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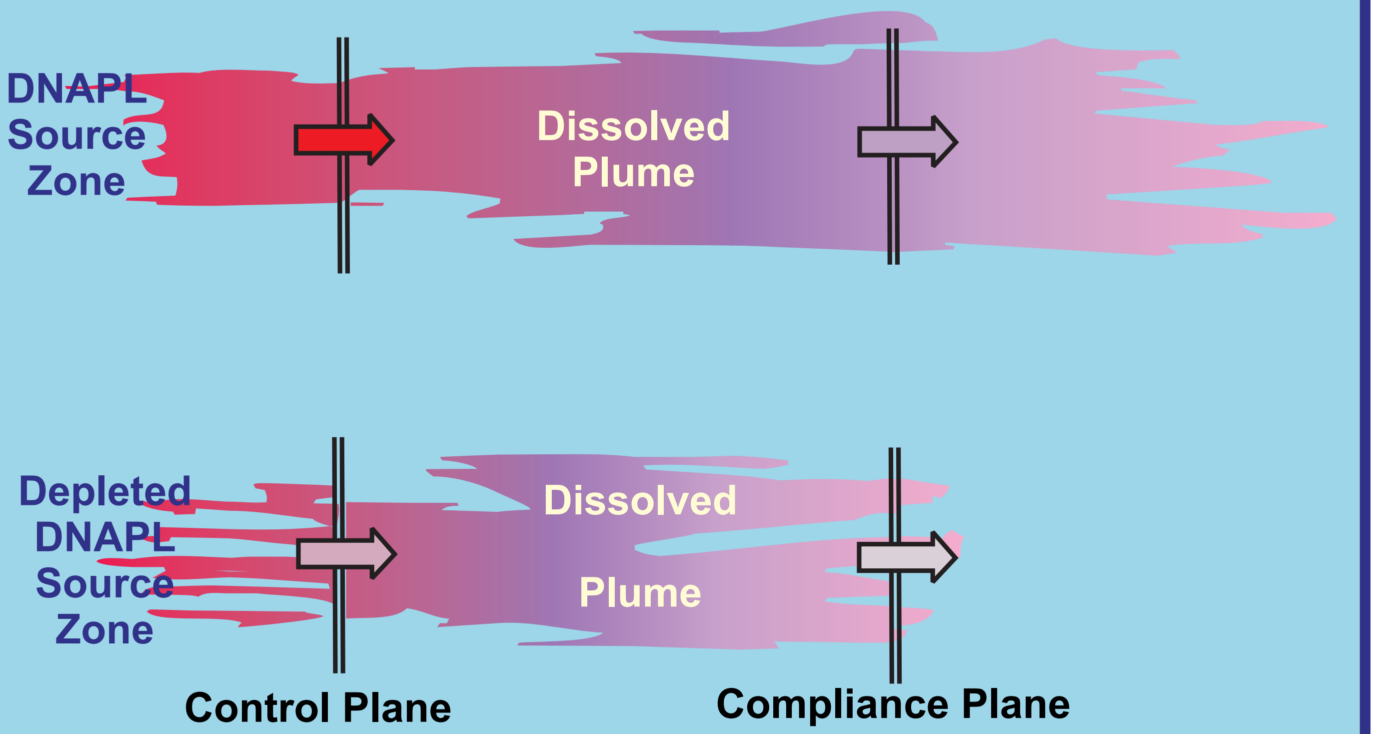
The DNAPL Remediation Challenge: Is There a Case for Source Depletion?



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The DNAPL Remediation Challenge:
Is There a Case for Source Depletion?

by

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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments, and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

At many hazardous waste sites contaminants reside in the subsurface as separate dense non-aqueous phase liquids (DNAPL). These DNAPL serve as persistent sources of dissolved phase contamination and are a major impediment to successful and cost-effective cleanup of sites. Commonly used pump-and-treat remediation systems have not been effective in removing DNAPL from these subsurface source areas or in restoring down-gradient contaminated groundwater to desired levels of cleanliness. However, field-scale research has demonstrated that a high percentage of the DNAPL mass can be removed by implementing aggressive *in-situ* technologies such as thermal or chemical flooding. These studies have shown that while a significant fraction of the DNAPL mass can be efficiently removed in a short period, the efficiency of DNAPL extraction often decays exponentially with increasing mass removal. As a result, there is currently no consensus in the academic, technical and regulatory communities on the ecological or environmental benefits of DNAPL source treatment or on the appropriate metrics for quantifying these benefits. To provide technical guidance regarding these critical environmental issues the US EPA convened a panel of national and international scientists and practitioners to conduct a critical, independent review of DNAPL remediation issues. This document contains the findings and recommendations of the panel. This report does not necessarily represent Agency views or policies and should not be interpreted as such. However, the information may be useful in developing appropriate research strategies and plans for solving this important environmental problem.

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Acknowledgments

This document was a joint effort of the Expert Panel on DNAPL Source Remediation consisting of the following members appointed by U.S. EPA.

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The Panel also wishes to acknowledge the thoughtful and constructive criticisms provided by reviewers selected by the U.S. EPA. While the Panel was commissioned and funded by the U.S. EPA, who also defined its general charge, the views expressed in this report reflect only the views of the Panel members, and not the official views of EPA or any other government agency, or Dynamac Corporation.

The Panel Co-Chairs extend their thanks to the Panel members for engaging in spirited debates about contentious issues, for providing insights based on their considerable experience and expertise, and for contribution and review of written material that formed the basis for the final report. The Panel Co-Chairs served as the editors for the final version, and made an attempt to represent divergent views on some topics when consensus could not be reached.

Executive Summary

Introduction

Releases of Dense Non-Aqueous Phase Liquids (DNAPLs) at a large number of public and private sector sites in the United States pose significant challenges in site remediation and long-term site management. Extensive contamination of groundwater occurs as a result of significant dissolved plumes generated from these DNAPL source zones that vary in size and complexity depending on site characteristics and DNAPL properties and distribution. Risk and liability management, consistent with regulatory compliance requirements, could involve remediation of the *source zone* as well as management of the dissolved plume. The *source zone* is defined here as the groundwater region (volume) in which DNAPL is present as a separate phase, either as randomly distributed sub-zones at residual saturations or "pools" of accumulation above confining units and includes the volume of the aquifer that has had contact with free-phase DNAPL at one time, but where all of the DNAPL mass is now present only in the dissolved or sorbed phases or diffused into the matrix in fractured systems. Over the past two decades, innovations in site characterization and remediation technologies have been developed and deployed at DNAPL sites. Several in-situ technologies are available which can achieve substantial DNAPL source depletion either by extraction or destruction. However, because of the risk of failure in achieving certain regulatory targets after implementing a source-depletion technology (e.g., MCLs in the source zone), combined with uncertainties in site characterization (i.e., the location and amount of DNAPL in groundwater at a site), in forecasting potential benefits and adverse impacts of partial source depletion, in prediction of life cycle costs, and uncertainties regarding the acceptability of alternative clean-up levels, many site owners have been reluctant to undertake aggressive source-depletion technologies. Thus, at the majority of DNAPL sites, containment of the source zone and/or management of the dissolved plume for cost-effective risk/liability reduction and regulatory compliance have been the dominant strategies of choice.

Charge to the Panel

As the continued annual costs and uncertainties associated with long-term management of DNAPL sites become more apparent, a reassessment of the factors controlling decisions on whether to implement DNAPL source depletion actions is needed. The long-term cost, reliability, and institutional requirements of the containment strategy for DNAPL source zones are thus topics of current scientific and policy debates, which provided the primary impetus for the U.S. Environmental Protection Agency (U.S. EPA) to establish an Expert Panel on these issues. In the summer of 2001, U.S. EPA formed an Expert Panel ("Panel") consisting of twelve recognized experts on DNAPL fate and transport and DNAPL site remediation to examine four specific issues regarding DNAPL source-zone treatment and management:

A. Status of technology development and deployment for DNAPL source remediation.

B. Assessment of source remediation performance goals and metrics.

C. Evaluation of costs and benefits of source remediation.

D. Research issues and needs.

In order to gather technical information and diverse views, the Panel participated in a two-day workshop involving Panel members and other invited experts (October 19 – 20, 2001; Dallas, TX), and then the Panel met for two days (February 2002; Orlando, FL) to deliberate. The Panel's discussions resulted in the identification of seven questions that cover three of the four issues for which EPA had sought guidance. Charge D, Research Issues and Needs, is addressed directly in Section 4.0 of this Report. These questions are as follows:

1. What are the potential benefits and the potential adverse impacts of DNAPL source depletion as a remediation strategy? (Charges A and C)
2. What are the appropriate performance metrics for assessment of DNAPL source depletion technologies? (Charge B)
3. Are available technologies adequate for DNAPL source characterization to select and evaluate depletion options? (Charges A and B)

4. What performance can be anticipated from source-zone mass depletion technologies? (Charge A)
5. Are currently available tools adequate to predict the performance of source depletion options? (Charges A and C)
6. What are the factors restricting the effective and appropriate application of source depletion technologies? (Charge A)
7. How should the decision be made whether to undertake source depletion? (Charge C)

Potential Benefits and Adverse Impacts of DNAPL Mass Depletion in the Source Zone

The potential benefits of DNAPL source depletion have been the subject of significant on-going technical and policy debates. Private site owners generally weigh remedies in terms of their risk management benefits and potential for reducing the total life-cycle cost to achieve site closure, assuming that the remedies under consideration meet all regulatory requirements for protection of human health and the environment. Government site owners, such as the Department of Defense (DOD), the Department of Energy (DOE), and EPA Superfund-lead sites generally follow a similar process, although the details of the remedy selection process may differ from decision processes at private sector sites, particularly with respect to assumptions regarding site institutional controls and the time value of money.

Regardless of the site owner, there is a range of benefits, from a risk management perspective, that may result from DNAPL source-zone depletion. These include explicit benefits such as: 1) mitigating the future potential for human contact and exposure through long-term reduction of volume, toxicity, and mobility of the DNAPL, 2) mitigating the future potential for unacceptable ecological impacts, 3) reducing the duration and cost of other technologies employed in conjunction with the source removal technology, and 4) reducing the life-cycle cost of site cleanup. These benefits can be achieved if the source depletion option can result in the following outcomes: 1) reduction of DNAPL mobility, if mobile DNAPL is present, 2) reduction in environmental risk to receptors; 3) reduced longevity of groundwater remediation, and 4) reduction of the rate of mass discharged from the DNAPL source zone. These outcomes could then lead to enhanced efficiency of complimentary technologies used for groundwater remediation as well as potential reduction in life-cycle costs. Implicit benefits of DNAPL source-zone depletion include: 1) minimizing risks of failure of long-term containment strategies, 2) mitigating public stakeholders' concerns, 3) enhancing a company's “green image” as stewards of the environment, and 4) minimizing future uncertain transaction costs associated with management of the site.

Adverse impacts of DNAPL source depletion could include: 1) expansion of the DNAPL source zone due to mobilization of the residual DNAPL, 2) undesirable changes in the DNAPL distribution (i.e., DNAPL architecture), and 3) undesirable changes in the physical, geochemical and microbial conditions that may cause long-term aquifer degradation, and/or may adversely impact subsequent remediation technologies. All of these adverse impacts could increase life-cycle costs of site cleanup.

Quantitative predictions of these potential benefits and adverse impacts to aid decision making on whether to implement DNAPL source depletion actions are highly uncertain. These uncertainties remain as significant barriers to more widespread use of source depletion options.

Appropriate Metrics for Performance Assessment

The Panel assessed the technical basis for using drinking water standards, such as Maximum Contaminant Levels (MCLs), as the single performance goal for successful DNAPL source-zone remediation and the use of chemical analyses in groundwater samples from monitoring wells as the primary metric by which to judge performance of groundwater remediation systems. Although an MCL goal may be consistent with prevailing state and federal laws for all groundwater considered a potential source of drinking water and is a goal that is easily comprehended by the public, this goal is not likely to be achieved within a reasonable time frame in source zones at the vast majority of DNAPL sites. Thus, the exclusive reliance on this goal inhibits the application of source depletion technologies because achieving MCLs in the source zone is beyond the capabilities of currently available in-situ technologies in most geologic settings.

In recent years, there has been a trend towards the adoption of a more pragmatic regulatory approach by some regulatory agencies that are considering alternate or intermediate performance goals and phased remedial action approaches for cleanup of contaminated sites. Such flexibility may result in implementing alternative strategies for groundwater cleanup, including: 1) establishment of management zones where cleanup goals other than drinking water standards may be applied, 2) groundwater classification schemes that permit alternative remedial action goals, and 3) other flexible regulatory approaches that do not impose non-degradation requirements or drinking water standards in DNAPL source zones. These new federal and state regulatory policies provide a more encouraging climate for implementation of innovative source-depletion technologies, in those situations where partial depletion of DNAPL sources is deemed an intermediate goal as a part of phased site cleanup.

In addition to alternative goals applied to DNAPL source zones, alternative metrics other than single-point measurements from groundwater monitoring wells should also be considered. One of the alternative metrics for judging the performance of source-mass depletion technologies is contaminant mass discharge, defined as the summation at a point in time of point values of contaminant mass flux (mass per time per area) across a vertical control plane encompassing the plume and perpendicular to the mean groundwater flow direction at a location downgradient of the DNAPL source zone. Both theoretical analyses and limited field data indicate that partial DNAPL mass depletion in the source zone reduces contaminant mass discharge. The magnitude and timing of such reduction are strongly governed by the site hydrogeology, the contaminant mass distribution (DNAPL and non-DNAPL masses), and the type and method of application of the source-depletion technology. Because a sufficient knowledge base does not yet exist to specify the level of mass discharge reduction needed to achieve site-specific benefits, such as risk reduction and reduction of the time lag between source remediation and mass discharge reduction, additional research will be necessary before this metric can be used to quantify the benefits of DNAPL source depletion.

Adequacy of Site Characterization Technologies

Site characterization tools are available to measure most of the performance metrics discussed. Because of the inherent complexities of DNAPL migration and distribution in subsurface environments, none of the available characterization tools is without limitations on suitability and accuracy. The current status of site characterization tools has been thoroughly reviewed in the literature, and several recent summaries provide adequate information for selection of the appropriate site characterization tools for the purposes of selection, design, and performance assessment of DNAPL source depletion technologies.

The Panel concluded that available technologies are adequate to locate and delineate the suspected DNAPL source zones. However, in practice, locating the DNAPL source zone and determining the actual mass and spatial distribution of the DNAPL mass is very difficult, and will only be possible with extensive sampling at the majority of sites. The cost and level of accuracy achievable by source-zone characterization tools can only be answered on a site-specific basis. Further investment by EPA and other governmental agencies in determining the level of accuracy required for source-zone characterization tools as a function of subsurface geologic conditions, DNAPL characteristics and distribution, and a specific DNAPL depletion technology is warranted.

New techniques for monitoring groundwater flow and contaminant mass flux and mass discharge rate have been developed, but to date, these methods have not been field tested at sufficiently diverse sites. Further guidance on the reliability, accuracy, and cost of mass flux and mass discharge rate monitoring techniques may be forthcoming based on research funded by DOD and other agencies.

Performance of Source-Zone Mass Depletion Technologies

Over the past two decades, a large body of information has been developed on the performance of source-zone mass depletion technologies. Hundreds of pilot-scale site trials using innovative in-situ technologies have been conducted in DNAPL source zones, although a much smaller number of full-scale source depletion projects have been reported. In addition, various federal (EPA, DOE, DOD) and state agencies (e.g., Interstate Technology Regulatory Council, "ITRC") have compiled information on source depletion technologies and case studies of the application of DNAPL source depletion technologies, and this information is available on the respective web sites of these organizations. Additional information on the cost and effectiveness of source-zone depletion technologies is expected within the next year based on reported surveys conducted by the U.S. Navy (at over 170 sites) and the ITRC committee on DNAPL source remediation case studies.

Many of these studies report that substantial quantities of DNAPL mass have been removed from the subsurface. A few case studies are included in this Report where Panel members had first-hand knowledge. Based on this body of knowledge, the Panel concluded that several technologies are sufficiently developed and ready for deployment at DNAPL-impacted sites. These include thermal technologies, in-situ surfactant/cosolvent flushing, and in-situ chemical oxidation. In-situ biodegradation is the one technology evaluated that is still in an early developmental stage although even this technology has been implemented as a final remedy at several DNAPL sites. Combinations of different source depletion technologies have also not been widely tested or evaluated.

Although the Panel did not have the resources to evaluate this information on technology performance and costs in detail, it is clear that large quantities of DNAPL can be removed from source zones, with the magnitude of the removal highly dependent on site-specific and technology-specific factors. However, it is highly uncertain that MCLs can be achieved in source zones impacted with DNAPLs in most geologic settings. Nonetheless, a number of DNAPL sites have received no further action letters, indicating that regulators were satisfied that the remedial action objectives had been achieved in the source zone. It is clear that site closure of DNAPL-impacted sites may be possible depending upon site conditions, but such cases may be the exceptions rather than the rule at this time.

Source-zone containment has been a goal adopted at a large number of DNAPL sites, and groundwater pump-and-treat, cut-off walls, or permeable reactive barriers have been effectively implemented. In the long term, containment has the disadvantage of requiring continued maintenance of effectiveness and the associated perpetual financial burden. In addition, long-term effectiveness of the containment strategies is not assured. The Panel found only a few case studies where rigorous monitoring data have been used to assess the benefits of source containment for long-term plume management.

Although source depletion technologies are capable of removing substantial amounts of the DNAPL in source zones at sites with favorable hydrogeologic conditions (i.e., less heterogeneous and more permeable subsurface conditions), achievement of drinking water MCLs in these source zones as well as source zones in more challenging heterogeneous hydrogeologic conditions (e.g., bedrock, karst systems, multiple stratigraphic units) is unlikely. However, these technologies are capable of achieving partial DNAPL depletion, which may provide other performance benefits, including eliminating the mobility of the DNAPL, and reduction in the mass discharge rate of DNAPL constituents from the source zone, which may reduce environmental risks and life cycle costs.

Factors Limiting Application of Source Depletion Technologies

Several obstacles have prevented widespread application of source-zone depletion technologies. These include: 1) setting of remedial action objectives (such as achieving MCLs in the source zone) that are likely to be technically impractical within a reasonable time frame, 2) uncertainty of the long-term effectiveness and cost of source depletion and length of time before site closure, 3) the lack of well-documented case studies that could reduce the uncertainties regarding the effectiveness of source depletion technologies, 4) lack of availability of insurance to mitigate the risks of failure of source-zone remedial actions, and 5) the limited number of technology vendors, which adds to uncertainties of cost, risk of failure, and risk of bankruptcy by the vendor. An additional uncertainty at most sites is the fraction of the contaminant mass in the DNAPL source zone that may be present in diffusion-controlled, low-permeability zones. If the metric for successful remediation is achievement of MCLs, the source depletion goal must include depletion of the dissolved and sorbed phase mass in addition to the DNAPL mass. In-situ technologies for source-zone depletion are generally limited in their ability to remove contaminant mass from these low-permeability zones; however, thermal technologies may overcome this limitation at some sites. On the other hand, it is likely that continued release of contaminants from these low-permeability zones will be at mass discharge rates substantially lower than those prior to source depletion. Whether this reduction in source-zone mass discharge would be sufficient to warrant implementation of the source depletion technology is not currently predictable, and remains an important research topic.

Adequacy of Tools to Predict Performance

Reliable (validated) modeling codes and decision tools along with associated data are not currently available to: 1) predict the performance of DNAPL source-zone remediation technologies, 2) predict the beneficial and adverse impacts after the remediation is attempted, and 3) guide the decision process for selecting technologies or end points. The Panel concluded that quantification of explicit benefits, such as the reduction of risks and cost liabilities after partial source depletion, is an exceptionally difficult task and that much of the difficulty results from the inherent uncertainty in determining the magnitude and distribution of the DNAPL source zone mass prior to remediation.

Uncertainties in predicting remedial performance, life cycle costs, and benefits confound both economic and technical analyses and comparison of technical options for DNAPL source-zone depletion. A strategy for achieving benefits from partial source mass depletion would be to reduce contaminant mass discharge to a level less than the natural attenuation capacity within the dissolved plume. Under such conditions, the contaminant mass discharge for the DNAPL constituents becomes less than the rate of contaminant degradation in the plume and, as a result, the plume gradually shrinks until a new, smaller steady state plume is achieved. Such a strategy is most likely to be beneficial for small DNAPL source zones at sites that are inactive. However, at many chlorinated solvent sites, natural attenuation by microbial degradation is ineffective because of inadequate microbial and geochemical conditions in the plume, and modifications of these conditions will be necessary to achieve acceptable degradation rates or dispersion to be protective of potential receptors.

On Making the Decision to Undertake Source Depletion

The Panel recognizes that the decision to implement source-zone depletion technologies for DNAPL site remediation is based on highly site-specific conditions and criteria, and that numerous regulatory, technology, and stakeholder factors must be considered. The current decision process, as practiced in the U.S., has generally resulted in selection of containment over source depletion. The Panel concluded that new approaches to this decision process are needed. Therefore, the Panel considered two distinct options for developing an improved decision analysis framework: one based on a qualitative, semi-empirical analysis, and the other based on a quantitative model-based analysis. The Panel recognizes that neither of these options has been formally used at DNAPL sites for decisions on whether to implement source-depletion technologies, but the Panel urges EPA to consider the utility of qualitative approaches as a screening level tool for evaluating the appropriateness of source depletion compared to containment, and to assess the feasibility of developing a quantitative model that can account for a broad range of potential costs, benefits, and negative impacts from implementing DNAPL source-depletion technologies.

Knowledge Gaps and Research Needs

The Panel found that although much information on DNAPL source depletion has been developed, knowledge gaps still exist regarding the effectiveness and cost of these technologies for DNAPL source removal in a wide range of hydrogeologic settings. Research is needed on the following topics: 1) development, verification, and comparison of alternative technologies for measuring mass flux and mass discharge from DNAPL source areas before and after source depletion, 2) development of improved predictive tools to estimate the benefits and adverse effects of partial source depletion for a range of DNAPL treatment technologies and DNAPL distribution and geologic scenarios, 3) continued field testing of DNAPL source-depletion technologies incorporating more than one technology (e.g., thermal, in-situ flushing, or in-situ chemical oxidation combined with biodegradation), 4) development of guidance on the conditions in which source depletion is not likely to be an effective strategy, 5) assessment of the long-term water quality impacts of source-depletion technologies, and 6) development of quantitative decision analysis tools that will permit an accounting of all potential costs, benefits, and adverse impacts of partial DNAPL source depletion.

A key knowledge gap is estimating the fraction of the total universe of DNAPL-impacted sites that would benefit from partial DNAPL depletion from the source zone. The Panel consensus was that partial DNAPL source depletion will have benefits at a portion of DNAPL-impacted sites, but the Panel did not have sufficient information to reach consensus, and was not willing to speculate. Resolution of this knowledge gap is a major research need and would provide the necessary foundation for expanded support of research and development programs on the issues raised in this Report. In the meantime, market forces and regulatory mandates will likely determine the extent to which DNAPL source-zone depletion technologies will be applied.

In the past decade, major advances have been made in technologies for characterization and performance assessment of remedial actions of DNAPL source zones, but there is need for additional advances. Part of the cost of applying an innovative technology for source mass depletion includes the cost of additional site characterization needed for technology selection and remedial design based on the choice of performance metrics. A major challenge is the identification of the degree of characterization and post-remediation monitoring necessary for effective application of each of the in-situ source depletion technologies. Research is needed to establish guidance for practical source-zone characterization keyed to the available technologies.

Conclusions

In the final analysis, the Panel concluded that partial mass depletion from DNAPL source zones has been a viable remediation strategy at certain sites and is likely to provide benefits at a number of additional sites. However, barriers to more widespread use of DNAPL source-zone technologies persist. Additional theoretical analysis and assessment tools (performance prediction tools; cost-benefit assessment tools; technology failure analysis; reliability of long-term management), improved monitoring techniques (site characterization; performance assessment), and field scale demonstrations that elucidate benefits of partial source depletion are needed to provide a more informed basis for decision-making on whether to undertake DNAPL source-zone depletion at both sites with a containment remedy in place and at new DNAPL sites. This information will also provide a basis to estimate the proportion of DNAPL-impacted sites that would be candidates for implementation of source-depletion technologies. At some DNAPL sites, containment may be the only viable remedial action, and at such sites, containment may be considered a “presumptive remedy” eliminating the need for costly additional studies. The Panel urges EPA to provide appropriate guidance for defining the conditions under which DNAPL source remediation would be a viable option for site cleanup compared to a containment-only option using the broader definition of benefits of this strategy as discussed in this Report.

The current strategy of source-zone containment has generally proven reliable for limiting routes of human and ecological exposure to chemical contaminants emanating from DNAPL-impacted sites, provided that the containment system (e.g., pump-and-treat, or permeable barriers) has been properly designed and maintained. However, this strategy poses long-term risks, transfers the burden of site management to future generations, and requires long-term financial stability of the responsible parties. Furthermore, these long-term risks are generally difficult or impossible to quantify accurately. It is thus imperative that sufficient resources be devoted to resolving the many uncertainties that this Panel has identified in DNAPL source-zone characterization and depletion technologies to ensure that source depletion at DNAPL sites is implemented to the maximum extent practicable.

Recommendations

The Panel’s specific recommendations to EPA are as follows:

1. Expand the existing EPA program for research, demonstration projects, and technology transfer to address and reduce the uncertainties in predicting and verifying the benefits and undesirable impacts from application of DNAPL source-zone depletion technologies.

2. Continue to support demonstration efforts to develop, test, and validate the most promising innovative and emerging technologies for DNAPL source-zone characterization and mass depletion.
3. Develop a new guidance document for source-zone response actions at DNAPL sites that provides a road map for decision makers to determine if implementation of source depletion technologies is appropriate.
4. Conduct a thorough and independent review of a selected number of DNAPL sites where sufficient documentation is available to assess the performance of source depletion using multiple metrics.
5. Develop and validate technologies for cost-effective and accurate measurement of mass flux and mass discharge from DNAPL source zones, and determine how these measurements relate to risk management decisions.
6. Evaluate impacts of source depletion technologies on long-term aquifer water quality.
7. Develop and validate cost-minimization and net benefit-maximization decision models suitable for evaluating the complete spectrum of costs, benefits, and negative impacts of source-depletion technologies.

1.0 Introduction

1.1 Background

It is well recognized by stakeholders that remediation of soil and groundwater contaminated by organic chemicals in the form of dense non-aqueous phase liquids (DNAPLs) represents major technical, economic, and institutional challenges. While the consequences of DNAPL releases on groundwater quality are easily observed and have been widely documented, the characterization and remediation of DNAPLs in groundwater remain problematic. At most sites, characterization of the location, distribution, and amount of DNAPL causing continued groundwater contamination is difficult, and often inaccurate. Removal or in-situ destruction of DNAPL, even when reasonably well characterized, has proven difficult in saturated zones with any significant degree of heterogeneity.

Since the early 1980s, the U.S. Environmental Protection Agency (U.S. EPA), the Department of Energy (DOE), the Department of Defense (DOD), and various private organizations have recognized that DNAPL site remediation entails significant technical challenges. For example, through fundamental and applied research directed by the Robert S. Kerr Environmental Research Center, in Ada, Oklahoma, the U.S. EPA prepared numerous technical guidance documents to advise stakeholders on characterization and remediation of DNAPL sites (*U.S. EPA, 1994, DNAPL Site Characterization Quick Reference Fact Sheet, EPA/540/F-94/049*). In addition to relevant guidance documents, EPA also developed policy guidance in recognition of the technical challenges confronting cleanup of DNAPL sites. The technical impracticability (TI) guidance document published in 1993 provided EPA's recommended approach for assessing the feasibility of meeting established performance goals at Superfund and RCRA sites where remediation was considered impracticable from "an engineering perspective, taking cost into consideration" (*U.S. EPA, 1993, TI Guidance Document*). However, since 1990 this policy instrument has been infrequently used and as of this date, only 48 TI waivers have been granted from a universe of approximately 1,500 Superfund sites. The number of TI applications over this period is unknown. Nonetheless, many Records of Decision at Superfund sites include containment remedies and as such likely contain analyses that are consistent with the technical bases presented in the TI guidance.

In 1994, a committee established by the National Research Council prepared a report on *Alternatives for Groundwater Cleanup (NRC, 1994*) summarizing the research knowledge and practical experiences of the past two decades on the use of the so-called "pump-and-treat" technology, the dominant approach at that time to remediation of groundwater contaminated by DNAPLs. Groundwater sites impacted by DNAPL were considered to be the most difficult sites to remediate, and at that time, none of the known or suspected DNAPL sites had achieved required cleanup levels.

While significant technical advances in DNAPL site characterization and remediation technologies have been achieved, there is still a lack of consensus regarding the ability of available technologies to achieve groundwater remediation performance goals at DNAPL sites within a reasonable time frame and at a cost commensurate with perceived benefits or risk reduction. In particular, there is a lack of consensus regarding the appropriateness of applying intensive and often costly remediation technologies for DNAPL extraction or destruction in the source zone, if such partial mass removal will not have a quantifiable and substantial impact on the duration and life-cycle cost of a containment remedy, such as pump-and-treat. Given the uncertainties associated with the application of innovative technologies and the risk of inadequate performance, combined with the difficulties of predicting the benefits of partial DNAPL source depletion, many potentially responsible parties in both the private sector (industry) and the public sector (government) are reluctant to undertake intensive source-zone remediation.

The current practical consequence of this lack of consensus is that for the vast majority of groundwater-contaminated sites where DNAPL is suspected or known to be present, site remediation strategies are dominated by containment technologies, coupled with long-term monitoring. This strategy has been effective at limiting the spread of contaminants at these sites and significantly reducing the risk of human and ecological exposures to these chemicals, but the failure to remove the DNAPL source from the groundwater requires that both long-term institutional controls and assurances of sufficient financial resources to maintain these controls must be in place. Stakeholder concerns over the long-term stability of these engineering and/or institutional controls, coupled with continuing issues related to natural resource damage claims, continue to provide a powerful incentive for improving our capabilities to remove or destroy DNAPLs found in soil and groundwater.

1.2 Expert Panel Formation

In the context of this debate regarding DNAPL source remediation, EPA, through its Ground Water and Ecosystems Restoration Division (GWERD), formed a DNAPL Expert Panel (“Panel”) to advise EPA on a number of key issues related to remediation of DNAPL source zones. The members of the Expert Panel and their affiliations are shown in Table 1-1, and short biographical sketches of the Panel members are included in Appendix B.

In the summer of 2001, the U.S. EPA’s Robert S. Kerr Environmental Research Center in Ada, Oklahoma, organized the Panel to provide independent advice to EPA on a series of issues regarding DNAPL source remediation. These four issues included the following:

A) Status of technology development and deployment for DNAPL source remediation.
B) Assessment of source remediation performance goals and metrics.
C) Evaluation of costs and benefit of source remediation.
D) Research issues and needs.

Table 1-1 Panel Participants

Name	Affiliation
Kavanaugh, Michael, Panel Co-Chair *mkavanaugh@pirnie.com*	Malcolm Pirnie, Inc.
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Udell, Kent *udell@me.berkeley.edu*	University of California, Berkeley

The Panel first participated in a two-day workshop organized by Dynamac Corporation for EPA in October 2001 in Dallas, Texas. The agenda for the two-day workshop is also included in Appendix C**,** and a list of attendees is included in Appendix D. Subsequently, the Panel held a two-day meeting in Orlando, Florida, in February 2002. The Panel decided at that meeting to define the technical issues as "DNAPL source-zone depletion" reflecting the general consensus that although complete or 100 percent DNAPL removal from source zones in the saturated zone is technically impracticable at all sites, partial DNAPL source depletion may be sufficient to meet site-specific remedial action objectives. In response to the charges from EPA to address the four key issues, the Panel generated a series of questions summarized in Table 1-2. Shown also in this table is the relationship between the questions posed and three of the four issues presented by EPA. Charge D, Research Needs, is the focus of Section 4.0 in the Report.

Table 1-2 Questions

Question 1: What are the potential benefits and potential negative impacts of DNAPL source depletion as a remediation strategy? *(Charges A and C)*

Question 2: What are the appropriate performance metrics for evaluation of source depletion technologies? *(Charge B)*

Question 3: Are available technologies adequate for DNAPL source characterization to select and evaluate source depletion options? *(Charges A and B)*

Question 4: What performance can be anticipated from source-zone mass depletion technologies? *(Charge A)*

Question 5: Are currently available tools adequate to predict the performance of source depletion options? *(Charges A and C)*

Question 6: What are the factors restricting the effective and appropriate application of source depletion strategies? *(Charge A)*

Question 7: How should the decision be made whether to undertake source depletion? *(Charge C)*

1.3 Organization of the Report

Based on review of the information provided at the October workshop, the knowledge and experience of the Panel members, and results of the Panel process, the Panel has prepared the following Report to the U.S. EPA ("Report"). To ensure common understanding in discussing DNAPL source remediation, Section 2.0 of this Report begins with an overview of the DNAPL problem. Section 3.0 presents the Panel's response to the seven questions generated to address each of the four issues raised by EPA in the charge to the Panel. In general, except where noted, these responses represent a consensus of the Panel. The final two sections of the Report summarize knowledge gaps and research needs, Section 4.0 (Charge D) and provide the Panel's conclusions and recommendations to EPA (Section 5.0).

2.0 Problem Description

2.1 DNAPLs as a Source of Groundwater Contamination

Dense Non-Aqueous Phase Liquids (DNAPLs) are water-immiscible organic liquids with a density greater than that of water at ambient temperature and pressure. The most prevalent types of DNAPLs are the halogenated organic solvents (including trichloroethene, "TCE", and tetrachloroethene, "PCE"), but many sites are contaminated with other types of DNAPLs including coal tar and creosotes (complex hydrocarbon mixtures consisting of polycyclic aromatic hydrocarbons and other aromatic hydrocarbons), polychlorinated biphenyl (PCBs), and certain pesticides (*Cohen and Mercer, 1993*). Numerous references provide detailed information on the physical and chemical properties of DNAPLs (e.g., *Hunt et al., 1988; Mercer and Cohen, 1990; Cohen and Mercer, 1993; Pankow and Cherry, 1996; and U.S. EPA, 1991*).

Although there was broad recognition of groundwater contamination from chlorinated solvents in the 1970s and early 1980s, the crucial role of DNAPLs as the primary source of this contamination was overlooked until the mid-1980s. The pioneering work on the fate of DNAPLs in the subsurface conducted by Schwille and his colleagues in Germany set the stage for an explosion in our understanding of the role of DNAPLs in groundwater contamination (*Schwille, 1988*). Pankow and Cherry (*1996*) provide a comprehensive history of the growth of knowledge regarding the role of DNAPLs in groundwater contamination. Since the early 1990s, however, the significance of the presence of DNAPL on the effectiveness of groundwater remediation has been fully recognized.

As is now well understood, the physical, chemical, and biotic degradation properties of DNAPLs determine the threats that such organic chemicals pose to the environment (*Pankow and Cherry, 1996*). DNAPLs can migrate relatively easily in the saturated zone under gravity forces, penetrate deeply into aquifers, and in some cases, travel substantial horizontal distances away from the original source area. Rates of migration are dependent on the properties of the DNAPLs (viscosity, density, interfacial tension), and the geologic characteristics of the subsurface (e.g., see *Pankow and Cherry, 1996*, for a review of the physics of DNAPL flow in various subsurface environments). DNAPLs exhibit relatively low aqueous solubility (typically in the milligrams per liter range or parts per million [ppm]), but the solubility levels generally exceed drinking water standards (typically in the microgram per liter range or parts per billion, ppb) by several orders of magnitude. Some DNAPL compounds, such as chlorinated solvents, are relatively volatile in pure phase, and can thus partition into soil gas, causing further migration of those DNAPL constituents in the vadose zone, and posing potential threats to air quality in confined spaces, an issue that has received national attention and has been addressed in recent regulatory guidance (see for example, http://www.epa.gov/epaoswer/hazwaste/ca/eis/vapor.htm).

DNAPL constituents slowly partition into the aqueous phase *(Eberhardt and Grathwohl, 2002)*, usually under mass transfer controlled conditions *(see e.g., Frind et al., 1999*) thus causing the development of a dissolved groundwater contaminant plume. In addition, under natural biogeochemical conditions found within dissolved plumes at most sites, chemical constituents of some DNAPLs (chlorinated solvents such as PCE and TCE) do not easily or rapidly degrade either biotically or abiotically. As a consequence, large and relatively mobile plumes of these chemicals will form and can migrate significant distances from the location of the original DNAPL release(s). Partial (biotic/abiotic) degradation of chlorinated solvents can transform the parent compound to by-products that are potentially of greater environmental concern (e.g., vinyl chloride and DCE). For coal tars and creosote DNAPLs, the primary constituents of concern are the polyaromatic hydrocarbons (PAHs), with a broad range of solubilities and susceptibility to biological degradation.

2.2 Magnitude of the Problem

Although DNAPL contamination of soil and groundwater is now widely recognized, there are few studies that have bounded the magnitude of the problem. EPA analyses (*U.S. EPA, 1993*) suggest that DNAPL is present at approximately 60 percent of Superfund sites where organic chemicals have been detected. However, the presence of DNAPLs is rarely observed directly, and must be inferred by comparing the maximum levels detected in soil or groundwater samples to the effective solubility in water or the residual saturation in soil of the DNAPL chemical of concern. It is probable, however, that DNAPLs are present at many sites where DNAPL constituents have been detected even with maximum concentrations in samples taken from groundwater monitoring wells below one percent of the effective aqueous solubility, which is generally used as a rule of thumb to infer the presence of the DNAPL at a site (*Feenstra and Cherry, 1988; U.S. EPA, 1992*). It should be noted that this widely used rule-of-thumb has no fundamental theoretical basis, but it is consistent with empirical observations and the impacts of dispersion on concentrations of chemicals dissolving from a DNAPL into water flowing past the material. Nonetheless, the presence of organic contaminants at levels below or above this threshold may or may not demonstrate the presence of DNAPLs.

The NRC study (*NRC, 1994*) on *Alternatives for Groundwater Cleanup* summarized various published estimates on the number of sites in the U.S. where groundwater was likely contaminated. The estimated number of sites with suspected groundwater contamination, excluding leaking underground storage tanks, which primarily contain petroleum hydrocarbons, ranged from 30,000 to 50,000 sites (*NRC, 1994*). For example, the State Coalition for Remediation of Drycleaners estimates that up to 75 percent of the 36,000 active dry cleaning establishments in the U.S. have experienced releases of PCE or other dry cleaning solvents (http://www.drycleancoalition.org/pubs.cfm "Conducting Contamination Assessment Work at Drycleaning Sites"). If one assumes that approximately 80 percent of the 30,000 to 50,000 sites with impacted groundwater are contaminated with organic chemicals, and of those organic chemicals, approximately 60 percent are DNAPLs as estimated by EPA, the total number of DNAPL impacted sites in the U.S. could range from 15,000 to 25,000 sites.

