FINAL REPORT

SERDP and ESTCP Expert Panel WORKSHOP ON REDUCING THE UNCERTAINTY OF DNAPL SOURCE ZONE REMEDIATION

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Acronyms and Abbreviations

CSM	conceptual site model
DARPA	Defense Advanced Research Projects Agency
DNAPL	dense nonaqueous phase liquids
DO	dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ITRC	Interstate Technology and Regulatory Council
LTM	long-term monitoring
MCL	maximum contaminant level
MNA	monitored natural attenuation
NRC	National Research Council
O&M	operations and maintenance
PCE	tetrachloroethene
R&D	research and development
RAO	remedial action objective
RDT&E	research, development, test, and evaluation
REV	representative element of volume
RPM	remedial project manager
SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethene

Acknowledgements

This report summarizes the results of a workshop sponsored by the Department of Defense's (DoD) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) that sought to determine the research, development, test, and evaluation (RDT&E) needs for reducing the uncertainty associated with dense nonaqueous phase liquid (DNAPL) source zone remediation at field sites.

A steering committee composed of Dr. Rob Hinchee, Dr. Paul Johnson, Dr. Mike Kavanaugh, Dr. Jim Mercer, and Dr. Hans Stroo assisted SERDP and ESTCP in determining the scope and structure of the workshop.

Dr. Hans Stroo and Dr. Andrea Leeson wrote background papers to communicate the current SERDP and ESTCP investments in DNAPL source zone characterization and remediation (Appendix D).

Dr. Rob Hinchee provided an opening presentation on management challenges at DNAPL sites. Dr. Mike Basel, Dr. Dick Brown, Dr. Charles Faust, Dr. Tom Sale, and Dr. Hans Stroo presented technology-specific field perspectives as a basis for identifying and prioritizing needs. Dr. Linda Abriola, Dr. Ron Falta, and Dr. Tissa Illangasekare provided overviews of their SERDP projects (Appendix C).

Breakout group discussions to identify key issues, barriers, and RDT&E needs were led by Dr. Rob Hinchee, Dr. Paul Johnson, Dr. Doug Mackay, Dr. Perry McCarty, Dr. Robert Siegrist, and Dr. Herb Ward. Discussions were documented by rapporteurs, including Ms. Deanne Rider, Ms. Alicia Shepard, Dr. Hans Stroo, and Ms. Kelly Woodworth.

Dr. Rob Hinchee and Dr. Paul Johnson guided the group discussions and led the effort to come to consensus on overarching issues arising from the breakout sessions.

Within SERDP and ESTCP, Dr. Jeffrey Marqusee, Mr. Bradley Smith, Dr. Andrea Leeson, and Dr. Hans Stroo provided leadership in the conception and implementation of this workshop. Mr. Amir Abyaneh, Ms. Veronica Rice, Ms. Deanne Rider, Ms. Alicia Shepard, and Ms. Kelly Woodworth from HGL facilitated all developmental activities for the workshop.

Most importantly, we acknowledge the input of all workshop participants, which has resulted in a strategic plan to guide investments in the area of DNAPL source zones over the next 5 to 10 years by SERDP and ESTCP. A list of participants appears in Appendix A.

Executive Summary

Chlorinated solvents are the most prevalent contaminants at Department of Defense (DoD) sites. These solvents are released into the subsurface as dense nonaqueous phase liquids (DNAPL) that can persist for centuries and are difficult and costly to remediate. There has been increasing regulatory and public interest in treatment of the source zones at DNAPL sites despite the difficulties and uncertainties involved. The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) have sponsored numerous research projects designed to provide useful guidance and develop innovative technologies for more effective and less costly source zone characterization and remediation. While great progress has been achieved, large challenges remain. With this, opportunities remain to advance better solutions for remediation of DNAPL source zones through focused research and development efforts. However, it is important to realize that DoD has set aggressive goals for installing final remedies at its sites, and therefore the greatest benefit from such research and development will be realized over a relatively short time (perhaps only the next 3 to 7 years).

SERDP and ESTCP convened a workshop on March 7-9, 2006, in Baltimore, Maryland, to define the future research needs in this area. The workshop was intended to define a path forward to further reduce the uncertainty surrounding DNAPL sites by providing (1) a critical review of the progress to date, including a consensus perspective on the implications of the funded research for practical remediation; (2) an overview of the current state of the science; and (3) a summary and prioritization of the remaining data gaps. More than 40 experts participated in the workshop, which was designed to define key issues and critical and high-priority needs for both research and demonstration projects.

The overarching issues that emerged from the discussions are listed below. In this list, as in all lists in this document, no priority is implied by the order of listing.

1. **Integrating decision-making processes for characterization and remediation.** The inherent uncertainties in addressing DNAPL source zones require an "observational approach," with continuous updating of the conceptual site model (CSM), constant evaluation of all new information, and contingency plans to address plausible variations from anticipated conditions.
2. **Improving understanding of source function and plume response.** The source function, or the rate of contaminant release into the groundwater flow, and the downgradient water quality response to source treatment are difficult to assess, yet they are key to understanding and assessing the benefits of source treatment.
3. **Developing more cost-effective methods.** There is a need to improve the effectiveness while reducing the costs for characterizing, remediating, and monitoring source zones, as well as to develop guidance in the optimal uses of existing methods.
4. **Establishing realistic expectations for treatment.** The impacts of treatment on remediation time frames are uncertain, and often overestimated. In addition, the

endpoints that can be achieved need to be realistically assessed. In many cases, treatment objectives will not require complete removal, only depleting the source enough to allow a transition to more passive approaches such as monitored natural attenuation (MNA).

5. **Analyzing existing data.** Critical evaluation of the rapidly increasing base of experience in source zone remediation could improve our understanding of real-world costs and performance (including technical impracticability) and provide valuable lessons learned for future projects.

6. **Transferring technology.** The programs can be helpful in disseminating information and developing best-practices manuals and other needed guidance and decision documents for project managers and remediation contractors.

The research and demonstration needs were prioritized into critical and high-priority needs (Table 1). The critical research needs included:

1. **Improved methods for characterization and monitoring.** Current tools are costly, limiting our ability to adequately characterize sources. Better methods are needed to assess source function, evaluate DNAPL distribution, and monitor sites.

2. **Improved understanding of plume response to source depletion**. Reponses to source depletion are not easy to predict or measure. Better predictive models are needed to assist decision making and evaluate the need for, and impacts of, aggressive remediation.

3. **Development of treatment and monitoring approaches for advective flow-limited portions of DNAPL source zones.** Remediation of advective low-flow portions of DNAPL sources is challenging because it is so difficult to deliver remedial agents to these areas. However, effective treatment is important because these zones can serve as long-term sources of contamination long after active treatment is stopped. Remedial designs or operational techniques that can better treat these low-flow zones would be helpful, as would technologies to contain or minimize any continuing discharge from these zones after treatment.

4. **Assessment of the impacts of implementing combined remedies**. The various general technological approaches to source zone treatment (e.g., thermal, chemical, biological) may be used together deliberately, in treatment trains or simultaneously. Such combinations have the potential to reduce costs or improve performance, but there has been little research to develop or demonstrate that potential.

5. **Improved remedial methods for karst and other complex sites.** Some sites are so challenging that finding sources, much less significantly depleting them, is highly unlikely. Guidance is needed for recognizing and managing sites where source treatment is likely to be inconsequential.

Table 1. Critical and High Priority Research and Demonstration Needs Identified

Research Needs	
Critical Priority	**High Priority**
Improved methods for characterization and monitoring	Better understanding of DNAPL architecture
Improved understanding of plume response to source depletion	Improved understanding of the relationship between mass removal and mass flux
Development of treatment and monitoring approaches for flow-limited portions of DNAPL source zones	Improved delivery mechanisms
Assessment of the impacts of implementing combined remedies	Quantification of uncertainty
Improved remedial methods for karst and other complex sites	Improved interaction and collaboration with state and federal regulatory agencies
Better understanding and monitoring of vapor transfer from sources	
Demonstration Needs	
Critical Priority	**High Priority**
Improved methods for reducing LTM/characterization costs	Improved methods for evaluating plume response
Focused data mining to assess long-term responses	Collection and publication of lessons learned from technologies
Development of decision guidelines for source zone characterization and remediation	Development of guidance on observational approach
Enhanced technology transfer	Better tools for handling industrial infrastructure

6. **Better understanding and monitoring of vapor transport from sources.** Research is needed to develop a better understanding of the processes controlling vapor attenuation within the vadose zone. In addition, improved monitoring techniques and methods are needed to discern between subsurface and surface sources of contaminants in indoor air.

The critical demonstration needs that were identified during the workshop included:

1. **Improved methods for reducing long-term monitoring (LTM) and characterization costs.** Low maintenance methods are needed to monitor long-term trends, and new probing techniques are needed for spatial characterization of complex sites.

2. **Focused data mining to assess long-term responses.** Post-mortem analyses of cost and performance at sites that have undergone source treatment would improve decision making and allow more realistic expectations of the long-term impacts of source depletion.

3. **Development of decision guidelines for source zone characterization and remediation.** Improved guidance directed at site managers could reduce the uncertainty involved in decision making. The guidance should be based on field-validated models and results from prior source treatment projects.

4. **Enhanced technology transfer.** Several initiatives were recommended, including (1) Develop best practices manuals; (2) Develop a web-based training course; (3) Identify opportunities to inform performance-based contracting in support of DNAPL source zone treatment; and (4) Engage regulators in establishing feasible approaches to DNAPL site monitoring and remediation.

The research and demonstration needs identified by the expert panel for reducing the uncertainty associated with the characterization and remediation of DNAPL source zones will guide the SERDP and ESTCP strategic plan for investments in this area over the next 5 to 10 years.

Because of the complex nature of DNAPLs and many subsurface settings, significant uncertainty reduction may not be possible and needs to be recognized up front. For this reason, decision guidelines and technology transfer should include policy and regulatory options for DNAPL sites that cannot be remediated in the near term (less than 30 to 50 years).

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) are designed to develop and transition innovative research and technology to help the Department of Defense (DoD) perform its mission in several environmental areas, including cleanup of contaminated sites. While DoD facilities may have several contaminants, chlorinated solvents are by far the most prevalent. Chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE) are found at approximately 80% of all Superfund sites with groundwater contamination and more than 3,000 DoD sites in the United States. The life-cycle costs to remediate these sites are uncertain but are likely to exceed several billions of dollars nationally. DoD could spend more than $100 million annually for hydraulic containment at these sites using pump-and-treat technologies. The U.S. Air Force alone spent approximately $25 million on operations and maintenance (O&M) costs for pump-and-treat systems in 2005. Total estimates of the life-cycle costs for pump-and-treat systems in use at DoD sites exceed $2 billion.

Chlorinated solvents can be extremely difficult to remediate, particularly at sites containing these compounds as dense nonaqueous phase liquids (DNAPL), where the DNAPL serves as a continuing long-term source of dissolved-phase groundwater contamination. Source zone treatment technologies such as surfactant/cosolvent flushing, thermal treatment, chemical oxidation, or enhanced bioremediation have been increasingly applied at sites, sometimes with impressive results, usually at sites with simple hydrogeology and small DNAPL sources. At sites with large source areas and/or complex hydrogeology, results have been less impressive. However, as the National Research Council (NRC) recently concluded (NRC, 2004), "The technical difficulties involved in characterizing and remediating source zones and the potential costs are so significant that there have been no reported cases of large chlorinated solvent sites where remediation has restored the site to drinking water standards."

The SERDP and ESTCP programs have funded basic and applied research over the past 4 years that was designed to address key questions relating to the efficacy and cost-effectiveness of chlorinated solvent source zone remediation. This work was funded in response to the recommendations from an earlier workshop (discussed in the SERDP Expert Panel Report on research and development needs for chlorinated solvent cleanup), and the work to date has provided valuable insights into chlorinated solvent source zone characterization and remediation. Background information on the projects can be found at: http://www.serdp-estcp.org/DNAPL.cfm. The background papers for the workshop (Appendix D) and the 2004 Annual Report provide greater detail on these projects.

Despite the progress to date, it remains difficult to greatly reduce the uncertainties involved in DNAPL site assessment and cleanup and, consequently, difficult to provide clear guidance to remedial project managers (RPM) who are considering DNAPL source zone remediation. The workshop described in this document was therefore convened on March 7-9, 2006, in Baltimore, Maryland, to define the future research and demonstration needs in this area. The workshop was intended to define a path forward to reduce the uncertainty surrounding DNAPL sites by

providing (1) a critical review of the progress to date, including a consensus perspective on the implications of the funded research for practical remediation; (2) an overview of the current state of the science; and (3) a summary and prioritization of the remaining data gaps.

2. METHOD

More than 40 experts participated in the workshop (see Appendix A for a list of the attendees). The participants were invited with the goal of including knowledgeable experts representing a broad range of perspectives, including academic researchers, regulators, remedial project managers, consultants, and government agency representatives.

Participants were provided background material on the SERDP and ESTCP programs, the workshop objectives, and the past and current SERDP- and ESTCP-funded projects related to DNAPL issues (Appendix D). Participants were also asked to consider several questions in three general areas: DNAPL site characterization, remediation, and remedial endpoints/long-term monitoring (LTM).

The objectives included defining future research and demonstration needs and providing useful guidance on (1) whether, and under what circumstances, source zone remediation should be attempted; (2) reasonable objectives for DNAPL source zone remediation at specific sites; and (3) how to measure progress toward achieving those objectives.

The agenda (see Appendix B) was designed to identify the most pressing needs in a focused manner, while ensuring that all participants could express their views. The workshop opened with several presentations intended to provide background information on DNAPL characterization and remediation technologies, as well as to highlight key issues.

Participants were then divided into smaller working groups to address specific questions regarding the state of the science and to develop and prioritize key research and demonstration needs. The entire group participated in the final discussions and selection of the key issues and the critical and high-priority research and demonstration needs. Several participants contributed sections to this report describing specific issues and needs and/or edited the draft versions.

3. Key Issues Associated with Characterization of DNAPL Source Zones

As described in Section 2 (Method), attendees were divided into three breakout sessions on each of the two meeting dates. The breakout session that was charged with discussing key issues associated with characterization of DNAPL of source zones was asked to address four questions as they related to the workshop objectives:

- What do we need to understand about the source area before selecting a remedial alternative?
- When is detailed characterization of a source area warranted?
- What are the practical limits to our ability to characterize sources?
- What tools are most useful for characterizing sources?

These questions were intended as a starting point for the discussions; therefore, the discussion was not necessarily limited to these four questions, and in some instances, these initial questions were modified to address issues the group believed were more relevant. The following sections provide a summary of the key issues identified during this breakout session on key issues associated with the characterization of DNAPL source zones.

3.1 Defining the Level of Characterization Required

The goal of any site characterization is to define the nature and extent of the contamination. However, it is being proposed that these are two distinct goals that can be accomplished at different stages or over different timelines. It is proposed that the **nature** of contamination refers to the **style** of the contaminant distribution relative to permeability and depth, and the nature or style of the contaminant distribution is of much more importance for source zone remedy selection and technical feasibility analysis than complete delineation (i.e., accurate determination of lateral and vertical extent and quantification of the total mass in the system). A second important feature is consideration of the **age of these source zones** because age should strongly influence the phase and relative position of the contaminant mass with respect to the high and lower permeability zones within the source zone or between the initial DNAPL areas versus the downgradient plume.

