes, and it is not clear that the ongoing ERH demonstration was the cause migration from the cell. This could help explain the lack of mass balance for the ERH cell (although a lack of mass balance is not surprising). These things may have a significant impact on percent removal estimates, and this point should be brought out. It also demonstrates why percent removed is not a good performance measure for remediation.

We agree that the writeup was somewhat confusing and have revised the case study.

250. Appendix B, Case Study 3: Salient points about the Young-Rainey remediation that I think would be useful to add to the case study:

- During the interim soil sampling, it was determined that one area was not being heated, and additional steam injection points were added in order to heat the entire target area.

- The actual objective of the remediation that was done at this site was to remove mobile NAPL. The soil and groundwater cleanup standards were set based on this goal; these concentrations were thought to demonstrate that no NAPL remained.

- The post-treatment soil sampling showed that all soil concentrations were significantly lower than the soil cleanup standards.

- This was a guaranteed remediation, and that likely effected the costs.

Also, I would recommend that all the lessons learned listed relate back to the objective of this document, which is performance monitoring. It's not clear to me that all of the lessons learned listed here relate to performance monitoring.

We have revised the case study to include these points.

251. Appendix B, Case Study 4: I think the table of performance measures (Table 2) is very useful, and adding a table like this to the other case studies would make all the case studies more useful. What was the shut down criteria used for this remediation? Again, I would recommend that all the lessons learned listed relate back to the objective of this document, which is performance monitoring. It's not clear to me that all of the lessons learned listed here relate to performance monitoring.

The shutdown criteria consisted of monitoring the TCE concentrations in the vapor stream until asymptotic conditions were achieved. Then the vendor recommended system shutdown and confirmatory soil and groundwater sampling performed. Groundwater monitoring was also performed during operations.

252. Appendix B, Case Study 5: Since this pilot study was performed within a highly contaminated area, what is the probability that final groundwater concentrations were affected by recontamination from surrounding areas? Was something done to prevent or reduce recontamination before the samples were obtained?

The probability is high that the ERH pilot test area will become recontaminated following the remediation because the pilot test was located on the periphery of a large TCE DNAPL source area. Nothing was done to prevent or reduce recontamination of the pilot test area before the samples were obtained.

Greg Lyssy - EPA Ground Water Forum Liaison

253. In Section 1.2.1 on Page 1, under the heading Document intent, the text states "It may very well be that decision makers decide that DNAPL treatment is not feasible for a particular site…" The text should be modified to indicate that it is possible that decision makers may select not to treat DNAPL. Use of the term "may very well be" suggests this practice would be considered standard, normal, and acceptable which it is not in many cases.

We have removed the sentence.

254. In Section 1.4.1 on page 5, under the heading Why is performance assessment important?, A more appropriate title for the section might be Potential goals and outcomes of performance assessment. The concepts expressed in this section are important and are well stated.

We concur and have changed the heading as suggested.

255. In Section 1.4.1 on page 6, under the heading To monitor potential impacts beyond the treatment zone, the second sentence indicates that the concern of project managers is the potential for unacceptable exposure to down-gradient receptors. In a more general sense, the concern would likely be that as a result of the DNAPL remedial action, contaminant migration outside of the DNAPL area would be enhanced and contaminants could be transported into previously uncontaminated areas.

Comment accepted. The text has been revised to include the more general case.

256. On Figure 2-1 on Page 9, this figure should be modified to clearly illustrate the difference between residual and pooled DNAPL as defined in the text. The current illustration is unclear.

See response to Comment 105.

257. In Section 2.1.2, on Page 10, Partitioning Theory, the text states that "Using these partitioning relationships and the concepts of conservation of mass and volume, the amount of each component in each of the four phases can be calculated. The text should be modified to indicate the amount of each component in each of the four phases can be estimated assuming equilibrium conditions have been met.

We concur and have revised the end of the sentence to read "...can be estimated, assuming equilibrium conditions have been met."

258. In Section 2.1.2, on Page 11, Saturation Concept, the text states "In the field, saturation values are averaged over large areas so that typical residual saturation of DNAPL will be substantially lower…". It is unclear if this is referring to measured residual concentrations or estimations based on calculations. The overall meaning of the sentence is unclear and should be revised.

We have revised the text to highlight the difference between saturation values in the vadose zone versus those in the saturated zone.

259. In Section 2.1.2 on page 12, under the heading Matrix diffusion, the first sentence can be read to define matrix diffusion as a process that applies to ground-water flow in fractured media. The text of this discussion later clarifies that matrix diffusion is not limited to fractured rock media. This discrepancy should be eliminated by revising the first sentence of the text. Additionally, matrix diffusion may have limited applicability to some fractured media, if the rock is completely impervious with the exception of the fractures. Such an impervious condition may not be common, but in practical terms, there are certain rock types that have effectively no primary porosity, potentially making the matrix diffusion process very limited or even inconsequential with respect to the DNAPL distribution.

There is a tendency to overuse the term "matrix diffusion" in the text. Advective flow is not limited for all rock types. For instance in poorly cemented sandstones such as the ST Petersburg, or in many arkoses, pore space can be significant and advective flux through the pore can be much greater than diffusion. In addition, not all rock types diffuse equally or simply. Where chemical weathering has proceeded along fractures, clay minerals may form. These clay minerals can retard contaminant movement. In an orthoquartzite such as the Tuscarora, there is virtually no porosity within beds. The silicate framework of quartz make diffusion fairly insignificant.

We concur. Based on this and other comments, the section on matrix diffusion has been removed.

260. On page 12, Section 2.1.2, Matrix diffusion. The text introducing Box 2-1 states that matrix diffusion made it infeasible to recover the source in a reasonable time frame. However, the text in the box indicates matrix diffusion was one of the many factors that reduced the feasibility of source recovery based on currently available technologies. The introductory text to Box 2-1 should be reworded accordingly.