The annual and life cycle costs to remediate the DNAPL sites could be quite high. Currently, at the majority of these sites, hydraulic containment using the conventional groundwater pump-and-treat technology is the dominant remedial technology of choice, without implementation of source depletion technologies. If pump-and-treat technologies remained in operation, or were applied to all DNAPL sites in the future, annual costs would be substantial. Based on data collected by EPA (*U.S. EPA, 1999a*), and on the experience of Panel members (see also, *NRC, 1994*), annual costs for operation and maintenance of pump-and-treat systems range from $30,000 to $4,000,000 per year, with a median value of roughly $180,000 (1999 dollars) per site, based on the EPA 28 Site Study (*U.S. EPA, 1999a*). Thus, using this median value, annual O&M costs for the 15,000 to 25,000 sites in the U.S. with DNAPL contamination could range from $2.7 to $4.5 billion dollars per year if all sites relied on groundwater pump-and-treat only as a containment remedy. The total life cycle costs for this remediation strategy depend on assumptions of equipment replacement frequency and costs and the net discount rate. The estimated life cycle costs for cleanup of DNAPL sites, assuming a net present value estimate based on 30 years of operation, would range from $50 to $100 billion dollars for discount rates ranging from 5 to 10 percent. *(It should be noted that the discount rate in public sector accounting could be as low as 3.9 percent compared to private sector present value discount rates ranging up to 12 percent)*.

Although a precise estimate of the total life cycle costs for remediation of DNAPL sites using a containment strategy is lacking, these order of magnitude estimates clearly show that the cleanup of groundwater DNAPL sites will require significant annual expenditures for the next several decades if hydraulic containment is the dominant strategy for groundwater remediation at these sites. These order of magnitude cost estimates suggest that development or implementation of existing and emerging source-depletion technologies could potentially reduce this annual liability by depleting the DNAPL source zone, resulting in reductions in life-cycle costs at those DNAPL sites with a containment remedy in place such as groundwater pump-and-treat as well as at those sites where no remedial actions have yet been selected. In addition to potential cost savings, source depletion would provide other benefits to site owners and the public, as discussed subsequently in this report.

2.3 Regulatory Framework

Among the principal drivers for undertaking remedial actions at groundwater sites contaminated with DNAPLs are federal and state statutes that have established methodologies for setting cleanup standards at sites managed under various regulatory regimes (see e.g., *U.S. EPA, 1996*). Source control is a critical component of site remediation strategies aimed at returning groundwater to maximum beneficial uses in a reasonable time frame and for achieving pollution prevention goals (see *U.S. EPA, 2002*; www.epa.gov/correctiveaction). For example, the CERCLA statute requires remedial actions to attain drinking water standards established under the Safe Drinking Water Act, or water quality criteria established under the Clean Water Act, *"...where such goals or criteria are relevant and appropriate under the circumstances of the release."* Superfund regulations, contained in the NCP (Final National Oil and Hazardous Substances Pollution Contingency Plan) establish that the cleanup goal for contaminated ground water is: "*...to return usable ground waters to their beneficial uses wherever practicable, within a timeframe that is reasonable given the particular circumstances of the site."* Superfund guidance further clarifies that drinking water standards are to be used as cleanup levels for ground waters that are determined to be current or potential sources of drinking water. For sites regulated under RCRA Corrective Action, similar final cleanup goals are established, although the point of compliance (POC) and various short-term and intermediate goals may be defined for the site (see *U.S. EPA, 2002*; www.epa.gov/correctiveaction). The regulatory context for groundwater cleanups is further complicated by state and local laws, which generally must be at least as stringent as federal requirements.

In recent years, however, many states have begun to adopt a more pragmatic regulatory approach, based on alternate or intermediate performance goals and phased remedial actions, for cleanup of contaminated sites. For example, revisions to Arizona state laws in 1997 now allow the Arizona Department of Environmental Quality ("ADEQ") increased flexibility in selection of groundwater cleanup methods and levels. ADEQ is "authorized to adopt rules for remedy selection that incorporate analysis of a range of cleanup alternatives, from remediation of the contamination to no action." Significantly, the statute clarifies that cleanup need not always result in achievement of drinking water standards in the aquifer itself. States such as Vermont, California, and New York among others are implementing alternative approaches to groundwater cleanup including establishment of management zones where cleanup goals other than drinking water standards may be applied, groundwater classification schemes that permit alternative remedial action goals, and other flexible regulatory approaches that do not impose non-degradation requirements or drinking water standards in source zones. These new federal and state regulatory policies and practices provide a more encouraging climate for implementation of innovative source-depletion technologies in those situations where partial depletion of DNAPL sources may be deemed an acceptable intermediate goal as a part of phased site cleanup. On the other hand, regulatory policies are also constrained by public concerns over leaving contamination in place and concerns over natural resource damages, and there is currently no accepted regulatory definition of qualitative terms such as "mass removal to the extent practicable." This results in significant uncertainty as to the extent of mass depletion that may be required in a DNAPL source zone.

The Panel has not undertaken an assessment of all new regulatory practices or changes in policies, but it is the experience of the consultants on the Panel that for groundwaters considered potential sources of drinking water, requirements for restoration or achieving MCLs in a source zone are the dominant regulatory approach across the country. Where alternative metrics or remedial actions are considered acceptable by the regulatory agency (e.g., remove mass to the extent practicable, eliminate DNAPL mobility, or achieve levels higher than MCLs), the potential for partial DNAPL source depletion to meet site-specific remedial action objectives is increased.

In addition to regulatory drivers, remedial actions in source zones may also be undertaken to eliminate long-term liability. Responsible parties can potentially be held liable for tort liability (e.g., human health impacts, nuisance, trespass, diminution of property values). Furthermore, as specified under CERCLA, states may sue responsible parties for natural resource damages, increasing the long-term risks that failure to cleanup a site would result in significant claims against such parties.

2.4 Technical Framework

To provide a consistent technical framework for addressing the four issues presented by EPA to the Panel, the following discussion addresses key factors that the Panel considers essential for a comprehensive understanding of the DNAPL source-zone remediation challenge. Before addressing questions such as what benefits can be obtained by depleting DNAPL mass from source zones, or which technology or technologies work best, it must first be recognized that source zones at DNAPL-impacted sites differ in important ways. These differences can have profound impacts on the technical and institutional approaches taken to groundwater remediation that are: 1) consistent with regulatory requirements, 2) mitigate stakeholder concerns, and 3) balance the benefits of risk reduction against life cycle costs. Benefit/cost balancing and the resultant risk management decisions related to the implementation of source depletion technologies can best be understood in the context of the technical framework presented below.

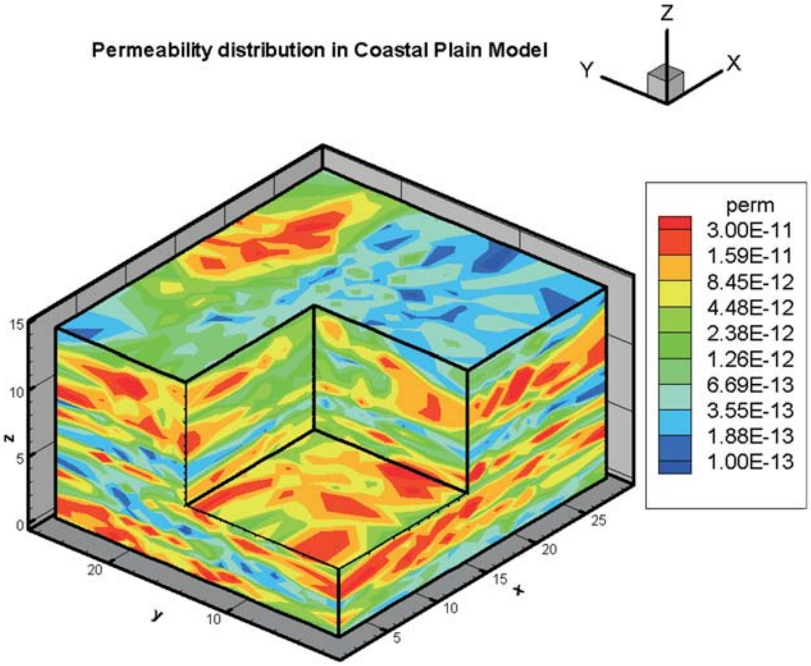
For purposes of this Report, the source zone has been defined as the groundwater region in which DNAPL is present as a separate phase, either as randomly distributed sub-zones at residual saturations or "pools" of accumulation above confining units (*Mackay and Cherry, 1989; Cohen and Mercer, 1993; Feenstra et al., 1996*). This earlier definition is extended here to include the volume of the aquifer that has had contact with free-phase DNAPL. This reflects the observation that diffusion can drive substantial contaminant mass into stagnant zones (e.g., clay) adjacent to DNAPL (*Parker, et al., 1994; Parker, et al., 1997; Reynolds and Kueper, 2002*). After depletion of DNAPL, back diffusion of sorbed and dissolved contaminants from stagnant zones can sustain plume concentrations (*Liu and Ball, 2002*). A good example of the cases to be included by this expanded definition is the source zones in fractured media discussed in the following paragraphs. The term source-zone architecture *(Sale and McWhorter*, 2001) is used to describe the geometry (shapes, sizes, spatial distribution, inter-connections) and DNAPL content of the sub-zones. The source-zone DNAPL architecture impacts the source strength (i.e., mass discharge rate), the evolution of the dissolved plume, and the efficiency of remediation. DNAPL sources in the vadose zone are not considered in this report.

The Panel determined that the primary factors differentiating source zones from other zones in the contaminated aquifer such as the dissolved plume include: a) site hydrogeology; b) DNAPL spatial distribution; c) size of the site and DNAPL release(s); d) composition and properties of the DNAPL (single- or multi-component); and e) the degree of ground surface interferences.

Site Hydrogeology: Hydrogeologic features—such as lithology and permeability—have a dominant effect on the rate and direction of groundwater flow and contaminant transport. DNAPL migration and distribution subsequent to a release are also strongly controlled by the hydrogeologic features. Two primary geologic conditions can be identified: 1) unconsolidated porous media, and 2) consolidated (fractured) porous media. For the unconsolidated media, we are particularly interested in three features of the medium: 1) the permeability, as represented by the mean hydraulic conductivity, 2) the degree of hydrologic heterogeneity, as represented by the variance of the distribution of values for the saturated hydraulic conductivity, and 3) the extent of anisotropy and spatial correlation, as represented by the ratio of the correlation lengths. For consolidated fractured media, advective transport occurs primarily in the fracture network, while the porosity of the rock matrix serves as stagnant zones connected to the advective flow paths via molecular diffusion; thus, these stagnant zones serve as long-term diffusion sinks/sources. Three specific features are of particular importance for fractured systems: 1) the porosity of the rock matrix, which gives an indication of the fraction of the pore volume that serves as the diffusive sink/source for contaminant transport, 2) the spatial organization of the fracture network, with an emphasis on the inter-connectedness of the fractures, and 3) the fracture-size distribution.

A typical heterogeneous unconsolidated medium is represented in Figure 2.1, and examples include deltaic deposits (e.g., Southeastern coastal plains hydrogeology; Garber Wellington Aquifer, Central Oklahoma) and glacial outwash. Such aquifer materials generally exhibit anisotropy in permeability (K_{sat}) values; that is, saturated hydraulic conductivity values in the x- or y-directions may be much larger than those in the z-direction, and as a result, preferential orientation of the stratigraphic layers occurs. This anisotropy is characterized by the ratio of the spatial correlation lengths in the x (or y) and z directions. Note that the larger the ratio, the more pronounced is the horizontal orientation of the layers, whereas, as the correlation length increases, the characteristic lengths of the inclusions increase.

Figure 2.1 Schematic representation of an unconsolidated heterogeneous geologic setting.



Fractured media may be grouped into two distinctly different types based on the porosity of the rock matrix (*Pankow and Cherry, 1996*). The first type has large matrix porosity, while the second type has small matrix porosity. The term "fractures" is used to evoke scenarios in which the bulk capacity to transmit fluids is primarily associated with flaws (e.g., fractures) in an otherwise low-permeability matrix. The porosity of the fractures is typically a very small fraction of the overall material volume. With large matrix porosity, contaminants (DNAPL and dissolved phase) are depleted from the fracture via diffusion into the matrix. Within the matrix, contaminant mass is stored as aqueous and sorbed phases. Molecular diffusion initially retards contaminant migration via advection, as the rock-matrix porosity serves as a sink. However, once the source is removed and the contaminant concentrations in the fracture network decrease, diffusion out of these stagnant intra-matrix regions can sustain contaminant concentration in the advective flow paths within the fracture network. Examples of such geologic media include limestone (e.g., the Niagara Escarpment, Niagara Falls, New York) and Lacustrine Clays (e.g., Sarnia, Ontario).

Alternatively, contaminants transmitted along fractures in matrix material with low matrix porosity are not attenuated by molecular diffusion. This limits the formation of an *in-situ* diffusion source. Unfortunately, it also allows contaminants to migrate much faster than in an equivalent fractured medium with large rock-matrix porosity. Examples of such geologic media include crystalline rock in the Piedmont region of the eastern U.S., and granitic bodies in the Rocky Mountains. A hypothetical depiction of a DNAPL source zone in a fractured medium is shown in Figure 2.2, after Davis and DeWeist (*1996*).

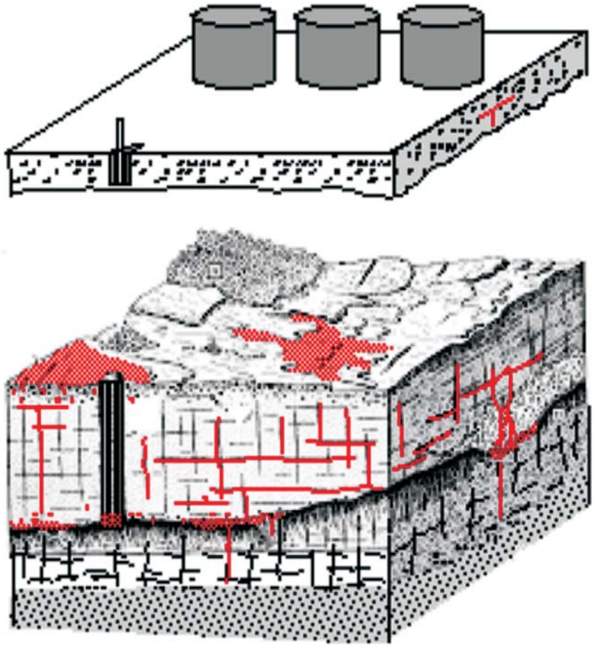


Figure 2.2 Schematic representation of fractured media site contamination DNAPL.

DNAPL Spatial Distribution: For a given DNAPL release scenario, very different spatial distributions of the DNAPL will occur depending upon the size of the release and the hydrogeologic settings. DNAPLs are present either as a free phase, and therefore, mobile liquid, or as residual liquids. Following the release(s), DNAPL constituents may partition into the water phase, the aquifer solids, or the soil vapor. Thus, DNAPL in a source zone may be distributed among four phases: 1) pure DNAPL, 2) DNAPL constituents sorbed on the surfaces of the aquifer solids, 3) dissolved in pore water, and 4) in soil vapor. Here, we do not consider the vapor-phase because remediation of DNAPL in the vadose zone is not the focus of this Report. Free-phase DNAPL may occur either as "pools" of an accumulation occupying most (but, not all) of void spaces in more-permeable zones or at "residual saturation" where disconnected globules are trapped by capillary forces (see e.g., *Imhoff et al., 2003*).

Size of the Site and DNAPL Release Volume: The size and frequency (release history) of DNAPL release(s) have a dominant effect in determining the distribution of "pools" and regions of residual saturation. The DNAPL source-zone architecture represents sizes, shapes, volumes, and connections of these DNAPL sub-zones and their hydrodynamic interactions with the more-permeable regions within the aquifers. That is, "architecture" defines both the morphological features (such as spatial distribution patterns, NAPL content, etc.) of the sub-zones and their "functions" in terms of hydrodynamic accessibility (i.e., rate of release by aqueous dissolution). DNAPL mass in stagnant regions (e.g., clay inclusions in unconsolidated media, intra-matrix porosity in fractured media) is stored primarily in the sorbed and dissolved phases, and mass-transfer via molecular diffusion is the primary transport mechanism (see e.g., *Parker et al., 1994; Parker et al., 1997*). It should be recognized that the source-zone architecture can and does change over time, especially when source remediation technologies are implemented; such changes have significant influence on the "source strength" (defined as the total mass discharge rate; MT^{-1}) and the manner in which the plume responds.

Properties and Composition of the DNAPL: Physical and chemical properties of the DNAPL, such as solubility, density, viscosity, interfacial tension, and composition, also play an important role in: 1) multi-phase flow behavior, which governs DNAPL source-zone architecture, 2) generation of a dissolved plume, and 3) performance of the remediation technologies. While many DNAPLs of interest are single-component liquids (e.g., chlorinated solvents, such as PCE or TCE), multi-component DNAPLs (e.g., creosote and coal tars) are also of significant practical interest. At many sites, chlorinated solvents are often found as mixtures, either with other hydrocarbons (e.g., fuels) or other solvents used in industrial operations, or may be released as spent solvents that contain a variety of chemical constituents.

While chlorinated solvents are generally considered to be non-wetting with respect to the aquifer solids, the presence of minor constituents (e.g., surfactants, organic acids) or “aging” after release can alter the interfacial tension and wetting behavior of a DNAPL (*Powers and Tamblin, 1995; Lord et al., 1997a,b*). Complex DNAPLs, such as coal tars and creosotes, also tend to behave as a wetting phase. Wetting DNAPLs are likely to be found at larger residual saturations, tend to exist as coatings rather than as dispersed globules, and are able to penetrate into low-permeability stagnant zones (*Abriola and Bradford, 1998; Bradford and Abriola, 2001; Abriola et al., 2002*). Such dramatic alterations in source-zone architecture must be evaluated in site assessment and remedial designs.

Degree of Surface Interferences: Surface structures including buildings, tanks, process units, buried utilities, and/or roadways limit access for investigation and installation of DNAPL source-zone depletion technologies. Generally, at sites with larger numbers of such interferences or “active” sites with on-going operations, one is more likely to encounter problems in deploying a selected source depletion technology.

In summary, the above five factors must be considered when evaluating appropriate technical and institutional strategies for groundwater remediation at DNAPL sites. The characteristics of individual sites must be carefully evaluated when considering site characterization efforts and potential remedial actions including the implementation of source-zone depletion technologies.

3.0 Questions

The following section summarizes responses to seven questions generated by the Panel in response to the charge from EPA on the issue of source-zone remediation at DNAPL sites.

3.1 Question 1: What are the Potential Benefits and Potential Adverse Impacts of DNAPL Source Depletion as a Remediation Strategy?

The potential benefits and the potential adverse impacts of DNAPL source-zone depletion have been the subject of on-going debates in the remediation field. The potential positive and negative outcomes discussed below are based on either theoretical considerations or laboratory and field data. However, the magnitude of these outcomes and the probability of their occurrence need to be determined from site-specific analysis. Analysis here is limited to a more generic description, and certain remediation technologies are mentioned only to illustrate potential outcomes. Furthermore, the intensity and persistence of the adverse impacts resulting from aggressive source-zone treatment are poorly understood, as is the resilience of a treated source zone to recover from such impacts. Similarly, experience with partial source depletion has not been sufficient to determine whether the benefits of partial source removal are seen only for a short duration before a rebound occurs to conditions similar to the pre-remediation scenario or some other unacceptable condition, as has often been the case when applying pump-and-treat technologies to DNAPL-impacted groundwater sites.

3.1.1 Potential Benefits of Partial Source Depletion

In many respects, the actual or perceived benefits of DNAPL source depletion depend on the view of the particular stakeholder. Private site owners generally weigh remedies in terms of their risk management benefits and potential for reducing the total life-cycle cost to achieve site closure, assuming that the remedies under consideration meet all regulatory requirements for protection of human health and the environment. Government site owners, such as the Department of Defense (DOD) or the Department of Energy (DOE) generally follow a similar process, although the details of the remedy selection process may differ from decision processes at private sector sites, particularly with respect to the time value of money.

In all cases, regardless of the site owner, there is a range of benefits, from a risk management perspective, that may result from source depletion. These include explicit benefits such as: 1) mitigating the future potential for human contact and exposure through long-term reduction of volume, toxicity, and mobility of the DNAPL, 2) mitigating the future potential for unacceptable ecological impacts, 3) reducing the duration and cost of other technologies employed in conjunction with the source depletion technology, and 4) reducing the life-cycle cost of site cleanup. These benefits can be achieved if the source depletion option can result in the following outcomes: 1) reduction of DNAPL mobility, if mobile DNAPL is present, 2) reduction in environmental risk to receptors; c) reduced longevity of groundwater remediation, and 3) reduction of the rate of mass discharged from the DNAPL source zone. These outcomes could then lead to enhanced efficiency of complimentary technologies used for groundwater remediation as well as reduction in life-cycle costs. Implicit risk management benefits include: 1) minimizing risks of failure of containment strategies, 2) mitigating public stakeholders' concerns, 3) enhancing a company's “green image” as stewards of the environment, and 4) minimizing future uncertain transaction costs associated with management of the site. In contrast to explicit benefits, these implicit benefits are often difficult to quantify in monetary terms. The following is a brief discussion of some of these benefits that may arise from mass depletion in a DNAPL source zone.

Reduction of DNAPL Mobility

The potential benefit of source depletion (such as by pumping free-phase DNAPL) to reduce free-phase DNAPL mobility and mitigate further spread of the source is clear. In some cases, free product mass removal may be necessary to prevent or reverse direct discharge of DNAPL to the land surface or surface water and thereby mitigate the associated risk potential to human and/or ecological receptors. The goal in such a case is to deplete the source sufficiently to reduce DNAPL to a residual saturation level, or at least to a point of relative stability. It may be possible, at least in principal, to achieve this objective through physical containment measures. However, the experience of the Panel has been that containment of DNAPL through physical measures (e.g., sheet pile barriers, slurry walls, etc.) is challenging and presents uncertainties regarding long-term reliability.

EPA (1998) evaluated the performance of subsurface engineered barriers, assessed 36 sites in detail, and concluded that if properly designed, such systems are effective containment systems primarily of the dissolved plume for the short and middle term, duration undefined. Presumably, "middle term" refers to a period of less than 10 years. However, at four of the 36 sites, contaminant leaks were detected at the interface between the barrier and anchor materials (i.e., barrier key), and at four other sites, evidence suggested that the containment objective had not been met. Two of the 36 sites had barrier walls installed with the objective to "contain" DNAPL, but the data were not sufficient to verify the success of these barriers, although at one barrier, EPA concluded that the containment objective may have been achieved. In those cases where source-zone containment is the goal, one uncertainty is whether the source zone containing DNAPL has been accurately defined. Thus, the success of physical containment strategies for mobile DNAPL is certainly not assured, and uncertainties remain regarding longer-term performance (>10 years).

In such cases, free product removal may provide an advantage by reducing the risks of barrier failure. In evaluating this benefit, however, the Panel concluded that at the vast majority of sites impacted with chlorinated solvent DNAPLs, the presence of highly mobile separate free phase cases is the exception rather than the rule since most chlorinated DNAPLs (PCE, TCE) generally come into hydraulic equilibrium relatively quickly following release. However, sites with wetting DNAPLs may be an exception to this general rule, and the Panel is aware of several reports of continued mobility of DNAPLS such as creosote and coal tars even though disposal may have occurred decades earlier.

Reduced Longevity

Source depletion provides a potential benefit in reducing the longevity of the DNAPL source and the associated dissolved plume. This potentially translates into risk reduction by shortening the time frame for site closure and thus reducing the overall potential for human or ecological exposure to the site DNAPL contaminants. The magnitude of this benefit is highly site-specific and will depend primarily on the degree of subsurface heterogeneity, DNAPL source distribution within the saturated zone (e.g., see previous discussion in Section 2.0), the extent of source depletion from high- and low-permeability zones, and the rate of other attenuation processes occurring at the site.

This potential benefit is common to all source depletion strategies, but difficult to predict and quantify at present due primarily to: 1) uncertainties in estimates of the initial and the residual DNAPL mass, and 2) characterization of the distribution of the DNAPL after source depletion has been implemented. These uncertainties are an inherent characteristic of subsurface systems because of highly heterogeneous geologic properties of all aquifers.

In tandem with risk management benefits, the potential value of source depletion in the view of the site owner may be in reducing the life cycle cost to achieve cleanup goals and site closure. For contaminated groundwater, the classic risk management approach has been to institute hydraulic controls (e.g., a pump-and-treat remedy) to stop plume growth coupled with restriction of groundwater use to prevent public exposure (*U.S. EPA, 1996; NRC, 1994; U.S. EPA, 2001*). This approach has generally been an effective risk management strategy, preventing unacceptable exposure to DNAPL chemicals, and containing plume migration. Long-term success of this strategy, however, depends on providing the appropriate controls and restrictions effectively over very long time frames (i.e., many decades).

On the other hand, this strategy of long-term management is often expensive. The current default assumption is that DNAPL sites will require several decades to centuries of plume management with significant cost and future uncertainty. Adding to the site owner's liability is the potential for permanently reduced land value for DNAPL-contaminated property as well as threats of natural resource damage claims. Viewed in these terms, source mass depletion has the potential benefit of reducing the time required for maintaining active controls and the associated life cycle cost of cleanup at a DNAPL site. This evaluation can be looked at from the standpoint of balancing the upfront cost and effectiveness of source removal vs. the long-term cost of controls, compared on a present worth cost basis. A brief discussion of this balancing process is presented under Question 4.

Reduction of Contaminant Mass Discharge to Receptors

Depleting the DNAPL source zone may result in near-term reduction in contaminant *mass discharge rate*, which is the total contaminant mass leaving the source zone per unit time. This mass discharge rate can be thought of as the *source strength* (M_d) and is defined as the mass of contaminant per unit time migrating across a hypothetical vertical cross section (a "control" plane) in the aquifer downgradient of the source zone, and perpendicular to the direction of groundwater flow (See Figure 3.1). This mass discharge rate divided by the total cross-sectional area of the source control plane yields an estimate of the *average contaminant flux* ($M\ L^{-2}\ T^{-1}$).

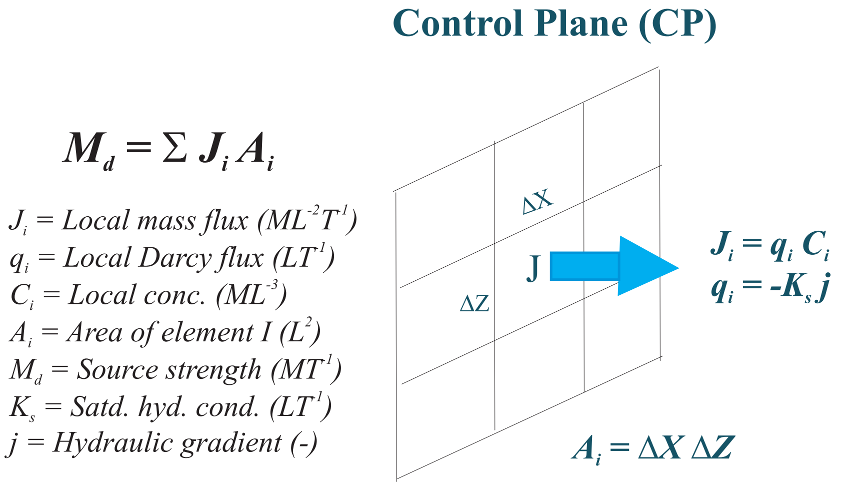


Figure 3.1 Schematic representation of a control plane, and a definition of the source strength (M_d) and local values for ground-water flux (q_i), and contaminant flux (J_i).

A classic example is the case of a dissolved-phase plume emanating from a DNAPL source discharging to a surface water body or public water supply well. Depleting the mass of DNAPL in the source zone may be useful in eventually reducing the total mass discharge rate to the surface water body or supply well, thereby mitigating the risks of unacceptable human or ecological exposure to the chemicals of concern from the site. Reduction of the mass discharge rate leaving the source zone may also result in near-term plume assimilation and enhanced efficacy of a natural attenuation remedy vs. active plume control measures.

Recent theoretical analyses (*Rao and Jawitz, 2003; Rao et al., 2001*) and field experiments (*Brooks et al., 2002*) suggest that partial depletion of DNAPL mass by in-situ flushing within the source zone located in unconsolidated heterogeneous geologic media can also result in a measurable reduction of the contaminant mass discharge rate at the downgradient control planes. In contrast, other modeling analyses have indicated that nearly complete removal of DNAPL in homogeneous geologic media is required before measurable reduction in the mass discharge rate is observed *(Sale and McWhorter, 2001*). However, more recent analytical and numerical analyses concluded that mass discharge rates are expected to decline as the DNAPL mass is depleted *(Falta*, *2003*). Thus, benefits from partial source depletion are uncertain, and measurement of the mass discharge rate achieved as a function of the degree of source depletion achieved becomes a critical issue for evaluating this benefit when considering source depletion options. The changes in the spatial distribution of the local contaminant fluxes and the magnitude of the resulting mass discharge rate are explicitly related to the hydrologic heterogeneity, the initial DNAPL architecture, and the correlation between hydraulic conductivity and the DNAPL saturation at the local scale.

In general, the relationship between the fractional reduction in source-zone contaminant mass (*X*) and the fractional reduction in contaminant mass discharge rate (*Y*) may be described using an empirical relationship (*Rao et al., 2001*): $Y = X^{1/\beta}$. The β value represents the “efficiency” of remediation in terms of mass discharge reduction. Its value ($\beta > 0$) depends on the degree of heterogeneity of the flow field, source-zone architecture (correlation between DNAPL content and permeability), and the remediation technology and its implementation. Note that small values of β represent low efficiency (usually the case for the less heterogeneous media), while larger values of β indicate more efficient contaminant mass discharge-rate reduction with mass removal, as is the case for more heterogeneous media. More recent theoretical analyses (*Enfield et al., 2003*; personal communication) suggest that these curves can take on more complex shapes, depending on the nature of the interactions between hydrogeologic heterogeneity and the source architecture.

While the benefits of a reduction in contaminant mass discharge rate are not necessarily unique to source depletion strategies (e.g., source containment could generate similar results), the opportunity for permanence at least conceptually should be considered as a potential unique risk management benefit for source depletion options. Additionally, the potential benefits in reducing the costs of complementary groundwater remediation technologies should also be accounted for as discussed below:

Enhanced Efficiency and Effectiveness of Complementary Technologies

Source depletion coupled with attenuation processes to reduce or eliminate receptor concentrations is a prime example, but not the only example, of potential benefits of DNAPL source removal. The most important attenuation processes of interest for DNAPLs include biodegradation and hydrodynamic dispersion. Another benefit is the reduction in the contaminant mass discharge rates entering a permeable reactive barrier used for plume containment. This reduction may increase the life of a permeable reactive barrier, thereby reducing the frequency (and costs) of barrier replacement or regeneration. The thickness of the permeable barrier and thus its capital costs might also be reduced if the overall mass discharge rate from the source zone was reduced. The potential for preferential pathways must be accounted for, however. In addition, a reduction in mass discharge rate from the source zone may reduce the costs of ex-situ groundwater treatment in those cases where hydraulic containment continues to be required to meet regulatory cleanup standards at downgradient points of compliance.

Economic Benefits

The economic benefits of source depletion could include the following:

- early site closure and return of the groundwater to beneficial use (the definition of site closure will vary depending on the site, from unrestricted to restricted use);
- lower annual overall life-cycle costs (i.e., reduction in annual and long-term operation and maintenance (O&M), or creating conditions that allow application of more passive remediation technologies);
- removal of long-term liability and accrued reserves for remediation;
- enhanced land value through reduction or removal of contingencies that reduce land value; and
- land transactions that would not otherwise occur due to the restrictions on land use, or need to retain liability and access associated with remedies requiring long-term management.

Although these potential economic benefits of source depletion could provide cost savings, generally, source depletion technologies will not likely be implemented unless the cost to achieve the benefit will be less than the beneficial value recovered, taking the risk of failure of the depletion technology into account. Also, the differences between the respective accounting practices of government entities (e.g., cost-to-completion) and commercial organizations (e.g., net present value) for the reporting of environmental liabilities to their stakeholders can lead to different conclusions on the economic benefits of the application of source depletion options. In addition, the private sector and the public sector use widely different net discount rates when conducting net present value analyses. For commercial organizations, an additional factor is the tax consequences of different remediation options, since O&M costs are considered deductible business expenses (*NRC, 1997a*). These two factors will lead to very different conclusions regarding the economic benefits of source depletion, as will be illustrated in Question 4.

Environmental Stewardship

Stewardship implies “good governance,” which when well executed yields both intangible and tangible benefits. Major tangible benefits include the following: 1) the earlier recovery of natural resources and placing those resources at the disposal of current and future generations, 2) removing a long-term risk, and 3) reducing the likelihood of natural resource damage assessments and subsequent claims. Intangible benefits are more aligned with features associated with leadership versus management. “Picking the right thing to do” is a leadership quality, while “doing the right thing well” is associated with management. Responsible parties perceived by the public as picking the right thing to do, and being transparent in their decision-making will be supported, and this could be transferred into improved market share, increased share value, or support of their policies and positions.

3.1.2 Potential Adverse Impacts from Use of Aggressive Technologies for Source Depletion

Here, we consider a range of negative impacts that are possible or likely when aggressive technologies for DNAPL source depletion are implemented. Since source containment is not a depletion strategy, we exclude this from our discussion, and focus below on various in-situ, innovative technologies that involve some type of aggressive treatment of the source zone.

Expansion of the Source Zone

Injection of remedial fluids containing surfactants or co-solvents, or thermal treatments (e.g., steam, resistive heating) has the potential to expand the source zone if adequate hydraulic controls are not in place, or if unexpected mobilization of otherwise trapped DNAPL occurs. For example, lowering the interfacial tension by adding surfactants or co-solvents may lead to mobilization of DNAPL into zones previously not contaminated. Penetration into low-permeability zones or transport to deeper permeable zones is of concern to practitioners, regulators, and site owners.

Changes in DNAPL Architecture

It is possible that certain in-situ remediation technologies can alter the DNAPL architecture in undesirable ways, causing either an increase in DNAPL mass transfer to flowing groundwater or a reduction in the potential for DNAPL mass removal. Mobilization of DNAPL at residual saturations can result in pools of new accumulations above confining units, thus potentially decreasing efficiency of mass removal. Injection of certain oxidants (e.g., permanganate) can result in formation of precipitates (e.g., MnO_2) that can form coatings on DNAPL ganglia or pools; this also diminishes access to DNAPL mass, thus reducing mass removal efficiency. Alternatively, removal of some DNAPL mass can actually enhance access by altering the permeability distribution, which, in turn, results in an increased contaminant flux and concentrations (at least, temporarily). This is viewed, by some, as a negative consequence. However, this may only be a transient effect.

Changes in Physical Conditions

Aggressive treatment of source zone can, in some cases, result in significant changes in physical properties of the treated aquifer zone. For example, in-situ chemical oxidation can lead to formation of precipitates (e.g., MnO_2) and mobilization of colloidal particles; in both cases, plugging of the permeable zones can reduce formation permeability, thus leading to difficulties in maintaining subsurface fluids delivery or access to remaining DNAPL mass. Bio-fouling during bioremediation can have similar undesirable consequences. Heating may cause the formation of mineral deposits as low permeability layers or hard pancakes depending on the geochemistry, as observed at the NASA LC34 demonstration.

Changes in Geochemical Conditions

The injected remedial agents (e.g., chemical, heat) can also alter the geochemical properties within the treated zone and downgradient within the dissolved plume. For example, introduction of oxidants and reductants or electron acceptors/donors can modify redox conditions (Eh) or pH or salinity. Similarly, byproducts of the intended reactions (e.g., organic acids from partial degradation of DNAPL constituents) may also alter geochemistry. Such modifications can limit (or enhance) microbial processes, enhance mobilization of colloids, and in some cases, promote transport of certain metals whose solubility and retardation are strongly dependent on pH and the oxidation/reduction conditions. Formation of degradation by-products that are more toxic than the parent compounds is also a concern when altering the geochemical environment; for example, the formation of vinyl chloride during reductive dehalogenation of chlorinated solvents, PCE and TCE.

Additional concerns include trace elements present in injected solutions. For example, permanganate-based solutions can contain trace amounts of chromium, which could result in unacceptable concentrations of this heavy metal in the groundwater. Adverse effects can be mitigated by selection of solutions with acceptably low levels of trace elements and applications of these solutions at sites where the geochemical conditions will immobilize/attenuate these constituents.

Changes in Microbial Ecology

Aggressive treatment of source zones can, in some cases, lead to at least a temporary reduction in microbial biomass, biodiversity, or functions. Technologies particularly prone to such adverse effects are in-situ chemical oxidation and thermal technologies. Flushing with surfactants and co-solvents can also result in alteration of microbiological processes. Limited data are available in assessing such changes, and how, if any, recovery occurs from an initial “insult.” For example, $KMnO_4$ residuals can inhibit the formation of anaerobic zones after treatment and increase the time required to re-establish biological reductive dechlorination processes. In contrast, residual amounts of remedial agents left in the source zone may actually be beneficial to microbial processes, as is the case with residual ethanol or surfactant fermentation products acting as electron donors to promote reductive dechlorination of chlorinated solvents (e.g., see discussion on Sages and Bachman sites, Appendix A). Reduction in contaminant concentrations may reduce “toxic” effects and permit faster degradation of certain contaminant classes as well.

Deleterious Impacts on the Deployment of Other Technologies

Some or all of the above-discussed potential adverse effects may inhibit or limit the use of other, perhaps less-aggressive “polishing,” technologies. For example, if geochemical and microbial alterations are too severe, long-term natural attenuation capacity may actually decrease. That being the case, either more source-mass depletion would be required, or the dissolved plumes would be longer for a given contaminant mass discharge.

Additional negative impacts could conceivably include the following: 1) inability to commercially develop or use the site, both during remediation and even after, if desired endpoints are not reached or adverse effects are deemed too great; 2) financial and legal consequences of failure to meet target endpoints, and 3) stakeholder concerns when remediation of source is judged to have “failed” by not reaching target endpoint in a projected timeline.

3.1.3 Summary

In summary, source-zone depletion of DNAPL has both potential benefits and potential adverse impacts. Careful consideration of all intended and unintended consequences, as a part of the remedial design process, is essential for successful application of source-zone depletion technologies and further assessment of both the desired and undesired consequences of implementing DNAPL source-zone depletion technologies is needed. Quantification of these positive and negative consequences will significantly improve the quality of decision-making when considering DNAPL source depletion options.

3.2 Question 2: What are the Appropriate Performance Metrics for Assessment of DNAPL Source Depletion Technologies?

Choosing and quantifying the appropriate metrics for evaluating the performance of DNAPL source depletion technologies is a critical, but difficult, task. The Panel is aware of a wide variety of goals and metrics that have been applied to address the issue of determining if a remedial action is successful. These goals have included: 1) halting migration of contaminants beyond a property boundary, 2) removing mass to the extent "practical," 3) removing a certain fraction of the initial mass, and demonstrating plume stability, and 4) reducing overall human health and environmental risks to levels commensurate with the planned land use.