The level of detail required for characterization will necessarily depend on the specific questions or cleanup goals being considered for the site and the complexity of the site conditions (hydrogeologic systems and contaminant characteristics). In addition to the variability in contaminant distribution, the biogeochemical properties of the subsurface may also vary widely. The hydrodynamics within and around the source zone can also be highly complex. All of these properties can affect the selection and design of remedies, and need to be understood well enough to select and design appropriate remedies.

A common situation for DNAPL source zones is the entry of the DNAPL into the subsurface during periods at least 20 and as many as 60 years ago. In the case of aquifers, we can expect that groundwater flow has removed much or nearly all of the initial DNAPL mass from the high permeability zones. It follows that the remnant DNAPL phase is persistent in the less flushed

zones and, furthermore, substantial mass has likely been transferred into the lower permeability zones by diffusion or combinations of advection and diffusion. For example, in granular aquifers (i.e., sand and gravel) field investigations at aged sites show that large fractions of the total mass can be found in the aquitard above or below the aquifer or in the lower permeability beds within the aquifer itself (Chapman and Parker, 2005; Parker et al, 2003; Parker et al, 2004).

In fractured aquitards (i.e., silts/clays and shales/mudstones), where the bulk hydraulic conductivity is relatively low, DNAPL can readily migrate into these units via the fractures and, after a few years to decades, nearly all the mass resides in the low permeability matrix blocks between fractures (Goldstein et al, 2004; O'Hara et al, 2000). In fractured sedimentary rock aquifers (sandstones, dolostones, limestones), substantial mass typically exists in the low permeability yet porous matrix blocks between the fractures that once contained the DNAPL phase (Parker et al, 1994; Parker et al, 2006; Sterling et al, 2005). However, in crystalline rocks (i.e., granites, basalts, diorites), most of the mass likely resides as DNAPL in dead-end fractures or smaller aperture fractures (lower transmissivity sections of the rock mass).

The conceptualizations of DNAPL source zones presented above are not necessarily accepted by all experts in the field. However, this picture of the nature of present-day source zones suggests it will be essential to examine the lower permeability zones that can either entrap or store substantial mass. This generally cannot be accomplished by groundwater sampling of wells or other groundwater monitoring systems because these devices preferentially sample the higher permeability layers or units. Therefore, there is interest in greater use of cores, preferably continuous cores. Examination of the permeabilities, textures, and fractures in core samples at a fine scale can provide insight into the small-scale geologic features that could have provided preferential pathways for DNAPL migration during the early stages of source zone formation. Analyses of cores can also help in understanding the distribution of lower permeability zones that serve as reservoirs for mass storage by mass transfer or entrapment of residual DNAPL that is not readily flushed by active groundwater flow.

The location and distribution of detailed spatial sampling of continuous cores for contaminants can be aided or complemented with a variety of qualitative tools or complementary tools, depending on the geologic environment being studied. In granular media, even the remnant DNAPL is likely present in very thin layers less than 1 cm to 10 cm thick (Parker et al, 2003). Because the mass distribution is typically controlled by small-scale features, high resolution sampling of cores is an essential part of determining the **nature or style** of contaminant mass distributions in most geologic types of source zones, and the actual sampling scale would vary for geologic systems as well as contaminant age and type.

It is proposed that the selection of an appropriate remediation technology or suite of technologies should be governed by the style or nature of the source zone mass distribution (i.e., position of mass phase and concentration with respect to permeability and depth) and that the goal of delineation relates more to feasibility and total cost to achieve a desired level of cleanup. Determination of the style of contaminant distribution is much easier than complete delineation and determination of total mass. Insights regarding the full extent of source zone contamination can be dealt with over a longer time period as one proceeds with remediation implementation and concurrent performance assessment (refer to Section 3.5). By far the largest uncertainty in

source zone site delineation (i.e., extent) is the estimation of the total mass, and in general, these estimates will likely remain uncertain by a factor of 10 or more given the complexity of contaminant distributions in natural subsurface systems.

3.2 Assessing Source Function

Defining the need for, optimal approach to, and progress of source zone remediation all benefit from the best possible assessment of the source function, defined as the total contaminant mass released into the groundwater flow per unit time (e.g., kg/day). Clearly, one major goal of source remediation is a significant reduction of the source function. However, the source function is dependent on a variety of factors, such as subsurface geologic heterogeneity, soil textures, DNAPL entrapment architecture, source aging, composition of the DNAPL, and groundwater flow. None of these factors are easily characterized, some are variable over time, and others are dramatically altered during remediation.

For obvious practical reasons, there is mounting interest in developing monitoring approaches to allow reliable estimation of the source function before, during, and after remediation of source zones. However, past experiences suggest that there is considerable uncertainty in estimates of source function using typical monitoring tools and approaches, because the contaminants often emanate from sources in complex distributions that cannot be sufficiently defined.

The source function can be even more difficult to estimate reliably during and after remediation if the distribution of the contaminant emanation becomes significantly sparser and more difficult to detect. In such cases, practitioners and regulators may be left with considerable uncertainty as to whether or not the source function has been dramatically reduced or simply altered such that a significant portion of it continues to migrate largely undetected.

3.3 Increasing Cost-Effectiveness of Tools

Participants agreed on the need for better, faster, and cheaper methods to characterize and monitor DNAPL sites. They also agreed on the need for guidance in the best use of existing tools. Finally, there was support for investigating opportunities to make more cost-effective use of existing tools, notably using existing wells in new ways (e.g., retrofitting wells to provide more information). The large infrastructure of existing wells may be a valuable resource but one that is currently underutilized and in some cases misinterpreted.

3.4 Understanding the Impact of Vadose Zone Processes

Federal and state regulators have expressed increasing concern about vapor intrusion from groundwater plumes into the indoor air space of overlying buildings. There are several well-publicized sites where this “indoor-air” pathway has been shown to cause elevated human health risk due to the migration of chlorinated solvent vapors through the vadose zone. In November 2002, the U.S. Environmental Protection Agency (EPA) issued the Vapor Intrusion Guide, which provides conservative groundwater concentration screening limits for the groundwater-to-indoor-air exposure pathway and recommends application of site-specific vapor sampling and/or modeling analyses if these screening limits are exceeded (U.S. EPA, 2002). These conservative

screening limits suggest that the presence of low ppb levels of chlorinated solvents in groundwater could pose an unsafe indoor air exposure at some sites, triggering the need for a site-specific evaluation at nearly all sites where buildings overlie solvent plumes.

The participants felt that current research challenges associated with vapor intrusion issues include (1) discerning between subsurface and surface sources of chlorinated solvents in indoor air; (2) developing improved monitoring methods; and (3) developing a better understanding of vapor attenuation processes in the vadose zone.

In addition to vapor intrusion issues, the participants concluded that there is a general need for better understanding of migration and attenuation processes in the vadose zone. As with submerged sources, the source function for vadose zone sources needs to be understood in more detail so that the remediation performance and remediation time frame can be predicted more accurately.

3.5 Integrating Site Characterization and Remediation

Given the inherent complexity of even simple lithologies and of contaminant architectures, and given the real limitation of time and money, site characterizations are incomplete if not significantly flawed. With limited numbers of wells and samples, it is not uncommon to miss the presence of smaller DNAPL areas or to improperly estimate (over or under) the quantity of DNAPL present. As discussed in Section 3.1, an "observational approach," which continuously updates and adapts the conceptual site model (CSM) to new data, is the best way to minimize characterization problems at DNAPL sites.

The observational approach, founded on basic scientific principles and described first by Terzaghi and Peck (1948), involves an iterative process of constructing a site model, testing the model against data obtained from the site, modifying the model to compensate for deviations in expected contaminant behavior, and contingency plans to address plausible variations from anticipated conditions. Any measurement of site conditions (sampling), any removal of subsurface material (recovery), or any intrusive activity (soil boring, well installation) should be seen as an opportunity to gather additional data which can be used to confirm or modify the CSM.

Remedial activities provide an excellent opportunity to update the CSM. For example, the installation of wells provides subsurface samples that can be used for contaminant or lithological delineation. Response to the injection of treatment agents or to the extraction of material (water, vapor, soils) can provide an indication of lithological barriers or of persistent contamination. However, to extract characterization data from remedial activities requires an integration of the two activities, which unfortunately is not a common practice. Too often, and to the detriment of cost-effective site characterization, remedial activities are viewed and managed as being distinct from site characterization. They are commonly seen as sequential, characterization then remediation, when, in fact, they can and should be integrated. Adaptation of the TRIAD approach (e.g., rapid site characterization) to remedial construction activities would be a means of more fully integrating site characterization and remediation.

4. Key Issues Associated with Remediation of DNAPL Source Zones

The breakout session charged with discussing key issues associated with remediation of DNAPL source zones was asked to address six questions as they related to the workshop objectives:

- Under what circumstances should source zone remediation be attempted?
- What objectives are reasonable for DNAPL source zone remediation at a given site?
- How should progress towards achieving those objectives be measured?
- What site conditions support innovative approaches to DNAPL source zone treatment rather than excavation or pump-and-treat approaches?
- What site conditions support containment rather than active remediation?
- Does combining treatment technologies make sense, and how can we combine technologies more effectively?

As described in Section 3, these questions were intended as a starting point for the discussions. Discussion was not limited to these six questions, and in some instances, these initial questions were modified to address issues the group believed were more relevant. The following sections provide a summary of the key issues identified during this breakout session on key issues associated with the remediation of DNAPL source zones.

4.1 Guidance on When Source Treatment is Warranted

There is currently a lack of guidance and technical support for site managers faced with the decision of whether or not to attempt aggressive source treatment (i.e., using technologies designed to remove significant mass instead of containing or monitoring). In many cases, treatment may provide relatively little value in terms of risk reduction with no commensurate reduction in life-cycle costs or reduction of site care requirements. However, there is a rapidly expanding knowledge base from research and demonstration, case studies, and site experiences. This knowledge base should be a valuable resource for useful, retrospective analyses and verification of model predictions. The overall goal should be to reduce uncertainty regarding the likely outcomes of treatment strategies and thereby stimulate appropriate uses of treatment technologies.

4.2 Relative Cost Comparisons for Remedial Technologies

The decision regarding which technology or set of technologies to choose to remediate a DNAPL source area is based primarily on the technical and economic factors to achieve the remedial objectives and to meet other political and social requirements. Given that available DNAPL treatment technologies can meet most remedial objectives, providing sufficient time and budget is allocated, a key factor is the relative cost between technologies to achieve the stated remedial goals.

It is typical to compare technologies based on the lowest treatment unit cost metric, such as cost per unit volume/mass, cost per unit mass of DNAPL treated, or cost per unit volume/mass per time. However, unit costs can be misleading because they are often derived from assumptions of

treatment effectiveness, which is impacted by the uncertainty of a variety of scale-dependent variables (e.g., geologic heterogeneity and DNAPL distribution) that cannot be adequately resolved using currently available characterization tools. Furthermore, overall remedy costs are driven by the uncertainty of the DNAPL distribution. Only by increasing the volume of soil that is treated can this uncertainty be overcome, resulting in the treatment of significant volumes of soil that did not contain DNAPL. Finally, initial estimates of total or unit costs are affected by the time it takes for the technology to meet the remedial goals.

The above discussion highlights the current difficulty in comparing the relative cost between technologies because of the interplay between the uncertainty of DNAPL distribution, the time value of money, and remedial objectives. RPMs need a better cost basis to compare remediation technologies versus the uncertainty of achieving the remedial objectives. This could be achieved through (1) retrospective analysis (i.e., postmortem or data mining analysis) of technology costs vis-à-vis the effectiveness and limitations of current technologies; (2) developing protocols for quantifying the cost and benefits associated with remedial technologies; and (3) collecting new data on cost versus performance.

4.3 Prohibitive Costs to Reach Some Remedial Action Objectives

The technical difficulties involved in targeting source zone treatment and implementing many of the remedial technologies can make it technically impracticable to reach many typical remedial action objectives (RAO). In most cases, achieving maximum contaminant levels (MCL) within the DNAPL source zone is practically impossible, but even more modest goals such as removing sufficient mass to allow natural attenuation to control any residuals and gradually reduce concentrations in the down gradient plume can be extremely expensive. In many cases, the objectives of source remediation are therefore to deplete the source to the extent possible, given available funds and time, and then to assess the post-treatment site management needs. This approach can understandably concern site managers and make it difficult to develop performance-based contracts tied to risk-based RAOs. Attainable remedial endpoints and performance measurements need to be specified before initiating remediation.

4.4 Potential Benefits of Combining Remedies

Because source zone remediation can be so costly and generally results in only partial source depletion, there has been interest in combining remedies in a planned manner. Treatment trains are often necessary, even if this involves only monitored natural attenuation (MNA) following engineered aggressive treatment. However, in some cases, a highly aggressive technology such as surfactant flushing may be followed by a more passive one such as active bioremediation. Guidance on when and how to best transition between technologies is lacking and could be valuable.

However, many believe that there are or can be synergies between different technologies that can improve performance and reduce costs. For example, low amounts of cosolvents along with bioremediation could increase overall mass removal and reduce the time needed for bioremediation to be effective. Bioremediation rates also could be enhanced by increasing temperatures via application of low-enthalpy thermal treatment. Numerous combinations of

technologies are possible, but there is little experience to date with deliberately combining remedies that is well-documented and carefully evaluated.

4.5 Challenges Posed by Complex Sites

Complex hydrogeology, in particular karst and fractured bedrock settings, contributes to difficulty in characterizing and remediating DNAPL source zones. In a recent study by NRC, hydrogeologic settings were classified into five types based on the spatial variation of permeability and porosity (NRC, 2004), as shown in Table 2.

Table 2. Classification of Hydrogeologic Settings (Adapted from NRC, 2004)

Type	Media	Heterogeneity	Permeability	Matrix Porosity	Example
I	Granular	Mild[1]	Moderate to high[3]	--	Eolian sands
II	Granular	Mild[1]	Low[4]	--	Lacustrine clay
III	Granular	Moderate to high[2]	All	--	Deltaic deposition
IV	Fractured	High	--	Low[5]	Crystalline rock
V	Fractured	High	--	High[6]	Limestone (e.g., karst), sandstone, or fractured clays

[1] Less than three orders of magnitude of spatial variability in permeability
[2] Greater than three orders of magnitude of spatial variability in permeability
[3] Permeability between 10^{-14} m^2 and 10^{-10} m^2
[4] Permeability less than 10^{-14} m^2
[5] Less than 1%
[6] From 1 to 40%

Type IV or Type V settings are complex sites. Fractured aquifers provide preferential pathways for contaminant transport and also serve as locations for mass storage. DNAPL source zones in a Type IV setting can be large due to the low effective matrix porosity. Groundwater can also be impacted over a large area because of the high aqueous flow rates that are possible within fractures (Type IV) or in conduit flow settings (Type V). Site characterization is typically difficult and costly, and resulting parameter estimates may be highly uncertain. For example, estimates of contaminant mass present in fractured settings typically vary by more than an order of magnitude. It may not be possible to significantly reduce the uncertainties of the conceptual site model by performing more site characterization. Contaminant remediation of DNAPL in a fractured setting is likely to be difficult and costly, and remediation to standard treatment goals may be technically impracticable in some instances. Furthermore, remediation time frames may be excessive due to reverse diffusion rates in fractured settings.

The management of DNAPL at complex sites therefore presents significant technical challenges and requires a disproportionately large portion of cleanup resources. A preliminary review by the Army Environmental Center of cleanup efforts indicated that of 34 installations where aquifer restoration may be technically impractical, 26 are underlain by karst or fractured rock aquifers. The projected cleanup costs for these 34 installations are approximately 50% of the Army's total projected environmental restoration costs, or $3 billion, emphasizing the high costs associated with characterizing and remediating complex sites.