Box 2-1 has been deleted.

261. On Page 18, Section 2.2, under the heading Secondary impact, the text indicates source remedies that lower pH mobilize naturally occurring metals. Please cite examples of where this condition has occurred.

The concern with mobilizing metals at low pH is based on basic water chemistry and not on any particular experience or observation. The concern is also qualified by the adjective "potential." No change is warranted.

262. On page 19, under the heading Gas generation, the third sentence states that through exothermic conditions associated with in situ chemical oxidation, VOCs may be generated. This statement should probably be reworded to indicate that the VOCs can be volatilized rather than generated through this process.

We concur. The subheading has been changed to "VOC off-gassing" and the term "stripping" substituted for the word "generation."

263. On page 19, in the first paragraph under the Section 2.3 heading Addressing Rebound, the text indicates or implies that vapor or ground-water extraction technologies are primarily a process involving diffusive mass transfer of contaminants. This wording needs to be either removed or modified, as advection is the primary process through which contaminant mass is transported through the subsurface. At some point in the removal processes, diffusion may control the rate of mass removal from the subsurface, but this condition is not necessarily the case, as there are other processes that limit contaminant mass transfer.

We concur. The sentence has been rewritten.

264. On Page 19, Section 2.3 Addressing Rebound, rebound indicates the need for long term monitoring. Site conditions will change. It may be the behavior of the source terms after treatment or it can be because of many other reasons such as drought, water supply wells etc. Long term monitoring is needed to assess performance. Temporal considerations should be a major point.

We agree. Mention of the need for long-term monitoring has been included.

265. In the second paragraph of Section 2.4 on page 21, the text states that some EPA documents encourage the use of TI waivers. Although the referenced documents may allow TI waivers, they do not necessarily encourage them unless the are appropriate. Please modify text.

We do not agree. The referenced EPA document do encourage the use of TI waivers.

266. In the second paragraph of Section 3.2.1 on page 29, the wording implies that the percent DNAPL reduction is an important element of any assessment of DNAPL removal efficiency. There are likely to be sites where the amount of DNAPL present under the baseline conditions will be extremely difficult to ascertain with any reasonable degree of certainty. For such conditions, the percent DNAPL reduction criterion may not be a good measure of DNAPL removal efficiency. Under these conditions, it may be best to either use a mass flux reduction/ground-water concentration reduction criterion to assess removal efficiency or to establish, as applicable, the reduction in DNAPL removal over time relative to the initial DNAPL removal rate and terminate or modify the DNAPL remedial action at a predetermined ratio of current to initial DNAPL removal rate.

We agree that percent removal is a source reduction metric that is difficult to quantify. The intent of this section is to describe some of the objectives of a pilot test; a perfectly valid outcome may be realizing that the goal of achieving a minimum percent removal is not appropriate for the full-scale because of the amount of uncertainty in the baseline mass estimate. Section 3.2 has been move to Appendix B.

267. The text of Section 3.2.2 states that some estimate of the mass and distribution of DNAPL and the uncertainty of that estimate, should be determined pre and post-treatment. The mass estimate and distribution of DNAPL are likely to be very uncertain at a number of DNAPL sites. The potential error of the DNAPL mass estimate should be provided when making these calculations.

It may, however be possible at some sites that specific subareas of DNAPL contamination can be reasonably well characterized prior to DNAPL remediation. Then, depending on the site hydrogeologic conditions, it may be possible to recharacterize those subareas following treatment and use that information as a surrogate for the overall DNAPL removal efficiency for the entire source area. At sites where there is considerable uncertainty about the nature of DNAPL distribution, total mass of DNAPL, et cetera, it may be advantageous to select such subareas as the locations for pilot-scale testing and establish such pilot-scale testing as an essential element prior to establishing performance criteria or treatment details for the full-scale DNAPL removal.

We have revised the text somewhat to downplay the importance and expectations of mass estimates. Section 3.2 has been move to Appendix B.

268. Section 3.2.3 on page 30 advocates locating the pilot test in either a representative portion of a site or in a section of the site that is considered to be more challenging than average.

If there are any criteria that can be used to decide which of these two options would be more appropriate for a particular site, they should be mentioned in this discussion. It may be difficult to define what constitutes a "representative" area of DNAPL contamination for many sites, based on DNAPL geometries and other contaminant-specific factors. There should probably be some mention of the value in having a well defined picture of the site geology as a means of assessing if identified subareas of DNAPL contamination are likely representative of the DNAPL contamination in general.

We concur and have revised the text. Section 3.2 has been move to Appendix B.

269. On Page 33, Section 3.3, "Developing an Exit Strategy", it may be prudent to not call a section an "exit" strategy. Perhaps an optimization strategy, especially since the text acknowledges that modifications to the remedy may be appropriate.

We agree. The term exit strategy has been changed to "completion or optimization strategy."

270. On Page 34, Section 3.3.2 is titled "Contingency planning and adaptation". While this title captures a part of the discussion in that section, the title is for the most part inconsistent with the text in the section. Some of the Section 3.3.2 text should probably be moved into Section 3.3.1 and the remainder of the text should probably be amended with additional language that describes contingency planning and implementation.

We concur and have reorganized the text as suggested.

271. In Section 3.4.2 on page 35, the second sentence poses the question "...which should be selected first: the statistical model to be used for the data analyses or the sampling program?" The appropriate statistical model to be used will depend upon the nature of the data being collected (e.g. is there seasonality in data; do the data follow some identifiable distribution?) The sampling program should be initially specified, with an agreement to review the data being collected and modify that plan, if necessary. Any statistical approach to analyze the collected data should be selected on the basis of the nature of the data that have been obtained.