The metrics used to confirm these goals are usually estimated from measurements of DNAPL constituents in soil and groundwater using standard site characterization techniques. For DNAPL sites where the groundwater is considered a potential source of drinking water, the concentration of the chemicals of concern in samples from individual groundwater monitoring wells located at agreed upon points of compliance is the current approach for assessing success. Generally, these concentrations must be at or below the agreed upon cleanup criteria (e.g., MCLs) for some fixed period of time, determined by site-specific conditions. While the Panel realizes that this metric will remain a keystone metric in evaluating the success of any remedial strategy on a site-wide basis, exclusive reliance on this single metric may be misleading in assessing the performance and potential benefits of source depletion technologies. Other performance metrics may also be appropriate, especially if they are included as assessment tools in determining progress towards the desired end states, as milestones in "pay for performance" contracts, and to define intermediate remedial action goals.

The Panel offers the following general considerations related to selection of the most appropriate source depletion performance metrics:

- No single metric by itself is likely to be adequate for assessing the performance and potential benefits of DNAPL source depletion technologies; thus, conjunctive use of multiple metrics should be used to evaluate performance. However, the relative significance or "weight" of each metric as it relates to decisions on site closure has yet to be developed.
- Some metrics are inherently more variable than others; thus, they are subject to greater uncertainty in measurement. The degree of uncertainty may also not be known.
- Often, performance metrics must be inferred from other data. That is, performance metrics are determined using primary data from characterization or monitoring efforts. Error propagation must be considered.
- Accuracy and reliability of techniques to measure the metrics must be considered when selecting metrics for performance assessment (i.e., agreement between multiple methods or validity of a single method).
- For a few metrics, multiple measurement methods are available, but for others, methods are not proven, and are currently under development.
- Some performance metrics, while desirable or appropriate, may be prohibitively expensive to measure. Thus, methods to estimate these metrics indirectly may be necessary. In such cases, the issue of reliability must be considered.

The last point is especially important. There are several types of distributed and integrated measures of source depletion performance assessment that are theoretically possible. It must be recognized, however, that it may not be feasible to measure some of these quantities under field conditions, due to cost or implementation constraints.

With this background, performance metrics are grouped below into three categories: Type I metrics that can usually be measured reliably, and are commonly used; Type II metrics that can sometimes be measured, but are not in wide use; and Type III metrics that are theoretically possible and are under development, but that have not yet been demonstrated at multiple field sites.

3.2.1 Type I Metrics

a. Source Mass Removal

This metric is defined as the contaminant mass recovered or destroyed during source depletion. Direct measurement is not possible for destruction, and the mass destroyed must be inferred from either mass balance of the byproducts generated or based on the difference between the estimated initial and final DNAPL mass. This metric may be less important than the mass remaining, but it is easier to quantify in most cases. There are a number of source depletion technologies that remove mass (as opposed to in-situ destruction). For these technologies, quantifying mass removal should be attempted. Although relatively simple to quantify, the relationship between this metric and the prediction of long-term success is difficult due to inherent uncertainties in estimates of the original mass, and the distribution of that DNAPL mass, as well as limitations in modeling tools as will be discussed in response to Question 5.

b. Change in Dissolved Concentrations Within and Downgradient from the Source Zone of DNAPL constituents

This metric is relatively easy to measure using multiple methods, but can be highly variable in space and time. In heterogeneous formations, this metric is not linearly related either to the mass remaining in the source zone or to the contaminant mass discharge rate. The interpretation of the data from use of this metric is complicated by the three-dimensional nature of the contaminated zones in the subsurface, the potential presence of preferential flow pathways, and fluctuations in the rate and direction of groundwater flow. This is the most common metric used to measure performance of a remediation system addressing groundwater contamination.

3.2.2 Type II Metrics

a. Mass Remaining (Parent and Byproducts)

This metric is defined as the contaminant mass not recovered (or byproducts created) following implementation of a source depletion technology. Contaminant mass can include DNAPL sorbed phase contaminants in stagnant zones and dissolved phase contaminants in stagnant zones in addition to the free or residual DNAPL phase. Direct and indirect measurement techniques for determining this metric are subject to large errors as discussed under Question 3.

b. Change in DNAPL Distribution Relative to Geological Features (i.e., the DNAPL Architecture)

Direct contact with or diffusive mass transfer from the DNAPL sub-zones to the primary groundwater flow channels is critical to downgradient impacts in the dissolved plume. In a quantitative approach, source-zone architecture may be characterized by multiple parameters that define the spatial statistics of the DNAPL distribution (e.g., mean, variance, correlation length) as well as the spatial cross-correlation between the distribution of DNAPL content, hydraulic conductivity, lithology, and other aquifer characteristics. In practice, however, it is either difficult or too expensive to measure such statistical parameters to describe quantitatively the source-zone architecture.

The spatial distribution of NAPL content within the source zone can be determined either by intensive soil-core sampling (*Rao et al., 1997; Meinardus et al., 2002*) or sampling at a number of multilevel sampling locations during partitioning interwell tracer tests (PITT) (*Sillan et al., 1998; Meinardus et al., 2002*). The inference of NAPL spatial distribution from inverse stochastic modeling of PITT tracer data has also been attempted (*James et al., 1997; Zhang and Graham, 2001*).

c. Change in DNAPL Composition and Properties

Some remediation technologies can change the composition and behavior of DNAPLs, making them more or less mobile, soluble, volatile, and more or less recalcitrant or toxic with changing composition. For multi-component DNAPLs, total mass reduction may not necessarily be the relevant objective. Rather, the removal of certain target compounds from the mixture may be more appropriate. For example, for coal tar source zones, thermal or flushing techniques can generally lead to selective removal of the more soluble or more volatile constituents, leaving behind some components (usually of higher molecular weight) as the residuals. The environmental and health risks posed by these residuals need to be considered in assessing the likely benefits of source-zone mass depletion. For example, bioavailability of some chemicals may decrease after source depletion, reducing the environmental risks of the remaining mass of chemicals of concern.

d. Physical, Microbial, and Geochemical Changes

As performance metrics, measurement of these parameters is useful to assess the ability to apply follow-on technologies, or to evaluate the effect of natural degradation processes on the remaining DNAPL source and corresponding mass flux. Aggressive source depletion activities may cause changes in the physical, chemical, and microbial subsurface environment. The changes may occur in the source zone, as well as downstream of the source zone. Changes in these three types of parameters can be assessed through physical examination of cores and hydraulic measurements (for assessment of physical changes), groundwater samples for geochemical/microbial analysis using conventional analytical techniques for geochemical analysis, and traditional and molecular techniques for microbial evaluations. These changes may be beneficial (e.g., improved porosity to flush reactants or nutrients), neutral, or negative (e.g., decreased porosity, or decimation of key microbial species). They may be short-term effects, or they may be permanent. These changes may also interfere with measurement of other performance metrics.

3.2.3 Type III Metrics

Type III metrics are theoretically possible, but technologies to quantify these metrics are still under development and have not yet been widely demonstrated in the field.

a. Change in Contaminant Mass Flux Distribution Downstream of the Source Zone

Contaminant mass flux is the *locally defined* contaminant discharge per unit area (the product of the mass concentration and the Darcy flux). The change of the contaminant mass flux can have a large impact on local biogeochemical reactions downgradient of the source. Currently, mass flux as a metric is being evaluated in a number of research settings, and as discussed under Question 1, a number of innovative approaches to quantifying this parameter are under investigation. However, it must be stressed that the use of the reduction of mass flux as a performance metric to evaluate source depletion technologies is not generally accepted practice, and has not yet been embraced by the regulatory community. State regulators, working through the ITRC, have expressed interest in this metric and are currently (2003) preparing a guidance document on the application of mass flux measurements to performance assessment of source-zone depletion technologies (see ITRC website for details). However, the majority of regulators still consider point measurements of contaminant concentrations as the primary metric for determining the success of any remedial action. In addition, the feasibility of measuring mass flux distributions in some geologic settings such as fractured systems is still uncertain, and research efforts are needed to address these uncertainties regarding the accuracy and feasibility of quantifying this metric.

b. Change in Mass Discharge Rate Downstream

This metric provides information on the total rate of contaminant mass discharge from the source to the groundwater. The mass discharge rate is calculated using the measured spatial integral of the contaminant flux distribution (*Hatfield et al., 2001, 2002*), or measured using pumping wells that capture the dissolved plume (*Bockelmann et al., 2001; Ptak and Teutsch, 2000*). The contaminant mass discharge rate, in units of mass per time, can be used to calculate the flux-weighted averaged concentration over the control plane of interest. Measurement at multiple control planes in a plume can be used to infer the attenuation rate and to distinguish the attenuation mechanisms, differentiating between dilution and degradation processes (*Bockelmann et al., 2001; Ptak and Teutsch, 2000*).

c. Change in Stable Isotopes

Technologies that destroy DNAPL mass may also enrich carbon isotopes of the parent chemicals. Comparing the composition of products and reactants in the dissolved phase (near or downgradient of the source) can be used to estimate the amount of source depletion.

3.2.4 Summary

Determining the most appropriate metrics for performance assessment of DNAPL depletion technologies compared to selected remedial action goals is a non-trivial task. Regulators are likely to continue to rely on point measurements at points of compliance as the primary metric of success when the remedial action goal in a source zone is specified as the concentration of the chemical of concern in groundwater. Use of this point measurement as the only metric does not provide sufficient information to assess the overall performance and thus overall benefits of source depletion technologies as it relates to life cycle costs and overall risk reduction. The Panel urges EPA to consider other performance metrics as discussed above to ensure that a broader range of potential benefits of source depletion can be quantified. Details of the Panel's recommendation on this matter are presented in Section 4.0.

3.3 Question 3: Are Available Technologies Adequate for DNAPL Source Characterization to Select and Evaluate Depletion Options?

Pre- and post-remediation characterization of the DNAPL source zones is an essential component of contaminated site assessment and selection/implementation of remedial options. Investment of time and resources in site characterization provides: 1) more reliable risk assessments, 2) more informed decisions being made about choices among remedial options, 3) development of optimal designs for remediation, 4) more efficient deployment of remediation technologies, and 5) more accurate post-remediation audits to judge performance and achievement of the interim cleanup goals or the final end points required for full closure.

Locating the DNAPL is required in order to characterize and remediate it. Over the last few years, several tools have been developed and significant advances have been made in the characterization of DNAPL sites. However, given historical and potentially large and multiple releases combined with complex subsurface DNAPL migration patterns, DNAPL sources are still difficult to characterize with the available tools, and the level of uncertainty can be as high as an order of magnitude or more.

3.3.1 Innovations in Site Characterization Approaches

Traditional, phased approaches to site characterization – constrained by the use of prescriptive protocols and analytical methods – have placed an undue emphasis on the process rather than the purpose of site characterization. Such approaches have, in the recent past, limited the faster adoption of innovative site characterization and remediation technologies, and have often added to the costs and delays in undertaking site remediation at contaminated sites. Even when prompt decisions have been made, various types of uncertainties in characterization data have contributed to concerns about the quality of the decisions made. In a linear process, where the site characterization issues are decoupled from the remedial design and assessment, decisions made tend to be sub-optimal, both in terms of cost-effectiveness and the achievement of target remediation goals in a timely fashion.

An ideal approach to site characterization should have the following elements (see *Crumbling, 2001; EPA 542-R-01-016*): 1) emphasis on achieving performance (e.g., meeting remedial goals), not on a regimented process and check lists, 2) uses transparent, logical reasoning to develop site plans, 3) engages multi-disciplinary teams to manage the complex issues, 4) requires continual education and training of the teams engaged in site work, 5) site professionals deal with various uncertainties and can evaluate the appropriateness of using innovative technologies, 6) rewards responsible risk-taking, and 7) uses the concept of “keeping the end in mind” to improve decision-making on the extent of characterization required.

The *Triad* approach (*Crumbling, 2001; Crumbling et al., 2001*) to site characterization attempts to incorporate these elements by integrating systematic planning, dynamic work plans, and real-time analyses into a comprehensive and more effective approach. Planning engages multi-disciplinary teams to develop and articulate multiple project goals, and involves the identification of various uncertainties that can influence decision-making. Dynamic work plans (also referred to as accelerated, or adaptive, or expedited characterization) are “choreographed” by the project’s multi-disciplinary teams.

3.3.2 Innovations in Site Characterization Tools

The first step in locating DNAPL sources is development of the site history concerning chemical storage, usage, and disposal. The next step is to characterize subsurface conditions away from any potential DNAPL sources. This is referred to as an “outside-in” approach. Such an approach allows development of an understanding of stratigraphy, groundwater flow, and contaminant distribution while minimizing the risk of cross contamination by drilling through a DNAPL zone. Dissolved concentrations in groundwater, which is an integrator of contamination, can be used along with site history information to “backtrack” to potential DNAPL source zones. The next step in the characterization process is to characterize the DNAPL zone, if appropriate, where the focus is more on soil data. Characterization will likely continue into the remediation stage.

During this initial work, a realistic site conceptual model is developed based on stratigraphy. Noninvasive and minimally invasive methods are used first, and plume information is used to infer up-hydraulic gradient source conditions. Source investigation methods are then selected that provide desired remediation data and minimize the risk of DNAPL mobilization. The following discussion provides a summary of available tools for site characterization in DNAPL source zones. A compilation of literature citations and information sources for site characterization is provided in Section 6.0.

Non-Invasive Tools: Non-invasive tools that can be used for DNAPL characterization include: 1) site history information (e.g., chemical use, inventory and disposal records), 2) historical aerial photographs, 3) geological fractures and outcrops, 4) soil gas analysis, 5) surface geophysics, 6) site infrastructure information (e.g., sewers) and 7) employee/witness interviews. Soil gas surveys can be either passive or active. For DNAPL source identification, old releases, particularly in hot environments, may have a limited soil gas signal due to weathering. Measurement of naturally occurring radon (radon-222), which partitions into DNAPL, has been used at a few sites to infer DNAPL presence. Conventional surface geophysical methods are used to delineate stratigraphy, buried metal and conductive fluids. Subsurface DNAPL is a poor target for geophysical methods; thus, direct detection of DNAPL is unlikely by this technology.

Invasive Tools: Invasive tools that can be used for DNAPL characterization include: 1) test pits, 2) probing and drilling, 3) soil examination methods, 4) downhole methods, 5) groundwater quality profiling using direct push (DP) and multilevel wells, 6) well measurements for DNAPL distribution, 7) characterization of DNAPL samples, 8) borehole geophysics, and 9) partitioning interwell tracer tests (PITTs). Test pits are an efficient way to observe shallow stratigraphy and DNAPL contamination distribution. All of these tools with the exception of the PITT have been widely used to characterize DNAPL zones. The PITT has also received extensive testing and demonstration, but its high cost tends to limit the widespread deployment of this technology except at very large sites such as DNAPL source areas at DOE or DOD facilities. Also, uncertainties still persist on the accuracy of the PITT where significant DNAPL mass may be present in low permeability zones in the subsurface. Other invasive tools are discussed below.

For probing, two widely used direct-push (DP) sampling techniques are rotary hammer or percussion methods (Geoprobe®) and cone penetration testing (CPT). The benefits of direct-push sampling include: 1) a variety of tools that can be used, 2) rapid stratigraphic logging and contaminant detection using sensor systems, 3) rapid, depth-discrete sampling of soil, soil gas, and water, 4) no drill cuttings and little investigation-derived waste (IDW), 5) minimally invasive with effective grouting and sealing capabilities, 6) reduced potential for contaminant drag-down, and 7) the availability of standard methods (ASTM D-6282 for direct-push soil sampling, ASTM D-6001 for direct-push groundwater sampling, and ASTM D-3441 for cone penetration testing). The advantages and limitations of the direct push sampling techniques are listed in Table 3-1.

For drilling, there are several technologies available. One newer drilling technology is rotasonic drilling. It employs use of high-frequency mechanical vibration and limited rotary power to drill. This technology is fast, can provide excellent quality, large diameter, relatively undisturbed cores of soil and rock for characterization, and minimizes IDW. Contaminant drag-down is a reduced concern because an outer casing is advanced as drilling proceeds, but the technology has limited availability and relatively high cost and may bias sampling because of heat generated during the drilling process.

Methods to examine soil cuttings/core above ground include: 1) organic vapor analysis (OVA), 2) ultraviolet (UV) fluorescence, 3) hydrophobic dye shake test, 4) Ribbon NAPL Sampler (RNS) core strip test, and 5) chemical and partitioning analyses. Chlorinated solvents do not fluoresce unless they are mixed with petroleum products (e.g., cutting oil), coal tar, or naturally occurring humic compounds that do fluoresce. The hydrophobic dye shake test involves mixing the soil sample with water and hydrophobic dye powder (e.g., Sudan IV). The RNS cover is a hydrophobic dye-striped tubular fabric designed to contact soil core extruded from a core barrel. Advantages and limitations of these methods are listed in Table 3-1.

For chemical analysis of soil core samples, it is important to minimize volatility losses (e.g., by using methanol as a preservative – EPA SW846 Method 5035). Equilibrium partitioning calculations can then be performed using the code NAPLANAL www.dnapl.com/publications.html) or similar methods to infer NAPL presence. Based on equilibrium partitioning calculations, the presence of DNAPL may be inferred from soil concentrations as low as a few hundred mg/kg.

Down-hole Methods for Detecting DNAPLs: Down-hole methods include 1) membrane interface probe (MIP), 2) RNS (aka NAPL FLUTe), and 3) cone penetrometer technology (CPT)/laser induced fluorescence (LIF). The MIP is a direct push-logging tool that records continuous relative VOC concentrations. It is used in combination with the electrical conductivity to provide rapid, real-time, detailed characterization of stratigraphy and VOC contamination. The RNS uses a pressurized flexible liner to support and seal a borehole and force a dye-striped NAPL absorbent ribbon against the borehole wall. Advantages and limitations of these methods are listed in Table 3-1.

Three different downhole fluorescence detection systems have been developed: 1) Site Characterization and Analysis cone Penetrometer Systems (SCAPS), 2) Rapid Optical Screening Tool (ROST), and 3) Fuel Fluorescence Detector (FFD). CPT uses strain gauges to measure soil behavior properties while LIF provides real-time logging of fluorescent contaminants. Thus, like MIP, CPT/LIF provides real-time characterization of stratigraphy and fluorescent contamination. The SCAPS CPT/LIF was developed by the Navy, Army, Air Force, and DOE; there are approximately eight units available for federal government use. ROST was developed by Dakota Technologies, Inc. (DTI) and marketed by Fugro, which operates seven ROST systems in the U.S. and Europe. FFD was developed by Applied Research Associates (ARA), which operates more than 20 FFD units in the U.S. Advantages and limitations of these systems are listed in Table 3-1.

Groundwater Profiling: Groundwater profiling downgradient of DNAPL source areas is used to backtrack to the source area. The profiling can be performed with either DP tools or multilevel wells. DP tools are used to collect multiple discrete groundwater samples from coarse sediments at multiple depths in a single hole. Available tools include 1) Waterloo Profiler®, 2) Geoprobe® Dual Tube and GW Profilers, and 3) VERTEK ConeSipper™. In order to apply these tools, one needs to know the stratigraphy to select sampling zones. Advantages and limitations of these tools are listed in Table 3-1.

For measuring groundwater quality, hydraulic head, and hydraulic conductivity in overburden and bedrock over time, multilevel groundwater monitoring systems can be used. Multilevel groundwater monitoring systems include: 1) conventional well clusters, 2) Continuous Multichannel Tubing™(www.solinst.com), 3) Waterloo Multilevel System (www.solinst.com), and 4) Westbay MP System® (www.westbay.com), and 5) Water FLUTe™(www.flut.com). Interpreting dissolved concentrations may be difficult due to non-uniform DNAPL distribution, mixing of groundwater in the well (a function of the well screen length), and effective solubility when dealing with multi-component DNAPLs. For conventional wells, the general guidance is that concentrations greater than 1% of the effective solubility suggest the presence of DNAPL, and concentrations exceeding 10% of the effective solubility indicate a very high probability of DNAPL. Unfortunately, the exact location of the DNAPL is not easily inferred from the aqueous phase concentration data, and estimates of the source-zone volume may be overestimated using these empirical rules of thumb regarding DNAPL presence.

Table 3-1. Advantages and Limitations of Various Site Characterization Technologies

TOOL	ADVANTAGES	LIMITATIONS
Percussion Probing (Geoprobe®)	-Less expensive -More mobile and available -Well developed sampling tools -Availability of certain sensors	-Difficult to penetrate hard dense soils -Depth limitation
Cone penetration	-Greater depth penetration -Certain sensors better developed (LIF, tip resistance, sleeve friction, etc.)	-More expensive -Less available -Less maneuverable
Organic vapor analysis Screening of soil cores	-Rapid and inexpensive -High concentrations of VOCs associated with NAPL presence -Useful to focus sampling -Readings sensitive to effective contaminant volatility, water content, sample temperature, and sample handling	
UV fluorescence detection methods	-Quick and inexpensive -Many NAPLs fluoresce -Can provide detailed information on relationship between stratigraphy and contaminant distribution -Can document using a digital camera	-Requires fluorescent NAPL -Indiscriminant -Interfere from non-target fluorescent materials (such as shell fragments in coastal sediment) -Significant potential for false positives and false negatives
Hydrophobic dye shake Test use and limitations	-Simple, quick, and inexpensive field methods for qualitative assessment and visual confirmation -Does not require analytical equipment	-Known background and NAPL-contaminated samples should be examined to check for interference and site-specific response -Can only detect NAPL if present in samples -Potential for false positives (reaction with other organic matter) and false negatives (not enough NAPL present) -Visual contrast can be difficult to discern in dark soil
Using RNS strips to detect NAPL in soil core	-Relatively simple, direct, and cost-effective (~$4/ft for hydrophobic dye-impregnated cover) -Can provide detailed information on relationship between stratigraphy and contaminant distribution -Amendable to rapid documentation via photography	-Minor discoloration of liner associated with handling and contact with plastic core sleeves -Relatively faint reaction to some NAPLs -Color fading and/or non detection due to evaporation -Potential for false positives and false negatives -Potential for cross contamination (open hole)
Membrane interface probe (MIP)	-Widely available -Simultaneous log of VOCs and soil conductivity -Operates in vadose zone and soil conductivity -Useful for delineating NAPL source zones -Rapid site screening (100s of feet per day). -Cost savings	-High detection limits, qualitative analytical data -Designed for volatile contaminants -Contaminant carryover can be high -Penetration resistance limitations -Shallow use

Table 3-1. Advantages and Limitations of Various Site Characterization Technologies, continued

TOOL	ADVANTAGES	LIMITATIONS
Downhole RNS (aka NAPL FLUTe™)	-Provides continuous record of NAPL distribution with depth at borehole location -Can be deployed in variety of hole types -Can provide cost savings	-Heterogeneity may limit value of information -Relatively ambiguous reaction to some NAPLs may be difficult to interpret -Wicking may exaggerate NAPL presence -Potential for false positives and false negatives -Potential for cross contamination
CPT/LIF UV fluorescence probes	-Real-time delineation of stratigraphy and fluorescent contamination -Typical daily productivity of 300 to 400 feet at 10 to 15 locations -LIF waveforms offer product identification/verification and rejection of non-contaminant fluorescence -Reduced IDW and exposure to site contaminants -Potential cost savings	-Primarily applicable to PAHs -Subject to interferences -NAPL has to be adjacent to sapphire window -Limited availability -Cost
DP groundwater profiling	-No drill cuttings and little purge water -Can pump clean water out through screen during advancement to minimize clogging and drag-down of contaminants -Can collect multiple samples (at any spacing) with depth using peristaltic or pneumatic low-flow pumping methods -Can perform K tests -Can develop well screen -Holes can be grouted through rods -Provides detailed concentration profiles that can be used for backtracking to NAPL source -Rapid and relatively cost-effective	-Limited by lithology (clogging, turbidity, and lack of yield problematic in fine-grained sediments) and depth (depending on drilling and sample collection methods) -Only provides a snapshot in time of water quality -Concentrations of metals and hydrophobic compounds likely to be biased due to sample turbidity -Vertical hydraulic gradients can impact backtracking interpretation -Due to heterogeneity and dilution effects can still be difficult to define morphology of DNAPL sources -Concentration > effective solubility indicates NAPL in sample -Concentration < effective solubility requires interpretation
PITT	-Can estimate DNAPL saturation	-Need to know DNAPL location -Need sufficient hydraulic conductivity for tracer test -Need small enough source to allow adequate well spacing to conduct tracer test in reasonable time frame -The presence of natural organic carbon may cause some difficulty with the interpretation of the results -For heterogeneous DNAPL distribution (especially pools), underestimates DNAPL volume -Expensive and regulatory concerns may require recovery of tracers

DNAPL Mass and Distribution: If DNAPL does flow into a well, it is important to determine DNAPL thickness and collect a DNAPL sample to determine its properties (e.g., density, viscosity, composition, interfacial tension.). Other invasive tools include borehole geophysics. Unfortunately, DNAPL is a poor target for geophysical methods, and they are unlikely to detect DNAPL. Residual DNAPL saturations may be estimated using a PITT by comparing the retardation of tracers that partition into the DNAPL (e.g., alcohols) to tracers that are not retarded (e.g., bromide). Advantages and limitations of PITT are listed in Table 3-1. Another way to estimate DNAPL saturation is the push-pull partitioning tracer test using naturally occurring radon-222 *(Davis et al., 2003)*.

DNAPL Mass Discharge Rate and Flux Distribution: As discussed in earlier sections, it is important to estimate the downgradient contaminant mass discharge rate or flux distribution. This estimate could be important as a metric to assess DNAPL source remediation and/or as a key input to evaluate monitored natural attenuation. There are three methods to estimate mass flux: 1) use water quality data from transects (multiple location and depths) combined with groundwater velocity, 2) use downgradient aquifer tests in a transect of wells, tracking mass pumped, and 3) use sorptive permeable media placed in downgradient wells to intercept contaminated groundwater and release resident tracers. Additional information on these approaches was discussed in Question 2.

3.3.3 Summary

DNAPL site characterization tools are available to collect data and information for most of the performance metrics identified in Question 2. Because of the inherent complexities of DNAPL migration and distribution in subsurface environments, as discussed in Section 2.0, none of the characterization tools is without accuracy limitations. This topic has been thoroughly reviewed in the literature, and several recent summaries provide adequate information for selection of the appropriate site characterization tools for the purposes of selection, design, and performance assessment of DNAPL source depletion technologies.

The Panel concluded that although available technologies are adequate to locate DNAPL source zones (e.g., footprint of the suspected source zone), in practice, delineating the DNAPL source zone and determining the actual mass of DNAPL is very difficult, particularly in fractured systems, and will only be possible with extensive sampling at the majority of sites. This could involve soil-core analysis on a very small interval, perhaps as small as a few inches in the vertical and a few feet in the horizontal. As the geological setting becomes more complex, and the scale of the potential source area increases, this level of detailed sampling becomes impractical, resulting in uncertainty in source-zone characterization. The cost and level of accuracy achievable by source-zone characterization tools can only be answered on a site- specific basis. Further investment by EPA in determining the level of accuracy required for source-zone characterization tools as a function of subsurface geologic conditions, the specific DNAPL depletion technology, and the remediation goals and metrics is warranted.

New techniques for monitoring groundwater flow and contaminant mass discharge rate or local mass fluxes have been developed, but to date, these methods have been field tested at a limited number of sites. Comparative testing of these new methods is just getting underway with funding from SERDP and other agencies. Further guidance on reliability of mass flux and discharge rate monitoring must wait for completion of these investigations. EPA support of these efforts is encouraged.

To better evaluate the success of source-zone depletion technologies at DNAPL sites, a set of diagnostic tools is needed for application at hydrogeologically distinct sites employing a range of innovative in-situ chemical, biological, and thermal treatment technologies. Mass flux or discharge rate measurement may serve as a useful metric of overall system performance, independent of the mass depletion technology used, because these measurements can demonstrate a reduction in the rate of contaminant mass release from the treated zone. Innovative technology-specific tools (e.g., molecular tools for in-situ bioremediation), and geology-specific tools are also needed for a real-time diagnosis of remedial technology performance.

3.4 Question 4: What Performance can be Anticipated from DNAPL Source-Zone Depletion Technologies?

EPA asked the Panel to assess the “status of technology development and deployment for DNAPL source remediation” and to evaluate the costs of using these technologies. In addressing these issues, the Panel recognizes that many technologies have been implemented for DNAPL source-zone remediation as a component of site groundwater remediation strategies, and substantial information is available on the effectiveness and costs of these systems. The Panel is also familiar with the substantial efforts of various federal agencies to document DNAPL remediation projects. EPA’s Office of Research and Development (ORD) has funded research on the development of new technologies for DNAPL source remediation through EPA labs, the SITE program, or through university research programs. Development and deployment of DNAPL source-zone technologies have also been supported by the DOE, the Department of Defense (DOD) through the Strategic Environmental Research and Development Program (SERDP), and various international agencies.

Over the past two decades, a number of technologies have emerged with the potential to achieve substantial reduction in the mass of DNAPLs found in either the vadose zone or the saturated zone, depending on the geologic conditions in the subsurface. EPA's Technology Innovation Office (TIO) and EPA's SITE program have compiled numerous reports and other documentation on the effectiveness of these technologies for remediation of DNAPL impacted sites. The DOE has also documented DNAPL removal technology demonstrations at DOE facilities (see e.g., *NRC, 1999*). Since 1994, several committees of the National Research Council have also compiled summaries of groundwater remediation technologies (*NRC, 1994; 1997; 1999; 2003*) with some focus on source remediation options (*NRC, 1997b; 1999; 2003*).

Other sources of information on the status of technology development and deployment of source remediation technologies include the peer-reviewed literature and vendor or consultant non-peer reviewed reports. Numerous web sites also provide access to large amounts of information on source depletion options (e.g., Interstate Technology Regulatory Council, [ITRC], www.itrcweb.org; the Strategic Environmental Research and Development Program, [SERDP], www.serdp.org; Federal Remediation Technologies Roundtable, [FRTR], www.frtr.gov; Ground-Water Remediation Technologies Analysis Center, [GWRTAC], www.gwrtac.org.; various EPA web sites, including Technology Innovation Office [TIO]).

However, the Panel was not provided the resources to undertake a thorough assessment of this extensive body of information. Instead, we provide here the collective judgment of the Panel on three issues related to the performance of technologies for DNAPL source-zone mass depletion, namely, a) the status of development and deployment of the technologies, b) the anticipated performance of these technologies for different DNAPL release and distribution scenarios, and c) a brief commentary on cost of these technologies relative to containment options.

3.4.1 Status of Development and Deployment of DNAPL Source-Zone Depletion Technologies

In addition to DNAPL pumping, the four major generic categories of technologies applicable to DNAPL source depletion are fluid flushing and recovery technologies, thermal technologies, chemical degradation (oxidation or reduction) technologies, and biodegradation technologies. Table 3-2 lists some of the specific technologies within these categories that have been deployed in either small scale controlled field experiments, pilot studies at DNAPL-impacted sites, or as part of a final remedial action at the full field scale level. Several of the listed technologies have demonstrated the potential to achieve substantial DNAPL depletion from source zones.

The following material presents a brief technical description of each of these technologies.

***Water Floods**:* Water floods involve the injection of water to mobilize DNAPL towards an extraction well and to improve the rate of DNAPL dissolution. We consider this technology, which has been widely used in the petroleum industry, to be sufficiently developed and available for deployment in DNAPL source depletion applications. The technology is applicable at sites where DNAPL may be mobile, such as coal tar and creosote sites *(e.g., see Sale and Applegate, 1997*). The technology may be suitable for source-zone applications if stabilization of the DNAPL mass is one of the remedial action objectives since the mobile DNAPL will then be extracted. The technology is not capable of removing residual DNAPL.

Steam Enhanced Extraction: Steam enhanced extraction (SEE) is a thermal technology that utilizes steam to heat the subsurface environment, combined with vapor and liquid extraction to recover vapors, contaminated water, and DNAPL. Air co-injection with the steam increases the recovery rate of volatile DNAPLs during the time between the beginning of steam injection and the arrival of the thermal front to the extraction wells (see *Hunt et al., 1988; Udell et al., 1997*). Because the injected air facilitates the removal of the DNAPL mass as a vapor, remobilization of NAPL due to condensation at the edge of the heated zone can be minimized. Steam injection can achieve uniform heating of the source zone to the steam temperature that causes complete vaporization of the more volatile DNAPLs including chlorinated solvents (such as PCE) with boiling points greater than that of water. This technology is most applicable to hydraulically accessible media with DNAPL in pools of significant mass and DNAPL distributed as residuals with small total mass. For hydraulically inaccessible zones that can be heated to steam temperature (modest thickness heated from two sides), it is also applicable to DNAPL of significant mass and significant dissolved mass.

In Appendix A, one case study of SEE is presented. Substantial amounts of a mixture of LNAPLs and DNAPLs were removed, but MCLs in the source zone were not achieved at the conclusion of the SEE demonstration. Subsequent monitoring appears to show that chemicals of concern have decreased below detection limits within the remediation zone (*Udell, 2002*). Cost data were not available for this case study.

Another case study of the use of steam-enhanced extraction is the Visalia Pole Yard Site in California. This site is a former wood-treating facility that exhibited extensive creosote and pentachlorophenol contamination in the saturated zone. Over 170,000 gallons of DNAPL have been removed or destroyed at this site where the source zone is approximately 1.8 acres in areal extent. Reportedly, concentrations of chemicals of concern at the site are not yet below regulatory levels at all points of compliance, but site managers are optimistic that site closeout will be achieved within the next few years (*Sciarrota, 2002*; see also TIO website for more details). The cost to date appears to exceed $25 million dollars. Independent verification of these costs has not been reported. Final projected costs to site closure have also not been reported.

EPA's Technology Innovation Office (TIO) of the Office of Solid Waste and Emergency Response (OSWER) recently published a compilation of case studies on the use of thermal technologies for soil and groundwater remediation at chlorinated solvent impacted sites (*U.S. EPA, 2003*). This report provides case studies on several full-scale SEE case studies involving chlorinated solvents in unconsolidated media and indicates that SEE has been implemented for DNAPL depletion in source zones at 14 sites in either full- or pilot-scale. At these sites substantial amounts of chlorinated solvent DNAPLs were removed, and for a few sites, no further action letters were issued by regulators.

Table 3-2 Summary of DNAPL Source Depletion Technologies Currently Available or Under Development

CATEGORY	TECHNOLOGY	PRIMARY MODE OF ACTION
Fluid Flushing	Water Flooding and Extraction	Removal of mobile DNAPL through application of sufficient hydraulic forces for DNAPL recovery, commonly used for oil recovery.
	Surfactants/Cosolvents	Solubilization/mobilization and recovery via extraction wells with use of a variety of surfactants, foams, cosolvents.
	Air Sparging	Injection of air into saturated zone, and volatilization of DNAPL with recovery of vapors by soil vapor extraction.
Thermal	Steam	Steam injection into saturated zone, heating of groundwater to steam temperature, mobilization/volatilization of DNAPL and recovery via water and vapor extraction wells.
	Electrical Resistance Heating - Vertical Electrodes	Three-phase or six-phase electrode arrays to provide thermal energy to subsurface formation (soil or groundwater), with recovery of fluids by vapor extraction or fluid extraction wells.
	Conductive Heating - Thermal Blankets or Thermal Wells	Electrical heating via thermal "blankets" placed horizontally at ground surface or vertical thermal wells.
Chemical	Chemical Oxidation with Various Chemical Solutions	Abiotic direct chemical oxidation of DNAPL by chemical solutions (sodium or potassium permanganate, persulfate, Fenton's reagent) injected into subsurface.
	Zone Source Encapsulation and Chemical Reduction	Injection of clay/zero valent iron into source zone to produce hydraulically inaccessible zone, reduction of DNAPL by diffusion and reaction with zero valent iron.
Microbial	In-situ Biodegradation	Injection of electron donor solutions (e.g., lactate) in source zone for stimulation of indigenous anaerobic dechlorination microbes that accelerate dissolution of DNAPL and subsequent microbial reduction of chemicals.
Combined	Cosolvent Flushing and Enhanced Microbial Anaerobic Reduction	DNAPL removal by solubilization/ mobilization followed by enhanced anaerobic dechlorination to ethene.
	Steam with Air/Oxygen Injection	Hydrolysis/pyrolysis technology for DNAPL removal and abiotic oxidation of DNAPL constituents.
	Thermal Methods Combined with Microbial Degradation	Steam, conductive or resistive heating followed by microbial degradation at appropriate temperatures.

Electrical Resistance and Thermal Conductive Heating: Introduction of thermal energy into the subsurface through conductive heating by placement of electrodes, and application of AC voltage (typically 440V), has been used as a thermal-based source depletion technology at several DNAPL sites. Electrical resistance heating (ERH) technologies utilize vertical electrodes to introduce thermal energy. Heating by electrical current has been applied using three-phase AC, six-phase AC, and DC voltage. *(See TIO website for details; also see U.S. EPA, 1999b).* Thermal Conductive Heating (TCH) technologies use horizontal electrodes placed on the ground surface to inject heat into the subsurface by conduction through the soil. Since the electrical current follows the most conductive pathway, and the heat dissipation occurs in zones of high current density, electrical heating by conduction is independent of the hydraulic properties of the aquifer material.

One of the THC technologies, known as In-Situ Thermal Desorption (ISTD), has been primarily used to remove organic contamination in the vadose zone (see e.g., *Stegemeier and Vinegar, 2001*). Significant removals of DNAPLs in soils have been demonstrated. Soil temperatures can reach levels of several hundred degrees Celsius using this technology. There is also compelling data that suggests that accelerated oxidation of chlorinated compounds may occur at elevated temperatures, giving rise to the possibility of abiotic destruction after heating has ceased.

All of the electrical heating technologies are commercially available, and sufficient information is available to conduct feasibility assessments on the use of these technologies for DNAPL source-zone depletion.

One of the case studies in Appendix A (Cape Canaveral) evaluated the performance (effectiveness and cost) of electrical heating to remove TCE present as DNAPL from the aquifer. This study did not demonstrate that the ERH technology was likely to be a cost-effective approach to source depletion at this site. See Appendix A for details. Other reports including commercial literature from the vendors of these technologies indicate removal of large amounts of NAPL from several sites, and several case studies reported in the non-peer reviewed literature, (e.g., various Battelle Conference Proceedings) indicate that site closure has been achieved using electrical heating technologies. EPA's recent report *(U.S. EPA, 2003)* summarizes the use of these technologies for soil and groundwater at chlorinated solvent impacted sites. ERH technologies have reportedly been implemented at full scale at eight sites and at pilot scale at nine sites, with data through 2002. The ISTD technology reportedly was implemented at full scale at four sites. Both performance and cost data are provided. At least one of the sites using the ERH technology *(*Skokie, Illinois, *see U.S. EPA, 1999b, U.S. EPA, 2003)* reportedly received a no-further-action letter from Illinois regulators, and source-zone concentrations of TCE reportedly were reduced to levels below the target concentration of 25 ppb for TCE. Costs for this site are reported to be $1.1 million dollars, for a 0.6-acre site.