5. Key Issues Associated with Remedial Endpoints and Long-Term Monitoring

The breakout session that was charged with discussing key issues associated with remedial endpoints and long-term monitoring was asked to address three questions as they related to the workshop objectives:

- How do we determine when to discontinue a remedial approach and transition to long-term monitoring?
- What are the limitations of existing qualitative and quantitative approaches to assessing the impacts of DNAPL source zone treatment?
- Can we improve estimates of the effects of treatment on plume longevity?

The following sections provide a summary of the key issues identified.

5.1 Transition from Aggressive Treatment to Long-Term Monitoring

In most cases, source treatment will not result in complete closure of a site (e.g., meeting MCLs site-wide or having no further liability or monitoring requirements) and will yield diminishing returns (i.e., decreasing risk reduction or mass removal) over time. Aggressive treatment will have to stop at some point, and less aggressive approaches such as MNA will have to be initiated. It is currently unclear when to stop aggressive treatment or to switch to a more passive technology. Guidance is also needed on the key parameters that should be measured before and after the transition.

5.2 Reduction of Long-Term Monitoring Costs

As DoD proceeds with remediation at sites, it is becoming apparent that long-term monitoring is a very significant part of the remediation life-cycle costs. For example, the U.S. Air Force spent 32% of its 2005 budget on LTM systems, or $24.8 million (compared to $51.8 million for remedial systems). The need for LTM is due in part to the reality that complete cleanup of significant DNAPL source zones has not been and, in the foreseeable future, will not be possible. Typically, even after the most successful remediation, some LTM is required.

Currently, most LTM approaches are relatively conventional, usually based in large part on groundwater monitoring using samples collected from wells and analyzed by laboratory EPA methods. This requires installation and maintenance of the wells, labor intensive sampling, and costly laboratory analysis. Some more recent developments such as diffusion samplers have marginally increased efficiency; however, the most common sampling and analysis approaches are based on technology originally developed for site characterization efforts 25 to 30 years ago. In addition, the analytical techniques typically used today were designed to detect a wide range of organics for characterization; however, once a site is in the LTM phase, the list of contaminants of concern is much shorter. Often monitoring is required for only a single compound, such as TCE, or a limited list of compounds.

Significant opportunities exist to improve upon this conventional approach. These opportunities generally fall into two categories—more efficient use of data that has already been collected and more efficient data collection methods.

At many DoD sites, years of site data exists, much of which has been utilized little since it was initially collected and reported. Often, LTM programs fail to take advantage of these data to improve understanding of the site and its dynamics. Better data utilization can lead to reduced need for expensive sampling and analysis, while still achieving LTM goals. Better data utilization could be accomplished through data mining, better statistical data management, or better site-specific modeling to refine the understanding of how a site is behaving and how it could be monitored more efficiently. However, there may well be difficulties in obtaining usable data of sufficient quality for the intended purposes.

Recent advances in industrial and other DoD sensor applications offer opportunities for application to long-term monitoring. Other organizations such as the Defense Advanced Research Projects Agency (DARPA) and the Department of Energy (DOE) have made significant investments in developing sensors and sensor systems. Opportunities exist to explore the development and use of sensors or sensor systems designed for the more limited and specific needs of long-term monitoring. This may lead to more field-based real-time monitoring systems, perhaps with implanted sensors not requiring conventional sampling. In addition, optimization applied to data networks will allow redundant data to be eliminated, reducing the required number of samples for long-term monitoring.

5.3 How (or If) to Use Mass Flux

Mass flux (contaminant mass per unit area per unit time, or mass discharge [mass per unit time]) has received considerable attention from researchers. Mass flux is a fundamental hydrogeological concept, and an estimate of mass flux should be performed for almost any site because it determines both the rate of source depletion and the impact to groundwater or receptors downgradient from the source or measurement transect. Mass flux estimates integrate knowledge about subsurface hydrodynamics, source strength, and attenuation rates. However, there are several methods proposed to measure mass flux or discharge, each with its own strengths and limitation. Further, most estimates involve significant uncertainty, and this uncertainty is seldom quantified or addressed. Because of this uncertainty, if the groundwater flow system does not change, a thoughtfully averaged concentration change following source remediation is a good estimator for flux change. If absolute flux values are not required and only relative flux change is of interest, averaged concentration change is all that needs to be measured. The trick is figuring out whether a weighted or simple average is sufficient.

Techniques to directly measure or estimate mass flux are still in development, but the concept has been applied to other contaminants, such as petroleum hydrocarbons, to evaluate risks and assess the performance of remediation actions. However, for DNAPL sites, in most cases the regulatory decisions are based on the maximum concentrations detected in monitoring wells, and mass flux is rarely estimated or used in making site management decisions.

Some participants expressed skepticism regarding the use of mass flux as a regulatory metric. This skepticism has limited the use of mass flux information in the past and continues to limit its current use primarily to the research community. What constitutes an "acceptable flux," for example? What reduction in mass flux would warrant stopping active treatment, or what mass flux can be handled by the natural attenuation capacity of an aquifer?

It can be argued that mass flux is a more appropriate measure of the potential impact of a contaminant moving away from a source zone, rather than the traditional point source measurements within the source zone. It also can be argued that there are many sites where there is insignificant risk, yet remediation is still required. Having a better estimator of risk at those sites may be a moot point. A certain degree of uncertainty is also associated with point-source measurements, as there is with any field measurement. Guidance is needed on when and how to best measure and analyze mass flux data, and collaboration with regulators is needed to determine how mass flux can be incorporated into existing or modified regulatory frameworks.

5.4 Use of Contaminant Assimilative Capacity of the Aquifer as a Management Strategy

Management of sites contaminated with DNAPL will likely require remedial objective alternatives to MCLs. One approach is to manage the site, through natural or engineered methods, to achieve a condition in which natural processes attenuate the contaminant present. In fact, MNA fundamentally relies on predictions of the assimilative capacity, though it is rarely explicitly defined that way. MNA determinations are generally based on measurements of dissolved contaminant levels in groundwater that indicate plume stability and estimates of the rates of transport and attenuation processes.

This approach is similar to management strategies employed for decades in surface water systems (Shifrin, 2005). The assimilative capacity of receiving waters concept is defined as the ability of the system to attenuate the pollutant load to meet water quality standards after a defined mixing zone. In surface water systems, it is accepted that a mixing or treatment zone is required to attenuate the contaminants. Within this zone, water quality standards will not be achieved. This conceptual framework needs to be applied to aquifers contaminated with DNAPL. The concept of a contaminant assimilative capacity of the aquifer needs to be further developed. The concept has been applied at a limited number of sites (Curtis and Lammey, 1998; Powers et al, 2001).

In aquifers, the volume of media impacted by contaminants is a function of the DNAPL source zone size, the advective flow, and the dispersive characteristics of the aquifer. Thus, characterization of the assimilative capacity of the aquifer will require a measure of the contaminant mass discharge from the source zone [M/T] and the contributing area perpendicular to flow. Alternatively, the local flux [$M/L^2/T$] distribution may be used to determine the maximum local mass flux and the average flux with the plume defined by some low concentration or mass flux. The assimilative capacity of an aquifer could then be characterized using a lumped mass loss term such as a first order decay parameter (though more advanced approaches may be needed when the first order approximation is not appropriate).

With assimilation capacity quantified and using a measured or estimated mass flux, the length of the mixing zone (or distance) required to meet some objective (such as MCLs or a specific mass flux) could be quantified. Alternatively, given some compliance point of interest (perhaps a property boundary) and a desired concentration or flux objective defined, the assimilative capacity of the aquifer could be used to determine an acceptable mass discharge (or maximum local mass flux) at the source zone. This approach will allow alternative flux-based remedial objectives for source zone treatment of DNAPL contaminated sites. It is possible that this approach could show that the existing mass flux (pre-remediation) is treated by the existing aquifer assimilative capacity, indicating that no source remediation is necessary. Finally, contaminant assimilative capacities of aquifers could be compared at a number of sites to assess variability and site characteristics correlating to assimilative capacity.

5.5 Remediation-Induced Effects on Subsurface Properties

Implementation of source zone depletion technologies can lead to changes in subsurface properties that can have complex and far-reaching impacts. Changes can occur in the subsurface within the source zone that is targeted for treatment. Alternatively, changes can evolve in the subsurface away from the source zone, as groundwater and soil vapors migrate through and away from the source zone during and after treatment. Prime examples of the types of changes that can occur include (1) changes in water chemistry (e.g., depressed pH, increased ionic strength); (2) changes in microbial populations (e.g., reduced biomass, increased activity, and changes in community structure); (3) changes in porous media properties (e.g., reduced permeability, altered surface chemistry); and (4) changes in subsurface temperatures (e.g., elevated temperatures) (Crimi and Siegrist, 2003; Kavanaugh et al, 2003; Siegrist et al, 2001).

The nature, magnitude, and consequences of remediation-induced changes depend on the contaminant and site conditions as well as the type of remediation technology implemented. Changes may be short-term perturbations, lasting not much longer than the duration of active remediation (e.g., elevated dissolved oxygen [DO] levels following treatment using catalyzed hydrogen peroxide). On the other hand, they can be long-lasting, persisting for months following active remediation (e.g., elevated temperatures following thermal treatment).

Remediation-induced changes can have positive or negative consequences on performance with respect to achieving a cleanup goal (e.g., achieving a percent mass depletion in the source zone or a reduced flux from the source following treatment). Positive effects can be realized if source zone depletion using one method tends to enhance the rate or extent of another passive or active method (see Section 4.4). For example, surfactant/cosolvent flushing or chemical oxidation can provide residual substrates that help build microbial biomass and support degradative activity. In contrast, in some cases, even if such a synergist effect is realized and a cleanup goal is achieved, remediation-induced changes can lead to consequences that may be undesirable and in some cases negate the risk-reduction benefits of the source zone treatment. For example, altered and uncontrolled mobility of untreated residual DNAPLs can be caused by treatment agent delivery and the absence of adequate hydraulic control or changes in water chemistry. In addition, water quality deterioration may result from chemical injection, such that increased metal or mineral contents, or elevated turbidity can interfere with ongoing or planned water uses (e.g., agricultural irrigation).

Remediation-induced effects on subsurface properties can also complicate contaminant behavior, system monitoring, and performance assessment (Siegrist and Satijn, 2002; Siegrist et al, 2006). For example, sampling intact cores can be subject to high bias due to volatilization losses, and these effects may be exacerbated under elevated temperatures. Alternatively, chemical oxidation may alter f_{oc} or K_{oc} such that partitioning properties change as a result of remediation and equilibrium partitioning approaches commonly used to infer a percent mass depletion or the contaminant mass level remaining may be invalid.

It is clear that source zone remediation can lead to changes in subsurface properties within a source zone and downgradient from it. However, it is less clear as to if and how remediation can be implemented to predictably gain potential synergistic benefits while avoiding negative consequences.

5.6 Opportunities to Use Historical Data

DoD now has many sites with 25 years or more of monitoring data. Many millions of dollars have been invested in these data, and much of it has been used little beyond the purpose for which it was originally collected, if indeed it was fully used for those purposes. This represents a huge investment in data that to date has been underutilized. There is an opportunity to mine these data for empirical insight into source longevity and natural attenuation processes (assuming there are data available of a type and quality suitable for these purposes). On many, but not all, of the sites, some form of remediation has been applied. There is an opportunity to return to sites where remediation was done to develop a better understanding of its benefits and impacts.

Demonstration of the value of mass flux measurements and mass flux reduction is often difficult within the lifetime of a typical research project because of the long time frame required to observe impacts on a dissolved plume. Returning to sites where remediation was done 10 or more years ago may well prove quite valuable in gaining a better understanding of the value of mass flux reduction. There are also sites with a long monitoring history where little or no remediation has been implemented. These sites have the potential to provide insight into natural attenuation and natural attenuation processes.

It was a consensus of the workshop that historical data and data mining offer a very real opportunity to improve our understanding of the long-term behavior of DNAPL source zones and plumes. These retrospective analyses can be done using data already collected and paid for at a fraction of the original cost of acquiring the data.

It must be recognized that there can be significant barriers to obtaining and utilizing historic data. The data itself can be difficult to access due to poor record keeping. Methods may have been poorly documented or, they may have significantly improved over the years, making the comparison of historic data to current data difficult at best. In addition, data that are considered essential today may not have been collected in the past, or the collection frequency may have been insufficient for today's purposes. Historic data must be carefully assessed to obtain genuine benefit from the information.

6. Research and Demonstration Needs to Reduce Uncertainty

During the second day of the workshop, participants were divided into breakout sessions, each with the same charge. Participants were asked to integrate the key issues identified from the three specific breakout sessions (characterization, remediation, and remedial endpoints/LTM) into discussions of research, development, test, and evaluation (RDT&E) needs to reduce the uncertainty of DNAPL source zone remediation. Specifically, participants were asked to:

- Identify and prioritize critical research paths to reduce uncertainty.
- Identify and prioritize critical demonstrations that could be conducted in the near-term to achieve design, monitoring, or performance assessment goals.

Research and demonstration needs were classified as either critical or high priority, according to the definitions in Table 3.

Table 3. Criteria for Prioritizing RDT&E Needs

	Critical	High
Research	Research that potentially could have a significant impact on reducing the uncertainty of DNAPL source zone treatment (e.g., through characterization or the design, implementation, monitoring, and performance assessment of remedial technologies)	Research that is of high priority but may not be able to be initiated until critical research needs are addressed or may be more clearly defined after critical research needs are addressed
Demonstration	Field demonstrations or assessments that can impact our near-term (3- to 5-year) ability to reduce the uncertainty of DNAPL source zone treatment in the field	Field demonstrations or assessments that are of high priority but may not be able to be implemented until critical demonstrations or assessments are completed

The following sections describe the research and demonstration needs identified by the workshop participants. Discussions are generally brief and refer to the discussions of key issues presented in prior sections. There is some overlap between the more basic research and development needs and the technology demonstration and validation needs, such as in the areas of sites with complex geology (e.g., karst sites), predicting and assessing the responses of plumes to source depletion, and the use of mass flux.

6.1 Research Needs: Critical

6.1.1 Improved Methods for Characterization and Monitoring

Current tools for characterization and monitoring are often very expensive, limiting our ability to adequately evaluate source conditions and treatment performance. In particular, better methods to evaluate the source function (Section 3.2) and to assess DNAPL distribution in the subsurface are needed. More cost-effective long-term monitoring is also a priority need (Section 5.2). Improved methods would also allow more comprehensive source characterization, which should improve remedial designs and operations (Section 3.1).

6.1.2 Improved Understanding of Plume Response to Source Depletion

The response of plumes to source depletion is not easy to predict or monitor (Section 3.2). New equilibrium conditions may take years to become established. Sorption and diffusion into low-permeability matrices are not well understood, and the diffusive processes may effectively determine the restoration time frames and control the concentrations in monitored (more permeable) media over time, whether or not source depletion is attempted. In addition, participants supported development of better predictive models to assist in making decisions since the impact on plume size, strength, and longevity are usually key objectives.

6.1.3 Development of Treatment and Monitoring Approaches for Flow-Limited Portions of DNAPL Source Zones

With the exception of excavation, all DNAPL source zone treatment schemes involve the movement of fluids through DNAPL source zones, though the fluid type, rate, and duration vary widely. For example, engineered bioremediation involves the delivery of nutrients, substrates, and sometimes specialized bacteria by groundwater flow; in situ chemical oxidation involves the delivery of chemical reactants by fluid flow; thermal treatment technologies involve the capture and/or injection of fluids; and the dissolution and biodegradation processes that occur during natural attenuation also rely on fluid flow.