We have added the sentence, "Because the appropriate statistical model to be used will depend upon the nature and form of the data being collected (e.g., seasonality, data distribution), the sampling program should be designed initially using some assumptions about the data, with an agreement to review the data as it is being collected and to modify that plan, if necessary."

272. Section 3.4.3 presents several data analysis procedures without providing any information as to how those statistical approaches might relate to monitoring DNAPL source zone remedies. The discussion would be improved if some examples were given for how

each statistical approach might be applied to the DNAPL source remediation problem.

We have moved the discussion on statistics (Section 3.4) to Appendix C.

273. Section 3.4.5 presents one type of trend analysis. Through omission of any alternative approaches, the text implies that this trend analysis approach will be universally applicable to problems involving DNAPL source zone remedies. This position is clearly invalid. Some statement should at least be added that other trend analyses are potentially applicable to data analyses involving DNAPL source remediation.

We concur and have added language to that affect.

274. Section 3.6, Keeping an Eye Toward Site Closure. The text presents ITRC's (a state organization) interpretation of federal regulations, including CERCLA and RCRA. The description of the programs is not necessary to understanding performance assessment or site closure. Even the description of other programs includes potentially erroneous statements about some state programs. The description of different programs is not needed, simply a statement that all regulatory programs may lead to and allow for site closure provided certain conditions have been met as determined by the program area would probably suffice.

We concur and have deleted the three paragraphs.

275. It would be useful if under the Purging considerations discussion of Section 4.2.2, the text stated that consistency in purging techniques between different sampling events is important to monitoring changes in ground-water chemistry in response to remedial actions addressing DNAPL.

We concur and have added the following sentence: "In addition, when considering changing the purging methods, it is important to evaluate if a change in analytical values results because of changing purging methods by performing a comparison of results from each method."

276. In the last part of the Purging considerations discussion of Section 4.2.2 on page 56, it would be useful if the text mentioned the use of passive diffusion samplers for some applications involving monitoring of low permeability formations where there is contamination related to chlorinated solvent DNAPL contamination. In particular, purging and sampling with a bailer can often introduce unacceptable ground-water entrance velocities in monitoring wells, yielding turbid samples. While text on page 58 notes that passive diffusion samplers have limited applications in aquifer materials with hydraulic conductivity less than 1 × 10-6 cm/sec, there are also limitations in such aquifer materials to using any type of sampling device. There is probably an optimal sampling approach for low hydraulic conductivity materials depending on site-specific considerations, and it may be best to note the universal difficulty in conducting ground-water monitoring of such earth materials.

We thank you for the comment, however we feel the document includes the information.

277. Section 4.2.3 discusses measurement of soil vapor concentrations in the context of a DNAPL removal from the vadose zone using SVE as the remedial process. Measurement of soil vapor concentration changes may also have some applicability where other types of DNAPL removal/treatment processes are used in the vadose zone, and perhaps in some limited circumstances, for DNAPL removal/treatment in the saturated zone. The latter part of the discussion notes the limitations of measurement of soil vapor concentrations. The discussion of this possible approach for assessment of DNAPL source treatment progress should note its benefits, particularly relative to monitoring soil contaminant concentrations through direct measurement of soil concentrations. Specifically, soil vapor monitoring can be done in a manner that produces a result per sample that is applicable to a larger volume of soil than a direct soil sampling technique, which may be important in comparing pre and post-treatment concentrations where there is considerable spatial variability in the contaminant distribution. As noted in the prior discussion regarding measurement of soil concentrations by direct soil sampling (page 54) "If the goal is to assess performance of a remediation technology, a direct comparison of conditions before and after treatment cannot be made."

We thank you for the comment, however we feel the document includes the information.

278. Under the heading Monitoring well network design and installation on page 56, the second paragraph should identify what "shutdown" refers to.

Shutdown refers to cessation of active source treatment.

279. The third "bullet" in the PDB discussion on page 58 needs to be reworded to indicate that the well screen/sand pack is the material that may be less permeable than the surrounding aquifer materials.

We have deleted the third bullet because it is not specific to PDBs and more generally applies to well construction.

280. The wording is awkward in the last sentence of the next to last paragraph of Section 4.2.2.

We concur. The text has been revised to clarify its meaning.

281. The last sentence of the first paragraph under Section 4.4.2 needs word added in order to be a complete sentence.

We concur.

282. Section 5.1 appears to omit a discussion on remedial effectiveness monitoring. The discussion also identifies one type of performance monitoring as "System efficiency monitoring," yet the text describes "System process monitoring." Terminology should be consistent.

We have revised the text in Section 5.1 and have changed process monitoring to efficiency monitoring.

283. In the last paragraph of Section 5.3.5, the term "ISTD" probably needs to be spelled out.

We have deleted Section 5.3.5 to reduce the length of the document.

284. In the discussion under the heading Dissolved concentration near the close of Section 5.3.6, there is missing text in the last sentence of the first paragraph.

Reference to Box 5-1 has been removed.

285. The text of Section 5.6.1 would be improved if a statement was added regarding what types of DNAPLs are considered to be potentially amenable to treatment by enhanced in-situ bioremediation.

The first sentence states that ISB has been demonstrated in the field only at a few chlorinated solvent sites. The entire section is limited to discussion of PCE and its degradation products.

286. On Page 92, Sampling Hot Ground Water, it is generally not recommended to collect samples of excessively hot ground water since it is not going to be representative of overall water quality. What is the purpose of collecting the hot water samples, especially if VOCs are the target analyte. It would be prudent to wait until the system cools so that temperature does not become an issue and certainly not a dangerous/safety issue.

We are aware of several projects where groundwater sampling was performed while the aquifer was near 90°C. Hot sampling techniques were employed to minimize volatilization and prevent exposure to hot fluids.