Surfactant and Co-Solvent Flushing*:* Co-solvent and surfactant-enhanced extraction are flushing and recovery technologies that rely on mobilizing DNAPL by significantly increasing the aqueous solubility of DNAPL components and reducing interfacial tension to increase the rate of DNAPL extraction. The cost-effectiveness of the technologies depends, in part, on recovery of the flushing solutions following extraction. A summary of recent surfactant enhanced aquifer remediation (SEAR) demonstration projects is provided by Simpkin et al. *(1999*). In the last few years, additional research work on these technologies has demonstrated significant removal of chlorinated solvent DNAPLs in unconsolidated geologic settings (see e.g., *Jawitz, 1998*).

These technologies may be ready for deployment in some unconsolidated geologic settings, but to the Panel's knowledge, neither field-scale demonstrations nor full-scale applications have yet to achieve site closure at a DNAPL source zone. The Bachman Road and Sages sites, summarized in Appendix A, are examples of removing substantial amounts of DNAPL, with subsequent changes to the geochemical environment that enhance biodegradation of the remaining mass of DNAPL. These technologies are not likely to be effective at removing DNAPL present in low permeability source zones, such as fractured systems.

Air Sparging: Air sparging is a widely used technology for remediation of volatile organic compounds in the dissolved state in groundwater and has been widely used for groundwater cleanup at petroleum hydrocarbon release sites (*Fields, et al., 2002*). The technology is also potentially applicable to DNAPL source zones when the DNAPL constituents are sufficiently volatile such as chlorinated solvent-impacted sites. The technology involves injection of air into the saturated zone through wells located to provide sufficient areal coverage of the DNAPL source zone. Capture of the volatilized contaminants from the unsaturated zone is an essential component of this technology. This technology has been developed and is readily available for deployment. The technology may achieve significant DNAPL depletion in the source zones that are hydraulically accessible, but it will not be effective when DNAPL is present in hydraulically inaccessible regions such as fractured clays or bedrock. No reports of successful cleanups of DNAPL source zones using air sparging have been found.

Chemical Oxidation: Chemical oxidation using various chemical oxidants (e.g., sodium or potassium permanganate solutions, persulfate, Fenton's reagent) is another promising process for source-zone depletion of some DNAPLs (see e.g., a recent survey by *Siegrist, et al., 2000*; *Siegrist, et al., 2001*). Known as In-Situ Chemical Oxidation (ISCO), chemical oxidation relies on rapid chemical reactions that will occur between the oxidant or oxidant-derived chemical species (e.g., hydroxyl radicals) and the chemical constituents in some DNAPLs. Pilot-scale demonstrations and full-scale applications have attempted in-situ treatment of low levels of chlorinated solvents and petrochemicals, and to a lesser degree, dense non-aqueous phase liquids (DNAPLs) using oxidant delivery by vertical injection probes (e.g., *Siegrist et al., 1998a, 1998b; Moes et al., 2000; Nelson et al., 2000; Parker et al., 2002*), deep soil mixing (e.g., *Cline et al., 1997*), flushing by vertical and horizontal groundwater wells (e.g., *Schnarr et al., 1998; West et al., 1998a,b; Lowe et al., 2002*), and reactive zone emplacement by hydraulic fracturing (e.g., *Siegrist et al., 1999; Struse et al., 2002*).

Much is known about the reaction processes that govern chemical oxidation of many organics in aqueous solutions as well as the transport processes influencing application in-situ, but there are gaps in the current knowledge base regarding ISCO applications for DNAPL depletion in source zones, particularly in fractured systems. While there is a theoretical basis for the degradation of DNAPL residuals by ISCO, the expected realization of the high destruction efficiencies of DNAPL source zones has remained elusive (see e.g., *Urynowicz, 2000*).

For application of chemical oxidants to DNAPL source zones, the major factors controlling performance include: 1) subsurface delivery and distribution of potentially large quantities of oxidant chemicals to degrade the DNAPL mass present and also satisfy any natural oxidant demand, 2) acceptable reaction rates between the DNAPL and the oxidant, and 3) undesirable secondary effects when large quantities of oxidant chemicals are added to the subsurface (e.g., gas evolution and fugitive emissions, particle formation and permeability loss, water quality deterioration due to metal impurities in oxidant solutions). In addition, the potential for development of interfacial mass transfer resistance (e.g., with MnO_4^-, a MnO_2 skin can form at the DNAPL-water interface) and a resulting inability to oxidize the DNAPL must be considered. The latter mechanism even suggests an approach to in-situ immobilization of DNAPL mass.

The three case studies included in Appendix A provide examples of the performance of the application of permanganate based ISCO for DNAPL source-zone depletion in sandy aquifers. In each of these cases, the DNAPLs are chlorinated solvents.

In summary, ISCO shows promise for DNAPL source-zone depletion in unconsolidated geologies, and may be suitable for attacking chlorinated solvent DNAPLs in fractured systems, but continued uncertainties on the effectiveness and cost of these technologies currently limit greater deployment of this technology for DNAPL source-zone depletion. DOD-funded research is currently addressing some of these uncertainties, and useful results should be available within the next twelve to 24 months (*See SERDP website for details*).

Chemical Reduction: Chemical reduction source treatment is based on the physical mixing of Zero Valent Iron (ZVI) into the DNAPL source zone to provide close contact between the DNAPL constituents and the ZVI to achieve reductive dehalogenation of the chemicals of concern. This technology is applicable for chlorinated solvent DNAPLs but is not suitable for creosote or coal tar DNAPLs. ZVI source treatment involves mixing a slurry of clay (generally kaolinite, though others have applied bentonite) and ZVI (e.g., 95:5 weight ratio of clay to ZVI) directly into the source zone. This is intended to create a relatively stagnant environment in the source zone within which slow diffusional processes may play an important function in transfer of the DNAPL constituent to ZVI particle surfaces. Complete treatment does not occur immediately but requires an extended time for various processes such as DNAPL dissolution, desorption, and diffusion to occur. The most appropriate application of the technology would involve a relatively small, well-defined source area consisting of residual/trapped DNAPL consisting of chlorohydrocarbons (e.g., PCE, TCE, carbon tetrachloride) amenable to ZVI reductive dechlorination.

To allow mixing/delivery, the source zone needs to be composed of unconsolidated soils. The source zone may extend above and below the water table. The technology is limited to DNAPLs treatable by reductive processes, and would have limited applicability to fractured rock sources. It would be applicable to all types of media amenable to mixing. One case study discussed in Appendix A summarizes a recent experience with this source depletion technology. This patented technology is available for deployment, but has been tested at only a few sites.

Another technology utilizing ZVI is a NASA-patented process using encapsulated micro- or nano-scale particles of ZVI within a micelle composed of water and oil/emulsifiers. The micelles are attracted to the DNAPL phase and will form DNAPL/emulsified ZVI mixtures. The VOCs will dissolve into the micelle and react with the ZVI. The composition of the micelle also supports biological reductive dechlorination as it decomposes. NASA has completed one test of the technology at the LC 34 complex in Florida, and the EPA SITE program has also evaluated the technology for source depletion at a TCE DNAPL site (see EPA SITE Program website for details). This technology is in an early stage of development and additional research is required to verify performance and cost.

In-Situ Biodegradation for DNAPL Source Zones: Conceptually, biological treatment of DNAPL in source zones is based on the ability of microorganisms to transform chemical constituents within close proximity to the DNAPL surfaces (the order of 100 μm), thereby resulting in enhanced rate of dissolution of the DNAPL constituents. Laboratory results by Cope and Hughes *(2001)* and Yang and McCarty (*2001*) using completely mixed lab-scale systems have shown that the dissolution rate of PCE DNAPL can be enhanced by a factor of over 15 times compared to the rate of aqueous dissolution. Recently reported results from field studies have shown significantly lower rates of enhanced dissolution (*Borden, 2003*), however.

This technology is being evaluated under the DOD Environmental Security Technology Certification Program (ESTCP) and NASA SBIR programs. A recent pilot study at the DOE Laboratory in Idaho (INEEL) showed successful treatment of a presumed TCE DNAPL source, and full-scale application of the technology using lactate as the electron donor has been implemented at INEEL to replace the current pump-and-treat system *(Sorenson et al., 2001*). The key design factor is delivering sufficient electron donors to the source zone to encourage microbial growth as close as possible to the DNAPL. Various organizations/researchers are investigating the use of food substrates that can partition into DNAPLs to enhance microbial degradation near the DNAPL/water interface. This technology may be applicable as a stand-alone source depletion technology, in conjunction with other source-zone treatment technologies or as a polishing step. It has the potential advantage of lower capital and O&M costs compared to alternative technologies, although a longer period of operation is likely compared to abiotic technologies.

Although this technology is still in an early stage of development, it has been deployed as a full-scale technology at a few sites and is planned for several others. The technology is not yet widely deployed, however. Given the potential cost reductions using this technology, further research is needed to confirm these potential benefits.

Combined Depletion Technologies: Combinations of one or more of the above technologies can also be employed for DNAPL source depletion. Both the Sages Site and the Bachman Road site, presented in Appendix A, are examples of combining co-solvent or surfactant flushing for DNAPL removal from a source zone, followed by microbially mediated degradation of the remaining constituents. Another promising combination is the use of electrical heating and steam injection as a hybrid thermal technology, known as Dynamic Underground Stripping. This technology has been demonstrated at one site (LLNL Gas Pad) with less than 3% of the total energy input coming from electrical heating and has been employed at several DOE sites including Savannah River and also the Visalia site *(*see e.g., *DOE, 2000).* Case studies for these sites are summarized in the recent EPA compilation (*U.S. EPA, 2003*).

Other promising combinations include thermal technologies followed by microbial transformations, which may require bioaugmentation with cultures containing halo-respiring microorganisms. Thermal treatments will significantly reduce the indigenous microbial populations. However, after temperatures have been reduced to more moderate ranges, the environment may provide little competition to the added microorganisms, allowing them to dominate the treated area and improve the degradation activity towards the residual chemicals. Additional research on these phenomena is needed. Chemical oxidation followed by biodegradation may also be an effective combined system for DNAPL source depletion. In general, these combination technologies have not been sufficiently tested in pilot or field studies to be considered as demonstrated technologies, and further research and assessment of these combinations as DNAPL source-zone depletion options is warranted. Combination technologies other than those listed should also be considered.

Table 3-3 summarizes the consensus judgment of the Panel on the “status” of the development and deployment of selected DNAPL source-zone depletion technologies. *(This Table includes most of the source-zone DNAPL depletion technologies familiar to Panel members and those that we consider the most developed, but it is not meant to cover all technologies available or to indicate any preference for one technology over another).* A technology is considered “developed” and ready for “deployment” at DNAPL sites if it has moved past the proof-of-concept and laboratory studies stage of development, and if there is sufficient information on performance and cost such that a feasibility level analysis, similar to that specified in the National Contingency Plan (NCP), can be conducted to determine if source depletion should be undertaken, and to select one technology or combination of technologies compared to other options. We suggest that if the technology meets the following five criteria, then that technology is now ready to be “deployed.” These five criteria are as follows: 1) completion of numerous (more than 10) pilot-scale projects in representative geologic settings that verifiably demonstrate substantial DNAPL source-zone depletion, 2) completion of at least five (5) full-scale projects, 3) availability of non-research level predictive performance assessment tools that allow design scale-up from pilot studies, 4) adequate cost data to allow for feasibility level assessments in the context of selection of source-zone remedial strategies, and 5) more than two technology vendors available.

It must be stressed that “deployment” does not imply that the technology is suitable for all DNAPL types, release scenarios, and observed DNAPL architectures. While a technology may be ready for “deployment” and in fact has already been deployed at full scale, significant uncertainties persist on performance and cost that can only be resolved through site-specific studies. The scale-up of these studies still represents a major technical challenge, however, because of the heterogeneous nature of the problem as discussed in Section 2.0 and other portions of this Report.

Of the technologies listed in Table 3-3, biodegradation technologies and combined technologies have a more limited database of performance and cost data compared to thermal, surfactant/co-solvent flushing, and ISCO technologies. For these generic categories, several technologies satisfy criteria 1, 2, 4, and 5, noted above. However, as noted in response to Question 5, user-friendly, non-research level multiphase numerical models are not yet available for these source depletion technologies, although research level models have been developed and are deployed at some large

Table 3-3 Status of Development and Deployment of DNAPL Depletion Technologies

Technology	Pilot Studies	Full Scale	Predictive Models	Sufficient Cost Data	At Least One Site Closure	More than Two Vendors
Water Floods	Y	Y	Y	Y	N	Y
Surfactants/Co-solvents	Y	Y	Y	Y	N	Y
Air Sparging	Y	N	N	N	N	Y
Steam Injection	Y	Y	Y	Y	Y	Y
Electrical Resistance	Y	Y	Y	Y	Y	Y
Conductive Heating	Y	N	Y	N	N	N
Chemical Oxidation	Y	Y	Y	Y	Y	Y
ZVI/Clay	Y	N	N	N	N	N
Biodegradation	Y	N	N	N	N	Y
Combination - Co-solvent with Biodegradation	Y	N	N	N	N	N
Combination - Thermal with Chemical Oxidation	Y	N	N	N	Y	N

Note: Y = yes, meets criteria; N = no, does not meet criteria.

DOE and DOD site studies. Further development of these models to produce more easily accessible modeling tools will provide a more reliable basis for technology selection, scale-up design from the results of pilot studies, and performance assessment.

Finally, it must be stressed that much of the pilot- and full-scale experience with these technologies has been developed for chlorinated solvent DNAPLs in unconsolidated geologic settings. The experience base using these technologies to remove DNAPL from fractured systems is much more limited, and this represents an important data gap in our understanding of the performance of DNAPL source-zone depletion technologies.

3.4.2 Anticipated Effectiveness of DNAPL Source-Zone Depletion Technologies

In Table 3-4, we summarize the Panel's consensus opinions regarding the "effectiveness" of these technologies to achieve remedial action objectives in different DNAPL scenarios. This Table summarizes in a conceptual way, the potential effectiveness of DNAPL source-zone depletion technologies for representative DNAPL subsurface scenarios. Two different hydrogeologic scenarios are considered in this evaluation: hydraulically accessible (permeable zones hydraulically connected to wells), and hydraulically inaccessible (low permeability zones such as fractured systems or permeable zones not hydraulically connected to wells). For hydraulically accessible media, two different DNAPL distribution scenarios are considered: DNAPL in pools of significant mass, and DNAPL distributed as residuals with relatively small total mass. DNAPL in pools of significant mass implies free-phase, possibly mobile liquids, usually trapped above a major low-permeability capillary barrier. DNAPL distributed as residuals with small total mass represents a source-zone scenario with relatively small, discontinuous ganglia and diffused mass.

For hydraulically inaccessible zones (i.e., where advective flow is negligible), two distributions of mass loading are considered: the first, more significant scenario, is DNAPL of significant mass typically resulting from gravity flow into high permeability regions through otherwise insignificant vertical pathways, media wetting DNAPLs imbibing into low permeability zones, and low-permeability media with significant fracture volumes allowing substantial accumulation of DNAPL mass. Low-permeability media with significant dissolved mass may also be considered to be part of the source zone; thus, depletion technologies are also evaluated for their applicability to those soils.

The likely effectiveness of various source depletion technologies for an individual site can be inferred from current scientific understanding, laboratory tests, and past field performance. Based on the judgment of Panel members, Table 3-4 includes a judgment on the level of certainty of the effectiveness ratings. These are: E - Expected to be effective based on laboratory data and scientific knowledge, P - Possibly effective based on current scientific knowledge, and U - Unlikely to be effective based on current scientific knowledge.

The Table indicates that a number of technologies are capable of removing DNAPL from the saturated zone, depending upon the DNAPL distribution and the geologic conditions. Whether the technology will be successful depends in part on the remedial action objectives (RAOs) established for the source zone. If the RAO in the source zone is complete restoration (i.e, background levels of the DNAPL constituents), or MCLs, it is unlikely that any of the technologies currently available will be successful, except in situations involving small spills of DNAPL in relatively homogeneous saturated zones. However, if the RAOs focus on reduction of mass, reduction of mass discharge from a source area, or stabilization of the mobile DNAPL, several of these technologies could be candidates for implementation. Where significant uncertainties persist with respect to performance and costs of these technologies, additional R&D will be warranted given the potential for these technologies to meet alternative RAOs for the source zone other than MCLs or complete restoration.

Table 3-4 Potential Applicability of Various Source Depletion Technologies in Two Generic Hydrogeologic Situations

	Hydraulically Accessible (Permeable zones hydraulically connected to wells)		**Hydraulically Inaccessible (Low-permeability zones or permeable zones not hydraulically connected to wells)**	
	DNAPL in Pools, large mass (1)	**DNAPL distributed as residuals with small mass (2)**	**DNAPL of substantial mass**	**DNAPL distributed as residuals with small mass (2)**
Co-Solvent	P	E	U	U
Electrical Heating	E-P	E	E	P
Oxidation	P	E	U-P	P
Steam Injection	E	E	P	P
Surfactants	P	E	U	U
H_2O Flood	P	U	U	U
Chemical Reduction	U-P	P	U-P	P
Biological	U	P-E	P	P

E: Expected to be a candidate technology based on field and/or laboratory data and scientific knowledge
P: Possibly a candidate technology based on current scientific knowledge
U: Unlikely to be a candidate technology (i.e., impractical or not effective in a reasonable time frame) based on scientific knowledge
(Where two designations are shown, Panel members had differing opinions.)

(1) Defined as being free-phase and possibly mobile
(2) Defined as residual/distributed pools, relatively small, discontinuous, not connected pools, and diffused mass

3.4.3 Cost of DNAPL Source Depletion Technologies

Cost is a key factor in comparison of alternative remediation strategies at DNAPL sites. EPA and other organizations have compiled cost surveys on individual technologies, and information is available from the SITE Program and the TIO database, with cost data on most of the technologies discussed here. The recent EPA report on thermal technologies also provides some cost data for chlorinated solvent DNAPL-impacted sites. However, cost data are highly dependent on site-specific factors for all DNAPL source-zone depletion technologies. In addition, cost estimates are often provided by vendors without independent assessments of the accuracy of the reported numbers.

A brief review of the recent EPA report on thermal technologies for chlorinated solvents in source zones illustrates this problem. This report provides detailed case study summaries on over 15 sites. Cost data, if reported, are presented as total costs and unit costs (e.g., dollars/cubic yard of material). Unit costs for chlorinated solvents in soil ranged from $13/cubic yard to $118/cubic yard. Costs based on a per acre basis ranged from less than $.5 million to over $6.5 million per acre. In some cases, costs only included vendor costs, and costs incurred by the site (e.g., steam costs) were not included. At the Skokie site, which is one of the sites that has received a no-further-action letter, vendor-reported costs amounted to $1.8 million per acre ($1.1 million for an area of 0.6 acres). The estimated cost per acre for the Visalia site is currently about $15 million/acre.

Because of the site-specific nature of any cost estimates and the lack of independent reviews of vendor-reported costs, generalizations regarding the unit costs or total life cycle costs for any of these technologies applied to DNAPL source-zone depletion are subject to significant errors and can be misleading. In place of such an analysis, we present here a brief comparison of a source-zone depletion strategy compared to a hydraulic containment strategy for the Visalia DNAPL site. In this case study, information has been provided on both the costs for source depletion using steam-enhanced extraction combined with abiotic chemical oxidation and the costs for a pump-and-treat system in operation prior to the initiation of source removal. Reports provided by the Visalia operators indicate that the steam/oxidation technology has cost approximately $25 million to date. This investment may potentially eliminate the need for continued use of the hydraulic containment system costing $1.2 million annually. It is, therefore, instructive to compare the net present worth of these two alternatives, assuming that the cost data are accurate, and assuming that in the near future, the pump-and-treat system at Visalia will be shut down when the RAOs for the site are met.

Table 3-5 contains a net present value (NPV) comparison for varying annual costs and varying interest rates, assuming 100 years of O&M for the pump-and-treat system. While 30 years is the typical period used in such calculations, 100 years is more appropriate for expected indefinite operation of a hydraulic containment option. As shown in Table 3.5, for the $1.2 million annual costs, the NPV for the pump-and-treat system only exceeds the cost of the source depletion option if the interest rate decreases below 5 percent (a value of 3.9 percent is a typical value for the time value of money used by the public sector while 12 percent represents a typical discount rate used by the private sector to evaluate alternative investment options). Furthermore, O&M costs are tax-deductible expenses for private site owners and thus, even at an interest rate less than 5 percent, the annual O&M costs may have a net present value cost lower than the capital cost required for the thermal remedy.

It should also be noted that for the median pump-and-treat site, with annual costs of $180,000 according to EPA's 28 site study (*U.S. EPA*, *2001)*, the net present value cost of a source depletion strategy would need to be less than $3.6 million at a 5 percent discount rate or less than $1.5 million at 12 percent to show positive economic benefits compared to the continued use of the hydraulic containment option. In the final analysis, this comparison suggests

Table 3-5 Net Present Value of Annual O&M Costs for Pump-and-Treat Technologies

Annual Costs	**Interest Rate (%)**			
	2	**3.9**	**5**	**12**
$180,000	$7,779,953	$4,521,368	$3,575,490	$1,499,990
$500,000	$21,610,981	$12,559,355	$9,931,917	$4,166,639
$1,200,000	$51,866,353	$30,142,452	$23,836,601	$9,999,935

that for DNAPL-impacted sites where the source areas are small (less than a tenth of an acre), depth to groundwater is moderate (less than 20 feet), and the total source-zone volume is also moderate, with RAOs other than MCLs in the source-zone being acceptable to all parties, and the value of land is high (>$1 million per acre), a source-zone depletion strategy using the appropriate technology may be justified on economic grounds. On the other hand, for large, complex sites, with fractured systems, and DNAPL at depth, costs for the source depletion strategy may not be justified, and containment may be the logical option. Of course, there are other benefits to source depletion other than cost savings, and those benefits may shift the balance in favor of undertaking a source depletion remedy.

3.4.4 Summary

Over the past 15 years, a wide range of innovative in-situ technologies has been developed, and tested at the laboratory and small field- or pilot-scale for removal or destruction of all types of DNAPLs in a variety of geologic settings for the source zones. Some of these technologies have also been applied at larger field sites, although the number of such case studies is limited. These technologies can be broadly characterized as follows: flushing and fluid recovery technologies, thermal technologies, chemical oxidation or reduction technologies, and biodegradation technologies. Of these general categories, only the biodegradation technologies are still in early stages of development compared to physical/chemical-based technologies, but some biodegradation technologies have been deployed or are planned for deployment at several DNAPL sites. Nonetheless, questions on effectiveness, cost, and applicability to DNAPLs other than chlorinated solvents are still unanswered.

Based on the Panel's experience and knowledge of the published and unpublished literature on DNAPL source depletion technologies, including the case studies presented in this Report, the Panel's consensus position is that several technologies are clearly capable of removing substantial amounts of DNAPL from a selected range of geologic settings, primarily in unconsolidated media, regardless of the DNAPL properties. Thermal, surfactant flushing, and ISCO technologies are sufficiently developed and tested such that they should be considered available for deployment, with sufficient information on performance and cost to conduct feasibility level analyses for the purpose of remedial action decision-making. Cost and performance uncertainties for all technologies still persist, however, due to site-specific uncertainties at DNAPL-impacted sites, particularly with respect to DNAPL in fractured systems.

3.5 Question 5: Are Currently Available Tools Adequate to Predict the Performance of Source Depletion Options?

Among the many challenges facing the remediation of DNAPL sites is the difficulty in scaling up either laboratory- or pilot-scale investigations of DNAPL source-zone depletion technologies to the field scale. This is, in part, due to site heterogeneities, and, in part, due to difficulties in site characterization. In order to overcome this scaling problem, a number of tools have been developed to provide decision-makers with a quantitative basis for making decisions regarding the application of DNAPL source-zone depletion technologies. The adequacy of the currently available tools in forming the basis for these decisions is the focus of this section.

Most source-zone remediation technologies rely on the delivery of remedial agents to the contaminated region. The injected agents may be designed to extract contaminants (e.g., water flooding, solvent/surfactant flushing, air sparging, steam flushing), or they may be injected to promote in-situ reactions (e.g., chemical oxidation, reductive dechlorination). The performance of any of these technologies will depend on efficiently delivering the remedial agent (water, air, heat, surfactants, cosolvents, oxidants, electron donors, etc.), the extent of (local) contact with entrapped or pooled DNAPL within the swept zone, and the rates of reaction or inter-phase mass transfer subsequent to this contact. Various tools are available to the practitioner to assist in the design, field implementation, and performance assessment of these source depletion technologies. These tools include computer models of varying sophistication and complexity, technical and regulatory guidance documents, and documentation of case studies including pilot testing at either the lab- or field-scale. Each of these tools provides a different type and level of information for better remedial design or performance prediction.

3.5.1 Numerical Models: Deterministic Approaches

The most quantitative tools for remediation design are numerical models. Although there is an enormous range in complexity among the various available models, all are based upon the solution of mass, momentum, and in some cases, energy conservation equations. The simplest and most well-documented models are those that describe single-phase, multi-dimensional fluid flow in both homogeneous and heterogeneous unconsolidated media. The most complex are the models for DNAPL sources and plumes located in fractured media.

In the treatment of DNAPL sources within the saturated zone of unconsolidated media, several current models are useful for the hydraulic design of in-situ flushing schemes (water flooding, cosolvent or surfactant flushing, chemical oxidation, etc.). A number of commercial packages are available; most in common use are based upon the USGS finite-difference simulator MODFLOW. These packages are generally user-friendly and require parameter inputs that are familiar to most groundwater practitioners.

Implicit in the application of a single-phase, fluid flow model to a DNAPL source-zone extraction (by flushing) scenario, are a number of assumptions that may be violated at a particular site or not applicable for the implementation of a specific remedial technology. One important assumption is that the resident groundwater and the injected flushing solution are (hydraulically) indistinguishable. If the injected fluid has properties distinct from the resident groundwater (such as a different density or viscosity), prediction of the hydrodynamic sweep of the DNAPL source zone requires the application of a coupled, single-phase flow and transport simulators. Multi-contaminant transport simulation is also required if the technology performance ultimately depends on the delivered concentration of some remedial agent in the flushing fluid. Contaminant transport simulators that incorporate the compositional dependence of fluid density and viscosity are less commonly applied for the design of DNAPL source depletion technologies. A few codes, however, are commercially available and reasonably well documented (e.g., SUTRA). Although such codes can accommodate nonlinear reactions (e.g., sorption) and variable fluid density, they have not generally been applied to DNAPL source-zone depletion scenarios. Thus, application of these codes to source-zone depletion may require substantial parameterization input from the user, and in some applications, may even require model source code adaptation.

Application of a single-phase flow/transport model to a DNAPL site remediation scenario also implicitly assumes that the DNAPL is hydraulically immobile, and that its presence does not substantially influence the flow paths and rates of the injected fluids. A class of computer models alternatively conceptualizes the source zone as a multiphase fluid system. Codes within this class are the most complex and the most versatile of available modeling tools. A multiphase modeling approach is required for the design and evaluation of technologies based upon gas injection (e.g., air sparging, steam flooding) or technologies that attempt to mobilize the contaminants as a separate organic phase (e.g., low interfacial tension surfactant flushing). Although some commercial models are available (e.g., UTCHEM, TOUGH, MISER, COMPFLOW) for targeted multiphase remedial applications, use of these codes requires an experienced user and extensive site-specific information on system chemical and physical properties. Nonetheless, currently, some of these codes are being used to design and evaluate the performance of thermal and surfactant flushing DNAPL source depletion technologies, based on the experiences of the Panel. In addition, successful application of these codes requires site-specific data on permeability distribution and DNAPL distribution. An example application is the multiphase flow code, SWANFLOW, used to evaluate DNAPL behavior and recovery at the Hyde Park and S-Area landfills in Niagara Falls, NY (*Faust et al., 1989*).

Application of the above models to predict effectiveness of the sweep of an identified source zone can be relatively straightforward, particularly in a low-heterogeneity geologic setting. Model predictions of contaminant recovery or transformation within the source zone, however, are subject to a high level of uncertainty. The accuracy of such model predictions is predicated on knowledge of the total contaminant mass within the source zone and its spatial distribution, as well as the limiting rates of reaction or inter-phase mass exchange. In-situ rates of reaction or inter-phase mass exchange will generally be governed by a complex coupling of physical, chemical, and (sometimes) microbiological processes. The identification and relative importance of these processes for a particular remedial application will depend upon site-specific conditions, such as local groundwater geochemical conditions, DNAPL architecture, microbial populations, and geologic heterogeneity.

Another important debate (and a gap) in development and application of comprehensive simulation models deals with the need for a linkage of source-zone and plume-zone process models or alternatively the use a single code for modeling both regions of interest. The former strategy is perhaps the most optimal if the outputs from the source-zone model can be used as the input for the plume-zone model. Several attempts along these lines are currently the focus of several projects funded by SERDP under its DNAPL initiatives.

Although these models have been used at a limited number of research sites, or large DOE sites, the Panel believes that the models and modeling approaches are not yet sufficiently validated for performance predictions in real field situations. The models currently must be considered primarily as research tools, and are not yet widely deployed in practice.

3.5.2 Numerical/Analytical Models: Stochastic Approaches

The modeling approaches described above might be labeled as “process-based deterministic.” Given the practical difficulties in providing the required model parameters for all locations within the spatial domain of interest, alternate modeling strategies have been developed. Often, they are based on Lagrangian Stochastic Advective Reactive modeling approaches (e.g., *Cvetkovic and Dagan, 1994*). In such approaches, the first goal is to predict the arrival-time distribution of non-reactive tracer at a selected control plane normal to the mean flow direction. Second, the dominant processes governing contaminant transport, retardation, and transformation along a single streamline, represented by one possible physical tracer arrival time, are modeled using process-based and deterministic approaches. Third, the stochastic pdf representation of physical tracer arrival time and possible other randomly variable transport and reaction variables is coupled to the deterministic single-streamline process description, to explicitly account for the spatial variability and the correlation structure of primary variables (e.g., hydraulic conductivity, retardation factor, DNAPL content, etc.). Model predictions may then provide expected values (i.e., mean), variances, and co-variances of outputs such as arrival times, concentrations, and fluxes at any chosen downgradient control plane.

Berglund (*1997*) was among the first to employ this stochastic modeling approach for evaluating the effects of the spatial heterogeneity of hydraulic conductivity and its correlation to DNAPL content on the likely performance of pump-and-treat systems for groundwater remediation. Applications of such modeling approaches to predict performance of innovative source-zone remediation technologies have not been attempted to date. However, closely analogous approaches have been attempted in recent years (*Enfield et al., 2000* and *2003*; *Jawitz et al., 2003*). In these efforts, a basic assumption made is that the arrival-time probability density function (pdf) can be represented as a single or a superposition of multiple log-normal distributions, even though any other possible and site relevant arrival time pdf can equally well be used within the modeling approach. That the log-normal assumption is valid has been demonstrated from the results of numerical simulations using sophisticated 3-D flow/transport codes for heterogeneous, saturated, unconsolidated media (*Demmy et al., 2001*).

While some Lagrangian models may rely on knowledge of the spatial distribution of aquifer properties (e.g., hydraulic conductivity) for theoretically determining the required arrival time pdf, field data from a tracer test (e.g., PITTs) may also be used to infer (via inverse modeling) the parameters for the assumed log-normal distribution(s). Destouni et al. (*2001*) present and compare different possible ways to model analytically arrival time pdfs and also show that log-normal pdf is relevant. In the latter approach, site-specific parameters applicable only to the pumping strategy implemented during the tracer tests are estimated. Such values are then used in a forward model to predict remediation performance under the same pumping conditions, and these modeling approaches can predict remediation performance only in the tracer-sampled domain and only for injected remediation fluids of the same physical characteristics as the tracer fluids. Different chemical characteristics, however, may be investigated with the same physical arrival time pdf model, by coupling with different possible chemical reaction models along a single streamline (*Cvetkovic and Dagan, 1996*; *Dagan and Cvetkovic, 1996*). Later model developments have also demonstrated the possibility to couple any site-relevant physical arrival time pdf to multi-component reaction models in complex geochemical environments (*Yabusaki et al., 1998*), including to the widely used and useful general geochemical model PHREEQC (*Berglund et al., 2003*).

Examples of such modeling approaches being specifically applied to the DNAPL remediation problem have been recently presented by Enfield et al. (*2000 and 2003*) and Jawitz et al. (*2003*) for in-situ flushing with surfactants and cosolvents. Data from lab-scale and field tests were used to evaluate the utility of these stochastic modeling approaches. Models for other innovative technologies (e.g., oxidation) have not been reported, nor have the models for in-situ flushing been tested at other sites or compared with other models.

3.5.3 Guidance Documents

A number of guidance documents have been developed in recent years for the application of innovative source-zone remediation technologies. Among these are a manual for the application of surfactant and co-solvent flushing (*Simpkin, et al., 1999*), draft guidance on air sparging, U.S. EPA Technology Innovation Office guidance on in-situ bioremediation of chlorinated solvents (*U.S. EPA 542-R-00-008, 2000*), and the ITRC Group's guidance document on in-situ chemical oxidation (*ITRC, 2001*), and in-situ surfactant/cosolvent flushing ITRC (*2003*). For other guidance documents on remediation technologies and site characterization, see the ITRC website (www.itrcweb.org). Guidance documents are typically subject to peer review and can provide good general information on state-of-the-art. These guidance documents typically provide a good overview of the technologies, some useful examples of case studies, a delineation of the steps for the design, application, and assessment of a technology at a site, and information on cost analysis and regulatory acceptance.

While guidance documents are useful in highlighting important considerations for design and application of a particular remediation technology, they rarely offer quantitative approaches for performance prediction.

3.5.4 Case Studies and Pilot Tests

Some information on remediation technology performance can also be obtained from documented case studies of field applications or pilot tests under controlled lab or field conditions. The documents on case studies of field applications are typically lacking in detailed documentation and independent verification of recovery claims. In many instances, unexplained technology failures are also reported. Relatively few well-documented case studies have appeared in the peer-reviewed literature, and those that have appeared tend to focus on pilot-scale demonstrations. Recent EPA efforts have provided more details on certain technologies, however (*U.S. EPA, 2003*).

It is important to recognize that the rules governing the level of documentation required and the sufficiency of the evidence provided to support the claims of success of remediation technology testing depend on the intended readers or target audience. The level of documentation required to judge the adequacy or sufficiency may be very different for professional practice (e.g., a project completion report submitted to an agency or a client) compared to a manuscript submitted for a scientific journal. In the former case, only the level of documentation that satisfies the client(s) and is acceptable to the regulators is required. In the latter case, an independent panel of anonymous reviewers determines if the claims made are defensible and justified based on the evidence furnished. This difference in expectations has contributed to a disagreement and debate among remediation technology practitioners working at "real" sites and academics working on innovative technology testing at smaller pilot test sites.

Another important issue is the scale of field testing and the extent of data collection. The Panel has provided summaries of a few well-documented cases of small-scale pilot tests (Appendix A). Such pilot tests, are often undertaken at a small scale that may permit more detailed characterization of the source zone and remedial performance than is feasible at larger sites. Also, the small-scale field tests offer more homogeneous conditions than are typical of most contaminated sites. Furthermore, some of the well-documented pilot tests were conducted after controlled NAPL releases, under conditions that may not be representative of older release sites.

To be most useful for technology performance assessment, a case study would ideally contain the following components:

1. An accurate site conceptual model and a summary of site characteristics, including a thorough description of the hydrogeologic, geochemical, and microbial settings.
2. An estimate of extent of the source zone, the total DNAPL mass, and its distribution in three dimensions within that zone.
3. Pre-remediation spatial distributions of aqueous contaminant concentrations within the source zone.
4. Pre-remediation estimates of contaminant mass discharge rate for the source zone and at downgradient control planes.
5. A complete description of the technology implementation.
6. Quantification of contaminant mass recovery/destruction during operation.
7. Post-remediation audit of the remaining DNAPL mass, source zone concentrations, and downstream contaminant mass discharge rate.
8. Post-remediation assessment of hydrochemical and microbial conditions within the source and in the plume.
9. Results of long-term monitoring of source-zone concentration levels and downstream plume behavior.
10. An independent assessment of capital and O&M costs.

3.5.5 Limitations of Existing Tools

The available performance assessment tools summarized briefly above have a number of limitations that preclude their successful and widespread application for the field design and assessment of innovative source-zone remedial technologies. These limitations relate both to an incomplete understanding of the process/technology and to model implementation.

Numerical modeling tools are generally based upon laboratory and bench-scale observations of remedial performance in relatively homogeneous settings. While the simpler models have been verified and validated at the laboratory scale, the more complex models, incorporating a number of nonlinear and coupled processes, have generally been verified/validated for only a small subset of their intended range of application conditions. Furthermore, processes that dominate at the small scale may not be those processes that are significant at a larger scale or under more complex geochemical and hydrologic conditions. It is also likely that reaction rates and rates of inter-phase mass transfer measured in a laboratory setting will have little predictive value at the field scale. Unfortunately, to date, mathematical models have not been extensively applied or validated for DNAPL source-zone remedial design or performance assessment at the field scale. The lack of well-documented case studies has necessarily led to a lack of data for model application and validation, particularly under a range of chemical and geologic settings.

Even if a process-based model has been numerically verified and conceptually validated for a particular application scenario, it will generally have large data requirements that may be difficult to satisfy in a field setting. While bench-scale treatability studies may provide some opportunity for parameter estimation, the spatial variability of geologic properties and the complexity of DNAPL mass distributions at a typical field site calls for a highly detailed characterization of the site or a well-defined methodology to incorporate parameter uncertainty into model predictions. Unfortunately, there is very little guidance on field-scale parameter selection for models, and most modeling has been conducted within a deterministic, rather than probabilistic, framework using 'average' uniform parameters. Model simulations based upon average, uniform conditions, however, can yield dramatically different results from high-resolution model simulations under more realistic and heterogeneous conditions. Difficulties in parameter estimation are further compounded by the lack of knowledgeable and experienced model users within the engineering practitioner community.

The above discussion highlights the need for well-documented case studies of remedial technology application and performance in a variety of geologic and chemical settings. There is also a critical need for the validation of process-based model performance predictions at the field scale. More effort should also be directed toward the development of parameter estimation guidance and more simplified modeling tools that can reliably predict remedial aggregate performance behavior and its associated uncertainty under diverse conditions.

3.5.6 Summary

While significant progress has been made in the development of new numerical tools to predict DNAPL recovery/destruction in the subsurface, in both the saturated and unsaturated zones, these models are not widely used in practice, and are still in need of further verification/validation at the field scale. Before these tools will become as common in use as MODFLOW and other numerical tools, further validation and technology transfer are needed. With respect to the use of case studies as tools for decision-making regarding DNAPL source-zone depletion, the utility of these studies must be improved by providing sufficient technical details to provide independent verification of the performance and cost data provided.

3.6 Question 6: What are the Factors Limiting the Effective and Appropriate Application of Source Depletion Technologies?

DNAPL source depletion technologies at present are being applied infrequently, and long-term containment has been the alternative of choice at most DNAPL sites in the past, although anecdotal information indicates that there is a measurable increase in the deployment of source depletion technologies across the country. The Panel's response to this question led to the identification of the primary factors that have led to the current state of remediation practice regarding the application of available and emerging DNAPL source depletion technologies. Understanding these factors is critical to the future successful development and deployment of promising new source depletion technologies at sites where the strategy for groundwater cleanup has not yet been selected. Furthermore, understanding these barriers may open opportunities for implementation of source depletion technologies at sites where a pump-and-treat remedy is already in place. The Visalia site represents a case in point, where the site owners decided that source depletion was warranted given the high cost and minimal effectiveness of the pump-and-treat system in operation at the site.