Not all DNAPL source zone regions are equally accessible to fluid flow. The natural variability in soil structure and accompanying contrasts in hydraulic conductivity result in spatial differences in fluid flow strength through the DNAPL source zone. For example, alternating layers of fine and coarse materials result in limited flow through the finer-grained sequences during horizontal flow; little flow occurs in the secondary porosity in fractured bedrock settings; and high DNAPL saturations in DNAPL pools prevent flow through the DNAPL pool.

Zones most accessible to fluid flow tend to be remediated more quickly and more effectively, while flow-limited zones may not be sufficiently treated during the typical duration of a remediation project. Chemicals diffusing from flow-limited to flow-accessible zones then tend to be long-term sources of groundwater impacts in the post-treatment time frame.

Research in the past decade has looked at mathematical and physical modeling of the dissolution of DNAPL from these flow-limited regions, providing valuable insight into the long-term groundwater impacts. What is still not well understood are the opportunities for remediating flow-limited DNAPL source zone areas or controlling the potential long-term contaminant discharges from them.

For example, some remediation technologies may be better suited for treating flow-limited zones, and the performance of others might be severely limited by their presence. There may also be opportunities for improving the treatment of these flow-limited zones through innovative remediation system design or clever manipulation of the operating conditions with time during remediation. If that is the case, then better diagnostic tools will be needed to identify, characterize, and monitor remediation performance in flow-limited zones. For cases where remediation is not practicable, there may be low-cost/long-term solutions that manipulate the natural physical or biogeochemical processes in a way that contains or minimizes the contaminant discharge from flow-limited zones.

6.1.4 Assessment of the Impacts of Implementing Combined Remedies

As discussed in Section 4.4, there has been a growing interest in the potential value of combined remedies. Thermal, chemical, and biological technologies may be used together deliberately, either in treatment trains or simultaneously. Research is needed to assess the potential symbiotic and detrimental impacts of such strategies (see Section 5.5). In order to use combined remedies more cost-effectively, it will be necessary to develop ways to measure points of diminishing returns for transition from one remedial approach to another. Demonstrations of the value of combined remedies are needed to increase confidence that such an approach can actually reduce overall life-cycle costs.

6.1.5 Improved Remedial Methods for Karst and Other Complex Sites

Complex hydrogeologic regimes such as karst and fractured rock complicate the potential remediation of DNAPL. Though several reviews on remediation have emphasized the significance of complex sites, there has been no comprehensive assessment of approaches employed in these settings. Furthermore, disparate groups have undertaken efforts, but results have not been widely disseminated or in some cases even made public. An evaluation of characterization efforts and treatment achievements made to date at complex sites is necessary to determine future research needs and to assist in the management of complex sites.

Despite many significant advances in groundwater remediation technologies in the past decade, remediating DNAPL at complex sites poses the most extreme example of technical limitations to aquifer restoration. Alternative approaches are needed at each stage of site management for complex sites, including site characterization, remediation techniques, monitoring efforts and alternative paths to site closure. Of particular importance is the lack of precision in obtaining parameter estimates and mass quantification during site characterization (as discussed in Section 4.5, such estimates can vary by orders of magnitude). An improved cost evaluation and decision-making approach is needed for managing complex sites given the uncertainty of characterization and monitoring results.

6.1.6 Better Understanding and Monitoring of Vapor Transport from Sources

As discussed in Section 3.4, vapor transport through the vadose zone represents a key uncertainty and potential liability at chlorinated solvent sites. Research is needed to develop a better understanding of the processes controlling vapor attenuation, as well as improved monitoring techniques and methods to discern between subsurface and surface sources of chlorinated solvents in indoor air.

6.2 Research Needs: High Priority

6.2.1 Better Understanding of DNAPL Architecture

The geometry and distribution of DNAPL pools, ganglia, and sorbed residuals largely determine the source longevity and the difficulty of remediation. For example, it has become clear that the depletion possible is related to the distribution, as described by the ganglia-to-pool ratio. In addition, dissolved phase DNAPL constituents can diffuse into lower permeability materials within the source area and within the plume, and the back-diffusion from these sources can result in long-lived contaminant plumes.

However, definition of source architecture characteristics such as the ganglia-to-pool ratio is difficult and costly. Often, it is difficult enough to locate and delineate the source zone, and the cost of the careful vertical profiling of several borings that is needed to better characterize the architecture can be difficult to justify. Better characterization methods and better understanding of the impacts of DNAPL architecture could improve our ability to predict the outcomes of remediation approaches.

6.2.2 Improved Understanding of the Relationship Between Mass Removal and Mass Flux

Although there has been considerable research, our understanding of the relationship between the degree of mass removal and the reduction or increase in flux after treatment is incomplete. The relationship will vary to some degree, depending on technology-specific considerations. Validated predictive tools could improve decision making and remediation system performance.

6.2.3 Improved Delivery Technologies

Improving our ability to deliver remediation agents efficiently and effectively to contaminant sources remains a key challenge for several in situ remedial technologies. Often, delivery is the most significant constraint to the performance of source zone treatment technologies. It is particularly difficult to deliver agents to flow-limited zones within the subsurface (see Section 6.1.3). Accessing contaminants within less permeable zones, or contaminants that have diffused into the geologic matrix, can be difficult, and yet these contaminants can continue to serve as long-term sources after treatment is stopped (Saenton et al, 2001). Better delivery targeting contaminant accumulations or flow-limited zones should improve both the cost and performance of source zone treatment technologies.

6.2.4 Quantification of Uncertainty

The characterization, remediation, and monitoring of DNAPL source zones involve inherent uncertainties. The extent and distribution of the contaminants and the hydraulic/chemical/biological processes that control its migration and persistence in the subsurface are extremely difficult to quantify and assess. In addition, the significant heterogeneity of most subsurface environments dictates that critical site parameters (i.e., hydraulic conductivity, groundwater velocity, microbial activity, contaminant concentration, and sorption/desorption rates) can vary over orders of magnitude within relatively short spatial distances. This high degree of spatial variability in subsurface properties makes complete characterization of a site virtually impossible.

Consequently, predictions or decisions needed for the remediation of an environmentally impacted site that are made based on this knowledge are subject to a relatively high degree of

uncertainty. The mathematical models that are widely used to inform decision making may be complex, but often the critical parameters needed for these models must be assumed or estimated. These estimates may be highly inaccurate, but the level of uncertainty inherent in parameter estimation and model predictions is generally not recognized or expressed when these models are used. Determining the sensitivity of model predictions to key parameters could help practitioners understand which measurements are most important. Developing methods to quantify the uncertainty in the data from a given site could improve decision-making and guide future characterization and monitoring efforts.

6.3 Demonstration Needs: Critical

6.3.1 Improved Methods for Reducing LTM/Characterization Costs

The costs for adequate characterization and long-term monitoring of sites can be very high (see Sections 3.3 and 5.2). Reducing these costs can have a major impact on the life-cycle costs of site management and can lead to improved designs and operation of remedial systems by improving the understanding of site conditions.

Low-maintenance methods to monitor long-term trends are needed. In particular, there are opportunities to adapt and use advanced and innovative sensors or sensor systems originally developed for other purposes (e.g., homeland security). This approach may lead to more field-based, real-time monitoring systems, perhaps with implanted sensors not requiring conventional sampling. For characterizing sites, particularly complex sites, new techniques that could improve our three-dimensional conceptual models of source zones or our ability to locate source zones would be useful and could reduce both characterization and remediation costs.

6.3.2 Focused Data Mining to Assess Long-Term Responses

As discussed in Section 5.6 in particular, retrospective analyses of historical data can offer a cost-effective method to evaluate costs and performance of source zone remediation approaches. Further, data mining and postmortem analyses after several years offer an opportunity to study longer term responses to treatment. Mass discharge and plume responses after treatment can only be assessed after the system reaches a pseudo steady-state following remediation. In addition, some of the potential adverse impacts of treatment can be properly evaluated only long after active treatment is stopped. Identifying and characterizing past sites that have undergone different source remediation approaches and rigorously evaluating the past data and current conditions long after active treatment has ceased could provide valuable information for relatively low cost.

6.3.3 Development of Decision Guidelines for Source Zone Characterization and Remediation

As discussed in Section 4.1, in most cases there is too much uncertainty surrounding source zone decisions. This uncertainty leads to unnecessary costs and delays. In some cases, remediation performance has not met expectations, and in many cases, expected treatment outcomes were not even defined because of the uncertainties involved.

One of the best sources of information on treatment outcomes is the experience gained over the last few years from sites where source depletion has been tried. Quantifying the costs and benefits associated with characterization and remediation options would be valuable to future

decision makers. The guidance also should provide information on policy and regulatory options.

6.3.4 Enhanced Technology Transfer

Improved technology transfer was strongly supported. Specific efforts or products mentioned included:

- Development of best practices manuals for DNAPL site characterization and monitoring
- Development of a web-based training course, possibly including certification, on characterization of DNAPL sources
- Identification of opportunities to inform performance-based contracting in support of DNAPL source zone treatment
- Engagement of regulators in discussion and resolution of DNAPL monitoring and remediation dilemmas through organizations such as the Interstate Technology and Regulatory Council (ITRC).

6.4 Demonstration Needs: High Priority

6.4.1 Improved Methods for Evaluating Plume Response

Research to date has shed considerable light on the expected response of plumes to source depletion. Improved predictions should lead to expectations that are more realistic by all interested parties. However, the uncertainty remains high, and the research to date has not yielded products useful to site managers. For example, back-diffusion from low-permeability zones within the source and within the plume may be a critical process that is not well understood. In addition, accurate measures of source function before and after treatment are key to understanding the likely plume response. However, our ability to measure source function is limited, and the tools available are rarely used. Guidance is needed on monitoring techniques that can improve our predictions and assessments of the impacts on plume longevity and size. Retrospective studies could also provide valuable information on the long-term plume response under real-world conditions.

6.4.2 Collection and Publication of Lessons Learned from Technologies

Given the rapidly increasing base of experience and the ongoing evolution of many of the source zone technologies, it is important to capture the lessons learned from prior applications. As the technologies are attempted under more difficult conditions, it will be vital to examine successes and failures and transfer the findings to site managers. In particular, the participants stressed the need to evaluate the lessons learned from in situ thermal technologies, as this approach is developing rapidly, is increasingly being deployed for source depletion, and mistakes can be very expensive.

6.4.3 Development of Guidance on Observational Approach

The observational approach (Section 3.5) was stressed as the intelligent approach to source zone characterization and remediation. However, it often does not fit well in the generally linear regulatory process, and as a result, information gathered after a characterization phase (such as Remedial Investigations) is often not intentionally integrated into an updated conceptual site model. Guidance on how to incorporate the principles of the observational approach into site

management could be helpful to site managers, regulators, and the public. Again, involvement of experience regulators in developing such guidance would be invaluable.

6.4.4 Better Tools for Handling Industrial Infrastructure

At many sites, there is an existing infrastructure (buildings, piping, remnant structures) that can greatly complicate investigation and remediation. Better tools for dealing with these impediments are needed to overcome access limitations and obstructions to characterization and remedial equipment.

7. OVERARCHING ISSUES

This section provides a broad overview of overarching themes that were repeatedly mentioned during the discussions. These issues reflect critical needs in the area of reducing uncertainty associated with the characterization and remediation of DNAPL source zones. Overarching issues range from fundamental to applied questions.

7.1 Integrate Decision-Making Processes for Characterization and Remediation

Many DNAPL remediation decisions are made in the face of tremendous uncertainty. The location and distribution of DNAPL and residual source material within the subsurface is often poorly understood. The effects of treatment on source strength and longevity are also not clear, even when the source has been "well-characterized" by current standards. Performance monitoring often relies on a few monitoring wells that may not be ideally located and constructed, and generally sample only a small fraction of the groundwater within and down-gradient of a highly heterogeneous source zone. In general, we do not sufficiently define or quantify the uncertainties involved at DNAPL sites, or consciously attempt to reduce uncertainty to acceptable levels for given site management decisions.

Given these inherent uncertainties, participants stressed the value of an observational approach, also referred to as iterative or adaptive management. Areas the observational approach emphasizes include the following:

- Continuous updating of the conceptual site model
- A phased approach to treatment
- Contingency plans to address plausible variations from anticipated conditions
- Careful evaluation of the effects of each phase of treatment.

This philosophy differs from the classical approach of a step-wise process of characterization, remedy selection, design, operation, shut-down, and post-treatment monitoring. It may be difficult to implement such an iterative learn-as-you-go approach given the current emphasis on performance-based contracting within DoD and other government agencies.

7.2 Improved Understanding of Source Function in Relation to Plumes

A key measure of the source zone impact on the plume is the source function, which is defined as the total contaminant mass released into the flow of groundwater per unit time (e.g., kg/day). It is important to understand source function because it controls both source longevity and the mass flux (and therefore plume size). The source function depends on the source distribution within the subsurface, the contaminant dissolution rate, and the source zone hydrodynamics. Source function can vary widely depending on scale, including both space and time. Because of the complex and dynamic factors that govern the source function, estimates generally have a large uncertainty associated with them.

Subsurface hydrodynamics play an important role in determining the source function, both under natural conditions and during source zone remediation. Subsurface hydrodynamics in this case

are defined as the spatial and temporal distribution of saturated thickness and pore velocity within the source zone. It has been demonstrated that, in general, mass transfer processes at the DNAPL-water interfaces are rate-limited. In addition, the emission concentration and mass flux from the source zone depend on dispersion (hydrodynamic mixing and diffusion) of the dissolved constituents. Hence, the velocity at the pore scale that contributes to rate-limited behavior and the macro-scale velocity variations in the source zone that contribute to dispersion depend on the source zone hydrodynamics.

The hydrodynamics within and near the source zone contribute to plume concentrations during remediation in two fundamental ways. First, the flow velocity controls the treatment effectiveness in source zone mass removal technologies that rely on the delivery of treating agents (e.g., surfactants, oxidants, biological agents, nanoscale iron) to entrapped DNAPL or the diffused DNAPL mass that may be present in stagnant zones. Second, during remediation, the flow velocity could change as a result of changes in the relative permeability of water due to DNAPL removal and modification of pore configuration as a secondary effect of remediation (e.g., precipitation during chemical oxidation and biological growth during bioremediation). In SERDP-funded research on upscaling of mass transfer process for field-scale predictions, it has been demonstrated that the parameters that control the field-scale hydrodynamics appear in the upscaled mass transfer coefficients for both natural conditions and during remediation.

7.3 More Cost-Effective Characterization, Remediation, and Monitoring Methods

DNAPL source zone assessment and remediation can be extremely costly, given the difficulties involved. Site managers would benefit from more cost-effective use of the methods available as well as the development of less expensive methods. Guidance on the use of existing methods should first assess the level of precision required for varying site conditions and intended uses of the results. Guidance should also take into account the total costs because often cost information cannot be compared on a true apples-to-apples basis. Also, there is insufficient real-world baseline information on costs for different methods.

Finally, new methods are needed to maintain or improve remediation effectiveness while reducing costs. Notably, participants felt that there are opportunities to reduce the costs for long-term monitoring, delivery of reagents, and assessing complex sites such as karst or fractured bedrock.

7.4 Realistic Expectations for Remedial Time Frames and Transition Points

Regulators, site owners, and site managers want to know how long a source zone will require continued monitoring and management and how much reduction in the "remediation time frame" will be realized if the source is treated. However, there are no widely used or trusted methods for predicting remediation time frame (with or without source treatment), and there is considerable uncertainty in most of the input data required for the available estimation methods.