287. On Page 95, in Section 6.2.2, Estimating remediation time frames, there is a discussion about the Natural Attenuation Software (NAS). Please add a sentence discussing the potential limitations of the NAS.

We have added the following sentences: "Like most numerical modeling tools, NAS requires the input of detailed site information about hydrogeology, redox conditions, and the distribution of contaminants. For highly heterogeneous systems, the program may introduce unacceptable errors and more detailed, site-specific modeling may be required."

A. Lynn Wood - EPA Office of Research & Development

288. Executive Summary, Second Paragraph: Last sentence of this paragraph states "…rate of contaminant mass or flux emanating…" This would be more correctly stated as "… rate of contaminant mass discharge or flux emanating…"

We concur.

289. 1.3.1 Effectiveness, First paragraph, last sentence: Why limit this to wood-treater sites? These goals could apply to other types of DNAPL sites.

We agree. The text has been revised.

290. 1.3.2 Efficiency, First paragraph, last sentence: Replace "procedure" with "practice."

We concur.

291. 1.4 Planning for Performance Assessment, First paragraph, first sentence: Replace "…source zone removal…" with "…source zone treatment…".

We concur. The change has been made.

292. 1.4.1 Third paragraph, 4th sentence: What is meant by "plume strength"?

"Decrease in plume strength over time" has been changed to "decrease in plume longevity."

293. 2.1 Key Concepts Relating to DNAPLs, Second paragraph: MacKay and Cherry, 1989; Cohen and Mercer, 1993 and Feenstra et al., 1996 are not included in Reference Section.

These have been included.

294. 2.1.1 First paragraph: Mercer and Cohen, 1993 is not in Reference Section. Fourth paragraph: Hunt, Sitar and Udell, 1989 and McWhorter and Kueper, 1996 are not in Reference Section.

These have been included.

295. 2.1.2 Saturation concepts, First sentence: Saturation is more appropriately defined as the percentage of the pore space occupied by a fluid. "Available volume" could imply something other than the void volume of the medium.

We concur and have revised the text.

296. 2.1.2 Matrix diffusion, Second paragraph, third & fourth sentences: The fractured system described here is the DNAPL source. Thus, it is confusing to say "When a DNAPL source is discharging a high mass flux…" Perhaps better stated as: "When DNAPL is resident in fractures, the concentration gradient…" Likewise, successful remediation of the source zone could imply removal of contaminants from both fractures and matrix. I believe the point is that when contaminant concentrations in the fractures diminish, contaminants will diffuse out of the matrix and into the relatively clean water in the fractures.

We agree. Based on other comments and a desire to focus on unconsolidated sediments, all discussions on fractured bedrock and matrix diffusion and have been eliminated from the document.

297. 2.1.3 Source zone delineation, Third paragraph, second sentence: Citation should be (EPA, 1992a)

We have deleted the discussion of the "one-percent rule" and no longer need the citation.

298. 2.2 Changes in DNAPL Zone Resulting from Treatment, Second paragraph: Changes in architecture do not necessarily improve efficiencies. It is common to observe decreased removal efficiency as remediation progresses. I know heat-induced soil agitation has been demonstrated in the laboratory, but has it been confirmed as an important process in the field? If not, perhaps it should be stated as a hypothetical (likely) contributor to DNAPL removal. I suggest rewording the last sentence as follows: "The degree of the change in mass flux is in part a function of the magnitude and nature of formation heterogeneity and the distribution of DNAPL within the formation."

We concur.

299. 2.2 Redistribution of DNAPL, First paragraph: Most aggressive treatment technologies mobilize DNAPL to some extent. Some technologies do so by design. The key is to control or capture mobilized DNAPL and substantial attention has been given to this issue for thermal and flushing technologies. Thus, I believe the following more accurately describes the issue.

"Treatment technologies that modify DNAPL or interfacial properties or alter the subsurface structure will likely mobilize and redistribute previously immobile DNAPL. This redistribution can create a more extensive source zone. Consequently, monitoring and effective containment of DNAPL during remediation is of paramount importance. Since the inherent remediation objective is DNAPL mass removal, knowledge of the rate and extent of this redistribution can help in the design of subsequent remedial steps."

We concur and have modified the text.

300. 2.2 Redistribution of DNAPL, Second paragraph, first sentence: Delete "potentially."

We concur.

301. 2.2 Increase in solubility or dissolved phase constituents. It would be helpful to list citations to support the statement that elevated dissolved concentrations often accompany DNAPL treatment. Does this refer to concentrations during or subsequent to aggressive treatment. The implication is that these elevated concentrations occur after treatment. Most field data that I have seen suggests a reduction in dissolved concentrations upon system equilibration following aggressive treatment. Although in some cases, there may be short-term increases in groundwater concentrations during the equilibration period. Elevated concentrations are certainly likely to be seen during application of thermal, flushing and biostimulation treatments. Also, there is substantial evidence for enhanced degradation during and following implementation of some treatment technologies.

We are referring to increased concentrations during and immediately after treatment prior to equilibration. The meaning has been clarified.

302. 2.3 Addressing Rebound, First paragraph: Rebound usually refers to concentration increases with respect to concentrations measured at the completion of remediation. Rebound can be significant even if concentrations do not return to pre-remediation levels.

We concur and have revised the text.

303. 2.3 Addressing Rebound, Fourth paragraph: Failure to remediate the DNAPL source is the primary and underlying reason for rebound. The other factors listed here are essentially potential reasons for this failure.

We concur and have clarified the wording.

304. 3.1.3 Performance metrics and criteria, Determining the response boundary or control plane: What is meant by "groundwater plume anatomy"? I assume this refers to dimensions and structure (contaminant distribution) of the plume. Multiple control planes or response boundaries may be required. Would this include measurement of parameters such as contaminant flux or discharge from which plume properties and changes in these properties may be estimated?