3.6.1 Definition of Remedial Objectives Requiring Restoration in Source Zones

The national goal for contaminated aquifers remains returning the contaminated zones to the highest beneficial use, which is domestic drinking water supply in most cases; many states echo this goal through their individual state non-degradation policies. The difficulty and cost of achieving complete restoration of DNAPL-affected aquifers is well-documented (e.g., *NRC, 1994*), and in the early 1990s, EPA established the technical impracticability guidance setting aside the restoration goal where it is technically and/or economically justified and allowing for the designation of alternative cleanup goals. Other regulatory programs (e.g., RCRA Corrective Action) have provided similar options to establish alternative cleanup levels. Since that time, the number of sites where technical impracticability has been used to revise restoration cleanup levels is limited as discussed earlier in Section 2.0 of this Report. With perceived uncertainties in the cost and performance of aggressive source depletion technologies, and the view that these technologies cannot provide cost-effective solutions to achieving the endpoints required for regulatory compliance, long-term source-zone and plume containment has evolved into the generally recognized low-cost default strategy, but the long-term success of such a choice is uncertain and poses some long-term risk.

The Panel considers the objective of restoration in DNAPL source areas as a barrier to more widespread use of DNAPL source depletion technologies because of technical impracticability of achieving this goal, taking cost into consideration. As discussed in Section 2.0, however, we note some changes in the regulatory policies towards establishing alternative remedial action objectives in the source zones, and the appreciation from regulators that partial DNAPL source depletion may have significant benefits in lieu of complete restoration. Thus, a regulatory framework that is based on either relaxing the timelines, the compliance boundaries, or adopting alternative remedial action goals (such as reduction in the contaminant mass discharge rate) for evaluating the progress made towards the final goal will allow for an assessment of the benefits of partial source removal in DNAPL source zones. This evolving regulatory framework may lead to greater deployment of source-zone depletion technologies.

3.6.2 Uncertainty in Predicting Likelihood of Success at a Given Cost

Closely associated with the first factor is the current difficulty in predicting the likelihood of successful source depletion and the beneficial impacts of source removal on plume longevity as discussed in response to Question 5. This difficulty stems from two main factors. First, there are relatively few well-documented case studies relating the degree of DNAPL depletion achievable for the various technologies to the geologic setting, DNAPL characteristics, and the level of effort and cost required. Such a track record will be needed to give the user community confidence that capital investments in source depletion strategies will achieve a desired level of success. Second, there is an even more limited experience record relating source depletion to mass discharge reduction from DNAPL source zones and positive plume impacts. While modeling approaches are evolving to facilitate this analysis, documented experience in the form of case studies will be needed to validate these modeling approaches and provide data for extension to other sites. In addition, integrated modeling tools relating mass discharge reduction to natural attenuation mechanisms will need to be developed and validated with actual site data to provide a comprehensive assessment of the overall benefits of partial source removal for a range of DNAPL/geologic scenarios.

An integral part of such case studies must include better and more complete documentation of the costs to characterize sites and conduct source depletion. Without access to reliable tools to relate costs and benefits, site owners will be resistant to source depletion as a remedial objective. SERDP has recently funded a series of inter-related projects involving basic research, modeling, and field-testing to address some of these problems, but attention to this issue by EPA is also recommended.

3.6.3 Lack of Well-Documented Successes

While the Panel can point to quite a number of reasonably well-documented pilot-scale applications (see the Case Studies in Appendix A as well as case studies compiled through the various websites referenced in Question 4), there has been a decided lack of documented full-scale applications in the literature to date. A few full-scale projects employing source depletion technologies have reported significant mass removal from source areas, and have claimed significant benefits from these efforts (see also the recent EPA study on thermal technologies [*U.S. EPA, 2003*]). Even in these cases, a careful assessment of the effectiveness of the project has not been published in peer-reviewed literature. However, in some of these cases, the lead regulatory agency has approved site closure.

Particularly lacking have been integrated studies of full-scale source depletion and the resultant beneficial impact to the dissolved plume. Without such documented successes, site owners and regulators are reluctant to accept the risk of failure (or the perceived risk of making matters worse by destabilizing DNAPL or cutting off natural attenuation) given the potentially high costs involved. On the other hand, this knowledge will not be forthcoming without willingness by some to accept risk.

In response to this issue, the Panel is aware of a recent study being conducted for the U.S Navy to survey site studies of DNAPL remediation technologies. This survey has been completed as of April 2003, and the results of the survey should be available later this year (2003) (*Lebron, C., 2003, personal communication*). Preliminary results indicate that of the 175 sites included in the survey, over 50 percent of the respondents (vendors, users, regulators) claimed that the use of a source depletion technology for DNAPL was “successful” though “success” measures varied. Thermal technologies and chemical oxidation with permanganate were the most widely used technologies. This survey combined with recent EPA compilation (*U.S. EPA, 2003*), hopefully will provide some of the necessary data to demonstrate the actual benefits from partial source depletion as well as indicating the conditions under which source depletion may not be a suitable site strategy.

Another option to resolve the continued uncertainties regarding the performance of DNAPL source depletion technologies is investment in post-closure characterization to assess critically the performance of the technologies. Sites where remedial action objectives have been achieved in the source zone could be subjected to an additional level of site characterization to confirm the claimed success. Independent assessments of the performance and cost success of partial source depletion at these sites would enhance the credibility of claims of success.

3.6.4 Availability and Cost of Insurance

A standard vehicle for mitigating risk in virtually any situation is insurance, and new insurance instruments have been developed for the environmental remediation market. However, the concept of insuring the risk of failure of source depletion technologies is new, and the track record of these technologies is limited. While the panel has little experience with this subject, given the lack of documented successes of source depletion technologies, it is likely that insurance, if available, would be expensive. As the track record develops, use of insurance instruments to reduce the financial risks to site owners applying source depletion strategies may become a more realistic option. Certainly the growing use of fixed price or performance based contracts accepted by remediation contractors in the U.S. suggests that this barrier may become less onerous, although unresolved issues remain regarding long-term liability in the event of failure to achieve site closure.

3.6.5 Limited Number of Qualified Vendors

The limited number of qualified vendors raises the cost and limits the access to a technology. In addition, lack of financially stable vendors raises risks to site owners and presents a further barrier to technology use. The proprietary nature of the technologies and competition between few vendors also results in limited information sharing during the important development phase of the technologies. Again, as a positive track record develops, the situation should improve as additional vendors enter the market, and the economics improve. EPA should evaluate their role in this problem such that vendors of these technologies can have some assurance of financial stability. This, of course, is a controversial approach in the U.S., but we recommend that EPA give some consideration to innovative ways to overcome the market problems faced by vendors of environmental technologies, whose difficulties have been documented in several forums (see e.g., *NRC, 1997*).

3.7 Question 7: How Should Decisions Be Made Whether to Undertake DNAPL Source Depletion?

In addressing this question, the Panel recognizes that the decision to implement source-zone depletion technologies for DNAPL site remediation is a highly site-specific decision, and that numerous regulatory, technical, and stakeholder factors must be considered. The current decision process as practiced in the U.S. has generally resulted in selection of containment over source depletion, although as noted elsewhere, there is a growing number of DNAPL sites where source depletion technologies are being deployed. In addition, market forces in the remediation field are shifting the decision process for cleanup of groundwater towards the use of performance-based or fixed price remediation contracts, with the risk of failure covered by cost cap insurance policies. Whether this leads to a greater use of source depletion technologies at DNAPL sites is uncertain. The Panel concluded, however, that new approaches to this decision process are needed. Therefore, the Panel considered two distinct options for developing an improved decision analysis methodology, one based on a qualitative semi-empirical analysis, and the other based on a quantitative model-based analysis.

An example of the qualitative decision approaches is the “weight-of-evidence” analysis where multiple factors important in reaching a decision are assigned relative weight factors or numerical scores (based on consensus expert opinion), and the aggregate score is used to guide the choice among multiple remediation options. Thus, this “weight of evidence” allows numerous factors to be considered, without letting a single factor control the decision analysis. Figure 3.2 illustrates the qualitative approach to decisions regarding the selection of source depletion technologies for DNAPL sites instead of the selection of a containment remedy. Depending on the geologic conditions and the DNAPL architecture, the size of the release, and the extent of land use, a DNAPL source zone would have a greater or lesser potential to achieve benefits from source depletion. Use of this screening level tool requires considerable judgment, and application to site-specific decision-making, and further development is needed to confirm its utility. Sale (*Sale, 2003)* also recently presented an example of the use of such “decision charts” based on an assessment of various benefits accrued from full-scale deployment of source depletion at LNAPL sites.

In contrast to the qualitative decision approach, a quantitative decision framework would provide a basis for balancing all benefits and costs with the risks of failure of the proposed remedy. Such a framework is needed to determine the following: 1) how much remediation is needed to meet remediation objectives, 2) which technologies will be deployed to remediate the source, 3) how will performance be monitored, 4) how “benefits” accruing from source treatment will be assessed, 5) how the economic analysis will be performed, and 6) how “soft” or “intangible” factors (i.e., implicit benefits) will be considered.

Figure 3.3 presents a schematic flowchart of components of a quantitative decision support system that (1) integrates existing and new knowledge, (2) utilizes stochastic simulators to predict performance, (3) incorporates cost functions (i.e., marginal cost per unit benefit), and (4) considers cost-efficient optimal solutions in developing decision alternatives. Decision tools based on such a fundamental approach do not exist at this time, but are being developed and tested for selection of plume management options (e.g., *Bayer et al., 2001; Andersson and Destouni, 2001; Teutsch and Finkel, 2003*). Once developed, these tools need to be field-validated, especially for the assumed costs.

Quantitative decision approaches may provide more transparent and conceptually sound bases for decision-making regarding the selection of source depletion strategies. However, to the Panel’s knowledge, rigorous quantitative approaches have not been used for decision-making at DNAPL sites for choosing among multiple options for source-depletion and plume-containment strategies. The Panel recognizes that such rigorous cost-minimization and net-benefit-maximization approaches are still at a research level and have so far only been applied to few environmental problems (e.g., *National Research Council, 1997; Gren et al., 2000, 2002; Hart and Brady, 2002; Baresel et al., 2003*), however, not including DNAPL source depletion because of lack of sufficient data. It must be noted and understood that cost-minimization is different from net-benefit maximization and that both these basic economic decision rules, and modeling approaches need to be developed and investigated. The potential value of rigorous quantitative approaches to making rational DNAPL remediation decisions should be evaluated. Application of such approaches could prove to be useful in clarifying relevant and dominant factors and identifying research gaps associated with making remediation decisions that are economically efficient and consistent with remedial objectives required by state and/or federal regulations.

DESIRED REMEDIAL BENEFITS[1]	**MORE NEED** FOR SOURCE DEPLETION ←		**LESS NEED** FOR SOURCE DEPLETION →
Reduce potential for DNAPL migration as separate phase	1a. Expanding mobile DNAPL Zone (probably rare at chlorinated solvent sites)[2] *(containment addresses this problem too)*	1b. Free-Phase DNAPL present but stable in stratigraphic traps	1c. Immobile, residual DNAPL Zone
Reduce source longevity, and reduce long-term management requirements	2a. High life-cycle containment cost (for example, containment Net Present Value (NPV) >> cost of remediation) 3a. Low reliability of containment system 4a. High resource value that cannot be used due to DNAPL (for example, sole-source aquifer OR Well Yield > 144,000 gpd with TDS < 3000 mg/L)[3] 5a. High probability of a meaningful reduction in time to reach MCLs (for example, small sites with low complexity)	2b. Moderate life-cycle containment cost 3b. Moderate reliability of containment system 4b. Moderate resource value 5b. Moderate probability of a meaningful reduction in time to MCLs	2c. Low life-cycle containment cost (for example, containment Net Present Value (NPV) << cost of remediation) 3c. High reliability of containment system 4c. Low resource value (for example, resource not being used AND either Total Dissolved Solids > 10,000 mg/L or Well Yield < 150 gpd)[4] 5c. Low probability of meaningful reduction in time to reach MCLs (for example, large releases at complex sites)
Near-term enhanced natural attenuation due to reduced dissolved phase loading	6a. Expanding dissolved phase plume (source loading > assimilative capacity) *(containment addresses this problem too)*	6b. Stable dissolved phase plume (source loading ~ assimilative capacity)	6c. Shrinking dissolved phase plume (source loading < assimilative capacity)
Near-term reductions in dissolved phase loading to receptors (e.g., a well or a stream)	7a. Receptor impacted now or impacted soon (for example, < 2 years travel time)[5] *(containment addresses this problem too)*	7b. Potential longer-term risk to receptor (for example, >2 years travel time)	7c. No risk to receptors now or in the future
Near-term attainment of MCLs	8a. Need for rapid cleanup (for example, impending property transfer)	8b. Limited need for rapid cleanup	8c. No users of resource within expected time frame needed for restoration of aquifer and no other exposure pathways likely, e.g., vapor migration
Intangibles	9a. Desire for active remedy; desire to test new technologies; desire to reduce stewardship burden on future generations	9b. Neutral on intangible issues.	9c. Desire for low-impact remedy; desire to use proven technologies; desire to not expend financial resources for limited risk reduction benefits

References and background sources:
1. Sale, T.C., 2001.
2. Pankow, J.F., and J.A. Cherry (Eds), 1996.
3. American Petroleum Institute, 2002.
4. Texas Council on Environmental Quality, 2003.
5. Aziz, et al., 2000.

Figure 3.2 Decision chart: Benefits from full-scale applications of source depletion.

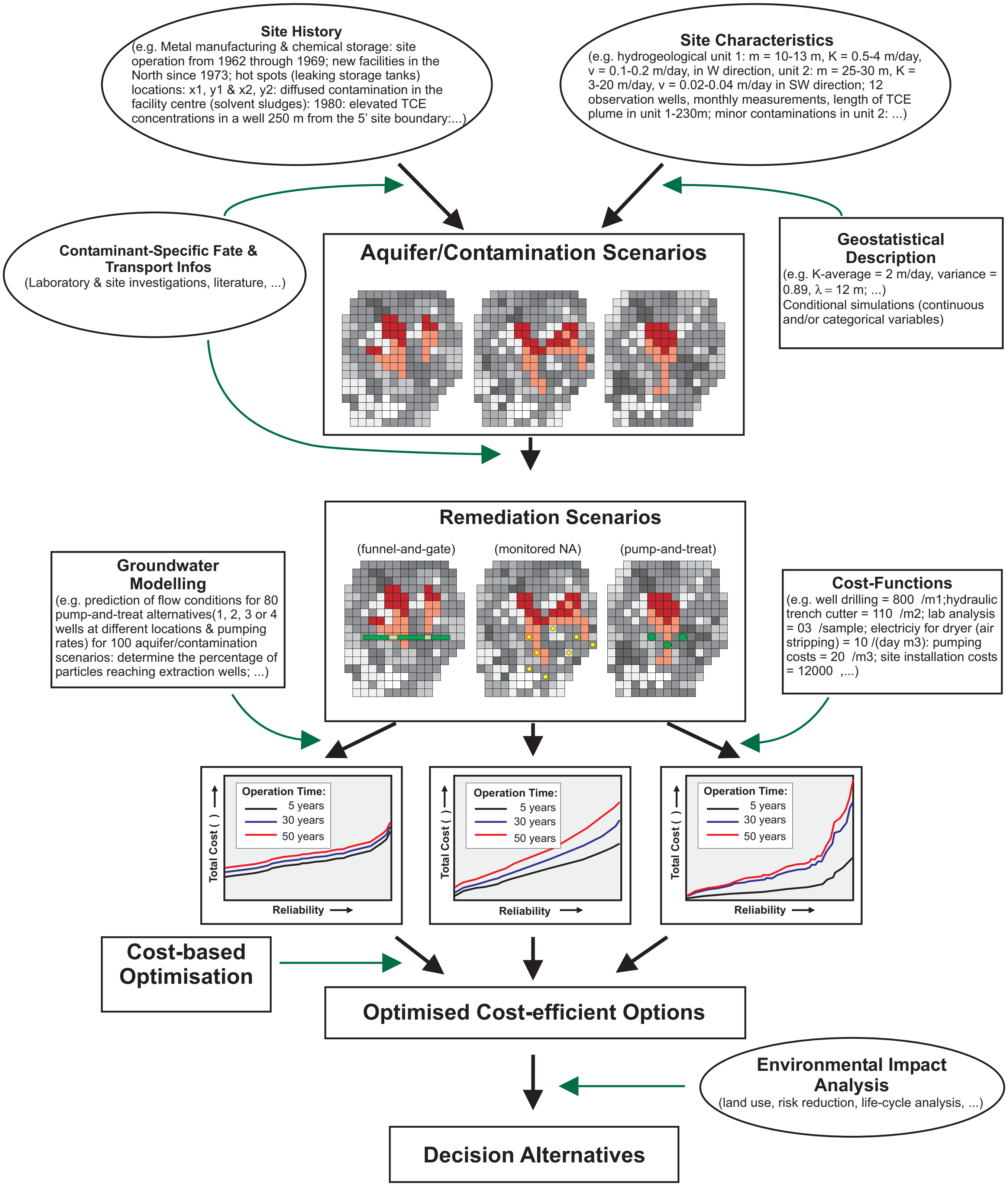


Figure 3.3 Schematic of quantitative decision framework (Teutsch and Finkel, 2003).

4.0 Knowledge Gaps and Research Needs

4.1 Introduction

This Report has identified a number of knowledge gaps and research needs related to the issue of DNAPL source depletion. The following section provides a brief summary of the gaps and research needs organized by the key questions addressed by the Panel, namely, a) performance metrics, b) site characterization, c) DNAPL source-zone depletion technologies, d) performance prediction tools, and e) decision-making tools.

4.2 Performance Metrics

4.2.1 Knowledge Gaps

A wide variety of metrics are available to assess the performance of DNAPL source-zone depletion technologies. Reliance on the metric of DNAPL constituent concentrations in the aqueous phase overlooks other metrics that will provide a more accurate assessment of the benefits of partial source-zone depletion. The utility of additional performance metrics for decision-making, performance assessment, and quantification of the benefits of partial source-zone depletion needs to be assessed.

4.2.2 Research Needs

Research needs for performance metrics include the following:

1. Conduct in-depth assessments of alternative performance metrics, and prioritize those alternative metrics that will improve the quantitative assessment of the overall benefits of DNAPL source depletion. Candidate alternative metrics include a) changes to the mass flux and mass discharge emanating from DNAPL source areas after source depletion b) residual DNAPL remaining, and c) changes to the biogeochemical environment in and around the source zone.
2. Conduct field scale comparisons of multiple methods for measuring contaminant mass flux (local) and mass discharge rates for a broad spectrum of hydrogeologic conditions and for various DNAPL types and DNAPL distribution (i.e., the DNAPL “architecture”).

4.3 Site Characterization

4.3.1 Knowledge Gaps

Site characterization tools are reasonably well developed for purposes of characterizing the nature and extent of DNAPL in the source zones. The inherent heterogeneities in the subsurface frustrate accurate quantification of the mass and distribution of DNAPL in many geologic systems, however. Some technologies are also prohibitively expensive for widespread use in DNAPL source-zone characterization and performance assessment. The key knowledge gaps in site characterization include: 1) continued need for low-cost characterization technologies to estimate DNAPL mass removal or destruction, 2) dealing with uncertainties in DNAPL characterization based on concentration measurements, and avoiding overestimation of the extent of DNAPL, and 3) advances in techniques to measure mass flux and mass discharge from DNAPL sources for a variety of DNAPL distribution scenarios.

4.3.2 Research Needs

Research needs to address these knowledge gaps for source-zone characterization include the following:

1. Conduct appropriate research projects to develop reliable methods for estimation of DNAPL mass and source distribution (i.e., DNAPL architecture), at appropriate spatial resolutions, both before and after remediation.
2. Conduct appropriate research projects to develop methods for estimation of contaminant mass flux building on research work to date, and support field verifications of these new mass flux technologies in a variety of hydrogeologic settings.

3. Provide updated guidance on interpretation of DNAPL source characterization based on water samples from appropriate sampling locations in the saturated zones for a variety of hydrogeologic settings.
4. Conduct appropriate research and development projects for development of source-zone characterization techniques in fractured systems and other highly complex hydrogeologic settings.

4.4 DNAPL Source-Zone Depletion Technologies

4.4.1 Knowledge Gaps

As discussed under Question 4, much information has been generated over the past two decades on the performance of various DNAPL source depletion technologies. Knowledge gaps persist, however, in part because of the highly heterogeneous characteristics of the subsurface. Some of the key knowledge gaps regarding these technologies include: 1) uncertainties regarding the DNAPL mobilization potential of thermal and surfactant/co-solvent technologies, 2) the impact of soil heating on the geotechnical properties of the soil horizon, and the impact of the heated subsurface on fate and transport of remaining constituents of the DNAPL, 3) long-term water quality impacts on source zones following aggressive source depletion, 4) effectiveness of any of the technologies in fractured clay, fractured bedrock, and karst saturated zones, 5) total life cycle costs of the technologies in complex geologic settings, 6) demonstration of the potential effectiveness of DNAPL source-zone bioremediation at the field scale, and 7) uncertainties in scale-up of pilot-scale studies to full-scale DNAPL source zones.

4.4.2 Research Needs

To address these knowledge gaps, the following research needs for source depletion technologies are suggested:

1. Determine the conditions under which mobilization of the DNAPL and spreading of the source zone may occur for thermal and surfactant/cosolvent flushing technologies.
2. Conduct appropriate laboratory and field-scale demonstrations of the most promising technology combinations for DNAPL source depletion. Support continued research and development efforts for those technologies not yet ready for deployment but with the potential for lower costs compared to thermal technologies such as in-situ biodegradation. Support development and assessment of low-cost, less-aggressive alternatives for source-mass depletion (e.g., ZVI mixing, oxidant mixing).
3. Conduct appropriate research studies on fate and transport of DNAPL constituents following source-zone treatment in both the vadose zone and the saturated zone to quantify the potential benefits of combined technologies (e.g., thermal and biodegradation, surfactants and biodegradation, ISCO, and biodegradation).
4. Conduct appropriate laboratory and field studies of alternative source depletion technologies in the most challenging hydrogeologic settings to determine the characteristics of the saturated zone that limit the effectiveness of these technologies in such settings (fractured systems, karst).
5. Conduct theoretical, laboratory, and field studies on the long-term water quality impacts of technologies requiring the injection of significant quantities of fluids to achieve the desired remedial objectives. Long-term water quality impacts are uncertain for surfactant/cosolvent technologies, injection of chemical oxidants, and injection of electron donor solutions for enhanced DNAPL removal using in-situ biodegradation.
6. Advance the state of the art in scale-up procedures for small-scale pilot studies of source-zone depletion that will result in a greater level of accuracy in design of full-scale source depletion applications.
7. Conduct technology failure analyses for containment systems based on reported field data and/or theoretical assessment of potential failure modes for containment technologies.

Technology transfer on DNAPL source depletion technologies is also desirable, and practitioners would benefit from guidance documents to allow: (a) determination of whether or not source remediation is appropriate for the site under consideration, and (b) selection of the source-depletion technology or technologies most appropriate for the site-specific conditions and remedial action objectives.

4.5 Performance Prediction Tools

4.5.1 Knowledge Gaps

In general, the Panel concluded that performance prediction tools were not sufficiently developed to provide an accurate methodology for assessing the likely performance of source-zone depletion technologies under a variety of DNAPL distribution and hydrogeologic settings. Although such algorithms exist, the input data and computational requirements limit the use of these algorithms in practice.

4.5.2 Research Needs

The primary research need is the development of more user-friendly prediction tools that provide a more reliable and accurate basis for assessing the likely performance of source-zone depletion technologies. This is especially important in the context of determining whether an existing hydraulic containment strategy should be changed after a remedy is in place and the benefits of source-zone depletion need to be quantified. Other needs include the following:

1. Support research on improved theoretical approaches for more accurate estimating of model input parameters.
2. Provide funding to validate multiphase numerical tools capable of predicting performance of source depletion technologies.
3. Conduct a review of existing and more recent case studies at DNAPL sites to evaluate performance based on several metrics of success including total mass depletion, reduction in mass discharge rates from the source zone, and whether reductions have been sufficient to transition the remedial strategy to natural attenuation. Publish this information in a form convenient for use by consultants and other decision-makers for assessing the applicability of source depletion technologies at their sites of interest.

4.6 Decision Analysis Tools

4.6.1 Knowledge Gaps

The most widely used model for decision analysis regarding the deployment of DNAPL source-zone depletion technologies is based on the National Contingency Plan (NCP) approach for comparison of alternatives at those DNAPL sites where feasibility analyses are required. That is, the remedy selected must meet the nine criteria established in the NCP in order to be selected for implementation where the site is under state or federal oversight. This decision model for assessing the options for DNAPL source-zone depletion is limited by the lack of a quantitative decision analysis tool or tools that can account for all quantifiable benefits and costs, taking uncertainty into account.

4.6.2 Research Needs

The Panel recommends that the feasibility of developing a quantitative decision analysis tool with the characteristics presented in response to Question 7 be evaluated. If such a tool can be shown to be reliable through testing against actual site conditions, EPA should support a research program to develop such a tool, and provide the necessary guidance and training for application of the tool to decision-making at DNAPL impacted sites, both those sites where a containment remedy is already in place, and sites where a remedy has not yet been selected.

5.0 Conclusions and Recommendations

The DNAPL Expert Panel was charged with evaluating the following four key issues related to source remediation at DNAPL impacted sites:

- **a)** Status of technology development and deployment for DNAPL source remediation.
- **b)** Assessment of source remediation performance goals and metrics.
- **c)** Evaluation of costs and benefits of source remediation.
- **d)** Research issues and needs.

In response to this charge, the Panel generated seven questions to provide the technical basis for addressing each of these issues and to provide recommendations on strategies to address the overarching issue posed in the title of this Report, namely, can a case be made for undertaking DNAPL source-zone depletion at sites with contaminated groundwater? Based on the Panel's responses to those questions and other information presented in this Report, the Panel presents the following conclusions and recommendations.

5.1 Conclusions

a) Status of Technology Development and Deployment for DNAPL Source Remediation

1. Substantial progress in development and deployment of technologies for DNAPL source-zone characterization and mass depletion has been made in North America and Europe over the past two decades.
2. Available site characterization technologies are capable of bounding the locations of DNAPL sources in the subsurface in both the horizontal and vertical directions. The accuracy of DNAPL source-zone definition, however, is highly site-specific.
3. Even when a large effort is conducted for DNAPL source-zone site characterization using the best available technologies, uncertainties in the estimate of the total DNAPL mass present in the source zone will be large at many DNAPL-impacted sites because of the effects of geologic heterogeneity and the spatial heterogeneities in DNAPL distribution.
4. Even at those sites where DNAPL source zones have been delineated, and the initial mass of DNAPL present has been estimated within a factor of two to four, it is difficult to determine if the DNAPL mass has actually been depleted from the subsurface, degraded into other chemicals, or been moved or displaced to another subsurface location following source depletion. This problem has been clearly demonstrated from the results of highly controlled DNAPL release studies at the Borden and the Dover Air Force Base sites or the recent source depletion tests at the Cape Canaveral site as summarized in Appendix A.
5. Both conventional technologies (pump-and-treat, excavation) as well as innovative in-situ technologies are capable of partial DNAPL source-zone depletion. In a large number of pilot-scale studies of source-zone DNAPL removal as well as in numerous full-scale implementation projects, mass depletion greater than 90 percent has been claimed. However, the Panel cautions that reported mass depletion levels as a percentage of the initial mass are highly uncertain due to the uncertainty in estimating the initial mass of DNAPL prior to source depletion.
6. As far as the Panel is aware, there is no documented, peer-reviewed case study of DNAPL source-zone depletion beneath the water table where U.S. drinking water standards or MCLs have been achieved and sustained throughout the affected subsurface volume, regardless of the in-situ technology applied. Nonetheless, at a number of DNAPL-impacted sites, closure of the sites has been reported signifying achievement of RAOs.
7. Although numerous site trials have been conducted by both private and government entities for DNAPL source-mass depletion using innovative technologies over the past 15 years, comprehensive documen-

tation on the effectiveness of source-mass depletion and resultant effects on groundwater quality within the source zone and in the downgradient plume is available for only a few sites. Documentation on plume improvements following source containment is also lacking. Such documentation would provide important insights on the benefits that could be achieved even with partial DNAPL source depletion. Recent EPA publications *(U.S. EPA, 2003)* and a recent (*2003*) survey being conducted by the U.S. Navy may fill some of the gaps in this information base.

8. Results of more recent laboratory and theoretical analyses have indicated that partial source depletion of DNAPL in certain geologic settings using available in-situ technologies may provide quantifiable benefits including: 1) more rapid achievement of conditions conducive to monitored natural attenuation as the accepted remedy for the groundwater at the site, and 2) lower life cycle costs associated with treatment trains used to remediate both the source zone and the dissolved plume.

b) Assessment of Source Remediation Performance Goals and Metrics

1. Source remediation performance goals and metrics currently used to evaluate the “success” of source depletion technologies are limited in number. The dominant goal employed by the regulatory community for groundwater considered a potential source of drinking water is U.S. drinking water standards for all regulated chemicals. Thus, achieving MCLs in the source zone is the primary goal of DNAPL source depletion in the U.S., and verification of achieving that goal is defined by groundwater point samples collected from compliance monitoring wells.
2. Although the MCL goal may be consistent with prevailing state and federal laws, and easy to communicate to public stakeholders, this goal is not likely to be achieved at the vast majority of DNAPL sites in the source zones. Thus, the exclusive reliance on this goal inhibits the application of source depletion technologies because achieving this goal is generally beyond the capabilities of available in-situ technologies in most geologic settings. Changes in the regulatory climate based on increased knowledge of the technical impracticability of achieving MCLs in the source zone and knowledge of the potential benefits of partial DNAPL depletion should establish a context for increased consideration of DNAPL source-zone depletion technologies at sites with a containment remedy (e.g., pump-and-treat) in place as well as new sites with no remedy in place.
3. The use of the MCL goal as the single measurement of “success” does not account for other potential benefits of DNAPL source depletion. These may include a number of risk management benefits including: a) reduction of DNAPL mobility, b) reduced longevity of the plume source, c) reduction in mass flux and mass discharge from the source zone, and d) enhanced efficiency and effectiveness of complementary source-zone control technologies.
4. Although the Panel did not conduct a detailed review of regulatory requirements at DNAPL sites throughout the U.S., the Panel is aware of other goals that have sometimes been used at sites for remediation of DNAPL source zones. These have included: 1) mass removal goals, 2) removal of DNAPL “to the extent practicable,” and 3) removal or stabilization of “mobile” DNAPL. It also appears that regulatory agencies at the state and local level are proposing more flexible regulatory strategies for DNAPL source zones, which may result in a greater range of acceptable remedial action objectives for the source zone other than meeting MCLs throughout the contaminated zone. The Panel cannot confirm how widespread this new flexibility exists, but at the least, regulators are becoming fully aware of the need to consider benefits of partial source depletion other than meeting MCLs in the source zones.
5. Multiple metrics will provide a more comprehensive basis for performance assessment of DNAPL source-zone depletion technologies. Use of alternative metrics such as reduction in mass flux and mass discharge from the source area is conceptually and scientifically appealing, but use of this metric is still in a research mode. This metric has not yet been embraced by the regulatory community for various reasons including uncertainties in the reliability and accuracy of current measurement techniques. Recently, regulators have expressed increased interest in these metrics, and efforts are now underway to assess their applicability for compliance and performance assessment purposes.
6. For a few metrics, multiple measurement methods are available, but for others, including mass flux and mass discharge, the methods are not proven, and are currently under development.

c) Evaluation of Costs and Benefits of Source Remediation

1. DNAPL source-zone depletion can provide explicit and implicit risk management benefits. Explicit benefits include: a) mitigating the potential for human contact and exposure, and the potential for unacceptable ecological impacts, b) reducing the duration and cost of other technologies employed in conjunction with the source removal technology, and c) reducing the life-cycle cost of site cleanup. Implicit benefits may include: a) minimizing risks of failure of containment strategies, b) satisfying public stakeholders'

concerns, c) enhancing companies' “green image” as stewards of the environment, and d) minimizing future uncertain transaction costs associated with management of the site.

2. Information on the costs and benefits of source depletion is limited. Cost data for source depletion are available from governmental agencies and from technology vendors, but it is difficult to translate these costs from one site to another. In addition, it is not yet possible to estimate life-cycle costs following source depletion because of uncertainties in predicting the impact of source depletion on duration of the groundwater remedial action.
3. Few, if any, studies on source-zone depletion have evaluated all costs associated with source-zone remediation. Because few DNAPL-impacted sites have achieved site closure, information on capital and annual O&M costs for successful source-zone remediation is limited.
4. Cost data can be obtained from vendors for several of the source-zone depletion technologies, and these data allow for the economic comparison of alternative strategies for remediation of the source zone. A simple engineering economics analysis presented in this Report compares the costs of DNAPL (creosote) source removal at the Visalia site with the life cycle costs of the pump-and-treat system previously employed for source containment. The relative economic benefits of source depletion options are strongly dependent on the net discount rate assumed when considering the time value of money. In a low discount rate environment, source depletion may be cost-effective, but at interest rates above five percent, the life cycle costs of the containment option appear to be lower than the costs for source depletion. Use of this simple engineering economics approach is helpful in bounding the range of costs for source depletion technologies that would potentially be cost-effective compared to containment remedies. An assessment of economic benefits is only one of the potential benefits that should be evaluated when making a source remediation decision.
5. Risk management benefits are difficult to quantify because of inherent uncertainties in predictions related to the effectiveness of source-zone depletion and the impact of DNAPL source-zone depletion on overall site closure. Translation of implicit risk management benefits into monetary terms presents even greater challenges that have not yet been addressed.
6. Because of the limitations in available tools for predicting the effectiveness of source depletion technologies, estimating the monetary value of all explicit and implicit benefits, and estimating the overall cost impact of applying these source-zone depletion technologies, decision-making based on classic risk/benefit calculations is inherently limited. The degree of uncertainty in the costs and benefits of applying source depletion technologies is currently at levels that discourage widespread use of the available source depletion technologies at DNAPL sites.

5.2 Recommendations

The Panel provides the following recommendations to the U.S. EPA.

1. **Fund research, demonstration projects, and technology transfer to address and reduce the uncertainties in quantifying the benefits from source-zone depletion**.

Uncertainties in quantifying the economic benefits of DNAPL source-zone depletion are a major barrier to the use of source remediation technologies. The research needs identified in Section 4.0 should be part of EPA’s program to address these uncertainties. To determine the appropriate level of funding, EPA should conduct an inventory of DNAPL sites throughout the U.S. to confirm the magnitude of the problem and to assess the potential reduction in life-cycle costs from increased application of source depletion technologies compared to containment strategies. EPA should build on the results of the recent survey conducted by the U.S. Navy on the use of DNAPL source depletion technologies at over 175 sites.

2. **EPA, in cooperation with other agencies and private industry, should continue support of demonstration efforts to develop, test, and validate the most promising technologies for DNAPL source-zone characterization and mass depletion.**

Cost-effective and reliable technologies are needed to improve the accuracy of locating DNAPL sources, estimating the magnitude of the DNAPL source, and quantifying the distribution of the DNAPL. Current techniques show promise but are limited in accuracy and/or are costly. All of the in-situ source depletion technologies have advantages and disadvantages, depending on the site-specific conditions. Knowledge of the effectiveness and cost of thermal technologies, surfactant and co-solvent technologies, and ISCO is most advanced for DNAPL source depletion. However, uncertainties persist, and additional demonstration projects that are fully documented are needed. There is a particular need for performance and cost data for DNAPL source-zone depletion technologies in fractured systems.

3. **EPA should provide a new guidance document for source-zone response actions at DNAPL sites that provides a road map for decision-makers to determine if implementation of source depletion technologies is appropriate.**

Given the sparse use of the TI waiver policy at DNAPL sites, and the limited number of source removal actions that have been undertaken, a new guidance document should be prepared for use by decision-makers to determine if source depletion technologies should be implemented given site conditions and the institutional setting. This document should build on the large amount of information compiled by various federal agencies, state agencies, universities, and private sector initiatives on the cost and effectiveness of DNAPL source depletion technologies. The document should include detailed guidance on how to conduct technology demonstrations in a credible manner. EPA should develop protocols to permit a quantitative assessment of the appropriate potential remediation category in which to assign a DNAPL site. As part of this protocol development, EPA should review a representative sample of DNAPL sites in the U.S. to determine the estimated proportion of sites that would be considered for three categories, namely: a) strong candidate for DNAPL source depletion, b) potential candidate for DNAPL source depletion, and c) not suitable for application of DNAPL source depletion technologies. The guidance document should also discuss the use of alternative remedial action goals other than achievement of target cleanup levels in the source zone and the value in using alternative performance assessment metrics.

4. **Conduct a thorough and independent review of a selected number of DNAPL sites where sufficient documentation is available to assess the performance of source depletion using a multiple of metrics.**

The need for well-documented case studies of remedial technology application and performance in a variety of geologic and DNAPL distribution scenarios is apparent. The currently available documentation on these studies is substantial, but limitations in the performance evaluation and accuracy of cost estimates contribute to the reluctance by decision-makers to implement source depletion technologies at many DNAPL sites. There is also a critical need for the validation of process-based model performance predictions at the field scale. Without these models, the long-term benefits of source depletion cannot be quantified in any meaningful way. This effort should include the development of parameter estimation guidance, guidance on scale-up of pilot scale studies, and more simplified modeling tools that can reliably predict remedial aggregate performance and its associated uncertainty under diverse geologic and chemical conditions.

5. **Develop and validate technologies for cost-effective and accurate measurement of mass flux and mass discharge from DNAPL sources zones.**

Measurements of the distribution of mass flux and the mass discharge from a source zone may provide new metrics for assessing the performance of source-zone depletion technologies. Research into technologies to measure these metrics accurately has only recently begun. Field experiments are needed to verify theoretical predictions that DNAPL removal from the more permeable zones in an aquifer may substantially reduce mass discharge from source zones. Furthermore, the benefits of this reduction as they relate to risk reduction must be quantified. EPA should support the development and validation of these technologies, building on research efforts currently funded by the Department of Defense through the Strategic Environmental Research and Development Program (SERDP).

6. **Evaluate impacts of source depletion technologies on long-term aquifer water quality.**

Demonstration projects conducted over the past decade have focused primarily on the effectiveness of DNAPL mass removal by candidate source depletion technologies. Few projects have considered the long-term water quality impacts of source depletion technologies. EPA should conduct necessary post-remediation studies to verify that long-term impacts of source depletion technologies will not be deleterious to future beneficial uses of the groundwater.