Currently, some regulators and practitioners assume that the reduction in remediation time frame will be directly proportional to the reduction in source mass. However, the participants concluded that source response is very complex, as there are multiple source processes (e.g., pool dissolution, ganglia dissolution, desorption, matrix diffusion, availability effects) that comprise

the source function. Overall, there is likely to be a nonlinear relationship between mass removal and the reduction in remediation time frame at most sites. Better predictive tools are needed to define the relationship between remediation time frame and mass removal at solvent sites.

While much of the research to date has focused on relatively strong sources (sources with pooled or residual DNAPL), future research may need to emphasize depleted sites (i.e., low concentration sites where matrix diffusion, low desorption, or other weak sources dominate). These exhausted sites may be the result of long-term natural attenuation processes or active treatment of the source. In addition, emerging research suggests that these weak sources may be formed throughout the entire plume, potentially creating a condition where "the entire plume is the source."

Treatment trains may be one method to attack source zones where long-term care requirements are not eliminated due to application of a single technology alone. The participants felt that identifying complimentary remediation technologies would be useful, through research and demonstration as well as data mining of existing sites where treatment trains had been applied.

The question of remediation endpoints was discussed. Participants agreed that one key transition point is reducing the mass flux from source zones to the point where natural attenuation processes can manage the plume, therefore reducing long-term care requirements. Better predictive tools are needed for predicting if a particular source treatment at a site will arrive at such a transition point.

7.5 Opportunities to Analyze Existing Data

There is a rapidly growing base of experience in several source zone remediation approaches. Several technologies are still in a developing phase. Participants stressed the large potential for learning from prior experiences since, in many cases, the data have not been fully analyzed or compared to results from other sites. Postmortem analyses could provide valuable information on the real-world costs and performance, and the lessons learned can improve future projects.

In addition, fully evaluating the plume response to source depletion may require significant time. A common objective of depletion is to reduce the restoration time frame, which is often estimated in centuries; however, the time course of restoration post-treatment is uncertain. The processes involved are often slow, and re-equilibration can take several years. Analyses of past projects could provide valuable data to elucidate the long-term responses.

7.6 Technology Transfer

The participants strongly supported an ongoing technology transfer effort. In particular, attendees recommended mining existing data, much of it supported by SERDP and ESTCP, to provide realistic data on the costs and benefits of different remediation approaches. Actively disseminating information from ongoing research was also recommended. Best practices manuals, protocols, guidance documents, and training materials should be developed to help DoD project managers, as well as the consultants responsible for site management under performance-based contracts. Finally, the participants recommended that SERDP and ESTCP participate in an outreach effort to the regulatory community on the use of mass flux estimates.

8. CONCLUDING THOUGHTS

There are more than 9,000 sites on former and current DoD installations requiring environmental restoration because of groundwater, soil, and sediment contamination. While DoD facilities may have several contaminants, chlorinated solvents are by far the most prevalent. Chlorinated solvents such as TCE and PCE are found at approximately 80% of all Superfund sites with groundwater contamination and more than 3,000 DoD sites in the United States. SERDP and ESTCP, as DoD programs that promote the development and demonstration of innovative, cost-effective environmental technologies, must determine how their limited funds can best be invested to improve DoD's ability to effectively address its cleanup requirements in consideration of and in collaboration with past, present, and planned initiatives of other funding organizations and research programs.

For the past 4 years, the SERDP and ESTCP programs have funded basic and applied research designed to address key questions relating to the efficacy and cost-effectiveness of chlorinated solvent source zone remediation. Despite the progress to date, it remains difficult to greatly reduce the uncertainties involved in DNAPL site assessment and cleanup. This workshop was intended to define a path forward to reduce the uncertainty surrounding DNAPL sites.

To address these uncertainties, research, demonstration, and technology transfer needs were identified and prioritized. Critical research needs included issues associated with characterization and monitoring methods, plume response, flow-limited portions of source zones, combined technologies, complex sites, and vapor transport. High priority research needs focused on DNAPL architecture, mass removal and mass flux, delivery mechanisms, and uncertainty. Critical demonstration needs included methods, data mining, decision guidelines, and technology transfer. High priority demonstration needs focused on methods for plume response, lessons learned, guidance on the observational approach, and industrial infrastructure.

The result of this workshop is a strategic plan to guide SERDP and ESTCP investments in research and demonstrations associated with the characterization and remediation of DNAPL source zones over the next 5 to 10 years, ultimately benefiting environmental restoration efforts at DoD sites.

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Appendix A

Attendees

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Tufts University
School of Engineering

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University of Florida
Department of Environmental
Engineering Sciences

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Haley & Aldrich, Inc.

Erica Becvar
HQ AFCEE/TDE

Richard Brown
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Southern Division

Charles Coyle
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Hazardous, Toxic and Radioactive Waste
Center

James Cummings
U.S. Environmental Protection Agency
Office of Solid Waste and Emergency
Response
Office of Superfund Remediation
Technology Innovation
Technology Assessment Branch

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Malcolm Pirnie, Inc.

Ron Falta
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Charles Faust
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Don Ficklen
HQ AFCEE/TDE

Laurie Haines
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Mark Hampton
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Rob Hinchee
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Joseph Hughes
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Tissa Illangasekare
Colorado School of Mines
Environmental Science and Engineering

Paul Johnson
Arizona State University
Civil and Environmental Engineering

Peter Kitanidis
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Bernard Kueper
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Restoration Development Branch

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SERDP and ESTCP

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Tamzen Macbeth
North Wind Inc.

Douglas Mackay
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Land, Air and Water Resources

David Major
GeoSyntec Consultants

Jeffrey Marqusee
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SERDP/ESTCP Support

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Engineering Research Center

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Thomas Simpkin
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Bradley Smith
SERDP and ESTCP

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Arizona State University
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Kent Udell
University of Utah
Department of Mechanical Engineering

Herb Ward
Rice University
Civil & Environmental Engineering

Kelly Woodworth
HydroGeoLogic, Inc.
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Appendix B

Agenda

WORKSHOP ON REDUCING THE UNCERTAINTY OF DNAPL SOURCE ZONE REMEDIATION

Harbor Court Hotel
550 Light Street, Baltimore, Maryland 21202
410-234-0550; www.harborcourt.com

TUESDAY, MARCH 7, 2006				
0730	Registration and Continental Breakfast			
0800	**Welcome and Introduction**	Mr. Bradley Smith SERDP Executive Director	Dr. Jeffrey Marqusee SERDP Technical Director ESTCP Director	Dr. Andrea Leeson Environmental Restoration Program Manager
0815	**Management Challenges at DNAPL Sites**			Dr. Rob Hinchee, IST Inc.
	Field Perspective:			
0835	Characterization			Dr. Charles Faust GeoTrans
0855	Biological Treatment			Dr. Hans Stroo HGL, Inc.
0915	Surfactants			Dr. Tom Sale Colorado State University
0935	Chemical Oxidation			Dr. Dick Brown ERM
0955	Thermal Treatment			Dr. Michael Basel Haley & Aldrich
1015	Break			
1045	**SERDP/ESTCP Investments in DNAPL Source Zone Treatment**			Dr. Andrea Leeson
	Research on Impacts of DNAPL Source Zone Treatment:			
1100	SERDP Project ER-1293			Dr. Linda Abriola Tufts University
1115	SERDP Project ER-1294			Dr. Tissa Illangasakare Colorado School of Mines
1130	SERDP Project ER-1295			Dr. Lynn Wood U.S. EPA, ORD/NRMRL
1145	**Poster Session Highlighting Relevant Projects (see Attachment) and Working Lunch**			
1330	**Breakout Session I Discussions: Key Issues as they Relate to Workshop Objectives; each breakout group has different charge** • Breakout Group A: Characterization • Breakout Group B: Remediation • Breakout Group C: LTM and Remedial Endpoints			Breakout Groups (divided by expertise)
1530	Break			

1545	**Breakout Session I Discussions (continued)**	Breakout Groups
1645	**Recap and Discuss Agenda for Next Day**	All Attendees
1700	**Poster Session Reception**	
1900	**Adjourn**	

WEDNESDAY, MARCH 8, 2006		
0730	Continental Breakfast	
800	**Reports from Breakout Session I**	Breakout Group Chairs
900	**Identification and Discussion of Key Issues**	Dr. Rob Hinchee, IST Inc.
1000	Break	
1015	**Breakout Session II Discussions: RDT&E to Reduce Uncertainty of DNAPL Source Zone Remediation; all groups have same charge**	Breakout Groups (mix initial groups)
1200	Working Lunch	
1300	**Breakout Session II Discussions (continued)**	Breakout Groups
1430	Break	
1500	**Reports from Breakout Session II**	Breakout Group Chairs
1600	**Prioritization of RDT&E Needs**	Dr. Paul Johnson, Arizona State University
1645	**Concluding Remarks**	Dr. Andrea Leeson
1700	**Adjourn**	

THURSDAY, MARCH 9, 2006	
0730	Continental Breakfast for Breakout Session Chairs/Scribes (i.e., Working Group)
0800	**Discuss Results and Preparation of Summary Document (Working Group)**
1100	**Adjourn**

Poster Session

Decision Support System to Evaluate Effectiveness and Cost of Source Zone Treatment (SERDP ER-1292) – Groundwater Services, Inc.

Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment (SERDP ER-1293) – Tufts University

Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (SERDP ER-1294) – Colorado School of Mines

Impacts of DNAPL Source Zone Treatment: Experimental and Modeling Assessment of Benefits of Partial Source Removal (SERDP ER-1295) – U.S. EPA, University of Florida, and Purdue University

A Field-Scale Model for DNAPL Source Depletion with Time: Model Development, Calibration, and Uncertainty (SERDP ER-1349) – Virginia Tech and Oak Ridge National Laboratory

Biodegradation of Dense Non-Aqueous Phase Liquids (DNAPL) through Bioaugmentation of Source Areas (ESTCP ER-0008) – NFESC and GeoSyntec Consultants

In Situ Bioremediation of Chlorinated Solvent Source Areas with Enhanced Mass Transfer (ESTCP ER-0218) – Camp Dresser & McKee, Inc.

Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment (ESTCP ER-0314) – Arizona State University

Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent-Contaminated Sites (ESTCP ER-0318) – Malcolm Pirnie, Inc.

Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (ESTCP ER-0424) – NFESC, Queens University, and GeoSyntec Consultants

Appendix C

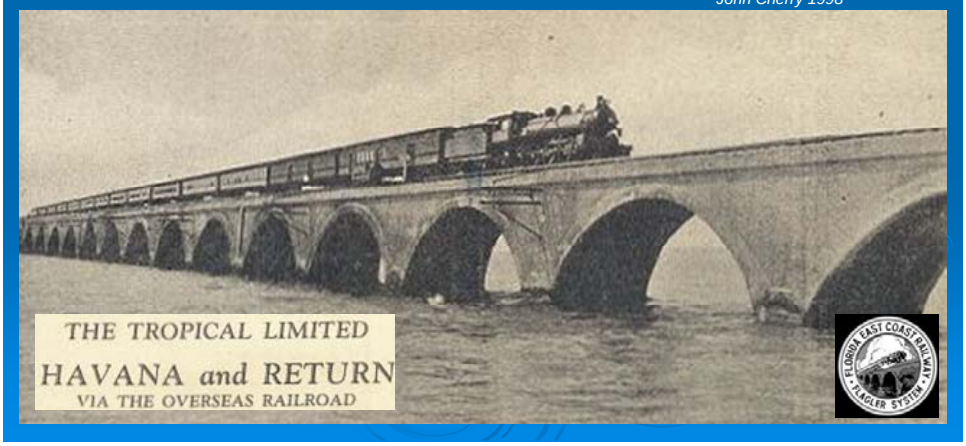
Presentations

Management Challenges at DNAPL Sites

Setting the Stage

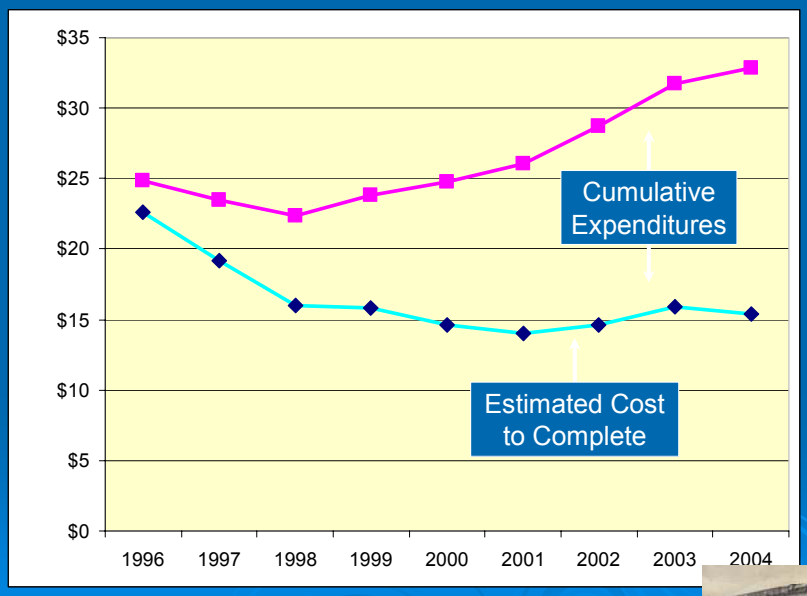
"DNAPL remediation is like building a bridge across a river but you can't see to the other side because it is too foggy. We are attempting to remediate DNAPLs anyway so that we can pass on a cleaner environment to the next generations. By the time our children are grown, they can continue building the DNAPL bridge to the other side of the river."

John Cherry 1998



Management Challenges at DNAPL Sites

- Overview of extent/scope of DNAPL issue
- Potential liability for DoD
- How is problem dealt with in the real world?
- What issues are RPMs struggling with?
- What are RPM decision challenges?
- What are regulatory challenges?
- What drives the push towards cleanup?



How Much of this is Chlorinated Solvent Related?

Hill AFB Costs

	Past Cost	FY05	Cost to Complete
Total	$295 million	$11.5 million	$348 million
DNAPL sites	$210 million	$8.3 million	$250 million

Hill AFB represents ~4% of Air Force
and ~0.1% of DoD ER budget.
At Hill chlorinated solvent sites represent
> 50% of ER costs.

So How Much?

Numbers are hard to tie down, but the DoD clearly faces spending **billions** on

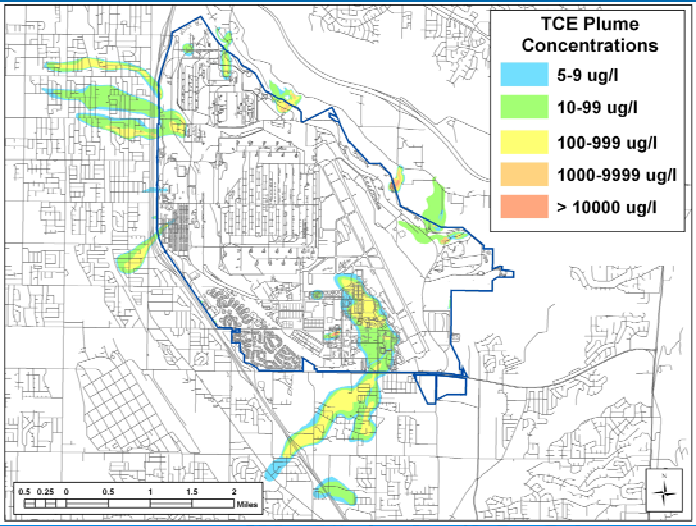
DNAPL and chlorinated site remediation.

$Really Big Bucks$

How is problem dealt with in the real world?