Plume anatomy does refer to the plume's dimensions and contaminant distribution both vertically and horizontally. Depending on the performance assessment strategy and response objective, contaminant mass flux or discharge may be the primary parameter of interest.

305. 3.2.3 Selecting the pilot study location, Second paragraph, second bullet: It is stated: "The practical pilot test limit is a reduction in the range of 95-99%". What is the basis for this range?

The phrase has been deleted. Section 3.2 has been removed to Appendix C.

306. 3.2.3 Selecting the pilot study location, Second paragraph, third bullet: Replace "Groundwater samples will rebound…" with "Groundwater concentrations will rebound…" The rate of rebound will be dependent upon hydrodynamic, geochemical, etc properties, and may not be rapid.

We concur and have changed "will rebound" to "may rebound..."

307. 3.2.3 Selecting the pilot study location, Second paragraph, fourth bullet: If rebound is measured in relation to concentrations at the termination of remediation (see comments for Section 2.3), soil concentrations may or may not rebound as contaminated groundwater reinvades the treated area. The extent of rebound will depend on the degree to which sorbed and dissolved concentrations were altered during remediation and the contaminant concentrations in the post-treatment groundwater . If post-treatment soil concentrations are compared to pre-treatment data, this may or may not be true. For locations from which NAPL was removed, rebound would be expected to be minimal (in comparison to pre-treatment concentrations). However, if compared to pre-treatment samples not containing NAPL, rebound could be substantial. Treatment-induced redistribution of DNAPL could also cause post-treatment soil concentrations to increase in some regions of the treated zone and influence post-sampling results in a manner suggestive of rebound. The bottom line is that it cannot be assumed, a priori, that soil concentrations do not demonstrate rebound, however significant rebound of soil concentrations is less likely.

We concur. The text has been revised accordingly. Section 3.2 has been removed to Appendix C.

308. 3.2.4 Addressing scale-up issues, Second paragraph: It may not always be possible to definitely answer all of these questions with a pilot study but it should be a goal. Better stated as: "Information essential for the design that should be collected during the pilot study includes:"

We have made the suggested change.

309. 3.2.5 Assessing costs, First paragraph: Does this refer to comparisons between sites or between technologies at a given site? There are other factors that complicate comparisons, such as stratigraphy, DNAPL composition and architecture. Also, it is very difficult to get accurate estimates of initial DNAPL mass.

We are referring to estimating the full-scale cost of various technologies that are being piloted at a given site, so site conditions (stratigraphy, etc.) should not be a complicating factor.

310. 3.2.5 Assessing costs, Second paragraph: What is meant by "total restoration costs". If the remedial goal is less than total restoration, would costs to achieve remedial objectives be the basis for comparison?

Yes, we mean costs to achieve whatever RAOs have been established for the project, not necessarily total restoration costs.

311. 3.2.5 Assessing costs, Third paragraph, first bullet: "prolonged treatment times" can imply longer than anticipated. I believe what is intended here is better stated as "The pilot study should be used to determine the source reduction technology duration and the potential costs for treatment times, as estimated from the pilot demonstration."

We concur and have made the changes.

312. 3.2.5 Assessing costs, Third paragraph, third bullet: There are potential scenarios in which some DNAPL-contaminated zones may be contributing very little to the total mass flux and may not need to be remediated to achieve remedial objectives.

We concur and have revised the text.

313. 3.2.5 Assessing costs, Third paragraph, fourth bullet: Post-treatment DNAPL mass estimates are difficult and/or expensive to get. It may be sufficient to know post-treatment fluxes or groundwater concentrations.

We have deleted the first sentence and have reworded the second.

314. 3.3 Statistical Approach to Evaluating Performance, Second paragraph: I did not find some of the cited EPA reports in the Reference Section. Also, the CRC citation is not in Section 7.

We have moved the entire section on statistics to Appendix D. The appendix has its own reference section.

315. 3.4.2 Sampling design, Second paragraph: What about flux-based goals?

The goals listed are only examples, but we have added "reduction in mass discharge" as a possible goal.

316. 3.4.2 Sampling design, Selecting sample size: What are the assumptions on which this equation is based? For example, does it assume randomly distributed DNAPL? What constitutes an "attempt". Does an attempt represent a discrete point. What if a larger volume sample (volume-integrated sample) is taken?

This equation assumes randomly distributed DNAPL. An "attempt" is a random, discrete point measurement.

317. 3.4.3 Geostatistical estimation techniques, Third paragraph: Should "…modeling variation in modeling complex systems" be "…modeling variability in complex systems"? Also, Milliken and Johnson (2001) and Lettell et al., 1996 are not in Reference Section.

We have made the changes you suggest.

318. 3.4.6 Integrated physical-geostatistical methods, First paragraph: "methods described above" – what methods are these?

The statistical methods described previously are those covered in the preceding subsections under data analysis procedures, geostatistical estimation techniques, trend analysis, etc.

319. 3.4.6 Integrated physical-geostatistical methods, First paragraph: Change "4)…(to reduce uncertainty and to reduce uncertainty in the estimate…" to "4)…(to reduce uncertainty in the estimate…".

We concur.

320. 3.4.6 Integrated physical-geostatistical methods, Second paragraph: The statistical methods are in Table 3-2, not Table 3-1.

We have revised the table numbering. The discussion on statistics has been removed to Appendix D.

321. 3.5.1 Setting data quality objectives, Third paragraph: Not sure I agree with this generalization. Probably depends on data application.

We agree that use of the term "high-quality data" may not be appropriate here. However, we do feel that the tolerance for error can be set higher when sampling in areas known to contain DNAPLs.

322. 4.0 Quantifying Performance with Field Metrics, Table 4-1: The relative accuracy of extracted source mass is reported as low in this table, extracted mass can be determined with relatively high accuracy. What cannot be estimated accurately is the fraction of the original mass that is removed, but this is due to difficulty in determining the original mass.