7. **Develop and assess the suitability of cost-minimization and net-benefit maximization decision models for evaluating the complete spectrum of costs and benefits of source depletion technologies.**

Current economic and financial models, used to make decisions on whether source depletion should be undertaken, have a number of limitations as discussed in this Report. The development and validation of a much more comprehensive economic model such as a cost-minimization or net-benefit maximization approach may provide important insights into the current tradeoffs between DNAPL source containment and long-term institutional controls compared to the generally significant capital cost of source depletion technologies. The practical benefits of this approach should be assessed by EPA, and if found to be feasible, such a model should be further developed, validated, and made available for practitioners and regulators.

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Joint Service Pollution Prevention Library: http://p2library.nfesc.navy.mil/

The Environmental Technology Commercialization Center: http://www.etc2.org/

University of Sheffield DNAPLs in Groundwater University: http://www.shef.ac.uk/~dnapl/

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APPENDIX A - CASE STUDIES

CASE STUDY

Application of Steam Enhanced Extraction
Site 5, Alameda Point, California

Application of Steam Enhanced Extraction, Site 5
Alameda Point, California

Introduction

The feasibility of Steam Enhanced Extraction (SEE) to remove chlorinated hydrocarbons from a Non-Aqueous Phase Liquid (NAPL) waste solvent source found in shallow fill soils was tested on a pilot scale at Site 5, Alameda Point, Alameda, California. The goals were to reduce chlorinated solvent concentrations in the groundwater in the treated zone to values comparable to the groundwater concentrations upgradient of the treatment zone, and to reduce soil petroleum hydrocarbon concentrations to levels which minimize migration potential. Without source removal, the NAPL mass was estimated to feed the groundwater plume for at least 600 years based on maximum aqueous solubilities of TCE dissolving from the multicomponent NAPL, the measured hydraulic gradients, measured transmissivities, upper-limit NAPL projected cross-sectional area, and measured TCE mass removed using SEE. Since this time frame was considered to be too long-term for monitored natural attenuation to be a viable option, source depletion was requested as a means of shortening the natural attenuation time frame of the site.

Application of SEE

The NAPL source zone was surrounded by six injection well clusters as shown in Figure A.1, with separate injection completions in the vadose zone and in the saturated zone. A single extraction well in the center of the hexagonal pattern was used to extract water, NAPL, and hot vapors. The surface concrete served as the cap for the process. The extracted fluids were cooled, separated, and treated. The NAPL was collected and stored in drums for eventual recycling, and the vapor and water streams were passed through carbon for treatment before discharge to the atmosphere and sewer, respectively.

In order to decrease the potential for NAPL condensation under the concrete cap, steam was first injected into the vadose zone for 10 days until hot vapors were observed in the extraction well. Steam was then injected into both the vadose and saturated zones at maximum rates possible for an additional 40 days until contaminant recovery rates dropped. Thereafter, and until the end of operations 20 days later, the injections and extractions occurred cyclically with a goal of inducing fluid pressure changes in the pores of the soil. Pressure reduction has been shown to induce in-situ boiling of water from soils of a wide range of permeabilities, which steam-strips VOC from the aqueous phase in a relatively homogeneous manner.

Operational data were collected to allow the quantification of the rates of removal of masses of solvents and other petroleum hydrocarbons from the subsurface. One hundred sixteen subsurface temperatures were measured daily and analyzed to track the development of the subsurface temperature field. Steam injection rates were closely monitored, and energy balances were tracked. Groundwater samples were taken from multipoint sampling locations before, and two months after, the application of SEE. Soil samples were taken aseptically before and after the steaming process to ascertain the impact of the steaming on microbial populations. All analytical data were obtained from analysis by an external certified laboratory, or analyzed at U.C. Berkeley, under the direction of an independent QAQC officer.

Results

A mass of 1,950 kilograms (kg), (or the equivalent of 600 gallons of hydrocarbon liquids), was removed during the operation of SEE. Of that mass, 83% was collected as NAPL and recycled, 2% was adsorbed on carbon in the water treatment system, and 15% was adsorbed on carbon in the vapor treatment line. The recovered TCE was mostly found in the gases exiting the last vapor/liquid separator, accounting for a mass of 192 kg. An additional 22 kg was removed in the water stream entering the treatment carbon. Only 18 kg of TCE was found in the recovered NAPL.

Soil concentrations of extractable petroleum hydrocarbons were reduced by about an order of magnitude by SEE with only low volatility components remaining in the soils that experienced ample steam fluxes. Only trace amounts of chlorinated compounds could be found in the steamed soils in shallow soils near the surface cap. Groundwater concentrations in the treatment zone were generally reduced to values about an order of magnitude lower than typical values found in the up-gradient groundwater. The VOC concentrations in water at the locations where NAPLs were observed before SEE decreased over two orders of magnitude from their initial concentrations (see Figure A.2). Microbial population counts in the steamed soils showed microbial rebound to pre-steaming levels upon cooling.

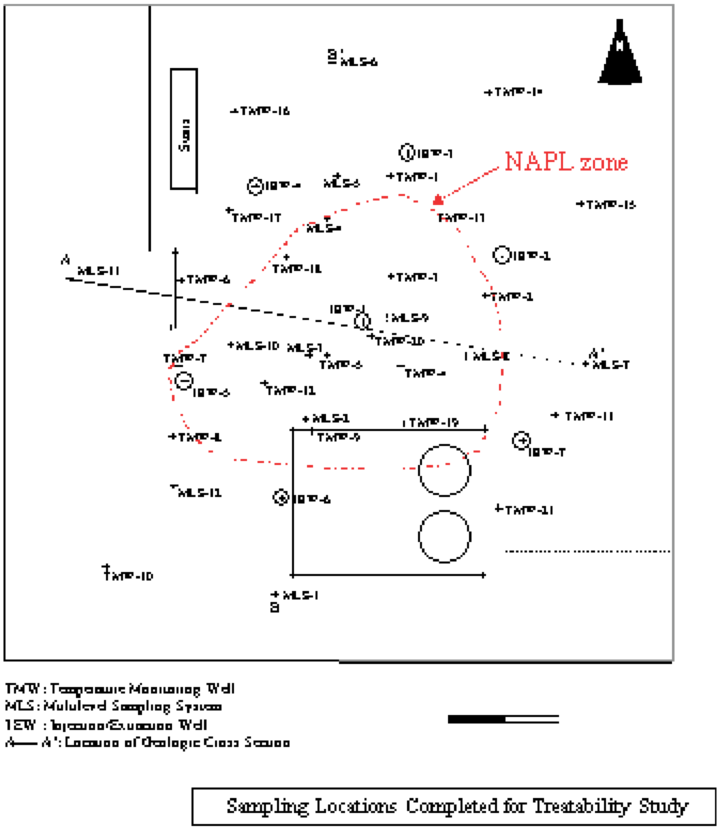

Figure A.1 NAPL extent, sampling locations, injection well location, and extraction well location.

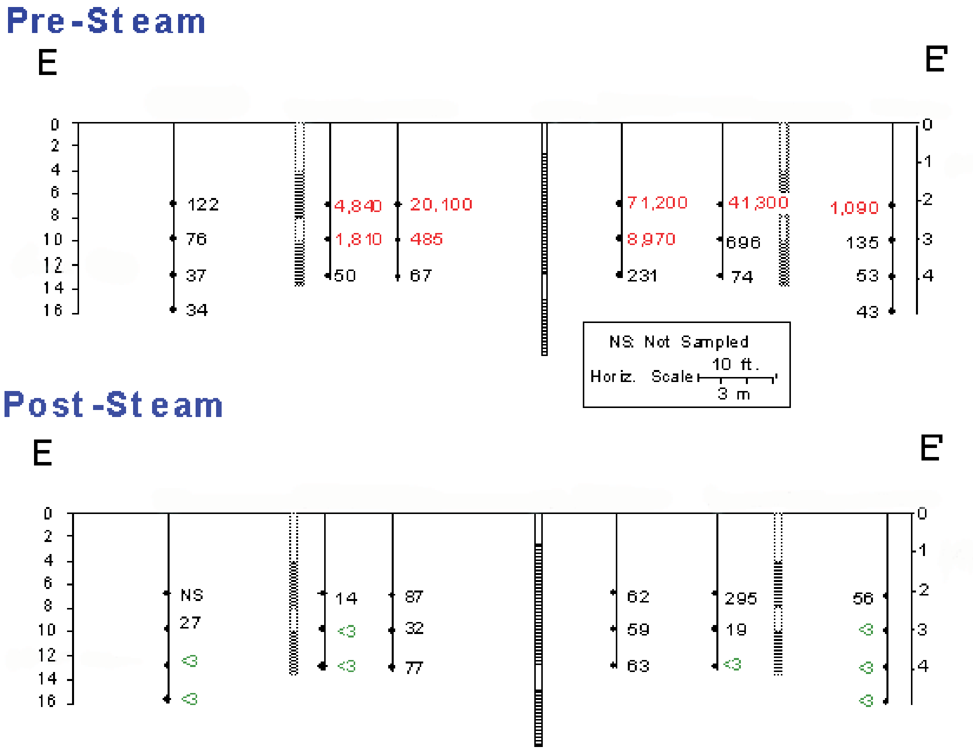

Figure A.2 Pre- and Post-Steam TCE concentrations in ground water (ppb).

Discussion

The treatability test showed that SEE can remove VOC constituents from a NAPL source and can reduce groundwater VOC concentrations in the source zone to levels below those of the surrounding plume. This result implies that source-zone depletion using SEE has the potential of reducing the site problem from one source zone existing for hundreds of years, to one where short-term monitored natural attenuation of the plume may be sufficient for long-term remedial needs.

The residual hydrocarbons (maximum soil concentration of 2000 mg/kg soil) remaining after the application of SEE had compositions similar to motor oils and greases. Those compounds have greatly reduced mobilities given their low volatilities and solubilities as compared to the initial mixture of volatile solvent wastes. The rebound of active microbial populations in soils taken from the steamed zone to levels near those found in un-steamed soils implies that natural attenuation processes will probably continue at this site in the zones that were steamed.

CASE STUDY

A Pilot-Scale Demonstration of Surfactant Enhanced PCE Recovery at the Bachman Road Site

A Pilot-Scale Demonstation of Surfactant Enhanced PCE Recovery at the Bachman Road Site

This brief summarizes results of a pilot-scale technology demonstration of surfactant enhanced aquifer remediation (SEAR) at the site of a former dry cleaning facility in Oscoda, MI. The demonstration was funded by the Michigan Department of Environmental Quality and involved researchers from the University of Michigan and Georgia Institute of Technology, in partnership with HSI Geotrans.

Site Description

The Bachman Road site is underlain by an unconfined aquifer composed of relatively homogeneous fine- to medium-grained glacial outwash sands. The aquifer has a saturated thickness of approximately 15 feet and is confined below by a thick clay layer. A sand/silt transition layer exists immediately above the clay. The shallow water table is at a depth of 11 feet. A narrow tetrachloroethylene (PCE) plume emanates from a suspected DNAPL source area, beneath a former dry cleaning building and discharges into Lake Huron, approximately 700 feet downgradient (Figure A.3). There are no co-contaminants at the site, and the aquifer sands are extremely low in organic carbon. PCE degradation by-products are essentially absent from the plume, suggesting little natural attenuation.

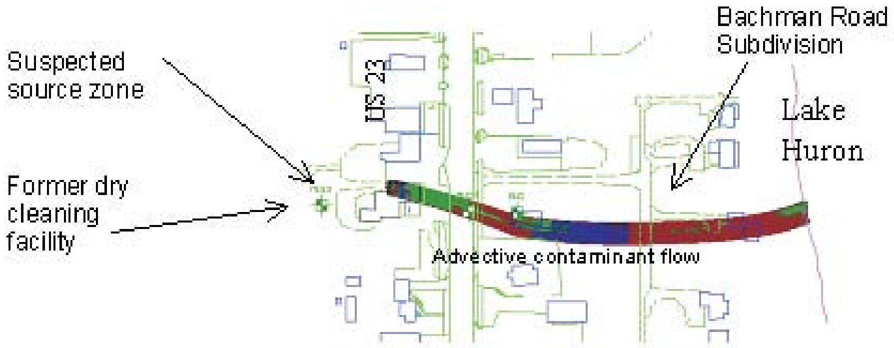

Figure A.3 Advective plume Bachman road SEAR pilot-scale test location. Shown is simulated contaminant advective flow to Lake Huron from suspected source zone.

Contamination from volatile organic contaminants was first detected in private water supply wells in the Bachman Road subdivision in 1980. In the mid-late 1980s, a remedial investigation was initiated by the MI DNR. Four groundwater plumes were delineated. The PCE plume described above was designated as Plume B. Additional characterization work was undertaken in 1992-94, including monitoring well installation and collection of water and unsaturated soil samples. Although free-phase PCE was not detected, aqueous PCE concentrations as high as 88 ppm were measured in front of the former dry cleaning facility (currently a printing business, with an adjacent private residence).

In 1999, additional site characterization work was undertaken in the vicinity of the former dry cleaning facility to explore the feasibility of applying SEAR at the site and to design a pilot-scale test. Intact cores were taken along eight vertical and angled borings. Cores were analyzed for PCE and sub-sampled for hydraulic conductivity and grain size distribution measurements. Hydraulic conductivity estimates ranged from 15-150 feet per day. Additional drive point and monitoring well samples indicated that the likely source of contamination was beneath the northwest corner of the former dry cleaning building, and this area was selected for the SEAR pilot-scale treatment zone. Further core sampling within the treatment zone (for installation of multilevel samplers) indicated that PCE contamination varied with depth. High PCE contamination levels were found consistently in two regions, about one to two feet beneath the water table and immediately above the aquitard. Only two soil sub-samples within the treatment zone conclusively indicated the presence of free-phase PCE. A small amount of free product was also detected in one multilevel sample prior to the start of the test. No PCE pools were encountered in site characterization, and meaningful mass estimation from core sampling was not possible.

SEAR Test Design

Tween 80, an ethoxylated sorbitan ester surfactant, was selected for the SEAR demonstration, based upon its high solubilization potential for PCE and its biodegradability. It performed well in laboratory tests with site materials. The pilot-scale test design (Figure A.4) consisted of a single extraction well (19.7 L min^{-1}), a row of three water injection wells (3.8 L min^{-1} each) to establish a flow field through the source zone, and a gallery of three surfactant injection wells (1.9 L min^{-1} each) positioned between the water supply and extraction wells. The selected pumping schedule involved start-up of the extraction well, followed shortly by all injection wells. For estimation of PCE mass within the swept zone, surfactant injection was preceded by a short-term partitioning tracer test (PITT). Following the PITT test, injection of a 6% (by volume) surfactant solution was initiated over the entire saturated thickness for five days. Operation of well S1 was then discontinued and a targeted injection of surfactant continued for an additional five days in wells S2 and S3, screened over the top and bottom 1.2 m of saturated depth. Simulations predicted that this targeted injection scheme would efficiently deliver surfactant to suspected highly contaminated regions and reduce overall surfactant cost. In total, 1.5 pore volumes of surfactant solution were injected. Water injection was continued for an additional two days after surfactant shut off, and the extraction well was then operated for one month to ensure surfactant and solubilized plume capture. Total test operation time was 60 days. Effluent from the extraction well was treated in above ground air strippers, and the treated fluid was then discharged to the community sewer system. Approximately 4,500 aqueous samples (excluding duplicates) were collected from the multilevel samplers during the test and analyzed for dissolved constituents (alcohols, PCE, and Tween 80) at the University of Michigan analytical laboratories (Figure A.4).

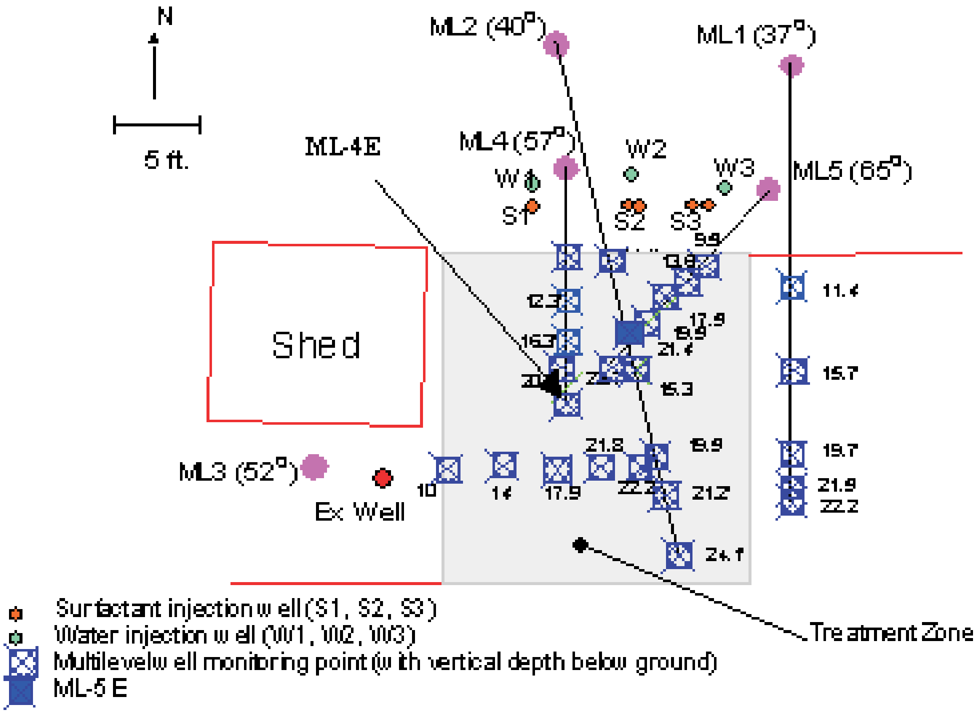

Figure A.4 Bachman road SEAR pilot-scale test site plan. SEAR treatment zone is shaded. Vertical depths for each monitoring point are shown.

Test Results

During the SEAR test, hydraulic capture of the solubilized plume was demonstrated with more than 95% of the injected surfactant recovered during the test. Surfactant sweep of the test zone was confirmed by multilevel sampler measurements of surfactant breakthrough. Approximately 19 L of PCE were extracted from the swept zone. This volume was consistent with results from the PITT test that indicated low average saturations of PCE (0.03% to 0.60%) within the swept volume. Significant PCE aqueous concentration tailing (at a level of 15 ppm) was observed in the extraction well, subsequent to surfactant plume capture. It is likely that these high tailing concentrations are associated with an additional DNAPL source region within the capture zone of the extraction well. This hypothesis has been confirmed by follow-on aqueous sampling within the surfactant swept region. Aqueous samples from the multilevels within this region have revealed a two order-of-magnitude reduction in aqueous concentrations subsequent to treatment. Highest concentrations, once nearing 100 ppm, are now below 1 ppm, with most sampling points below 0.1 ppm. (Note that these concentrations still exceed MCLs). Higher PCE concentrations appear to be associated with areas of persistent higher Tween 80 concentrations, suggesting stagnant zones within the source region. To date, no concentration rebound has been observed within the swept zone. PCE degradations products (TCE and *cis*-DCE) have recently been detected in significant concentrations within and downstream of the treatment zone, suggesting that the addition of the Tween 80 has stimulated microbial activity. (Neither ethene nor vinyl chloride have been detected to date). A halorespiration investigation and in-situ stimulation of halorespirers is ongoing at a near-by mixed BTX/PCE plume.

Contractor costs for the pilot-scale test totaled approximately $390,000. This included preliminary and final design costs, limited source characterization work, installation of multilevel piezometers for monitoring, system construction, system operation and maintenance (including treatment system sampling), treated effluent discharge costs, and system shutdown. This total excludes the costs for the intensive aqueous sampling of the swept zone and associated chemical analyses.

The MI DEQ has been encouraged by the pilot-scale test results, and a full-scale SEAR implementation for the site is currently being designed.

CASE STUDY

In-Situ Alcohol Flushing for Enhanced Remediation of PCE Source Zone: Sages Dry Cleaner Site

In-Situ Alcohol Flushing for Enhanced Remediation of PCE Source Zone: Sages Dry Cleaner Site

Sillan (*1998*) and Jawitz et al. (*1998*) reported on a pilot-scale field test of in-situ alcohol flushing for enhanced remediation of a DNAPL source zone where isolation of the test zone was achieved entirely by hydraulic containment (i.e., no sheet–pile walls). This field study was conducted at the site of a former dry cleaning operation in Jacksonville, FL, where the shallow, unconfined, sandy aquifer had become contaminated with tetrachloroethylene (PCE). The goals of the in-situ alcohol flushing strategy were to maximize the efficiency of DNAPL extraction, minimize the potential for DNAPL mobilization or fugitive emissions, and minimize waste disposal costs within the given financial and regulatory constraints.

The DNAPL source zone was delineated using soil cores, groundwater samples, partitioning tracer tests, and direct push cone penetrometer methods. Enhanced DNAPL solubilization was achieved by in-situ flushing with two pore volumes (PV) of a 95% ethanol/5% water mixture. The pilot test described here is the first field-scale demonstration of in-situ alcohol flushing for enhanced remediation of a DNAPL source zone. This pilot study was conducted and funded jointly by LFR Levine Fricke (Tallahassee, FL), the University of Florida, Florida Center for Solid and Hazardous Waste Management, Florida Department of Environmental Protection, and U.S. EPA (NRMRL, Ada, OK; TIO, Washington, DC).

Field Site

Fine to very fine sand occurred at the site to a depth of approximately 9 m below ground surface (bgs), below which a 1.7 m layer of very fine to silty sand was encountered. A thin discontinuous clay layer (0.15 to 0.3 m thick) was detected at approximately 10.7 m bgs in most soil borings. Very fine sand to silty fine sand was observed beneath the clay layer. The water table was approximately 3 m bgs, and the natural hydraulic gradient was measured to be approximately 0.0025. The average saturated hydraulic conductivity, estimated from slug test data, was about 6 m/day in the upper sand unit (0-9 m bgs) and about 3 m/day in the lower sand to silty sand zone (9-10.7 m bgs). The PCE release history at this site was unknown. Concentrations of PCE in groundwater samples collected from existing monitoring wells during the initial site assessment ranged from 70 to 150 mg/L. About 15 cm of free-phase PCE were detected in the former supply well.

Source-Zone Characterization

Preliminary CPT coring identified an oblong PCE source area of approximately 7.3 m × 2.7 m in the depth range of 7.9 m to 9.4 m bgs. The target DNAPL source zone was further characterized both before and after alcohol flushing using soil cores and inter-well partitioning tracer tests. Soil cores were collected using hollow-stem auger and split-spoon barrel methods during installation of the wells, and using CPT methods during installation of the multilevel samplers (MLSs). Soil cores were collected every 60 cm and sub-sampled at 3 cm intervals for methylene chloride extraction. A total of 196 sub-samples were collected from 16 borings (three injection wells; six recovery wells; and seven MLSs) prior to alcohol flooding while 61 sub-samples were collected from six CPT borings following alcohol flushing.

Partitioning tracer tests were conducted before and after alcohol flushing. In the pre-flushing tracer test, methanol was used as a non-partitioning tracer, and n-hexanol; 2,4-dimethyl-3-pentanol; and 2-ethyl-1-hexanol were used as partitioning tracers. For both the pre- and post-flushing tracer tests, a tracer pulse of approximately 0.20 pore volumes (3.8 hrs) was delivered to the IWs during steady water flow using the flow distribution described above. Throughout the tracer injection and displacement periods, samples were collected from the recovery wells (RWs), injection wells (IWs), and MLSs at frequent intervals (ranging from one to eight hrs). Data from analyses of these samples yielded tracer breakthrough curves (BTCs). Temporal moment analysis was applied, and the average PCE saturation, S_N, within the swept volume of each recovery well was determined.

Numerical simulations indicated that a well configuration of three IWs and six RWs would provide effective hydraulic containment and achieve adequate coverage of the NAPL source zone (Figure A.5). A total flow of 15.1 L/min was distributed equally to the three IWs. The interior wells (RWs 3, 4, 6, and 7) had extraction rates of 5.9 L/min, and the outer two wells (RWs 2 and 5) were assigned extraction rates of 3.4 L/min, resulting in a 2:1 extraction to injection ratio. The three IWs were screened from 7.6 to 9.9 m bgs, while the six RWs were screened from 7.9 to 9.6 m bgs. This design was selected to promote upward flow of the injected fluids. Seven MLSs were installed within the NAPL source zone, with five sampling depths at each MLS.

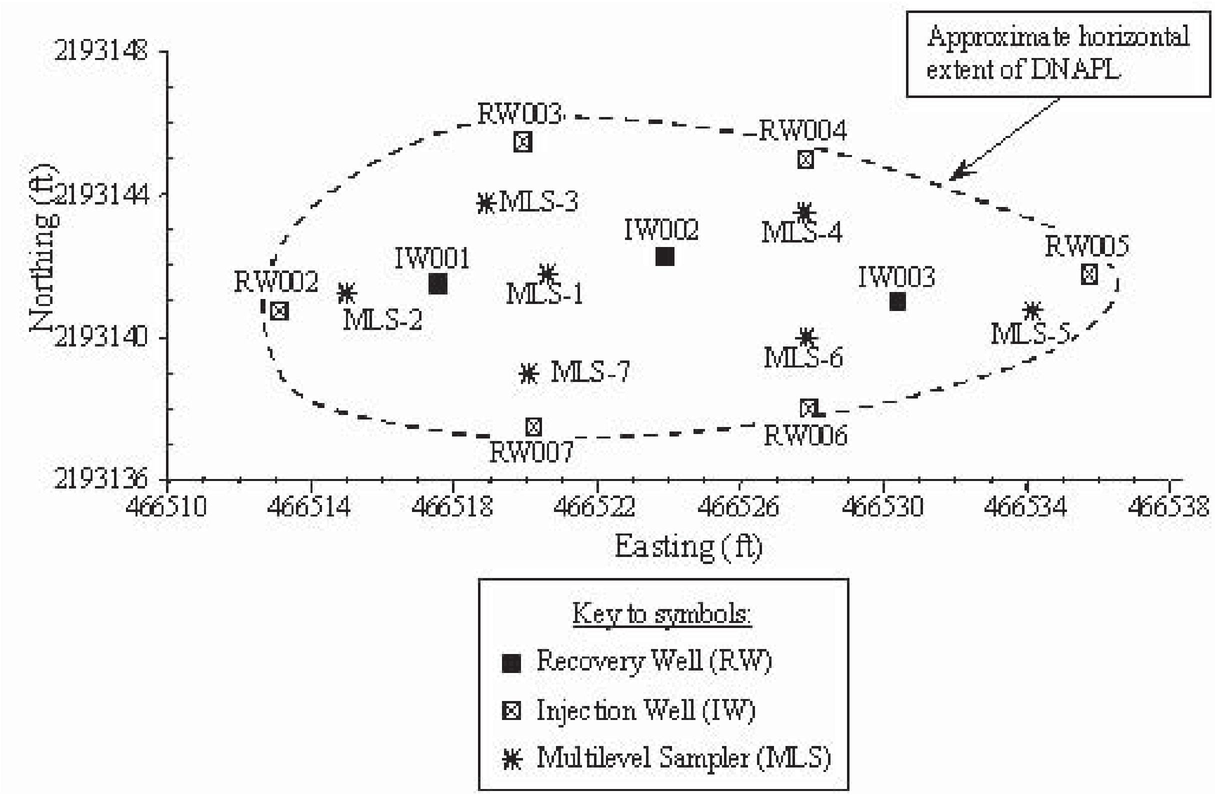

Figure A.5 PCE source zone with the well and sampling design used for in-situ alcohol flushing pilot Test at the Sages dry cleaner site, Jacksonville, Florida.

In-situ Flushing Protocols

A total of 34 kL (2 PV) of 95% ethanol was delivered to the three IWs during a period of about three days. A neoprene-rubber well packer was placed in each injection well in order to focus delivery of the alcohol to zones of high S_N. Alcohol was injected below the packer while potable water was injected above the packer to limit migration of the alcohol into the aquifer above the packer. The combined flow rate of water and alcohol was held constant at 4.2 L/min for IW-1 and IW-3 and at 6.8 L/min for IW-2. Initially, the packer height was set at 0.3 m in order to flush alcohol immediately below the deepest detected free-phase PCE. By flooding this region with alcohol before flushing the PCE-contaminated zone, a barrier to downward mobilization of free-phase PCE was established. Thus, if free-phase mobilization of PCE from the contaminated region above occurred at the alcohol injection front, a layer of alcohol solution was available below to solubilize the PCE that may have migrated from the contaminated region.

The ethanol concentration in the injection fluid was ramped from 0 to 95% over 10 hrs (0.5 PV) using a continuously stirred tank reactor (CSTR) that had a tank volume of 340 L. The gradient injection of alcohol was implemented to minimize fluid density differences between the resident groundwater and the injected fluids as a means of reducing flow instability effects. The 95% ethanol/5% water mixture was injected below the initial packer height for six hrs (0.3 PV), and the packers were then raised at a rate of approximately 15 cm/hr to a maximum height of 1.7 m at IW-1 and IW-2 and 0.9 m at IW-3. The maximum packer heights were chosen based on the locations of PCE detected in soil cores. After 70 hrs of flushing (3.73 PV), the packers were lowered at the same rate to a final height of 30 cm. This scheme was employed at the latter stages of the ethanol flood to facilitate the subsequent removal of the ethanol mixture from the swept zone by minimizing the potential for gravitational segregation of the ethanol mixture and the displacing water. Water flooding was initiated after 3.5 days (4.48 PV) to remove the remaining ethanol and was continued for 4.5 days (5.75 PV). Note that because of the efforts to minimize the potential for flow instabilities and uncontrolled NAPL migration, approximately 76 kL of water and ethanol were flushed through the NAPL source zone in order to deliver 34 kL of ethanol.

In order to minimize costs associated with the disposal of waste containing high levels of PCE, a macro-porous polymer extraction (MPPE) system, developed by Akzo Nobel, was used to separate PCE from the effluent solution that contained ethanol, water, and dissolved PCE. This technology uses a porous polyolefin material with a proprietary extraction fluid immobilized within its structure. During treatment, the waste stream was passed through a column containing MPPE material into which the PCE preferentially partitioned. After loading with PCE, the columns were regenerated with low-pressure steam stripping. The steam extracted the PCE from the MPPE material and was then condensed and separated into free-phase PCE for disposal. Waste fluids containing greater than 1% ethanol were transported for off-site disposal, while those containing less than 1% ethanol were processed through an air stripper and discharged on site.

Results

The high-frequency sub-sampling technique delineated thin (5 to 8 cm thick) layers of PCE that did not appear to be horizontally continuous over the extent of the target zone. The average concentration of PCE in the soil samples collected was 2,809 mg PCE/g soil with a standard deviation of 11,050 mg PCE/g soil (n = 147 samples). These data suggest a high degree of variability in the areal and vertical extent of the discontinuous NAPL source zone. Such source architecture—with a limited volume fraction with DNAPL— is fairly typical of DNAPL source zones. Thus, detection of source zones is difficult, and in-situ flushing remediation is likely to be an inefficient process. The tracer data suggest that the total estimated volume of PCE within the swept zone of the wells was approximately 69 L, equivalent to an overall average S_N of 0.004. The largest quantities of PCE (>50% of the total) were found in the swept volumes of two wells (RWs 3 and 7); these two wells were on opposite sides of a sump that was the suspected point of PCE entry into the subsurface. The total amount of PCE extracted was approximately 42 L (67 kg), determined from numerical integration of the PCE breakthrough curves at all extraction wells. Substantially more PCE was extracted from RWs 3, 6, and 7 than from RWs 2, 4, and 5, in general agreement with the pre-flushing partitioning tracer estimates of the amount of PCE within the swept volume of each well. Numerical integration of the ethanol BTCs indicated that approximately 92% of the injected alcohol had been recovered by the end of the 5.75 PV water flood. The 2:1 extraction ratio resulted in considerable dilution at the RWs and, consequently, produced a large volume of extracted groundwater containing ethanol, PCE, and tracers requiring considerable costs and management for treatment and disposal. Approximately 35 L of PCE were separated from the waste stream by the MPPE system, representing a recovery of 83% (the effluent contained approximately 42 L of PCE). The treated fluids had high ethanol contents but could not be re-injected because of state regulatory constraints. About 640 kL of waste liquid were transported off-site to an industrial wastewater treatment facility.

Performance Assessment

The average concentration of PCE in the 61 soil samples collected from six post-flushing borings was 936 mg PCE/g soil, with a standard deviation of 3200 mg PCE/g soil. Based on soil core data, the PCE removal effectiveness, defined as the fraction reduction in the amount of PCE initially present, was calculated to be 0.67. The post-flushing tracer tests indicated the total volume of PCE remaining in the swept volume was about 26 L, equivalent to an average S_N of 0.0014. Both the soil core and partitioning tracer data indicated that approximately 60% of the PCE was removed through two PV of in-situ alcohol flushing. However, a comparison between the concentrations of PCE in groundwater samples collected from the MLSs before and after the alcohol flood showed that the aqueous PCE concentrations were similar before and after alcohol flushing. This is the result of the presence of enough DNAPL to maintain elevated PCE concentrations. More recent monitoring data indicate that the average PCE concentration in multilevel source-zone sampler was about 49 mg/L, and after one year, the average concentration for PCE was reduced to about 26 mg/L. The estimated mass reduction was 62%, compared to an estimated reduction in mass discharge from the source zone of 47%, based on calculations completed by the University of Florida.

The goal of this study was the removal of a significant amount of PCE from the DNAPL source zone, and not necessarily the reduction of aqueous PCE concentrations in the NAPL source zone to below regulatory limits. A related objective was to monitor the source zone and the dissolved plume for an extended period (approximately two years) following in-situ flushing to examine changes in the geochemical processes and microbial dechlorination of PCE. Mravik et al. (*2000*) report the results of long-term monitoring to assess the decreases in PCE concentrations resulting from enhanced reductive dechlorination, possibly enhanced by the presence of ethanol serving as an electron donor. Such secondary benefits of source removal merit further careful evaluation.

CASE STUDY

In-situ Treatment of a TCE Source Area Using a Jetted Slurry of ZVI and Clay

In-situ Treatment of a TCE Source Area Using a Jetted Slurry of ZVI and Clay

Introduction

In September 1999, a project was completed at DuPont's Kinston, NC, plant involving use of high-pressure jetting to emplace a slurry of zero-valent iron (ZVI) and kaolinite into a small, well-defined trichloroethene (TCE) source area. This pilot scale project was completed in conjunction with emplacement of a thin ZVI permeable reactive barrier (PRB) across the plume downgradient of the source, also using high pressure jetting. Groundwater has been monitored periodically to track performance of the source treatment and PRB. In addition, source area soils were re-sampled approximately one year after emplacement to measure treatment effectiveness.

Site Description

The project site is a TCE plume in the Central Manufacturing Area at DuPont's Kinston facility. Figure A.6 shows a plume map from May 1998 as well as location of an existing groundwater extraction system that was put in operation in 1993. The plume originated in a relatively small source area near monitoring well MW-30A, apparently resulting from undocumented waste handling activity prior to 1980. Figure A.7 provides a geologic cross section through the source area. The water table lies at a depth of about four to five feet below ground surface. Based on average gradients and hydraulic conductivities from slug tests in the area, the average linear groundwater velocity is estimated to be 0.05 to 0.1 feet/day. The TCE plume is roughly 500 feet long and is 250 to 300 feet wide at a downgradient distance of 300 feet. Peak groundwater concentration in the source region prior to treatment was in the range of 50 to 60 mg/L (at BW-1), while peak concentration in the distal reach of the plume was roughly 100 to 150 mg/L (at MW-29).

The impacted zone is limited to a surficial sand unit roughly 15 feet deep overlying a thick mudstone confining layer. In May 1998, Geoprobe sampling was performed to better define soil TCE concentrations in the source area. Soil cores were collected from two soil depth intervals (near base of light grey sand horizon and near base of black silty sand horizon, respectively – refer to cross section) at 16 locations in the vicinity of the suspected source. Core samples were placed on ice and analyzed by GC/MS (EPA Method 8260) within an hour of collection in a mobile on-site lab. Results are shown in Figure A.8. TCE concentrations in the source ranged from roughly 10 mg/kg to 100 mg/kg (on a wet weight basis) with higher concentrations generally observed at the light grey sand/silty black sand horizon about two to three feet above the mudstone interface. No free-phase or residual-phase DNAPL was observed. From the results of this work, it was concluded that the source area apparently was limited to a 25-foot diameter area.

Technology Description

The dechlorinating properties of zero-valent iron for in-situ groundwater treatment of chloroethenes and other chlorocarbons are well documented. The technology applied at Kinston by DuPont involved mixing a water-based slurry of ZVI and kaolinite clay into the TCE-impacted source area sands as a "reactive stabilization" measure. Figure A.9 illustrates this concept. Unlike the standard PRB application of ZVI, groundwater velocity and reaction rate are not the overriding design concern since the addition of clay provides a relatively low hydraulic conductivity diffusional environment in which the treatment can take place. Given adequate mixing and sufficient ZVI relative to source mass, the treatment can proceed at any reasonable pace provided an acceptable treatment endpoint is reached consistent with site strategy and remedial objectives.

The slurry emplacement/mixing method chosen for Kinston was high-pressure jetting applied in an interlocking column configuration. Jetting uses a high-pressure stream of fluid to cut through soil and emplace slurry. The columnar jetting process is illustrated in Figure A.10. The process begins by drilling to the desired depth, in the Kinston case to the top of the mudstone horizon. Once at depth, the jetting process is activated. A small diameter, high-pressure jet of fluid exits from jetting nozzles located just above the tip of the drill string. Upon starting this process, the drill string is slowly rotated and extracted leaving a column of soil and entrained slurry in place. Some portion of the jetted material and native soil will come to the surface as spoil. At Kinston, this excess spoil was containerized in roll-offs and held until treatment rendered TCE concentrations non-detect.

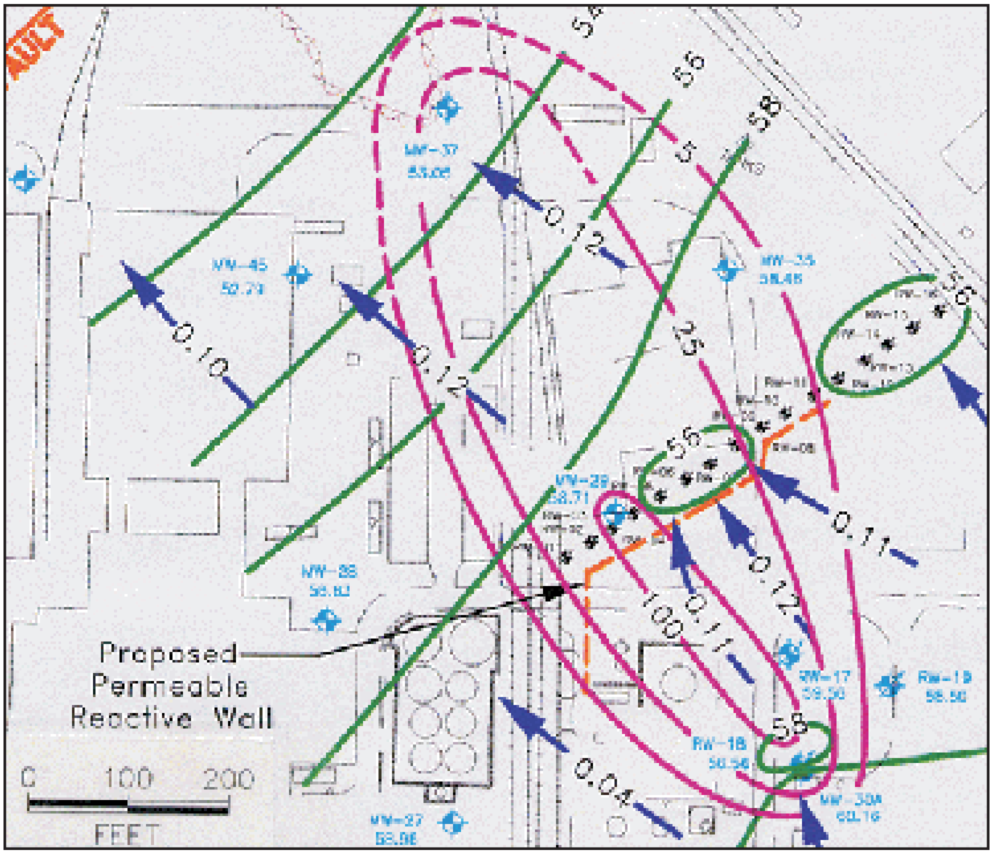

Figure A.6 Map of impacted area.