- Continue with the Hill AFB example
  - Hill has a long history of working with DNAPL problems
  - One of the larger DoD DNAPL problems
  - In some ways typical of many bases
- Lebron Study
  - Most comprehensive study of what RPMs think and are doing
- Non scientific pole
  - RPM opinions and thoughts

Areas of Groundwater Contamination Hill AFB, Utah



Hill AFB

- 11 OUs with chlorinated solvent contamination (main base)
  - 9 DNAPL or high concentration chlorinated
  - 2 LNAPL with chlorinated solvents
- 1 Well Characterized source area
- 2 Moderately characterized source areas
- 8 OUs without well defined source areas

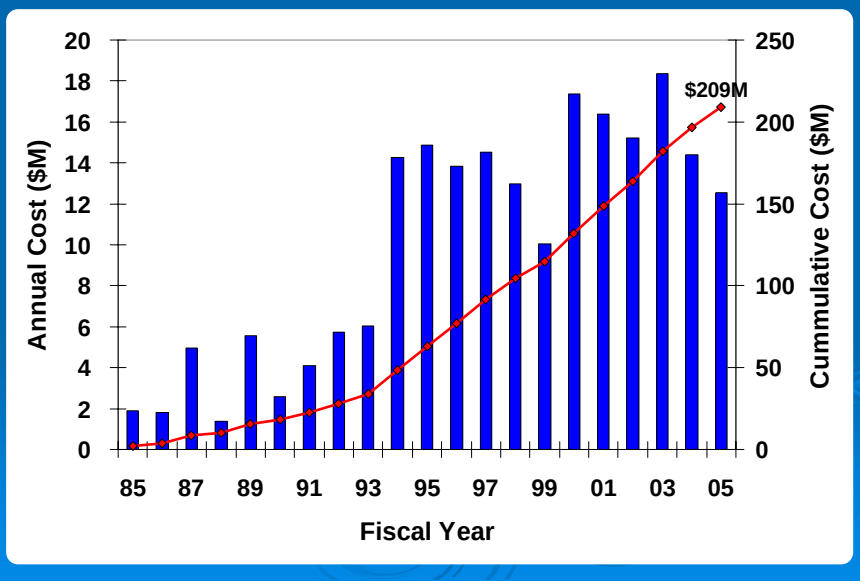
Hill AFB – Full Scale Implementation

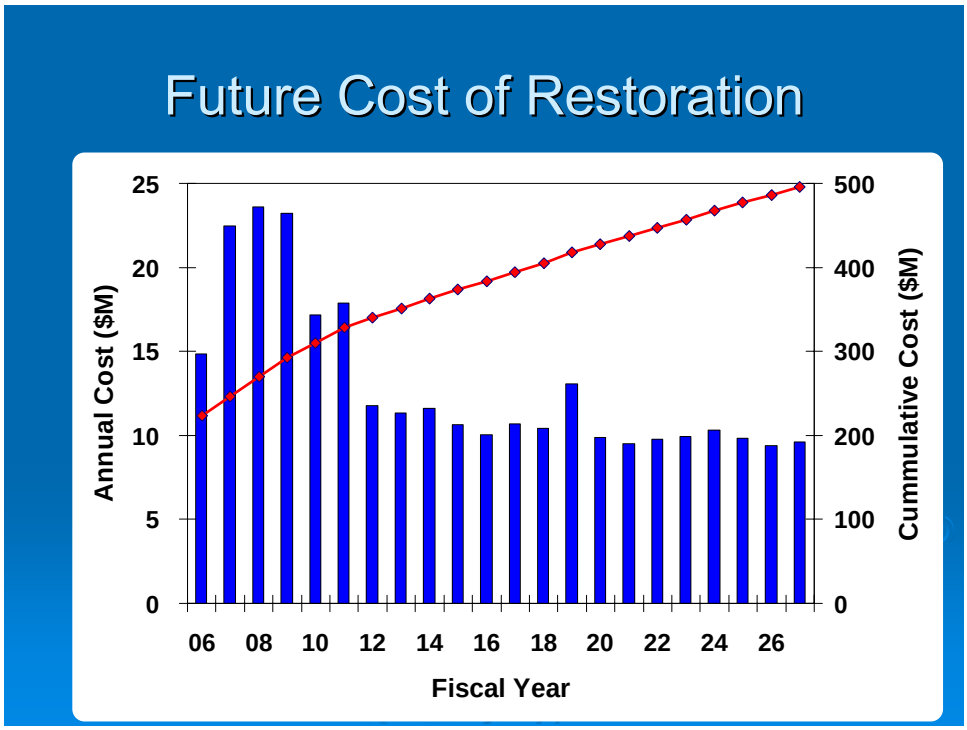
- 1 OU with DNAPL recovery
- 7 OUs with pump and treat
- 2 OUs with SVE
- 2 OUs with PRB
- 2 OUs with excavation
- 1 OU with slurry wall
- 1 OU with source treatment, surfactant flood at OU-2

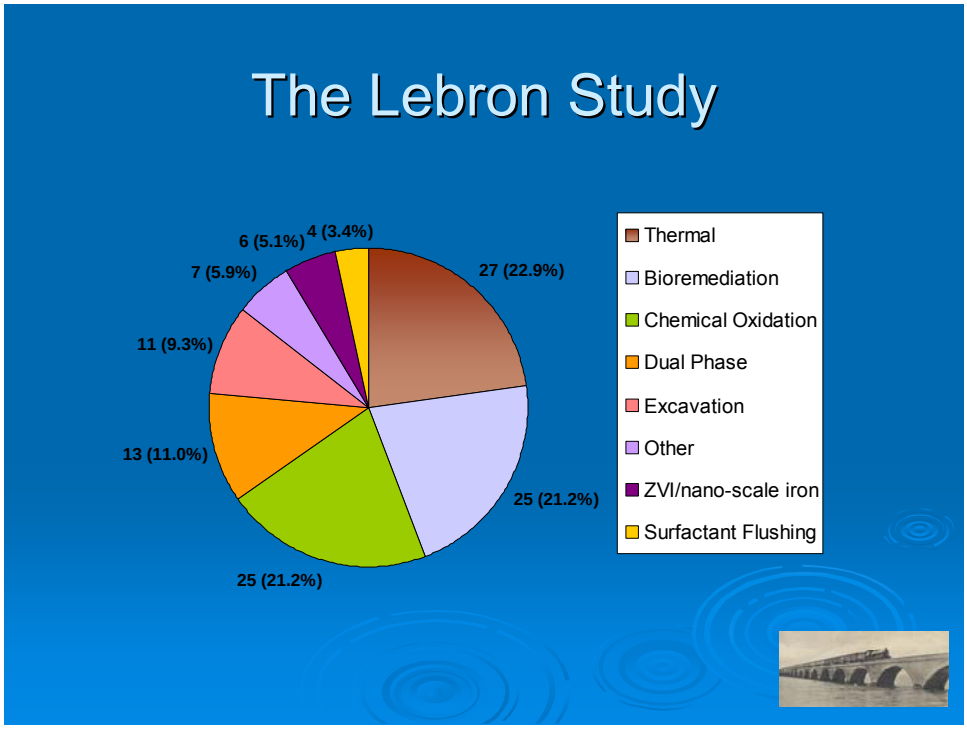
Hill AFB – Treatability Studies or Pilot Tests

- Surfactant flood
- Bioremediation
- Thermal treatment
- SVE
- Air Sparging
- Groundwater Circulation Wells

Restoration Cost-to-Date




Future Cost of Restoration
Annual Cost ($M)
Cummulative Cost ($M)
Fiscal Year
0
5
10
15
20
25
0
100
200
300
400
500
06
08
10
12
14
16
18
20
22
24
26


The Lebron Study
27 (22.9%)
25 (21.2%)
25 (21.2%)
13 (11.0%)
11 (9.3%)
7 (5.9%)
6 (5.1%)
4 (3.4%)
Thermal
Bioremediation
Chemical Oxidation
Dual Phase
Excavation
Other
ZVI/nano-scale iron
Surfactant Flushing

Results Summary

118 sites

Site Information

- Lithology
  - Unconsolidated = 104 (89%)
  - Consolidated = 13 (11%)
- Areal extent 10,000 ft^2 to 100,000 ft^2
- Volume greater than 100,000 ft^3
- DNAPL Distribution
  - 83% residual DNAPL
  - 61% sorbed DNAPL
  - 44% pooled DNAPL
- DNAPL Depth
  - 10 to < 100 ft bgs

Technology Information

- Thermal treatment, pump and treat, and dual-phase extraction applications appeared to be significantly more expensive than chemical oxidation cases on large sites
- Average full-scale application is $2.8M
- Treatment Duration:
  - Dual Phase Extraction: 60 years
  - Pump & Treat: 158 years
  - Chemical Oxidation: ~4 years
  - Thermal Technologies: ~4 years
  - ZVI Technologies: ~4 years
  - Bioremediation: ~4 years

Lebron Study - Did it work?

Mass removal	Reduced mass flux	Observed rebound	RPM opinion of success
technical			
30% >50%	26% >80%	26% no	70% fair or better
8% <50%	15% <60%	13% yes	2% poor
62% unknown	54% unknown	60% unknown	17% unknown

Performance Observations:

- None of the sites in the survey met MCL criteria
  - Meeting MCLs was not always the reason source reduction was attempted.
  - Some sites in the literature (ITRC, 2004) have met MCL criteria:
    - The ICN Pharmaceuticals, Inc. (ICN) site in Portland, Oregon (ITRC draft, 2004)
    - TCE site, ~120 X 80 X 20 ft. Used Electrical Resistance Heating (ERH).

Performance Observations (cont'd):

- None of the sites in the survey got closure or No Further Action (NFA) letters
  - Significant mass removal and mass flux was achieved in the majority of the cases that estimated mass removal and mass flux.
    - 26% of the sites (14 out of 53 completed) sites had >80% source removal
    - the majority of the cases that estimated mass flux achieved an 80 to 100% decrease in mass flux.
  - Some sites in the literature (EPA, 2003) have met NFA criteria:
    - Manufacturing Facility in Skokie, Illinois using ERH
    - Groundwater concentrations were reduced to below Illinois EPA Tier III groundwater levels

What issues are RPMs struggling with? – non technical

- How to deal with the need to clean up to MCLs
  - Slows some down; why spend $ if I can't
  - Speeds some up; better get started
  - Almost universal issue
- Budget constraints
  - Lean & Mean vs Skinny and PO'd
  - Living with Performance Based Contracting

What issues are RPMs struggling with? – technical

- How to predict the outcome of remediation?
  - Time to MCLs?
  - Mass removal?
  - Rebound?
  - No one mentioned mass flux…….
- How to work with uncertainty
- Vapor Intrusion – New Issue

Performance Monitoring

- Need for measurable criteria tied back to the Site Conceptual Model w/ feedback loop
- We frequently fail to analyze and mine our data sets
- Must invest in monitoring systems that will provide early feedback
  - Operational cost of failing system will outweigh the cost of added monitoring
  - A realization when looking at performance based contracts

What are RPM decision challenges?

- How much should I spend on source treatment and how do I decide what to do?
- How do I deal with dynamic issues?
  - Changes in regulatory standards and approaches
  - Dynamic conceptual models
  - Dynamic funding levels
  - Changing technical paradigms

What are regulatory challenges?

- Need to clean up to MCLs
  - Biggest single issue
  - Everyone talks about risk based and alternative clean up levels but it all seems to come back to MCLs
- Changing regulatory demands
- Worries about future changes in direction

What drives the push towards cleanup?

- Compliance with the law
- Doing my job
- Public or community pressure
- Preserving the military mission
- Advancing science & technology
- Cleaning up the environment
  - Legacy issues
  - Resource restoration
  - Paying for sins of the past

About that Bridge

- As a society we have made the decision to start building it
- RPMs are the folks with the responsibility to build it
- Our job is to help

CHARACTERIZATION
Field Perspective

Charles R. Faust, James W. Mercer, and Robert M. Cohen

GeoTrans, Inc

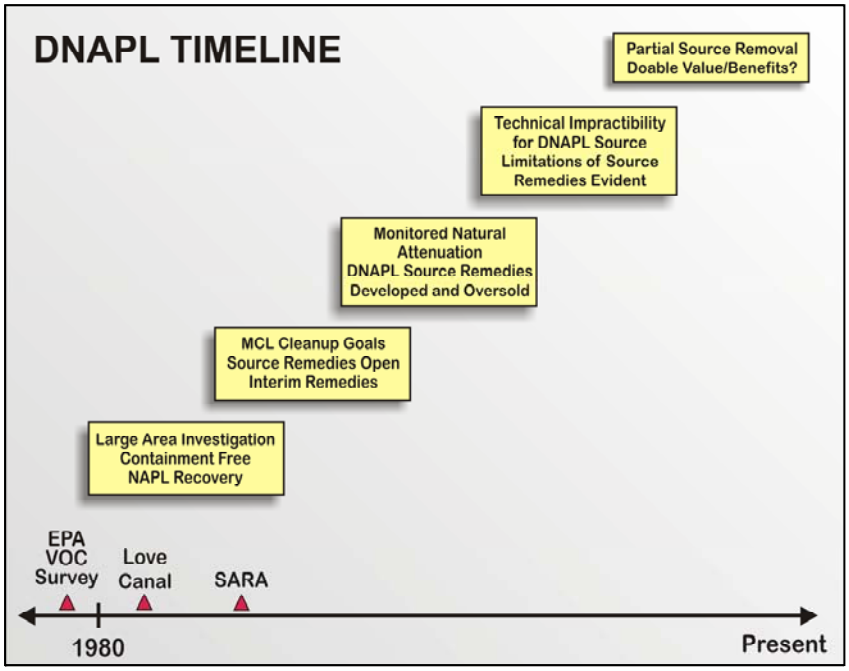
7 MAR 2006

Workshop on Reducing the Uncertainty
of DNAPL Source Zone Remediation

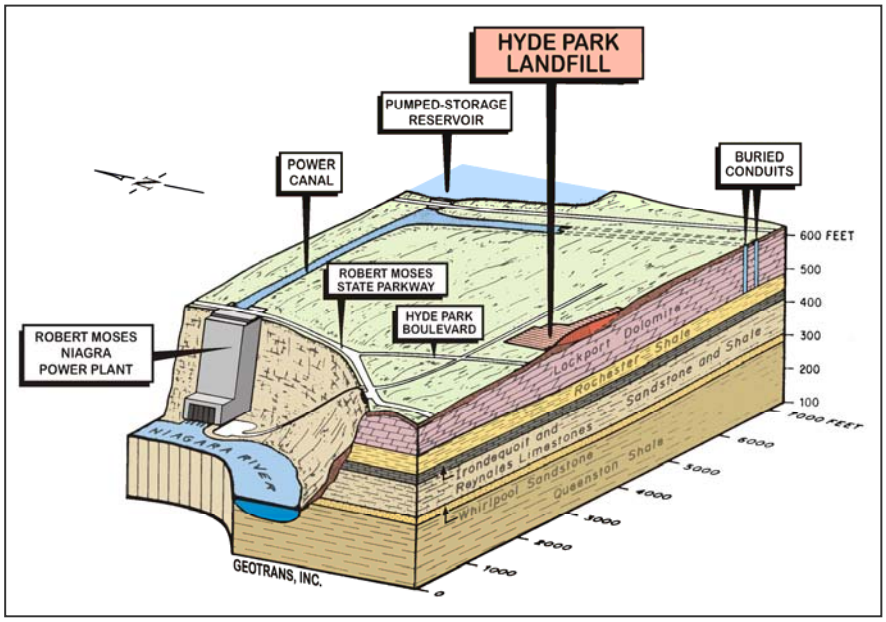
Baltimore, MD

Presentation Overview

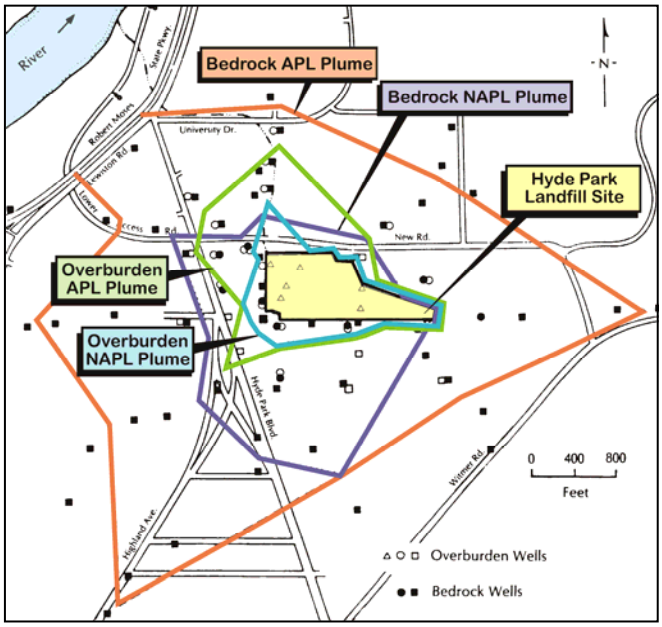
- DNAPL timeline and historical perspective
- Characterization objectives
- General characterization strategy
  - What are the key decision processes for determining which characterization approach to implement?
  - What are the metrics most commonly used in the field to assess effectiveness of the characterization process?
  - What are the data gaps/needs for more effective source zone characterization?
- Remediation characterization
  - Contaminant mass flux
- Case studies of remediation characterization
- Parting thoughts