Conversely, the accuracy with which source mass remaining can be determined with PITTs is shown as intermediate to high. I suggest that, the accuracy would likely be intermediate. If the remaining NAPL is relatively inaccessible (hydraulically), if NAPL saturation is low or if the NAPL is non-uniformly distributed, accuracy is likely to be low. The primary issue is often adequate resolution of the breakthrough, but other factors such tracer degradation or retardation by residual remedial agent can be important as well.

We concur. The table has been reorganized to clarify.

323. 4.2.1 Decrease in soil concentration, Limitations, Fourth paragraph, second sentence: False positives are much less likely than false negatives. In the absence of analytical problems, the primary reason for false positives would be inadequate information about DNAPL composition, soil organic carbon content or the partitioning behavior of the DNAPL constituents with the soil.

We agree that false negatives are more common than false positives. The text has been revised to mention some of the reasons for obtaining false positives and negatives.

324. 4.2.1 Decrease in soil concentration, Limitations, Fourth paragraph, third sentence: Setting upper limits are difficult not because chemical and soil properties must be considered, but because these properties are difficult to obtain.

We concur and the text has been revised.

325. 4.2.2 Decrease in dissolved concentration, Purging considerations, First paragraph, third sentence: I assume the isolated and stagnant water is in the well bore. Restate as: "However, water in the well bore above the screened section is relatively isolated and becomes stagnant."

The text has been revised as you suggest.

326. 4.2.2 Decrease in dissolved concentration, Monitoring well network design and installation, First paragraph: A single transect of wells parallel to flow will likely not be adequate to determine impact of remediation on groundwater concentration. Problems and limitations are similar to those for core samples. Cross-gradient well locations or transects are likely to be needed.

We agree; however the need for cross-gradient well locations is already addressed.

327. 4.2.2 Decrease in dissolved concentration, Monitoring well network design and installation, Second paragraph: Lateral spreading is not limited to flat groundwater gradients. Spreading as a result of diffusion will be more significant under low flow conditions, but this spreading is often small relative to that resulting from hydrodynamic variability. The post-treatment monitoring time examples (2, 4, 8 weeks) are unlikely to be sufficient for the system to re-equilibrate. System re-equilibration is dependent upon several factors but may require months to years in many cases.

We concur and have revised the text accordingly.

328. 4.2.2 Decrease in dissolved concentration, Multi-level sampling, Fourth paragraph, third sentence: The use of multi-level samplers to estimate flux is not dependent upon poorly distributed monitoring wells – reword to clarify. Also, it is important to note that contaminant flux estimates require knowledge of both contaminant concentrations and groundwater flux.

The word "poorly" has been changed to "properly." The need for groundwater flux information has been added.

329. 4.2.2 Decrease in dissolved concentration, Use of passive diffusion bag (PDB) samplers, Third paragraph, fourth bullet: I don't understand this bullet.

The bullet has been deleted.

330. 4.2.2 Decrease in dissolved concentration, Limitations, Third paragraph, third sentence: Suggest revising as follows: "Depending on the degree of heterogeneity, groundwater flow rates and size of the treated area, it may take years …"

We have made the suggested change.

331. 4.2.2 Decrease in dissolved concentration, Limitations, Third paragraph, last sentence: Groundwater concentrations in down-gradient wells could be higher prior to equilibration due to water passing through a more highly contaminated source zone or perhaps the presence of residual remedial agents that enhance solubility.

We concur and have added the potential for observing increased concentrations as another limitation.

332. 4.3.3 Mass remaining, Estimating mass remaining, First paragraph, last sentence & Box 4-3: Box 4-3 presents an example of mass estimates from core samples, but it does not illustrate or describe how soil core data can be used to estimate contaminant mass.

Box 4-3 and the last sentence of the first paragraph have been deleted.

333. 4.3.3 Mass remaining, Estimating mass remaining, Third paragraph: This discussion of tracer tests would be strengthened by adding information about the benefits and limitations of PITTs as well as information about field applications and assessments. For example see Brooks et al. Journal Contam. Hydrology 59:187-210.

The limitations of tracer tests are described under *Limitations*. The intent here is to make the readers aware of the mass estimation technique and provide references for further information. We will consider including the Brooks et al. reference.

334. 4.4.1 Decrease in DNAPL toxicity, First paragraph, last sentence: The issue of mass flux and associated risk is perhaps as important as (if not more so) toxicity. Concentrations and mass fluxes of low solubility components will be lower.

We do not think that mention of mass flux is appropriate here.

335. 4.4.2 Decrease in DNAPL mobility, Measuring NAPL saturation: The organization of this section implies that NAPL saturation can be used to estimate NAPL mobility. If so, what is the correlation between saturation and mobility? Also, saturation may be a more direct measure of remedial effectiveness but its determination is subject to same limitations as mass estimates from which it is derived.

We have added qualifying language to that effect.

336. Laboratory analysis of soil samples, Second paragraph: The procedure described here needs more detail.

We do not concur. The procedures are described in detail in the references.

337. Third paragraph: Jackson and Mariner, 1995 not in Reference Section.

These references have been included.

338. 4.4.3 Decrease in source mass flux, Third paragraph, second sentence: In fact, mass discharge is the primary or correct measure of source strength (as defined earlier in this section). Flux is a measure of loading over a specific area.

We have reorganized Section 4.4.3 and made revisions to improve consistency.

339. Figure 4-2: Labels on large arrows should be changed from "Contaminant Flux" to "Contaminant Discharge".

We have changed the label to read "Source Strength."

340. Measuring mass flux, Fifth paragraph: Schwarz et al., 1998 not in Reference section.

We have added Schwarz et al. to the references.