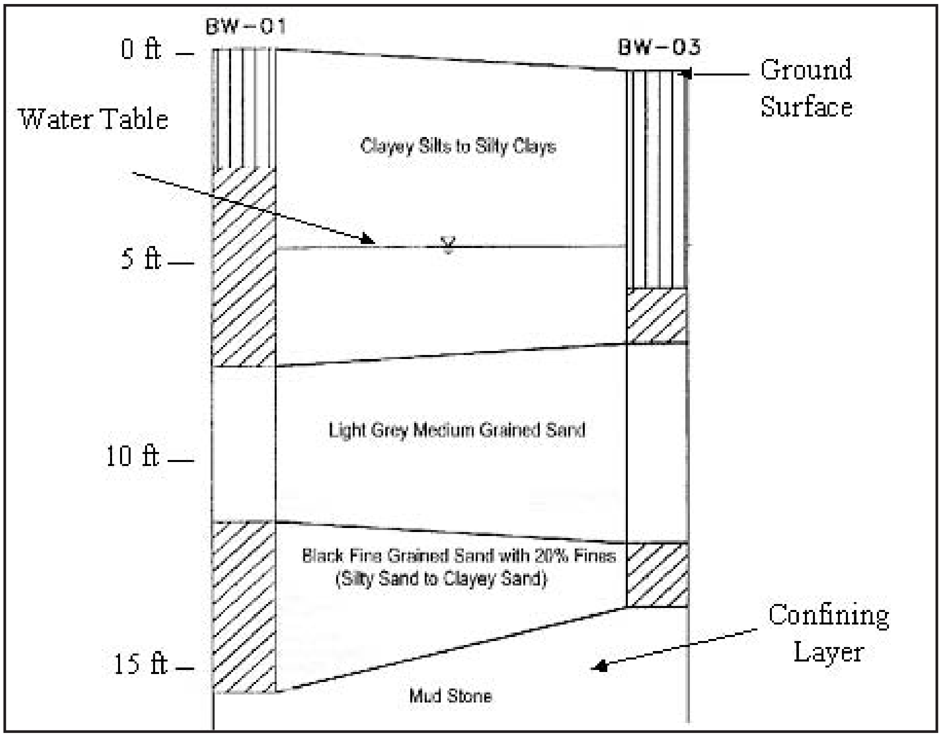

Figure A.7 Geologic cross section.

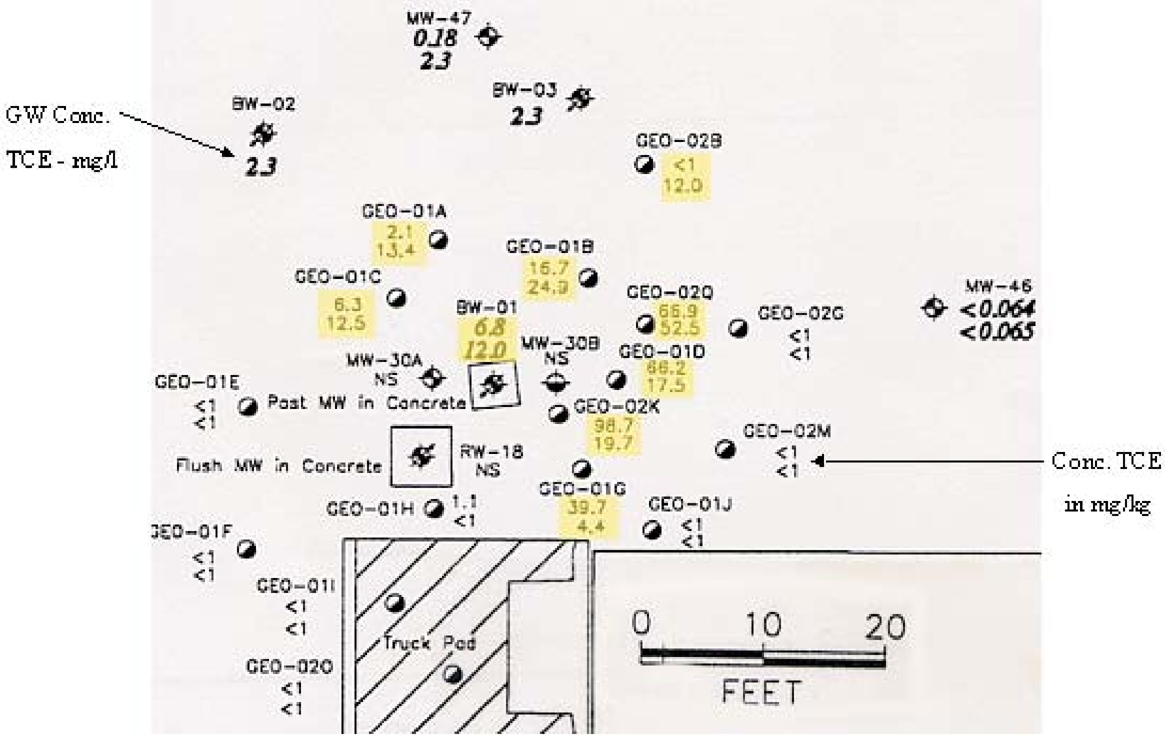

Figure A.8 Source-zone concentration map.

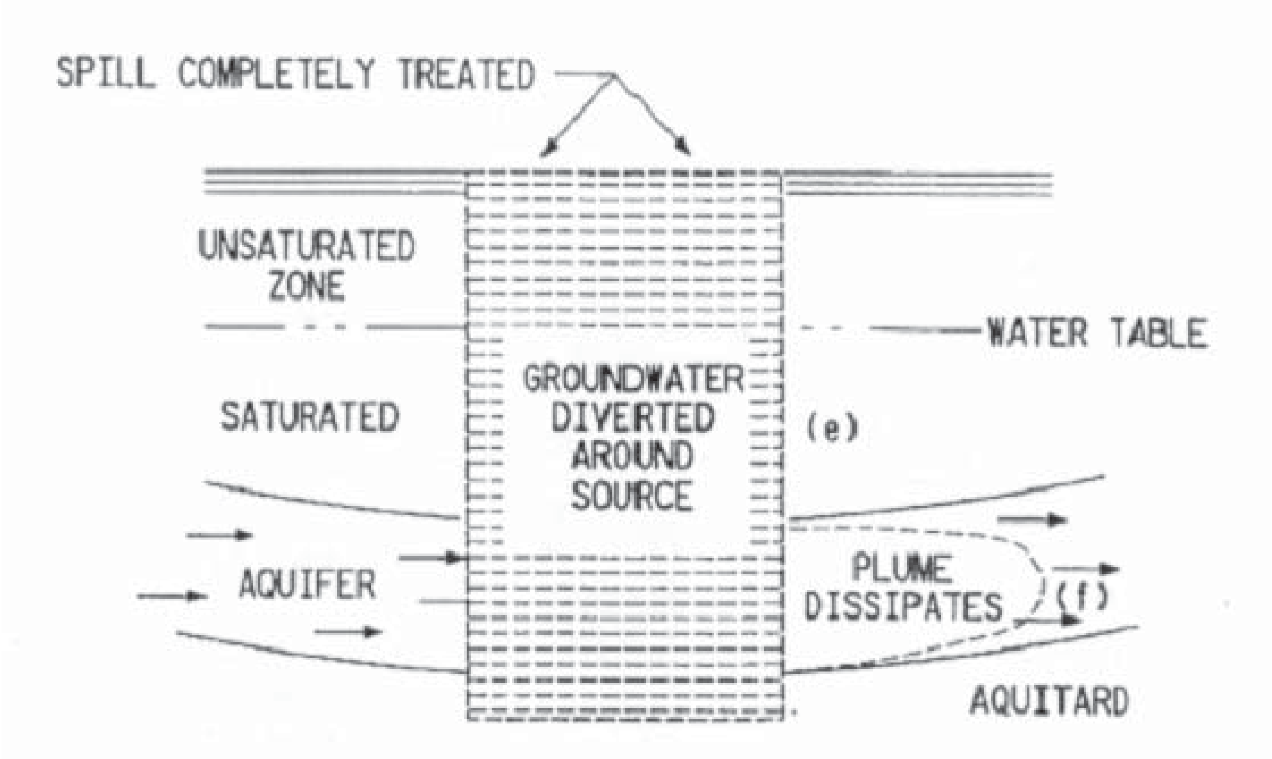

Figure A.9 Concept of treating DNAPL source area.

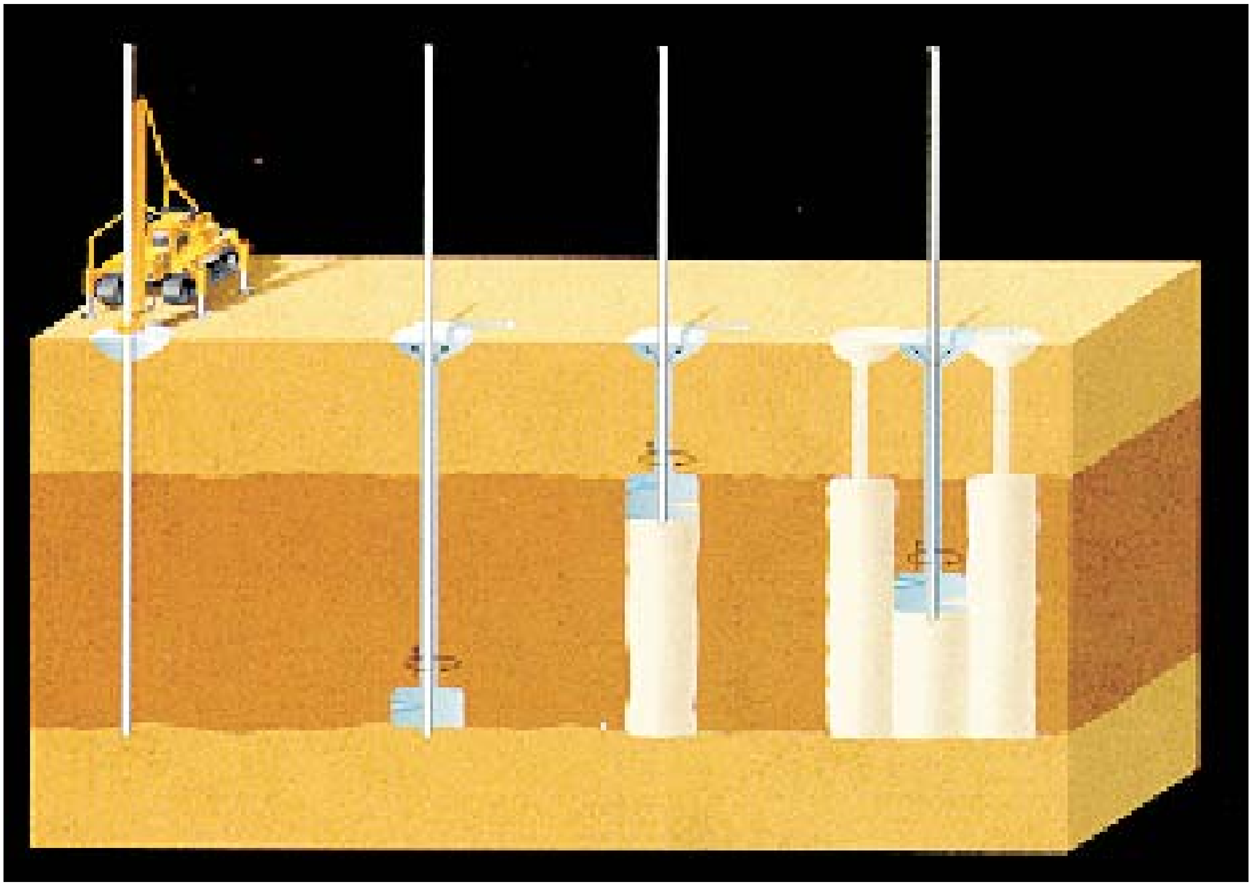

Figure A.10 Columnar jetting process.

Design and Application

The slurry applied at Kinston consisted of 95% kaolinite and 5% Peerless ZVI (-50 mesh) on a dry weight basis. In September 1999, a total of 11 treatment columns were emplaced to depths ranging from 15 to 18 feet. The estimated treatment column diameters ranged from five to six feet, and columns were placed at centerline distances of four to five feet. In addition, a low hydraulic conductivity cofferdam of jetted clay/ZVI slurry was placed completely around the source area perimeter. This was accomplished using the thin diaphragm wall emplacement technique in which the drill string is held stationary during extraction to emplace panels instead of columns. The cofferdam jetting centers were placed nine feet apart to create interlocking panels. Figure A.11 shows the layout of the treatment columns and cofferdam. Hayward-Baker of Baltimore, MD, was the jetting contractor.

As part of the same project, jetting was used to emplace a 400-foot long thin wall of ZVI across the distal portion of the plume about 300 feet downgradient of the source area. The PRB was accomplished using the thin wall emplacement technique similar to the cofferdam. However, the slurry design was changed to consist of –50 mesh Peerless ZVI in a guar gum slurry. The resulting PRB consisted of an effective thickness of two to three inches of ZVI.

Results

The source area was resampled by Geoprobe coring about 11 months after treatment. The resampling effort consisted of taking post-treatment cores at the same source area locations sampled in 1998 prior to treatment. Soil cores were screened immediately in the field by OVA followed by Encore sample collection and placement on ice. Lab analysis was conducted for TCE and daughter products by GC/MS EPA Method 8260. Figure A.12 shows results of the post-treatment samples side-by-side with the pre-treatment results. Only two out of 16 contained significant TCE and/or breakdown products in the post-treatment cores. Direct observation of cores indicates that intimate mixing on a particle scale was not achieved, but rather the mixing of entrained slurry within host soils was on the scale of inches. However, jetting appears to have been effective overall in creating sufficient mixing to achieve treatment through most of the source region.

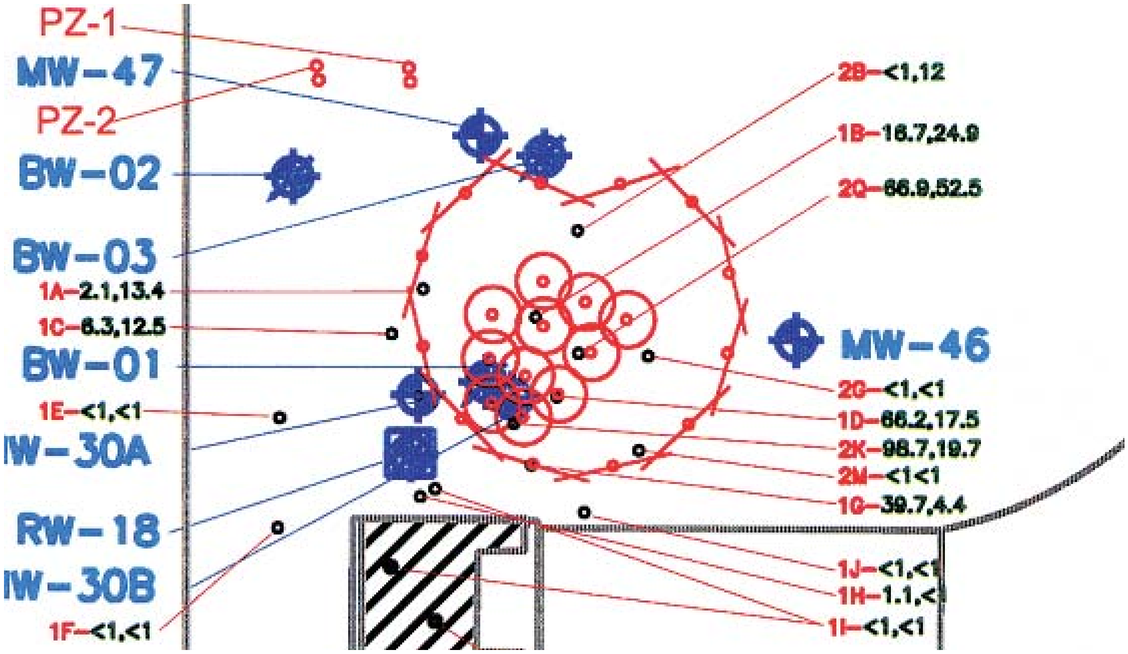

Figure A.11 Source-Zone treatment layout.

Figure A.12 Post-treatment coring (one year).

Periodic sampling of monitoring wells downgradient of the source has been ongoing since 1999. While TCE concentrations have declined generally, concentrations remain elevated. This result to date is not surprising considering the slow groundwater velocity through the area and relatively short time since treatment. Monitoring will continue in order to evaluate the long-term effectiveness of treatment on improving groundwater quality.

CASE STUDY

In-situ Chemical Oxidation of TCE Using $KMnO_4$ at the DOE Portsmouth X-701B Site

In-situ Chemical Oxidation of TCE using $KMnO_4$ at the DOE Portsmouth X-701B Site

Introduction

A field-scale test of in-situ chemical oxidation (ISCO) using $KMnO_4$ was completed at the DOE Portsmouth Gaseous Diffusion Plant in Piketon, OH, as part of the environmental restoration program at that site (*West et al., 1998a,b*). Oak Ridge National Laboratory (ORNL) coordinated the demonstration in collaboration with the site operating contractor, Lockheed Martin Energy Systems (LMES). Assistance with facets of the demonstration was provided by Carus Chemical and Schumacher Filters America. The field-scale ISCO test was implemented near the X-701B pond which was a source area for TCE DNAPLs and an associated 2000-ft long TCE plume with ground water concentrations of ~1000 mg/L near the source declining to 32 mg/L at the distal end of the plume (Figure A.13). The ISCO system utilized a pair of previously installed parallel horizontal wells that were 90 ft apart and had 200-ft screened sections consisting of 5-in. diameter, high-density porous polyethylene well screens (500 μm pore size). The horizontal wells were installed using directional drilling methods such that the screened sections were on top of the Sunbury shale and within the Gallia water-bearing unit. The goal of the field test was to determine the efficacy of flushing 2.5 to 4.0 wt.% $KMnO_4$ through the groundwater in the Gallia to degrade TCE DNAPL contamination. The field test was designed to use the existing wells and to occur over a duration of four weeks, and thus, cleanup of the entire zone between the horizontal wells was not a test objective. ISCO performance with respect to TCE degradation efficiency was evaluated by comparing pre- and post-treatment soil and groundwater TCE concentrations within the region between and just downgradient of the horizontal wells.

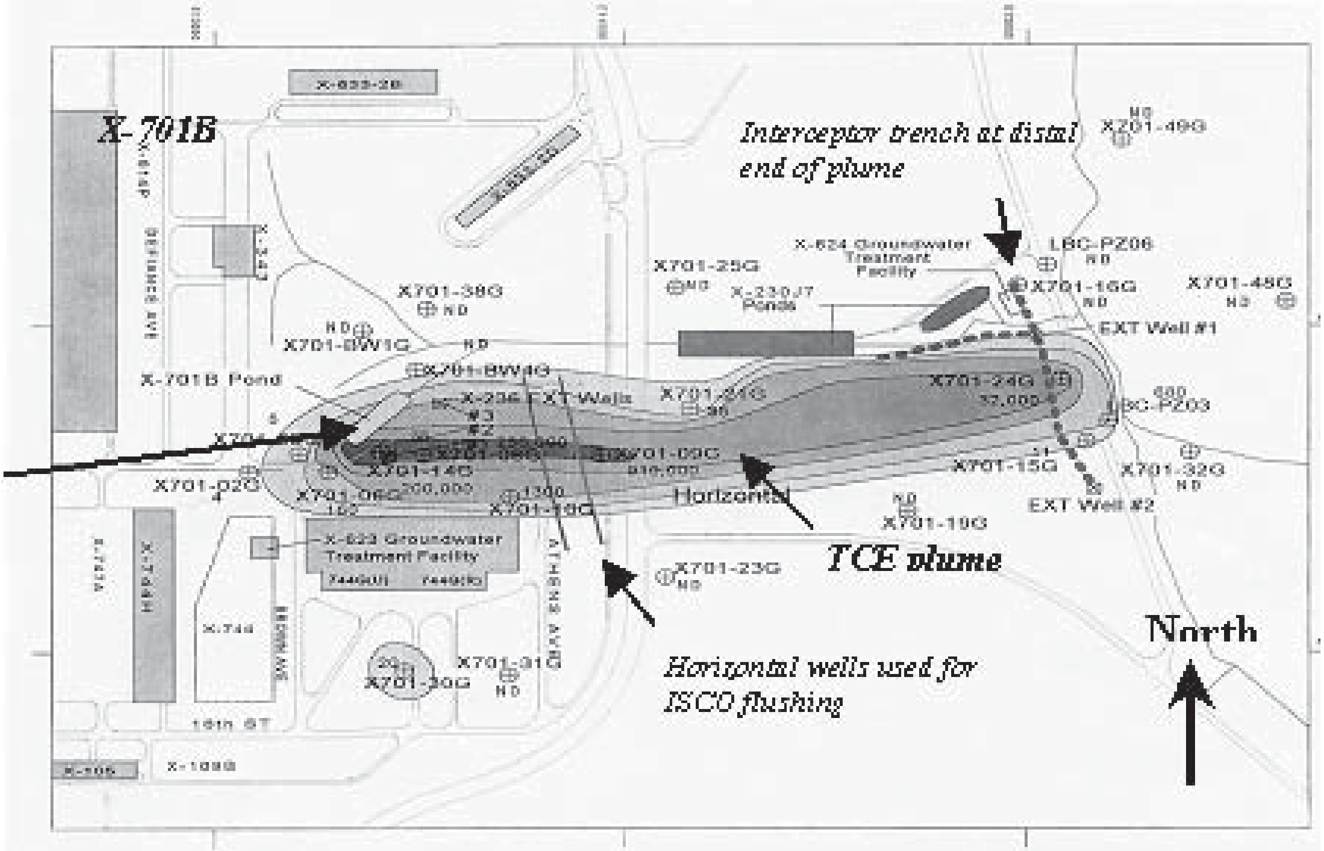

Figure A.13 Plan view of the X-701B site and the 2000-ft long TCE ground water plume.

Site Description

The stratigraphy underlying the X-701B site consists of the following layers proceeding downward from the surface (1) Minford silt and clay with a thickness of 25 to 30 ft, (2) Gallia silty gravel with a thickness varying from 2 to 10 ft, (3) Sunbury shale which is the first bedrock layer and consists of a 10 to 15-ft thick, moderately hard shale that often exhibits an upper weathered zone of gray, highly plastic clay, and (4) Berea sandstone which is present at an approximate depth of 47 ft in this area. The Minford silt and Sunbury shale layers have very low conductivities, while the Gallia and Berea layers are the main water-bearing units. Past characterization has shown TCE contamination to be present at high levels in the Minford, Gallia, and upper weathered region of the Sunbury shale, suggesting DNAPLs within the subsurface (Table A-1). The subsurface between the two horizontal wells encompassed an aquifer region where 1 pore volume was equal to ~ 1 million L.

Table A-1 TCE Concentrations in Pre-ISCO Samples from the X701B Site *(West et al., 1998a,b)*

Media and layer	No. of samples	Trichloroethylene concentration				
		Average	**Std. Dev.**	**Median**	**Min.**	**Max.**
Soil:		(µg/kg)**	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
Minford *	90	19,493	21,770	10,002	nondetect[#]	80,471
Gallia	163	53,596	52,713	43,320	nondetect	302,237
Sunbury*	13	132,405	269,791	46,932	32	1,048,174
Groundwater		(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
Gallia	26 wells	176,400	241,300	119,800	nondetect	820,600

* Minford based on samples at > 20 ft. bgs. Sunbury based on samples from the top weathered region. **Based on wet soil weight (avg. water content = 16%). [#] not detected at an approximate detection limit of 5 µg/kg or 5 µg/L.

ISCO System Implementation

Prior to design and implementation of the field application, a column-scale treatability test was completed at ORNL to test the flushing of $KMnO_4$ solution through a sandy media contaminated with DNAPL TCE. Results indicated a TCE treatment efficiency of nearly 99% with a $KMnO_4$ natural oxidant demand of 3.6 g-$KMnO_4$ per g-TCE. During the implementation of ISCO at the X-701B site, water extracted from the west (upgradient) horizontal well was sent through a nearby groundwater treatment facility before the addition of $KMnO_4$ (this was done to ensure compliance with the regulatory requirement that TCE in the re-injected groundwater was <5 ppb). Water for the oxidant injection solution was taken from a portion of the groundwater treatment facility effluent, and mixed with crystalline $KMnO_4$ using a solids feeder. The oxidant-laden water (~2.5 wt.%) was then injected without pressurization into the east horizontal well. As such, flow between the horizontal wells was opposite the direction of ambient groundwater flow. Extraction from the west horizontal well was set to ~10 gpm by flow regulators. The target injection flow rate at the east horizontal well was 10 gpm. However, this well could only take a maximum of 6 gpm as water backed up to the ground surface when higher injection flow rates were attempted. ISCO between the horizontal wells began operation on July 26, 1997, and continued through August 21, 1997. Simultaneous injections in the east horizontal well and a nearby vertical well (74G) were initiated on August 20, 1997, to attempt greater coverage of permanganate injection. Well 74G was selected because it is centrally located within the treatment region and had high levels of TCE (734 mg/L in groundwater) prior to the beginning of the ISCO field test. Injection and extraction from the horizontal wells were halted on August 21, 1997, while oxidant injection into well 74G was continued through August 28, 1997, approximately four weeks after the ISCO field test was initiated. As mentioned previously, the field test duration was preset at four weeks. The oxidant flow rate into 74G was 2 gpm. Thus, injection into well 74G, which had a screened section of 5 ft, was significantly more than injection into the 200-ft horizontal well that could only be sustained at a maximum of 6 gpm. A total of ~12,700 kg of $KMnO_4$ was delivered to the treatment region, 1,960 kg of which were introduced through vertical well 74G. Of the 206,000 gallons of oxidant solution, 14,000 gallons were delivered through well 74G. In total, the oxidant delivery was equal to ~0.8 pore volumes of the aquifer between the horizontal wells. At the completion of the oxidant flushing operation, there were increasing levels of colloidal particles coming from the extraction well, which the groundwater

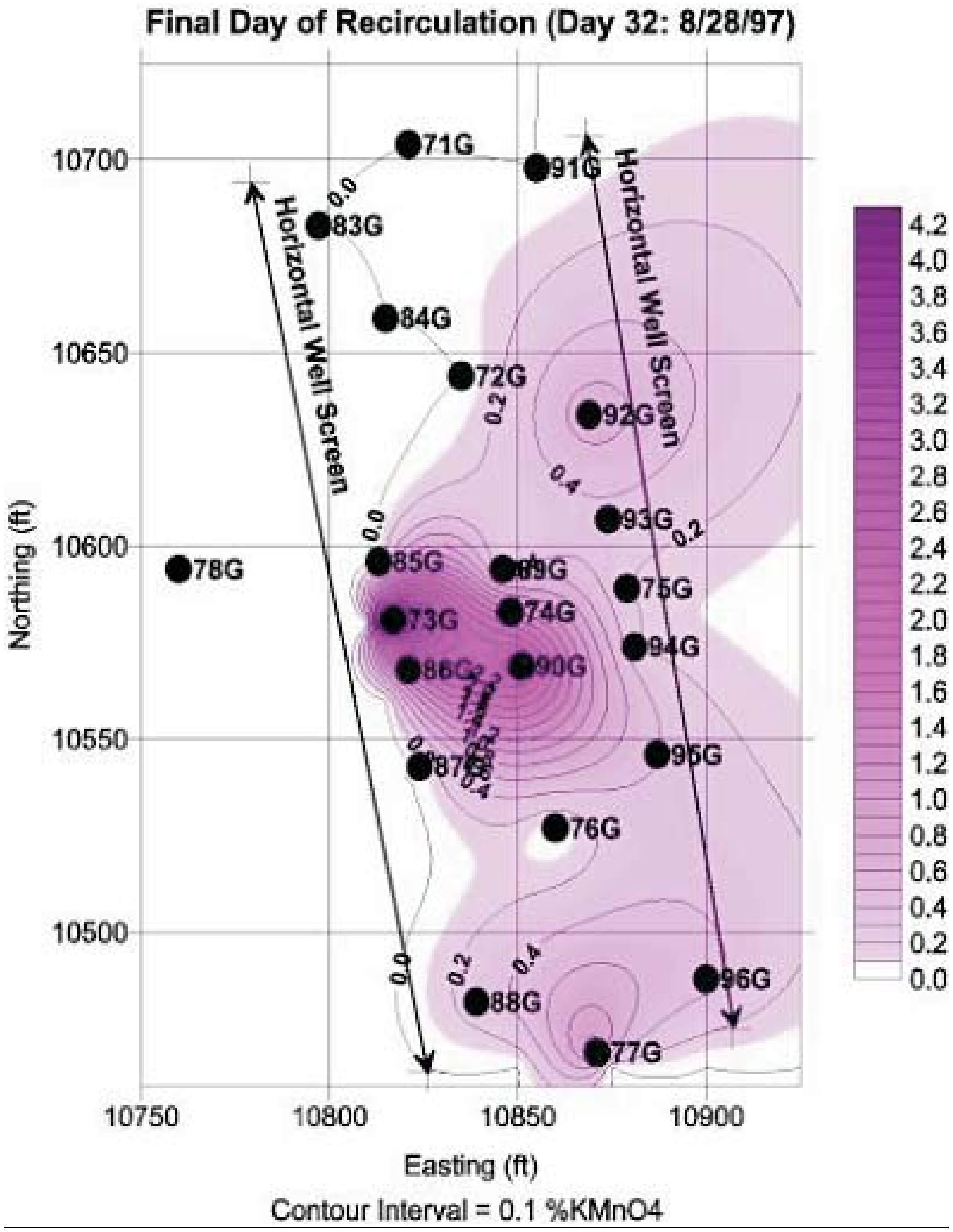

Figure A.14 Distribution of $KMnO_4$ in ground water at the ISCO field test site 32 days after initiation of oxidant delivery (West et al. 1998a,b). (Note: Oxidant delivery was initially conducted using the eastern and western horizontal wells for injection and extraction, respectively. Oxidant was injected into vertical well 74G toward the latter part of the field test).

treatment facility was not prepared to handle. These particles, on the order of 1 micron in size, were identified using a scanning electron microscope and energy dispersive x-ray as amorphous manganese oxides. The total cost of the field test was $562K (1997 dollars) divided among planning and management (~12%), pre-ISCO sampling and mobilization (~29%), ISCO operations (~29%), resistivity monitoring (~12%), and post-ISCO sampling and demobilization (~18%).

Operation and Performance Results

The process control and performance of the ISCO system were monitored through collection of water samples from the influent and effluent streams (daily) and from monitoring wells (daily to every three days) in the vicinity of the treatment region. The delivery of oxidant solution through the east horizontal well was not uniform through the length of the treatment region. After 21 days, the oxidant had been detected in all the monitoring wells that were within ~15-ft of the injection wells, except one well (Figure A.14). The oxidant was detected in the central area of the treatment zone after oxidant injection in vertical well 74G was initiated. The non-uniform distribution of MnO_4^- was probably due to spatially variable hydraulic conductivities that ranged from 24 to 411 ft/day as measured in monitoring wells within the treatment zone. The highest conductivity of 411 ft/day corresponds with the rapid detection of $KMnO_4$ in the wells in the southern portion of the treatment zone.

Overall, whenever MnO_4^- was detected in groundwater samples from the monitoring wells, TCE concentrations dropped to non-detectable (<5 µg/L) or low ppb levels (Table A-2). While this drop in groundwater TCE concentrations may be due to the degradation or removal of TCE, it could also be due in part to displacement of contaminated groundwater from the pore space and non-equilibrium between the pore water and residual TCE in the sediments at the time of sampling. Approximately two weeks after the ISCO field test ended, boreholes were drilled in locations where MnO_4^- was detected during treatment operations. All post-treatment boreholes revealed that TCE soil concentrations were significantly reduced in the Gallia layer wherever MnO_4^- was able to permeate. In the Minford silt and Sunbury shale layers, TCE levels did not significantly change with treatment because MnO_4^- did not permeate into those areas during the ISCO flushing. However, MnO_4^- was still detected at up to 93 mg/L in some of the monitoring wells more than three years after the ISCO field test, and subsequent diffusion of the oxidant into the Minford and Sunbury layers could have occurred.

Table A-2 TCE Concentrations in Post-ISCO Samples from the X701B Site (after West et al., 1998a)

Operation	No. of	Trichloroethylene Concentration (µg/L) *					
Date	Wells	Average	Std. Dev.	C.V.	Median	Min.	Max.
Pre-ISCO	25	183,400	243,600	1.33	129,400	5	820,600
Post-ISCO:							
0 weeks	24	107,500	234,300	2.18	6	5	797,700
2 weeks	19	41,000	90,900	2.22	230	32	339,500
8 weeks	22	65,200	158,100	2.43	5	5	621,500
12 weeks	23	98,500	238,200	2.42	5	5	923,300
20 weeks	23	54,900	82,100	1.50	5	5	220,800

* 5 indicates not detected at an approximate detection limit of 5 µg/L.

CASE STUDY

Cape Canaveral Launch Complex 34

Cape Canaveral Launch Complex 34

Introduction

The Interagency DNAPL Consortium (IDC), a group consisting of the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA), U.S. Department of Defense (DOD), U.S. Navy, and National Aeronautic and Space Administration (NASA), has completed two demonstrations and is currently conducting a third demonstration of innovative DNAPL remediation technologies at Launch Complex 34 (LC34), Cape Canaveral Air Station (CCAS), Florida. The demonstrations are carried out in adjacent 50 ft. by 75 ft. plots (<0.1 acre) and have taken place over a three-year period from 1998 to 2001. The technologies demonstrated at LC34 are potassium permanganate oxidation, Six-Phase Heating™ (SPH), and steam/air co-injection (in progress). Information on the Cape Canaveral project is available at http://www.getf.org/ dnaplguest/, then click on <Library>.

Several trichloroethene (TCE) hot spots have been identified at LC34. The one adjacent to the Engineering Support Bldg. (ESB) was selected for this technology demonstration. The subsurface at LC34 consists, in descending order, of (1) an upper sand unit, (2) a middle fine-grained unit, (3) a lower sand unit, (4) a lower clay unit, and (5) a lower confined aquifer. The targeted depth for the demonstration was above the lower clay unit, which consisted primarily of sandy material. Depth to groundwater is about six feet. The water table is fairly flat with a slight southeasterly flow direction in the vicinity of the test plots. The TCE distribution within the treatment zone had been fairly well characterized prior to the demonstrations; DNAPL TCE presence was estimated to correspond to soil concentrations >300 mg/kg.

The following discussion focuses on chemical oxidation and SPH. It illustrates the difficulties and uncertainties in performing technology demonstrations.

Chemical Oxidation

In the chemical oxidation plot, the initial DNAPL mass was estimated at 13,000 lbs (using soil boring data). Seventy-five tons (150,653 lbs) of potassium permanganate were injected into the plot using 841,650 gallons of solution, which is equivalent to 3.5 pore volumes. Such a large volume has the potential to cause displacement from the plot. The oxidation treatment generated 9,300 lbs of sludge (primarily insoluble permanganate reagent impurities). The total cost for the chemical oxidation demonstration (including preliminary design, field analytical support, utilities, and waste disposal) was $1,128,312.

Initially following treatment, there was significant reduction of TCE soil concentrations with some rebound after nine months. This is partly explained by soil sample variability. There was much less significant reduction of TCE groundwater concentrations, with TCE concentrations greater than 400,000 µg/L remaining. DNAPL TCE was still present in the plot. In addition, displacement occurred causing DNAPL migration outside the plot. This is based on (1) DNAPL detection in perimeter wells following treatment[1] and (2) significant increases in dissolved TCE detected outside the plot, (e.g., at PA-8D, TCE increased 1,322 mg/L)[2]. Calculated mass reduction is provided in Table A-3. As noted, these mass reduction calculations do not include TCE mass displaced (but not destroyed) from the plot. In addition, the rebound after nine months may be due to a redistribution of mass in the plot, or it could represent a migration of mass into the plot from TCE that was outside the plot following treatment.

Positive results from the treatment include (1) some of the contaminant mass was destroyed (although the mass reduction is uncertain), (2) chloride concentrations in the groundwater increased, a possible result of TCE oxidation, and (3) the microbial evaluation indicated that although the application of a strong oxidant is detrimental to anaerobic microbial populations in the short term, in the longer term, some microbial populations are re-established. Unfavorable consequences of the chemical oxidation include (1) chromium levels increased from ND to more than 10 times MCL, (2) copper, zinc, nickel, and silver all increased above MCLs (*Battelle, 2001b*), (3) TCE concentrations increased in middle fine-grained unit leading to more difficult follow-up treatment, and (4) displacement of TCE outside the plot.

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[1] DNAPL was observed at PA-2I, PA-2D, and PA-11D; it is uncertain whether the DNAPL in these wells migrated from the SPH or oxidation plot, or both.

[2] Thermal effects from the six-phase heating plot do not extend to PA-8D; the increase in TCE is due to the oxidation plot.

Table A-3 Oxidation (Permanganate) Plot Mass Reduction (Battelle, 2001b)

Computational Approach	Mass Reduction[1]	
Contouring (linear)	TCE Total	TCE DNAPL
Post demonstration	82%	84%
Extended (9 mo.)	77%	76%
Statistical (kriging)		
Post demonstration	62-84%	NA
Extended (9 mo.)	49-68%	NA

[1] Does not include TCE mass displaced from plot.

Six-Phase Heating

In the SPH plot, the initial DNAPL mass was estimated to be 24,888 lbs. For the SPH demonstration, the total cost (including preliminary design, electricity, and waste disposal) was $647,719.

Following treatment, there was significant reduction in soil TCE concentrations (soil sampling at one month after treatment is suspect due to elevated soil sample temperatures). There was insignificant reduction of TCE in groundwater. DNAPL migration outside the cell occurred or was suspected based on DNAPL (based on soil concentrations) detected in perimeter wells following treatment and DNAPL (based on soil concentrations) detected beneath the lower clay layer following treatment (not sampled prior to treatment). Estimated mass reduction in the SPH plot is provided in Table A-3.