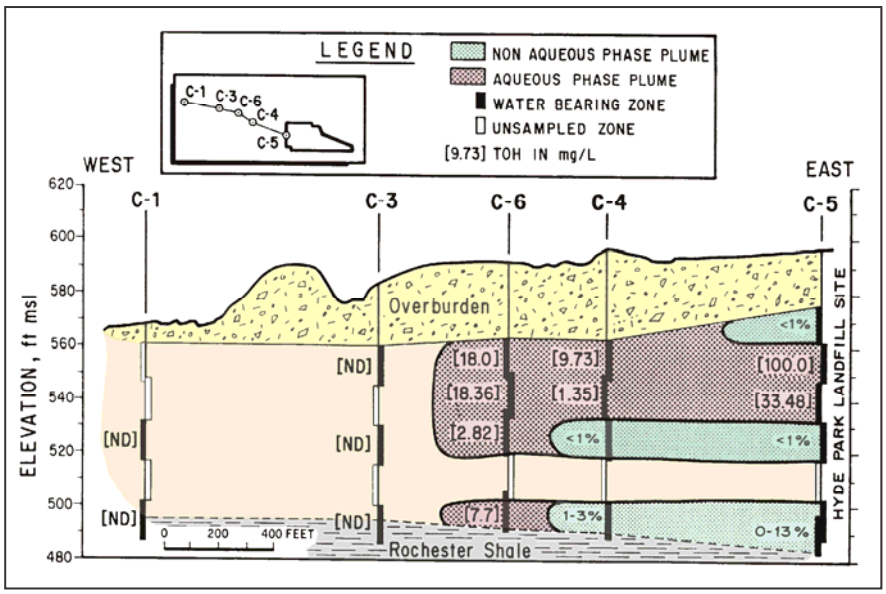
Generalized Block Diagram



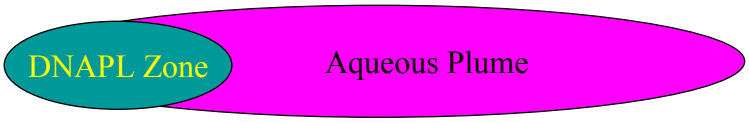
Boundaries of APL and NAPL Plume



Vertical Section of Lockport Dolomite



The Problem



DNAPL Zone can include (1) residual DNAPL, (2) pooled DNAPL, (3) sorbed contaminants, and (4) dissolved contaminants diffused into fine-grained media.

All are long-term, continuing sources to the downgradient, dissolved aqueous plume. Need to characterize both the DNAPL source zone and the aqueous plume.

DNAPL Characterization

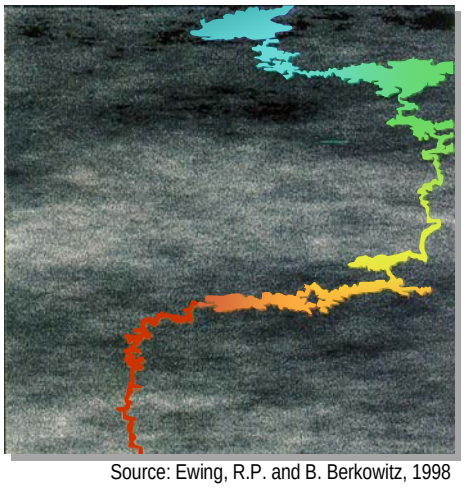
Determine:

- DNAPL distribution (architecture), if possible
- DNAPL characteristics for remediation (density, viscosity, composition . . .)
- DNAPL mobility and age
- Risks associated with DNAPL
- Aqueous plume characteristics (stable or expanding . . .)
- Remediation effects

DNAPL Characterization Challenges

- Limited information about sources/releases
- Complex migration patterns
- Small volumes, which can create persistent dissolved plumes, are difficult to delineate

  "needle in haystack" problem
- Risk of mobilization by intrusive characterization activities
- Composition and physical properties can change with age



Source: Ewing, R.P. and B. Berkowitz, 1998
Reproduced by permission of AGU

General Characterization Strategy

- What are the key decision processes for determining which characterization approach to implement?
- What are the metrics most commonly used in the field to assess effectiveness of the characterization process?
- What are the data gaps/needs for more effective source zone characterization?

DNAPL Characterization Key Decision Processes

- Health & Safety
- Don't make matters worse
- Define risks
- Determine remedial approach
- Meet regulatory requirements
- Resources
- Schedule
- Budget

DNAPL Characterization … Effectiveness Metrics

- It's a Boolean set.. not a set of linear measures
- General requirements
  - Quantify risk to within plus or minus one order of magnitude using EPA guidance
  - Provide sufficient data to evaluate remedial alternatives
- Minimum criteria
  - Define extent of subsurface where DNAPL is potentially present
  - Estimate of DNAPL mass, composition and physical properties
  - Qualitative description of distribution of DNAPL
    - Free, residual
    - Relationship to geologic characteristics
    - Trapping features
  - Characterize fate and transport in aqueous plume

DNAPL Characterization … Data Gaps/Needs

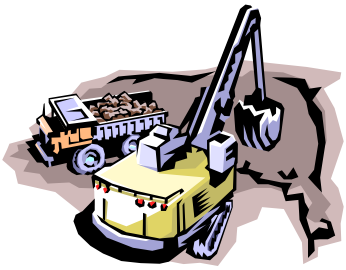
- Mass in Place estimation
- Quantification techniques for pool and ganglia volumes
- Field methods to estimate statistical measures of hydrologic properties of geologic media
- Flux method comparative assessment
- Field methods that can be up scaled to large sources and applied in deeper and consolidated media

Noninvasive Tools for DNAPL Characterization

- Site history information (e.g., chemical use, inventory and disposal records)
- Historical aerial photographs
- Geologic fractures/outcrops
- Soil gas analysis
- Surface geophysics
- Site infrastructure information (e.g., sewers)
- Employee/witness interviews

Invasive Tools for DNAPL Characterization

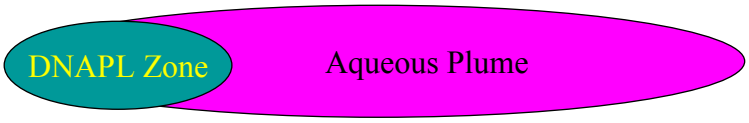
- **Test Pits**
- **Probing and Drilling**
- **Soil Examination Methods**
  - Organic vapor analysis (OVA)
  - Ultraviolet (UV) fluorescence
  - Hydrophobic dye shake test
  - Ribbon NAPL Sampler (RNS) core strip test
  - Chemical and partitioning analyses
- **Downhole Methods**
  - Membrane Interface Probe (MIP)
  - RNS (aka NAPL FLUTe)
  - Cone Penetrometer Technology (CPT)/Laser Induced Fluorescence (LIF)
- **Groundwater Quality Profiling using Direct Push (DP) and Multilevel Wells**
- **Well Measurements for NAPL Distribution**
- **Characterization of NAPL Samples**
- **Borehole Geophysics**
- **Partitioning Interwell Tracer Test (PITT)**
- **Flux Assessment**



DNAPL Characterization for Remediation

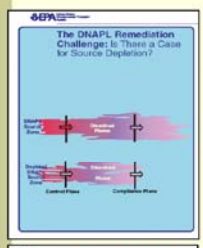
- Characterization efforts need to focus on traditional goals (e.g., nature and extent) and on remediation data needs (i.e. formulate goals and strategy early in process)
- Must locate DNAPL for removal/destruction; need to distinguish it from aqueous plume
- Must quantify DNAPL mass in place before and after remedy
- *In recent efforts, DNAPL characterization has focused on downgradient mass flux distributions; tools to characterize flux are emerging*
- DNAPL left after remediation is due to both incomplete characterization and remediation

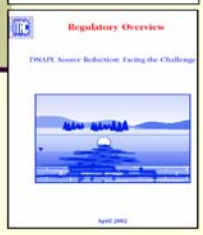
The Problem



- Alternative remedial strategies
  - Complete DNAPL removal/destruction to minimize aqueous plume effort
  - Aqueous plume treatment/containment with DNAPL left in place
  - Partial removal of DNAPL to facilitate aqueous plume remedy

EPA Expert Panel on DNAPL Remediation[1] (Dec. 2003)
&
ITRC DNAPL Source Remediation Report (April 2002)

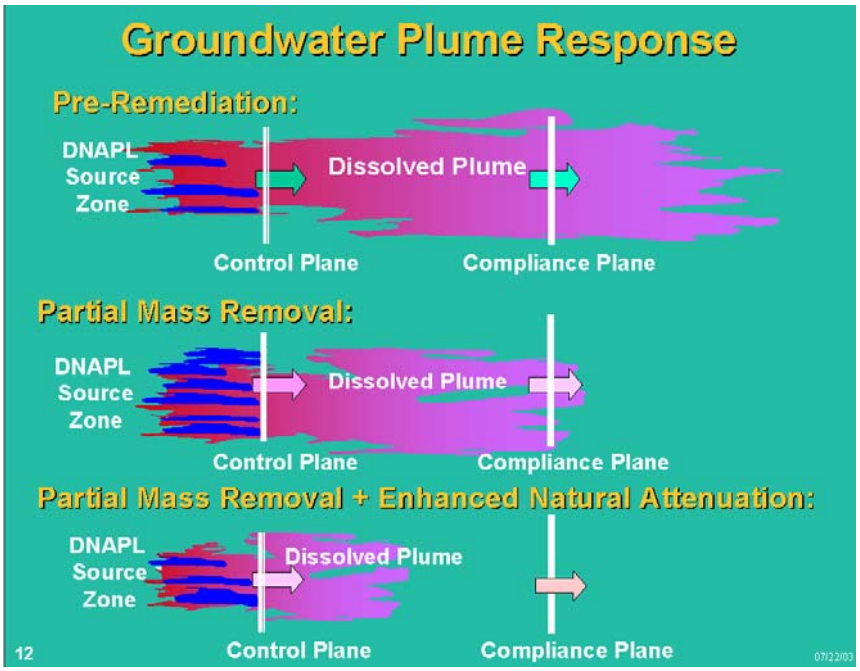




- *partial mass depletion from DNAPL source zones is likely to be a viable remediation strategy at certain sites*
- *DNAPL mass depletion in the source zone reduces contaminant mass discharge*
- *Contaminant mass discharge should be used as an alternate performance metric to assess benefits of source depletion*

[1] Kavanaugh M. and P.S.C. Rao (Eds) 2003

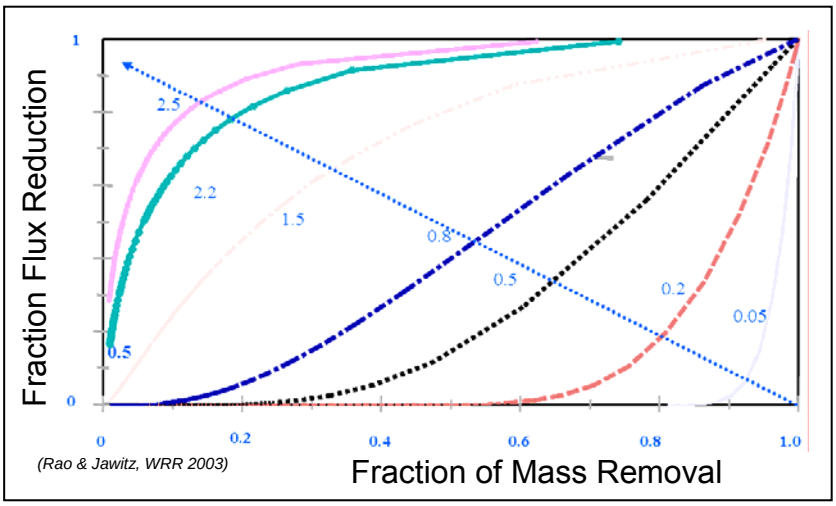
PURDUE



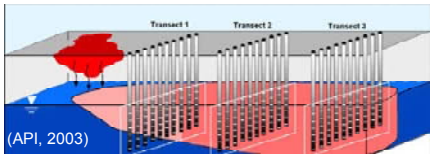
Analytical Model Results

(For a range of standard deviation σ)

(Arrow shows line in increasing heterogeneity)

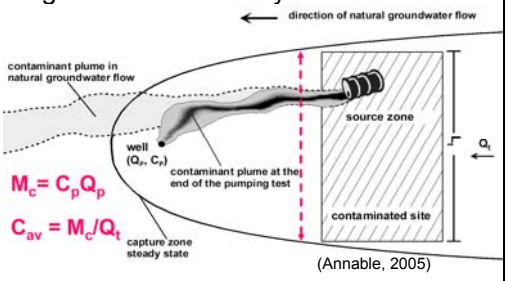


Methods to Measure Mass Flux



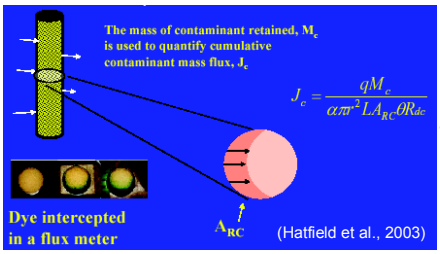
(API, 2003)

- Use water quality data from transects (multiple locations & depths) and groundwater velocity



(Annable, 2005)

- Use downgradient aquifer tests in a transect of wells (Bockelmann et al., 2001; Ptak & Teutsch, 2000)



(Hatfield et al., 2003)

- Use sorptive permeable media in downgradient wells to intercept contaminated groundwater & release resident tracers (Hatfield et al., 2001)

Limitations of Mass Flux Measurements

- Need to compare methods
- Scale of methods
  - Similar to issues comparing pump test, slug test, and lab values of hydraulic conductivity
- Uncertainty quantification
  - Assumptions
  - Data
    - Hydraulic conductivity
    - Hydraulic gradient
    - Spatial and temporal variability