341. 4.5 Summary of Performance Metrics Results From a Recent Survey, Fifth paragraph: Is there confidence that these sites were indeed measuring mass flux? This has not been a commonly measured metric and it is very surprising that 57% of the sites reported doing so.

Section 4.5 has been deleted and the information moved to Box 4-1. We agree that the concept of measuring mass flux is not common, but we refer the reader to the report to make their own conclusions regarding its accuracy.

342. 5.0 SUGGESTED TECHNOLOGY-SPECIFIC MONITORING TOOLS: The focus of this section is on technology descriptions and to a lesser extent monitoring parameters and needs for specific technologies. Tools should be deleted from section title.

We concur and have changed the title to "Technology-Specific Monitoring Considerations."

343. 5.1 Remedial Effectiveness vs. System Efficiency: The two types of performance monitoring are discussed briefly in Section 1.3, but the concepts are not adequately developed nor are they used in this section (Section 5.0). This section should be expanded and better developed or deleted.

We have expanded Section 5.1.

344. Effectiveness monitoring: This discussion focuses on geochemical and process monitoring which more appropriately fall under efficiency monitoring.

See response to previous comment.

345. 5.2 Conventional Source Zone Remedies: This section is introduced with "Although not innovative, we include these conventional source zone technologies to allow a comparison of performance monitoring tools." Only one sentence in the section deals with performance monitoring. It is essentially a description of conventional source remedial approaches. Comparison of performance monitoring is not possible with the information presented.

We have provided references to EPA and USACE guidance on assessing performance.

346. 5.3 Thermally Enhanced Remediation: Apparently subsection 5.3.1 (Technology description?) is missing.

We describe the three main types of thermal technologies under Sections 5.3.2 through 5.3.4. Section 5.3.1 consists of introductory material on the benefits of heat.

347. 5.3.6 Key monitoring parameters, Dissolved concentration: The sentence beginning with "Box 5-1" is incomplete. Also, Box 5-1 is missing.

We have corrected these errors.

348. 5.4 Surfactant/Cosolvent Flushing: To be consistent with the previous section, a subsection discussing enhanced in-situ degradation should be added. There is both lab and field data that suggests surfactants and cosolvents enhance in-situ degradation (Mravik et al., 2003 and Abriola et al., ?).

The discussion of thermally mediated increases in biodegradation rates has been removed from Section 5.3, therefore they should no longer be inconsistent.

349. 5.4.1 Technology description, First paragraph, seventh sentence: Suggest revising sentence as follows: "Both chemical solutions lower the interfacial tension between DNAPL and the aqueous phase and increase the apparent solubility of DNAPL constituents."

We concur.

350. 5.4.2 Key monitoring parameters, Surfactant/cosolvent contaminant analysis, Second sentence: The electrolyte issue is primarily associated with surfactant and is not an issue with cosolvents. Therefore, revise as follows: "In some cases when using surfactants as the remedial agent, small fluctuations in electrolyte…".

We concur.

351. Fourth sentence: To make applicable to both cosolvent and surfactant systems, revise as follows: "Thus, it is important to monitor both remedial agent and contaminant concentrations during a surfactant or cosolvent flood."

Comment accepted.

352. Groundwater quality: This discussion is also pertinent to thermal technologies but was not included in that section.

We agree that groundwater quality monitoring is often performed during thermal remediation, however it is not considered a key parameter.

353. Injection/extraction flow rate, Last sentence: I do not understand this sentence.

We have improved the readability of this sentence.

354. 5.5.1 Technology description, First paragraph: Schnarr et al., 1998 is not in Reference Section.

The sentence containing the reference to Schnarr's work has been deleted.

355. 5.5.1 Technology description, Groundwater quality, Second paragraph, fourth & fifth sentences: This issue is pertinent to other technologies as well. Solution concentrations associated with sorbed contaminant are likely to be substantially lower than those associated with DNAPL. Actually, for ISCO, dissolved concentrations could be low because of rapid and effective oxidation in the aqueous phase (if unreacted oxidant is present) even though substantial DNAPL is present. Solution concentrations would rebound when oxidant is depleted.

To address this issue, we refer the reader to Section 2.3 of this document and the ITRC ISCO document.

356. 5.6.2 Key monitoring parameters, First paragraph, last sentence: Time frame for ISB is more likely to be years to decades.

We have replaced the phrase with "several years."

357. 6.1 Health and Safety: Need to add a section dealing with the handling of flammable liquids such as alcohols used in cosolvent flushing.

We concur and have added text regarding flammable liquids.

358. 6.1 Health and Safety, Second paragraph: Incomplete sentences and paragraph.

We have corrected the error.

359. 6.1.1 Sampling hot media, Third sentence: "…this could take from 2 weeks to several months or longer."

We concur.

360. 6.2.1 Predicting plume response: It would be helpful to citations for the research described in this section.

We have provided a reference to the ESTCP web site.

361. Method 2, Simple Box Model: Aziz et al., 2000 is not in Reference Section.

We have added the reference.

362. Method 3, Process-Based Models, First sentence: Replace "Process-type models available are…" with "Available process-type models are…"

We concur.

363. 6.3 Regulatory Concerns, Concerns over potential for mobilization potential off site migration of DNAPLs: Change subsection title to: "Concerns over potential mobilization of DNAPLs".

Okay.

364. 6.4 Stakeholder/Public Involvement: This section reads as a selection of random, poorly coordinated thoughts.

This section has been edited and revised to make it more readable.

365. Case Study 1: Composition and grammar of this section need substantial improvement.

We have made many grammatical corrections to this case study.

366. Case Study 1, Figures are missing.

We have decided not to use any figures in Case Study 1; references to figures have been deleted.

367. Case Study 1, Groundwater quality monitoring: Where were monitoring locations? What criteria were used for determining plume stabilization or shrinkage?