As a result of the lateral and possible vertical TCE migration from the SPH plot, the amount of mass reduction is uncertain. Only 4,292 lbs of DNAPL were collected (19% of mass removal determined by contouring in Table A-4) by the extraction system. Some of the missing mass can be explained by surface vapor emissions (mass loss to the atmosphere), as verified by flux chamber. Accounting for the disparity in the mass balance by in-situ destruction of TCE is uncertain for the following reasons: increases in *cis*-1,2 DCE/VC concentrations could be the result of redistribution; chloride concentration increases could be partly due to water evaporation. Adding to the uncertainty was a sudden rise in the water table following a hurricane, causing a surface release of TCE from the plot.

Table A-4 Six-phase Heating Plot Mass Reduction (Battelle, 2001b)

COMPUTATIONAL APPROACH	Mass Reduction[1,2]	
Contouring (linear)	TCE Total	TCE DNAPL
Post demonstration	90%	97%
Statistical (kriging)		
Post demonstration	80-93%	NA

[1] Does not include TCE mass displaced from plot.

[2] Elevated temperature of soil cores, possible causing volatility loses causing mass reduction to be overestimated.

Vertical DNAPL migration is even more uncertain. The lower confined aquifer was not characterized prior to the demonstration to avoid potential cross contamination. Therefore, it is uncertain if DNAPL penetrated the lower clay unit before or after the demonstration. Although heating and volatilization of TCE would cause upward migration in the plot, cooling and condensation at the fringes could cause downward migration. DNAPL was found only in the lower confined aquifer beneath the SPH plot, even though sand lens or lenses were observed in the confining layer under both the SPH and oxidation plots.[3] The post-demonstration boring on the SPH plot (SB-52/PA-22) is located in the northern quadrant of the plot near the pre-demonstration boring SB-11. Prior to the demonstration, SB-11 had a maximum TCE concentration of 167 mg/kg (26-28 ft); the maximum TCE concentration in SB-52 is 40,498 mg/kg (56-58 ft). Thus, if pre-demonstration vertical DNAPL migration occurred, there is no evidence of it. Therefore, vertical DNAPL migration uncertainty must be considered in any mass reduction calculation.

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[3] In addition, the aquitard is thinnest under the oxidation plot; however, no DNAPL was found under this plot.

Some uncertain quantity of contaminant mass was removed as a result of SPH. Unfavorable events/consequences of the SPH test include electrode and transformer failures, surface release of TCE following water table rise, surface vapor emissions requiring plenum installation, well fouling from mineral precipitation, potential vertical and horizontal DNAPL migration, and safety issues related to monitoring well over-pressurization.

CASE STUDY

Permanganate Oxidation in Fractured Media

Permanganate Oxidation in Fractured Media

Preamble

The case study presented below, taken without modification, from the Proceedings of the 3rd International Battelle Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2002, Monterey, CA, pertains to a small TCE-TCA DNAPL contamination site in Fort Lauderdale, FL, where a passive potassium permanganate method is being used for source mass depletion. This publication covers the first phase of permanganate treatment that was conducted in 2000-2001. The purpose of this phase was to assess the performance of this technology applied at full scale during a time period specified by the State of Florida. In this phase, which comprised three injection episodes spread several weeks apart, more than 90% of the volume of the DNAPL source zone was successfully treated. In this successfully treated portion of the DNAPL source zone, the maximum VOC concentrations were reduced from > 10,000 µg/L to less than 100 µg/L. In the remaining 10%, the maximum concentration was reduced from > 600,000 µg/L to < 40,000 µg/L. Based on these encouraging results, the Florida Department of Environmental Protection approved a plan for a second and final phase of permanganate treatment. This final phase comprises a single permanganate injection episode during a two-week period in late September/October 2002 followed by monitoring. This final phase was in progress at the time of finalization of this Panel Report. The goal of this final phase is complete treatment of the DNAPL source zone to VOC concentrations < 100 µg/L everywhere and less than the MCLs for TCE and TCA at nearly all locations. Preliminary results from this phase indicate that this goal will likely be achieved, and that no further injections will be required. The VOC distribution in groundwater prior to the initiation of final permanganate injection episode was monitored in exceptional detail using a dense network of multilevel monitoring systems complemented with conventional monitoring wells. The TCE and TCA distributions following treatment, after a period allowing for rebound, will be determined in a manner that will enable the effects of the final treatment to be established rigorously.

Passive Permanganate Remediation of a Solvent DNAPL Source Zone

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Abstract

Permanganate remediation was conducted in southern Florida at a small industrial site with TCE and 1,1,1-TCA contamination down to 70 ft bgs in a sand aquifer. The permanganate solution was injected into the DNAPL source zone (30 ft diameter in plan view) where a small mass of residual TCE DNAPL caused this zone to have TCE concentrations exceeding 10,000 µg/L, with small zones approaching TCE saturation. This remediation project comprised three injection episodes, each occurring over several days during which small volumes of $KMnO_4$ solution were injected at depths between 5 and 65 ft bgs in each of 6-8 direct push holes. During the 2-3 months allowed between injection episodes, the large initial density contrast caused the permanganate to spread out laterally and move downward while fingering and diffusion occurred. The combination of these migration and mixing processes caused complete $KMnO_4$ coverage of the source zone, even though the coverage immediately after each episode was only 1-8% of the total pore volume of this zone. By keeping the initial injection volumes small relative to the total aquifer pore space within the targeted treatment zone, displacement of TCE mass outward from the source zone was avoided. The post-treatment monitoring showed that the combined effect of the three permanganate injection episodes was a 90% reduction in the aquifer volume where TCE in groundwater was above 100 µg/L and an even larger reduction in volume above 10,000 µg/L. The injections caused the maximum TCE concentration in groundwater to drop from 635,000 µg/L to 56,000 µg/L, with this latter value occurring only in a very small zone. These results indicate that all, or nearly all, of the DNAPL has been destroyed. These encouraging results are based on groundwater sampling of an exceptionally detailed network of depth-discrete multilevel monitoring systems. Based on the results of this initial phase, we expect that complete remediation of the source zone will be achieved with one additional injection episode focused on the two small zones where moderate TCE concentrations exist.

Introduction

Inadvertent releases of small volumes of free-product trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) occurred between 1995-early 1997 in the vicinity of spigots on an outside wall of an industrial building used to manage waste solvents from a vapor degreaser that was housed in the building located in Broward County, Florida. The site is underlain by medium-grained sand with a shallow water table (< 3 feet bgs). TCE- and TCA-contaminated soil and groundwater were discovered in April 1997 at which time solvent use was discontinued and more extensive groundwater investigations were initiated. Initial direct-push (Geoprobe) 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. This was followed by an attempt to remediate using *in situ* oxidation by injecting a Fenton's-type reagent into 30-ft screened injection wells in 1998 and early 1999. The site owner discontinued this trial after detailed monitoring showed ineffectiveness of this method.

This paper pertains to the next phase of remediation at this site in which the passive method of permanganate remediation was used for DNAPL source-zone remediation. This method was applied in combination with detailed depth-discrete monitoring to establish the pre-treatment conditions for design of the injections and for remediation progress tracking and post-treatment assessment. The permanganate injections accomplished near complete source-zone destruction of both TCE and TCA, and monitoring indicates that complete destruction can be expected with minimal addition of permanganate and effort.

Site Description and Background

The site is underlain by 85 ft of fine- and medium-grained sand resting on fossiliferous limestone. The sand has a near-shore marine origin and is nearly homogeneous, with hydraulic conductivity slightly greater than 10^{-2} cm/s. The upper 50 ft are nearly devoid of carbonate minerals and at greater depth, gravel-size limestone fragments occur with increasing size and frequency down to the top of competent bedrock at 90 ft bgs. The carbonate mineral content ranges from 0.3 to greater than 2% expressed as weight percent inorganic carbon.

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. The cores were obtained using the piston coring technique described by Starr and Ingleton (*1992*) and Zapico et al. (*1987*). Detailed sampling of these cores for DNAPL detection using the Sudan IV dye method and quantitative VOC analyses by gas chromatography showed no DNAPL occurrences and highest TCE values at half TCE solubility. Also, detailed depth discrete groundwater sampling was 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 permanganate 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 to 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 A.15 illustrates our conceptual model for the TCE contamination and also shows typical pre-treatment TCE results obtained from two bundle wells. DNAPL occurs in the source zone as dispersed globules representing the vertical trail of downward DNAPL migration. The DNAPL descended vertically until it entered a thin (8 in) 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. We refer to this area as the DNAPL source zone (Figure A.16). A zone of much lower TCE and TCA concentrations occurring beyond the source zone is the plume (Figure A.16). The horizontal gradient is slight, mainly stabilized by a locally controlled canal network and, therefore, the plume is small. The goal of the permanganate remediation is to oxidize the TCE mass in the DNAPL source zone so that the source for the plume no longer exists, allowing the plume to attenuate by natural processes.

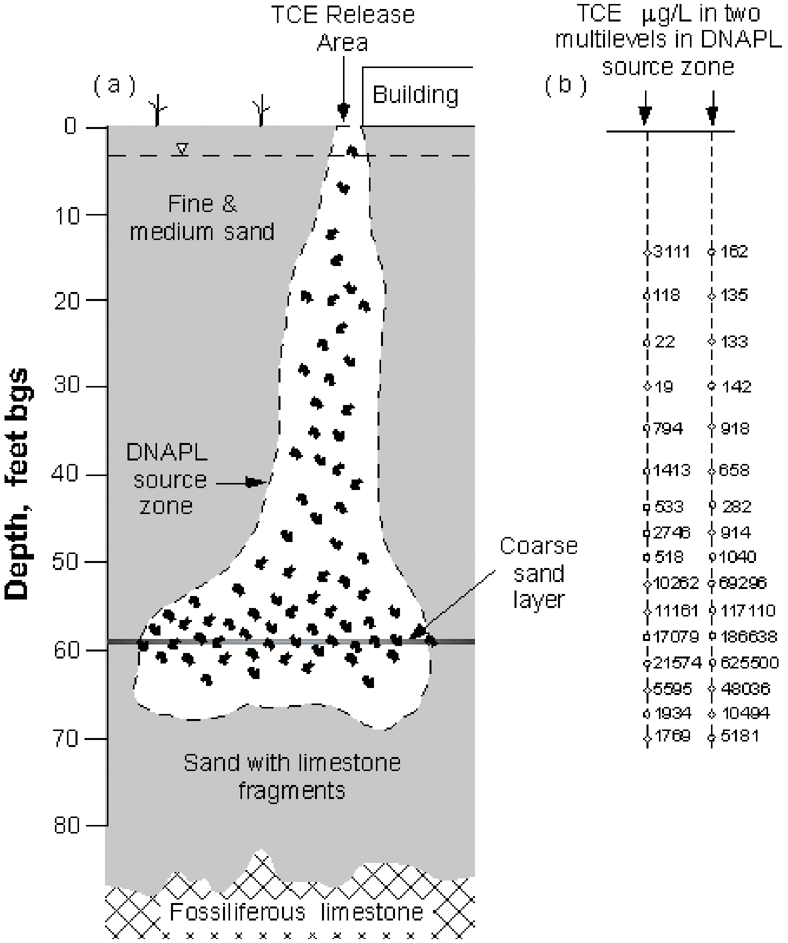

Figure A.15 Nature of the DNAPL source zone: a) geology and conceptualization of DNAPL occurrence, and b) TCE concentrations in two multilevel systems in the source zone prior to $KMnO_4$ treatment.

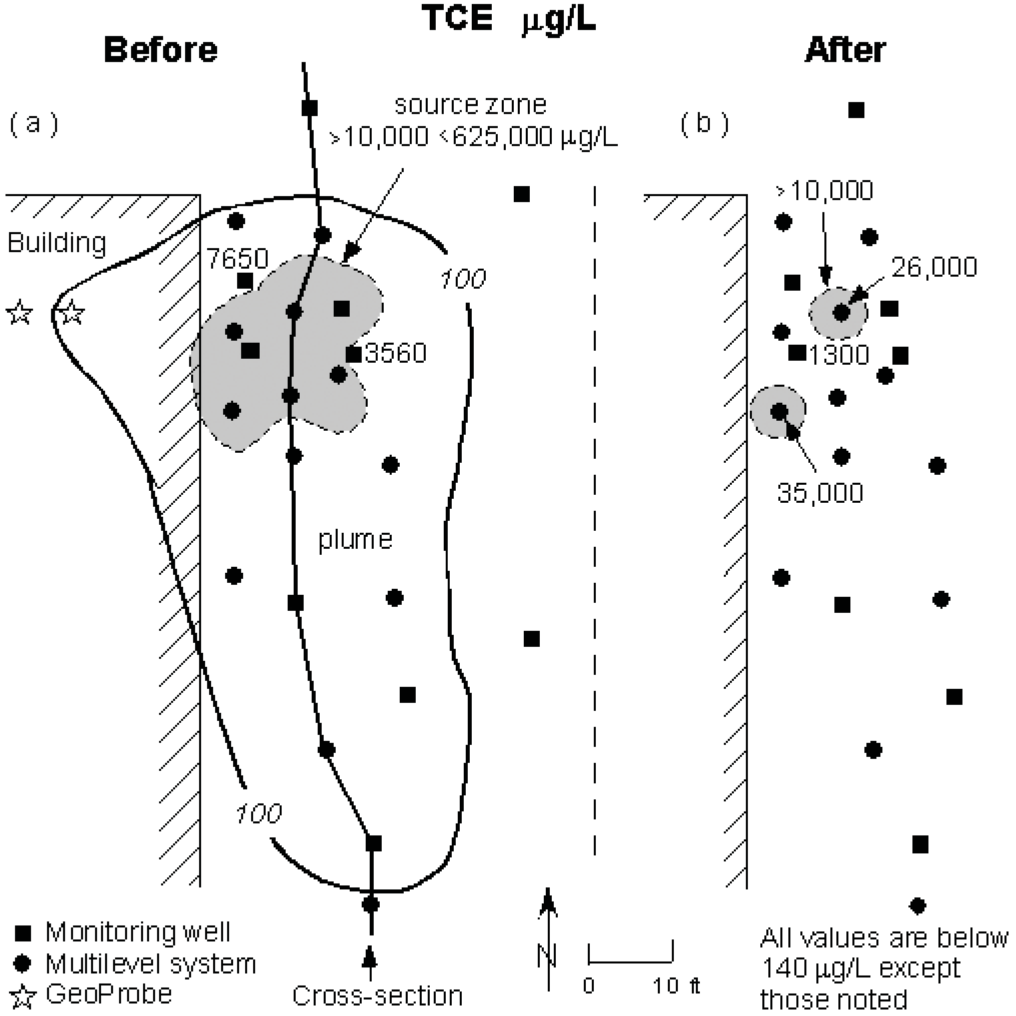

Figure A.16 Plan view of maximum TCE concentrations found at each monitoring location: a) prior to $KMnO_4$ injections and b) three months after.

Passive Approach for $KMnO_4$ Treatment

Our remediation approach used at the Broward County site is aimed at effective destruction of the TCE mass in the DNAPL source zone by $KMnO_4$ injections while minimizing the displacement of groundwater with high TCE concentrations away from the source zone into the surrounding plume. 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 (i.e., in the DNAPL source zone). At each injection point, a small volume of $KMnO_4$ solution is injected laterally to form an initial local zone (i.e., disc or ellipsoid). Stacked discs with vertical gaps in between are created in each hole using a short-screen well-point (7.6 cm length and 3.8 cm diameter) driven with a direct push rig. The time taken to create several discs per hole in several locations is referred to as an injection episode. 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 essence the dense permanganate solution sweeps through the source zone following each injection episode to cause destruction of TCE mass. A period of time is allowed after each injection episode for the redistribution and concurrent $KMnO_4$ consumption as TCE is oxidized.

In the DNAPL source zone at the site, the injection point, attached to drill rods, was driven to 60 ft bgs using the model SD-2 direct push rig manufactured by Precision Sampling Inc. The injection tool and system used at the site were developed previously by Nelson et al. (*2000, 2001*) and used at the Borden, Ontario, research site. 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 pounds (1,266 Kg) of KMnO4 dissolved in 9,166 gallons of water (34,703 liters) at a concentration of 40 g/L was injected into a total of 21 holes. The first episode took place during March 31 to April 10 at 6 locations, the second during June 1 to 7 at 8 locations and the third during September 29 to October 4 at 7 locations. 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.

Results

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. Figure A.15 shows that, before $KMnO_4$ treatment, all seven of the monitoring locations situated inside the 10,000 µg/L contour had TCE values above 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 less than 35,000 µg/L. Figure A.15 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. 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 A.17 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 A.16 for the cross section location. The cross sectional area above 100 µg/L declined markedly to 10% of the before treatment area, and the area above 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 A.17 shows that 20 sampling points had TCE in the 100 to 1,000 µg/L range before treatment; only four had such values after. Before treatment, 10 sampling points had TCE values above 10,000 µg/L but after, only two were above 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. Measurements of the carbon isotope ($^{13/12}C$) 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 et al., 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 feet 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.

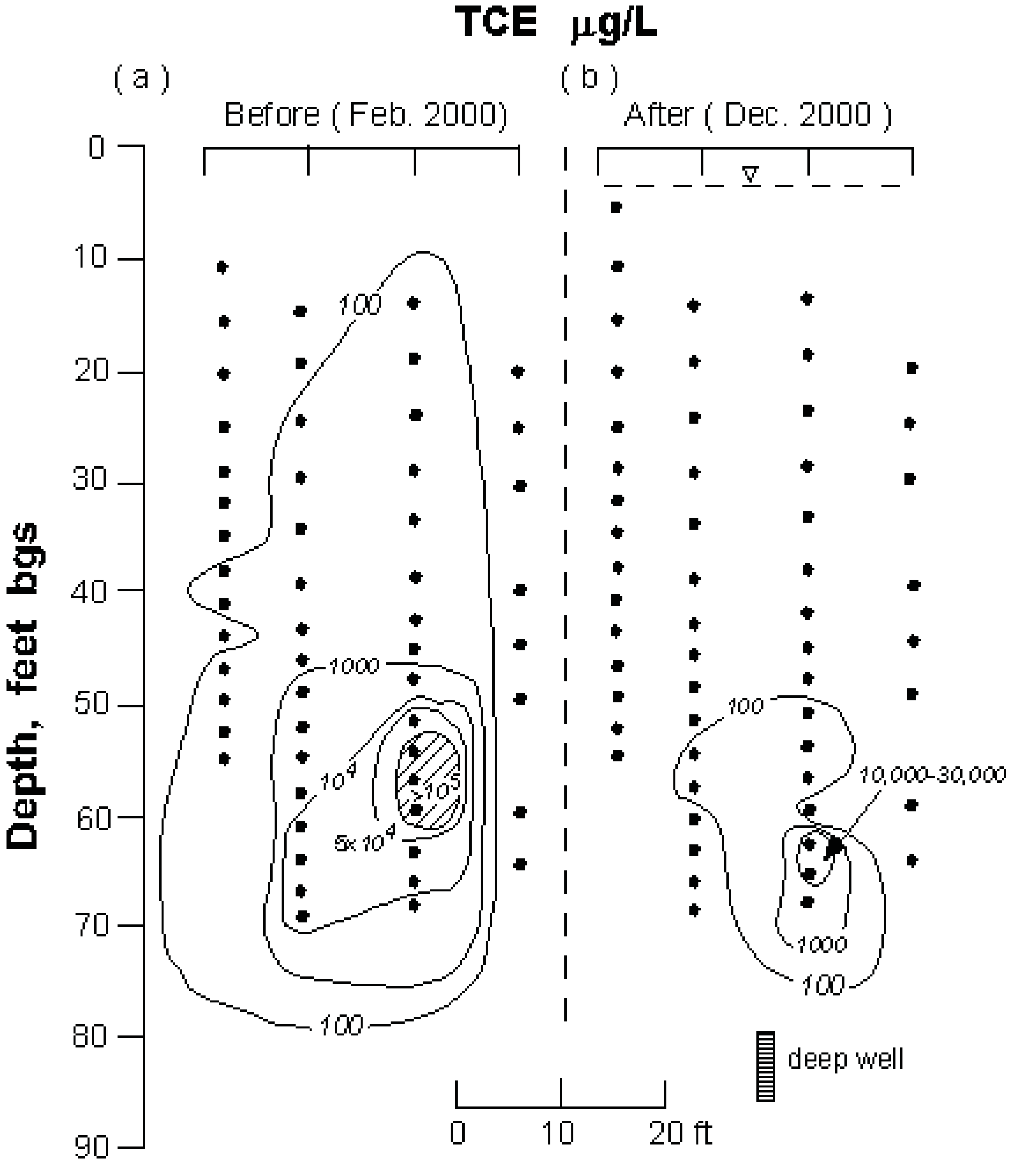

Figure A.17 Comparison of TCE concentrations one month before and three months after $KMnO_4$ treatment observed along cross section through DNAPL source zone.

The distribution of monitoring points (wells and multilevels) 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 A.17 shows this well situated in the depth range of 81.3 to 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 pre-injection Cl^- values in the source zone ranged from 20 to 60 mg/L. The maximum post-treatment Cl^- values were in the range of 150-260 mg/L in the zone where the pre-treatment TCE values were generally between 100–300 mg/L. The stoichiometric view for Cl^- production presented above considered only the dissolved-phase TCE in the source zone. We believe 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 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 above 100 µg/L and above 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 A.16 and A.17. Although not expected, the $KMnO_4$ treatments reduced the concentrations and volume of TCA contaminated aquifer similar to the TCE reductions.

Conclusions

Significant progress towards complete remediation was achieved by injecting small volumes of near-saturation $KMnO_4$ solution at several depths in each of six to eight holes during each of three episodes. These injections created an initial condition of many small, stacked $KMnO_4$ zones with large vertical gaps in between. Only 8% of the total pore volume in the lower half of the aquifer (high TCE concentration zone) was invaded by $KMnO_4$ solution immediately after each injection episode. However, during the few weeks following each injection episode, these many small $KMnO_4$ zones spread out and descended under the influence of density combined with fingering and diffusion to achieve complete coverage within the source zone. Use of this episodic, stacked-injection approach resulted in no observable displacement of high-concentration TCE water outward from the source zone into the surrounding plume. The post-treatment monitoring using an exceptionally detailed three-dimensional network of depth-discrete samplers showed the combined effect of the three permanganate injection episodes caused a 90% reduction in the aquifer volume where TCE in groundwater is above 100 µg/L, and an even greater reduction of the volume above 10,000 µg/L. Therefore, the passive approach achieved high-percentage remediation with minimal engineering effort that also minimized displacement.

Acknowledgments

The main crew from the University of Waterloo that conducted the field work included Matthew Nelson and Colin Meldrum, who also performed most of the data compilation and display; and Robert Ingleton and Paul Johnson. The VOC analyses were done by Maria Gorecka. The project benefited from the planning advice of William Pence and Robert Osar. Joseph Ghiold coordinated on-site activities and provided logistical support and Sun Belt Precision Products, Inc. supplied project funding.

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APPENDIX B - Biosketches of Panel Members

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Dr. Abriola is the Horace Williams King Collegiate Professor of Civil and Environmental Engineering at the University of Michigan. She received both Masters and Ph.D. degrees in Civil Engineering from Princeton University and a Bachelors degree in Civil Engineering from Drexel University. An author of more than 90 refereed publications, Dr. Abriola is an expert on the transport, fate, and recovery of dense nonaqueous phase contaminants in the subsurface. Her current and recent service activities include membership on the National Research Council Committee on Source Removal of Contaminants in the Subsurface and the DOE Natural and Accelerated Bioremediation Research Advisory Committee. Dr. Abriola has been the recipient of numerous awards, including the National Ground Water Association Distinguished Darcy Lecturer and the Association for Women Geoscientists' Outstanding Educator Award. She is an ISI Highly Cited Author in Ecology/Environment, a Fellow of the American Geophysical Union, and a member of the National Academy of Engineering.

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Dr. Cherry is a Professor and holder of the Chair in Contaminant Hydrogeology in the Department of Earth Sciences at the University of Waterloo. For his contributions to the study of groundwater contamination, he has received awards from professional organizations in the United States, Canada, and Britain. He began research on contaminants in fractured clayey aquitards in 1968, and since 1978, his studies have focused on field aspects of DNAPLs in fractured rocks and clayey aquitards. He has consulted widely on DNAPL issues, and has served on expert and advisory panels for both the corporate and public sectors. He holds patents for technologies for site monitoring, emphasizing multilevel monitoring approaches, and for remediation. He has been the director of the University Consortium Solvents-in-Groundwater Research Program since 1988.

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Dr. Kavanaugh is Vice President and the National Science and Technology Leader of Malcolm Pirnie, Inc., a 1400-person U.S. based private consulting firm specializing in environmental science and engineering. He is a chemical and environmental engineer with 29 years of consulting experience, providing a broad range of consulting services to private and public sector clients. His areas of expertise include hazardous waste management, site remediation with particular focus on ground-water remediation, risk and decision analysis, fate and transport of contaminants in the environment, water quality, water treatment, potable and non-potable water reuse, industrial and municipal wastewater treatment, strategic environmental management, and technology evaluations, including patent reviews on environmental technologies. Dr. Kavanaugh also has extensive litigation experience, both as a testifying expert and a fact witness on engineering and hydrogeologic issues related to hazardous waste sites, as well as on other issues related to his areas of expertise. He also has broad experience with alternative dispute resolution methods for settling environmental disputes and has participated on several mediation and arbitration panels as a neutral technical expert. Dr. Kavanaugh has been project engineer, project manager, principal-in-charge, technical director, or technical reviewer on over 190 projects covering a broad range of environmental problems. He has authored or co-authored approximately 35 peer-reviewed technical publications, edited and contributed to three books on water quality, water treatment, and ground-water cleanup, respectively, and has made over 100 presentations to technical audiences as well as public groups including testimony before congressional and legislative committees.

In addition to his consulting practice, Dr. Kavanaugh has been an active participant in various national committees advising the U.S. Environmental Protection Agency, the Department of Defense, the Department of Energy, as well as participating on various Boards and committees of the National Research Council. Between 1988 and 1991, Dr. Kavanaugh chaired the Water Science and Technology Board. He chaired the Board on Radioactive Waste Management between 1996 and 2000. Between 1992 and 1994, he was the Chair of the National Research Council (NRC) committee on alternatives for ground-water cleanup. From 1997 to 2001, Dr. Kavanaugh served on the Integration Project Expert Panel at the DOE Hanford Site, established by the Department of Energy to accelerate cleanup of soils and ground water at Hanford. He currently is a member of the Science Advisory Board of DOD's environmental research program, the Strategic Environmental Research and Development Program (SERDP). For his contributions to water quality and hazardous waste management, Dr. Kavanaugh was elected into the National Academy of Engineering in 1998.

Dr. Kavanaugh is a registered chemical engineer in California, Utah, and Michigan, and a Diplomate (DEE) of the American Academy of Environmental Engineers. He is also a consulting professor of Environmental Engineering at Stanford University. He has a Ph.D. in Civil/Environmental Engineering from the University of California at Berkeley, and B.S. and M.S. degrees in Chemical Engineering from Stanford and UC Berkeley, respectively.

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Dr. Major is a Principal at GeoSyntec Consultants, and received his Doctorate from the University of Waterloo for his thesis on the anaerobic biodegradation of aromatic hydrocarbons in ground water. For the past 15 years, he has worked with clients, researchers, and regulators to develop practical biological and chemical solutions to remediate contaminated sites. He has extensive experience in providing technical direction to complex remediation projects, third-party review of feasibility evaluations, and litigation support. Dr. Major serves on the steering committee of the Bioremediation Consortium of the Remediation Technologies Development Forum (RTDF), a collaboration between industry and government to develop innovative remediation technologies for chlorinated solvent and DNAPL sites. He is a co-developer of ITRC/RTDF Courses on Monitored Natural Attenuation and Enhanced In-Situ Bioremediation of chlorinated solvents, which are sponsored in part by Department of Defense Environmental Security Technology Certification Program (ESTCP). He is the Project Director/Principal Investigator of several ESTCP projects involving in situ remediation, including demonstrations of bioremediation/bioaugmentation with halorespiring microorganisms to enhance the dissolution rate of DNAPLs, and coupling in situ chemical oxidation (ISCO) with bioremediation. Dr. Major is also assisting the Navy to review DNAPL treatment technologies and case studies of their application. He is actively involved in the identification and evaluation of emerging environmental technologies, and was instrumental in commercialization of EnviroMetal Inc., which holds the patent for use of zero-valent metal in permeable reactive barriers to dechlorinate chlorinated solvents. He is continuing to further develop leading-edge remedial technologies, evident through his management of two laboratory and field demonstration projects, sponsored by NASA, to evaluate the application of bioaugmentation and emulsified nano-scale iron to treat DNAPLs.

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Dr. Mercer is a hydrogeologist with GeoTrans, Inc. He received a B.S. from Florida State University and a M.S. and Ph.D. from the University of Illinois; all of his degrees are in geology. He spent eight years with the U.S. Geological Survey in the Northeastern Research Group working on contaminant and heat transport issues, including multiphase flow. He co-founded GeoTrans in 1979, and in 1980, began working on DNAPL issues at Love Canal. In 1985, Dr. Mercer received the Wesley W. Horner Award of the American Society of Civil Engineers for the work performed at Love Canal. Dr. Mercer continued to work on DNAPL issues and co-authored a book on *DNAPL Site Evaluation* in 1993. In 1994, he received the American Institute of Hydrology's Theis Award for contributions to ground-water hydrology. Dr. Mercer has served on the National Research Council's Water Science and Technology Board and was a member of the U.S. EPA Science Advisory Board.

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Dr. Newell is a Vice President of Groundwater Services, Inc. He is a Diplomate in the American Academy of Environmental Engineers and is an Adjunct Professor at Rice University. He has co-authored three EPA publications, five environmental decision support software systems, numerous technical articles, and two books: Natural Attenuation of Fuels and Chlorinated Solvents and Ground Water Contamination: Transport and Remediation. His professional expertise includes site characterization, ground-water modeling, non-aqueous phase liquids, risk assessment, natural attenuation, bioremediation, non-point source studies, software development, and long-term monitoring projects._

He served on the EPA's DNAPL Workshop in 1991 and was one of four speakers who presented the EPA's Seminar on Characterizing and Remediating DNAPL at Hazardous Waste Sites in ten cities in 1993. He has also served as a nationwide Risk-Based Corrective Action (RCBA) trainer for the American Society for Testing and Materials (ASTM). Dr. Newell has been awarded the Hanson Excellence of Presentation Award by the American Association of Petroleum Geologists, the Outstanding Presentation Award by the American Institute of Chemical Engineers, and the 2001 Wesley W. Horner Award by the American Society of Civil Engineers (for the paper, "Modeling Natural Attenuation of Fuels with BIOPLUME III").

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Dr. Rao is the Lee A. Rieth Chair & Distinguished Professor of Environmental Engineering in the School of Civil Engineering at Purdue University, and he holds a joint appointment in the Agronomy Department in the School of Agriculture. Prior to arriving at Purdue, Dr. Rao was on the faculty at the University of Florida for 24 years, where he now holds an appointment as an Emeritus Graduate Research Professor. He teaches contaminant hydrology and remediation engineering. His research has involved development of innovative technologies for characterization of hazardous waste sites, and for enhanced remediation of contaminated soils and aquifers.

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Dr. Sale is an Assistant Professor in Civil Engineering at Colorado State University and an independent consulting hydrogeologist. He has been actively involved in the characterization and remediation of subsurface releases of Nonaqueous Phase Liquids (NAPLs) since 1981. Currently Dr. Sale is working on NAPL-related projects for the American Petroleum Institute, Department of Defense, and Union Pacific Railroad. His primary focus areas are pragmatic expectations for NAPL remedies and passive strategies for management of NAPL releases. He received his Ph.D. in 1998 from Colorado State University (Department of Chemical and Bioresource Engineering). The focus of his dissertation research was the effect of fractional NAPL removal from NAPL source zones on downgradient water quality and source longevity.

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Mr. Shoemaker joined DuPont in 1987 and holds the title of Senior Consultant in DuPont's Corporate Remediation Group. Mr. Shoemaker's responsibilities include directing remediation projects and developing strategies for DuPont plant sites; negotiating remediation programs with state and federal agencies; and evaluating appropriate remedial technologies for use by DuPont. For ten years he led a multi-disciplinary network in DuPont tasked with evaluating, developing, and demonstrating new in situ remediation technologies with particular emphasis on chlorinated solvents, including DNAPLs. He was a founding member of the Remediation Technologies Development Forum (RTDF) and co-founded the RTDF Permeable Reactive Barriers workgroup.

Mr. Shoemaker has over 24 years of experience in the study and remediation of subsurface contamination. He graduated from the University of Delaware in 1977 with a B.S. in Geology and from the University of Missouri-Rolla in 1978 with an M.S. in Geological Engineering.

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Dr. Siegrist earned his B.S. and M.S. in Civil Engineering (*High Honors*, 1972; 1975) and his Ph.D. in Environmental Engineering (1986) at the University of Wisconsin. During 20 years of experience, he has held research and teaching appointments with the Colorado School of Mines, Oak Ridge National Laboratory, the University of Wisconsin, and the Agricultural University of Norway. He has been a faculty member with CSM since January 1995, where he is currently Professor and Director of the Environmental Science & Engineering Division. During the past 15 years, his research has focused on characterization, assessment, and *in situ* remediation technologies for contaminated land. His research has encompassed *in situ* treatment processes (e.g., chemical oxidation, redox reactive barriers, bioremediation) as well as subsurface manipulation methods (e.g., vertical and horizontal recovery and recirculation wells, lance permeation, deep soil mixing, hydraulic fracturing). In related work, he has also continued research into the hydrodynamic and purification processes impacting land treatment and disposal of wastes. Since 1990, Dr. Siegrist has been leading a program of research concerning *in situ* chemical oxidation involving peroxide and permanganate systems. This program has involved fundamental studies of reaction chemistry, contaminant mass transfer, and oxidant delivery systems, as well as field evaluations through pilot- and full-scale technology demonstrations. Dr. Siegrist's research has been sponsored by DOE, EPA, DOD, NSF, and private industry, and he has published the results of his work in over 50 refereed articles and more than 150 conference proceedings and reports. He is a registered professional engineer and an active member of several national societies. He has served as an advisor and technical expert for state and federal agencies in the USA, Canada, Norway, and Sweden, and is currently a Fellow with the NATO Committee for Challenges to Modern Society. On the personal side, he is an expert rock climber and mountaineer, and has organized and led climbing expeditions to Alaska, Peru, and Nepal.

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Prof. Dr. Teutsch completed his study in geology and hydrogeology at the Universities of Tüebingen and Birmingham in 1980 with a M.Sc. in Hydrogeology. Following the completion of his study, he worked for several years nationally and internationally as a hydrogeologist concentrating on problems of water resources and water planning. In 1988 he gained his Ph.D. in the field of groundwater modeling in karst aquifers. Between 1986 and 1991 he led the ground-water research group at the University of Stuttgart. In 1991 he gained his post doctorate (Habilitation) thereafter becoming professor for Geohydrology at the University of Stuttgart. In 1993 he was appointed to the Chair of Applied Geology at the Geological Institute at the University of Tüebingen and is now in charge of the new Centre for Applied Geoscience which comprises more than 50 academics from different fields.

His professional expertise comprises innovative subsurface investigation methods, the development of numerical and analytical models for the flow and contaminant transport in porous and fractured media, the design and optimisation of ground-water remediation schemes, and also aquifer analog studies. He has published more than 50 technical papers in reviewed journals and is consulting environmental authorities and industry in Germany, at EU level, and in the U.S.

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Dr. Udell is a Professor of the Department of Mechanical Engineering at the University of California at Berkeley. He received his B.S. degree in Mechanical Engineering from Utah State University, and his M.S. and Ph.D. degrees in Mechanical Engineering from the University of Utah in Salt Lake City, Utah. He has been the Director of the Berkeley Environmental Restoration Center since 1993. He received the EPA Outstanding Remediation Technology Award in 1999 for technical excellence in the development of in situ thermal treatment technologies. He is presently a member of the Innovative Thermal Technology Advisory Panel for the U.S. EPA.

APPENDIX C - Workshop Agenda – Dallas, TX
DNAPL Source Remediation Workshop

Day 1

SESSION 1	Moderator - Bob Puls, U.S.EPA
8:00 AM	**Introduction of Objectives and Perspectives for Workshop**
	Lynn Wood, U.S.EPA
	James Cummings, U.S. EPA
8:30 AM	**DNAPL Remediation Issues and Workshop / Panel Objectives – Establish framework or boundaries for workshop**
	Mike Kavanaugh, Malcolm Pirnie, Inc.
SESSION 2	Moderator - Suresh Rao, Purdue University
8:45 AM	**Constraints to and Incentives for Source Remediation**
	Kevin Garon, Dupont TONA
	Dick Willey, U.S. EPA
	Jim Harrington, NYSDEC
	Discussion
9:45 AM	**BREAK**
10:15 AM	**Overview of Source Remediation Technologies**
	Carl Enfield, U.S. EPA
	Kent Udell, University of California, Berkley
	Bob Siegrist, Colorado School of Mines
	Discussion
11:45 AM	**LUNCH**
SESSION 3	Moderator - Mike Kavanaugh, Malcolm Pirnie, Inc.
1:00 PM	**Benefits of Source Mass Reduction**
	Linda Abriola, University of Michigan
	Tom Sale, Colorado State University
	Ron Falta, Clemson University
	Discussion
2:30 PM	**BREAK**
3:00 PM	**Integrated Remedial Approaches: Addressing the Residual Plume**
	Susan Mravik, U.S. EPA
	Guy Sewell, U.S. EPA
	Frank Chapelle, U.S. Geological Survey
	Chuck Newell, Groundwater Services, Inc.

Discussion

4:50 PM **Charge to Breakout Groups**

5:15 PM **Adjourn for dinner**

7-9:00 PM **Break Out Groups (3 sessions)**

Session 1: Remediation Technology	Leader – John Cherry
Session 2: Integrated Approaches to Cleanup	Leader – Steve Shoemaker
Session 3: Decision Analysis	Leader - Georg Teutsch

Day 2

SESSION 4

Moderator - Mike Kavanaugh, Malcolm Pirnie, Inc.

8:00 AM **Metrics for Source Remediation**

Georg Teutsch , University of Tuebingen, Germany

Suresh Rao, Purdue University

Ken Lovelace, U.S. EPA

Discussion

9:30 AM **Break**

10:00 AM **Reconvene Breakout Sessions**

11:30 AM **Lunch**

SESSION 5

Moderators - Suresh Rao & Mike Kavanaugh

1:00 PM **Breakout Discussion Group Reports:**

Group 1

Group 2

Group 3

SERDP Panel Report

2:00 PM **Discussion**

2:45 PM **Closure (end of workshop)**

Executive Session of the Panel with the Sponsors (closed meeting)

3:15 PM **Panel Discussion, Planning, Initial Report**

APPENDIX D - List of Attendees - Dallas, Texas

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