Determining plume stability or extent was a simple matter of creating contour plots of dissolved PCE concentrations and observing trends in these plume maps over time. We realize there are limitations to this approach. Numerical modeling would certainly be beneficial in predicting plume stability. Groundwater monitoring locations were not provided; please contact the project manager listed.

368. Case Study 1, Soil vapor monitoring, First sentence: Replace "…demonstrate that Soil Vapor was no longer present in the subsurface…" with "…demonstrate that contaminants were no longer in the soil vapor…" Also, how were the concentration levels determined below which the dissolved or vapor plumes did not expand.

We have revised the text. Evaluation of groundwater and vapor quality data is done by assessing trends using plume maps, as described above.

369. Case Study 1, Soil vapor monitoring, Second sentence: replace "soil vapor" with "vapor-phase contaminant."

We have made the change.

370. Case Study 2, Performance Monitoring and Verification, Seventh paragraph, second sentence (p. B-13): The report states "Only ERH met the performance criterion of 90% mass reduction of TCE DNAPL established for the tests, although both ISCO and SEE probably achieved this goal when measurement uncertainties are considered." I don't understand how consideration of measurement uncertainties would lead to the conclusion that the criterion was met.

We agree that the statement is misleading. The last part of the sentence has been deleted.

371. Case Study 2, Lessons Learned, ERH, fourth bullet: This bullet is unclear. I assume this is saying that <50% of the estimated pre-treatment mass was recovered during remediation.

There was greater than 90% removal from the ERH plot based on a comparison of pre- and post-treatment mass estimates. The point being made is that not all of the mass removed from the ERH plot was accounted for in the calculated mass recovered in the form of vapor, dissolved, and NAPL phases. The sentence has been revised to state that "... less than 50% of the TCE mass assumed to have been removed from the source zone was actually captured by the aboveground recovery systems."

372. Case Study 3, Performance Monitoring and Verification, Soil: Were precautions taken to prevent contaminant losses from hot samples?

Hot sampling techniques were employed to minimize contaminant loss. Methods have been added to the case study.

373. Case Study 3, Performance Monitoring and Verification, Groundwater: What were subsurface temperatures during 4-, 12- and 24-week sampling events? Why was it assumed that 24 weeks was sufficient to assess rebound?

A cool-down phase of operations was conducted following completion of active heating. Subsurface temperatures were below 100°C at all temperature monitoring locations following cool-down before confirmatory sampling began. Groundwater temperature was not measured during the confirmatory sampling events, however. A period of 24 weeks was determined to be sufficient to assess rebound based on consultation with NAPL remediation specialists, literature searches, etc. Additionally, the subcontract was performance-based, meaning that the contaminant concentrations in the subsurface had to be below the defined concentration goals, as modified by various statistical definitions. If, following the verification sampling at 24 week, concentrations exceeded the goals, the subcontractor would have been required to recommence remediation. Therefore, it was necessary to define a reasonable time frame until success could be determined. It was believed that 24 weeks would be a sufficient time period to observe any potential rebound.

374. Case Study 3, Performance Monitoring and Verification, Operational: Were data available to estimate total contaminant removal? If so, how did it compare to initial mass?

The table below lists the estimated contaminant mass before and after NAPL remediation.

375. Case Study 4, Background: A site map would be helpful.

Thanks for the suggestion, but to be consistent, we have not provided site maps.

376. Case Study 4, Remediation Results: How were groundwater and soil samples collected? How were losses of VOCs from hot samples minimized? Was the system allowed to equilibrate before post-remediation sample collection?

Sampling procedures are described under "ERH System Operations." To clarify that these procedures apply to performance monitoring, we have moved the paragraphs to the "Performance Monitoring and Verification" section.

377. Case Study 5, Technology Performance: Was rebound evaluated? Is cost information available?

Rebound was not evaluated due to monitoring and characterization data limitations. Cost information was not available.

378. Case Study 6, Performance Monitoring and Verification, Second paragraph: How was it determined that 98% of the chlorinated hydrocarbons were destroyed?

The percent reduction refers to a reduction in mean dissolved concentrations. The text has been changed.

379. Case Study 7, Performance Monitoring and Verification, Last paragraph: What were $KMnO_4$ concentrations during the post-treatment sampling events? Also, add references for this study.

This case study is based on a paper submitted by Dr. Beth Parker to the 2002 Battelle Conference. References have been added.

380. Case Study 8, Add references for this study.

This case study was written by the project manager from North Wind, Inc. based on data that has not been published. The reference has been added.

381. Case Study 8, Performance Objectives, Second paragraph, last sentence: What is the residual saturation at which natural attenuation processes will "address" the residual groundwater concentrations? How is this saturation determined or estimated?

The NAPL saturation has not been measured at this site and will not be used as a performance metric due to the difficult and complex hydrogeology. Groundwater concentrations constitute the performance metric that will be used to determine when ISB operations can be terminated. Operations will continue until MCLs are achieved for all VOCs and ethene production has ceased in the existing monitoring wells. Once ISB operations are terminated, continued monitoring will be conducted for an additional period of time to verify that concentrations do not rebound above unacceptable levels. This concentration threshold, which essentially represents the contamination level below which attenuation processes will address contamination, has not yet been defined.

382. Case Studies – General: I suggest adding a case study for in-situ flushing. The Sages site has several years of monitoring data

following cosolvent flooding. These data show substantial enhancement in post-treatment degradation. Primary contacts for information would be Susan Mravik with EPA or Mike Annable at the University of Florida.

We would welcome your help in pulling together the project team to generate this case study. Perhaps we can add a case study at a later date.

APPENDIX F

DNAPLs Team Contacts, ITRC Fact Sheet, and Product List

Appendix F. DNAPLs Team Contacts, ITRC Fact Sheet, and Product List

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