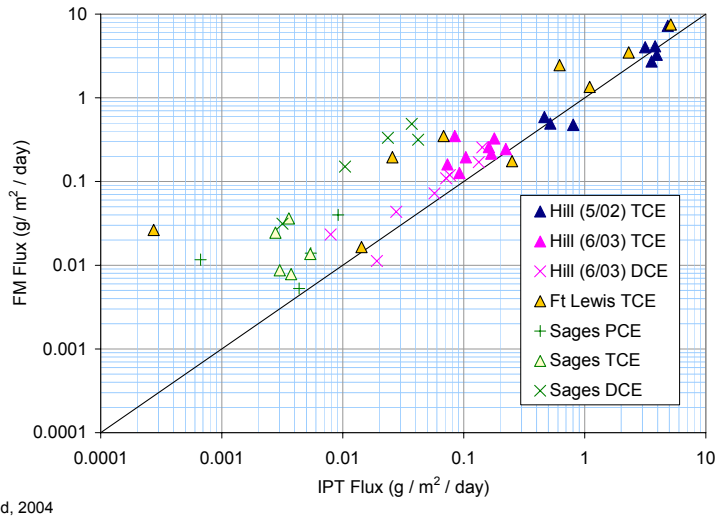
Flux Method Comparison … Summary

Sites	Darcy Velocity (cm/day)		Total Molar Discharge (moles/day)	
	PFM	IPT	PFM	IPT
Hill AFB	2.5	2.9	0.72	0.56
Borden	2.8-4.3	---	0.016	0.018
Sages	2.8	---	0.074	0.047
Ft. Lewis	27	23	6.3	6.5

Ft. Lewis
TCE Mass Discharge = 660 ± 110 g/day
DCE Mass Discharge = 130 ± 17 g/day

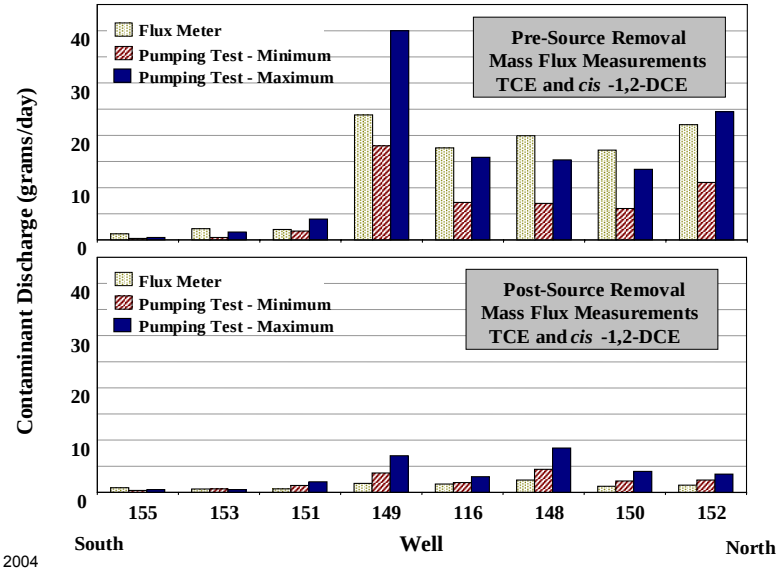
Wood and Jawitz, 2005

Flux Method Comparison … VOC Specific



Wood, 2004

Flux Method Comparison … Before and After Partial Mass Removal

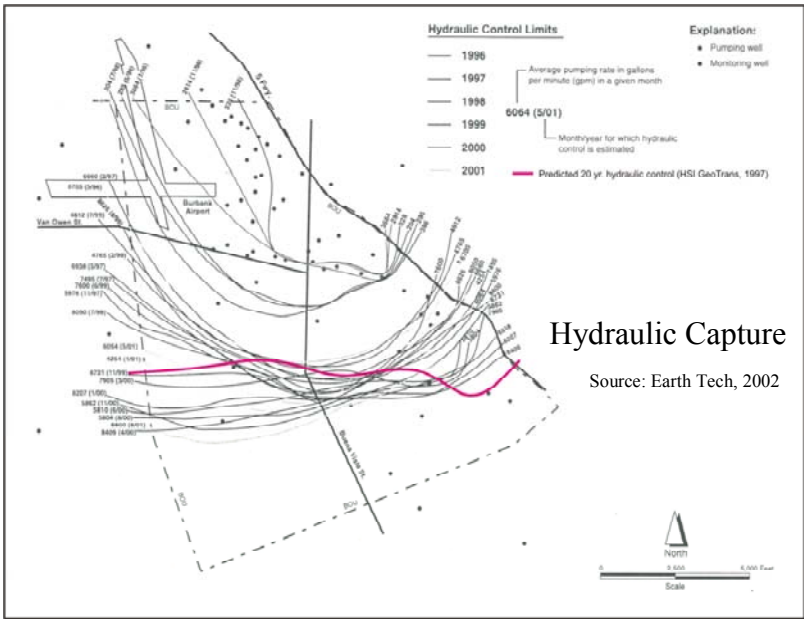


Wood, 2004

Flux Method Comparison

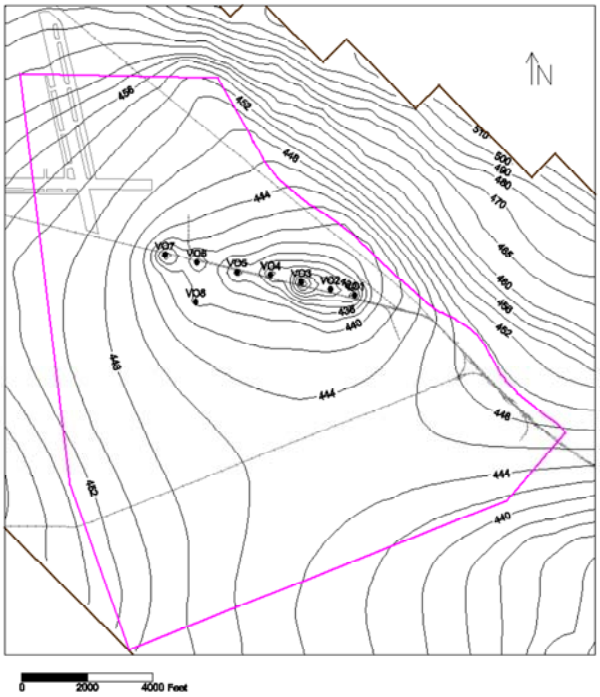
- More work needs to be done
- Differences should not be biased
- Relative flux reductions should be comparable
- Nonetheless, flux assessment and downgradient monitoring are important tools (if only relative) in assessing source reduction/containment

Mass Flux Case Study … Burbank Operable Unit, San Fernando Valley, CA



Hydraulic Capture

Source: Earth Tech, 2002



Mass Flux Case Study
Burbank Operable Unit,
San Fernando Valley, CA

Groundwater Model

Simulated Water Levels for the A Zone, 6000 gpm Total Pumping

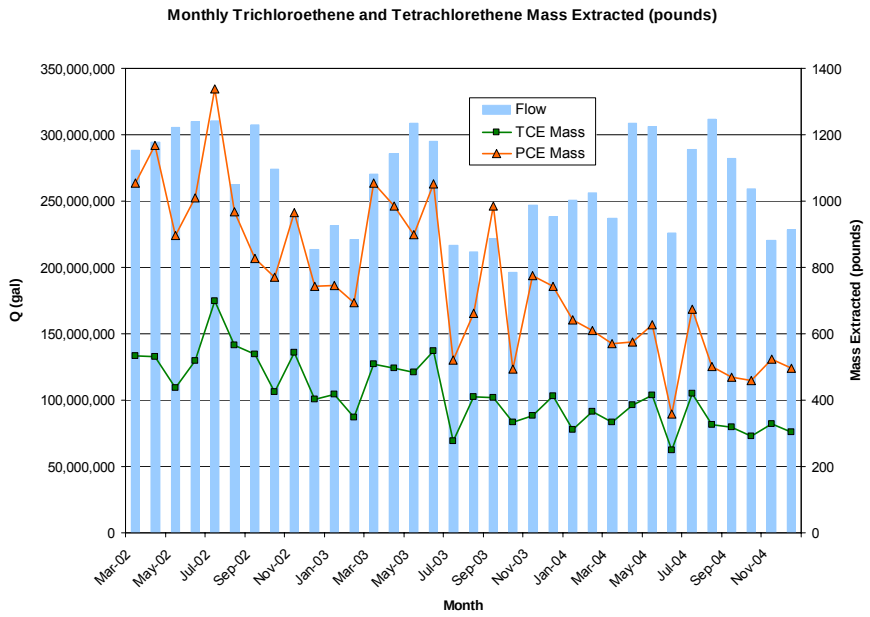
Legend

BOU boundary

Model grid boundary

Extraction well

Mass Flux Case Study … Burbank Operable Unit, San Fernando Valley, CA



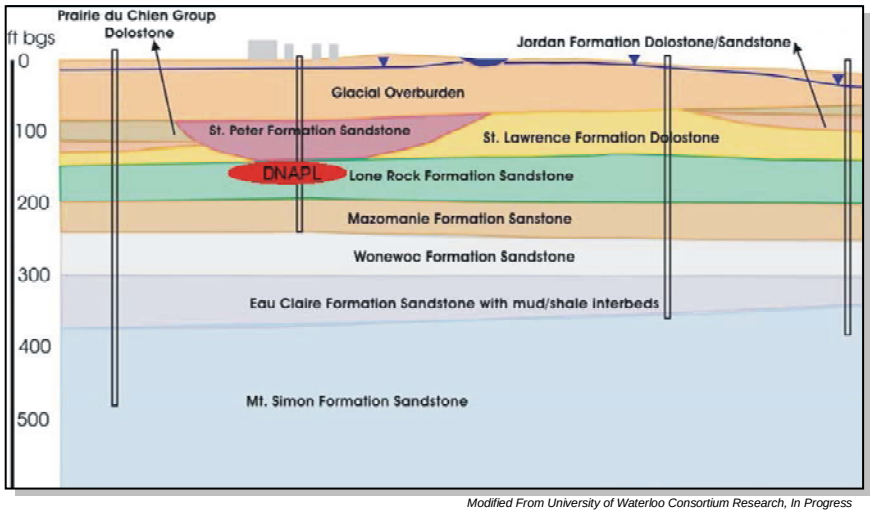
Mass Flux Case Study … Burbank Operable Unit, San Fernando Valley, CA

Average Mass Removal by Well
BOU Well Field Mar 02 – Dec 04

	Pumping (gal/month) or %	Mass Removed (pounds/month or %)				
		Total Cr	Nitrate	TCE	PCE	1,2,3 TCP
Well field	262,372,000	19	80,493	423	768	4.4
VO1	3.79%	9.12%	3.94%	3.16%	1.03%	0.04%
VO2	12.27%	23.00%	14.02%	24.95%	15.34%	0.82%
VO3	14.51%	19.26%	14.32%	20.21%	11.08%	0.42%
VO4	12.51%	12.42%	16.59%	19.58%	28.92%	2.34%
VO5	9.30%	10.01%	12.33%	11.78%	11.55%	5.85%
VO6	14.09%	8.79%	12.79%	7.77%	10.38%	77.94%
VO7	13.27%	6.79%	11.06%	6.77%	14.84%	11.90%
VO8	20.24%	10.61%	14.95%	5.78%	6.87%	0.69%

Adverse Impact, Case Study

Site Stratigraphy



Modified From University of Waterloo Consortium Research, In Progress

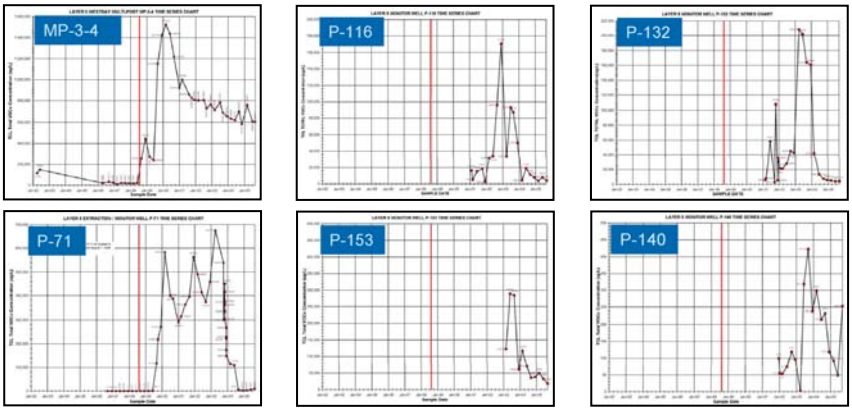
Adverse Impact, Case Study

DNAPL Investigation and Removal Procedure

- Rotosonic borehole drilled to top of Lone Rock Fm.
- Packer assembly installed and pumped (~1 gpm) at 10-foot intervals to identify DNAPL
- Recovery well installed
- Low-flow pumping used to remove DNAPL
- Pumping ceased when DNAPL was <2% of total liquid volume

Adverse Impact, Case Study

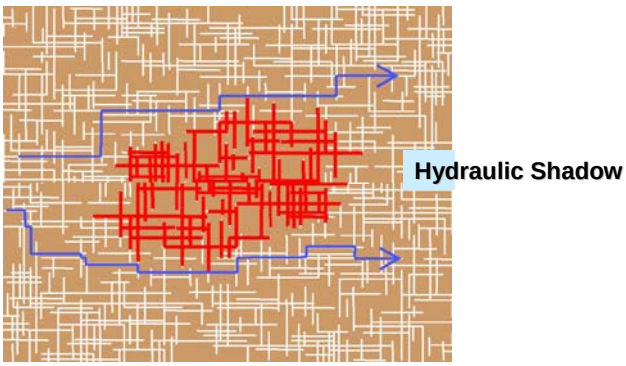
VOC Slug Moving Progressively Through Downgradient Monitoring Wells



Adverse Impact, Case Study

Conceptual Model Prior to DNAPL Removal

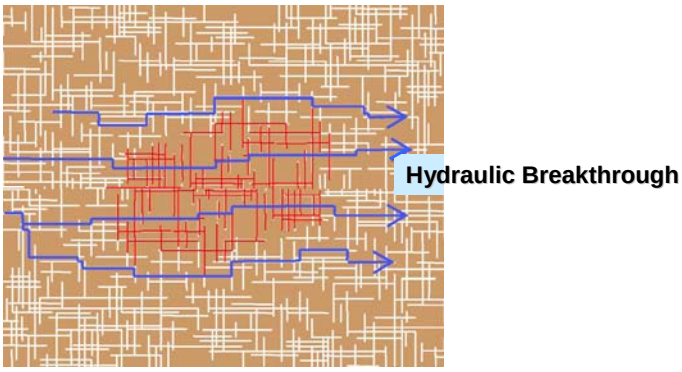
- DNAPL in rock fractures reduced fracture permeability
- Resulted in groundwater flow diversion around DNAPL zone
- Low DNAPL surface area contact with groundwater
- Minimized dissolution and contaminant mass transport



Adverse Impact, Case Study

Conceptual Model Following DNAPL Removal

- Increased DNAPL contact surface area and flow rate through source zone resulted in greater contaminant mass flux



Parting Thoughts

- DNAPL characterization techniques have advanced significantly over last 25 years
- Characterization still difficult and expensive
  - In particular for deep sources or consolidated media
- Partial source removal decision requires additional characterization
  - Mass in place
  - Downgradient flux
  - Distribution details (eg, ganglia to pool ratio)
- Monitor downgradient impacts
- Don't make matters worse

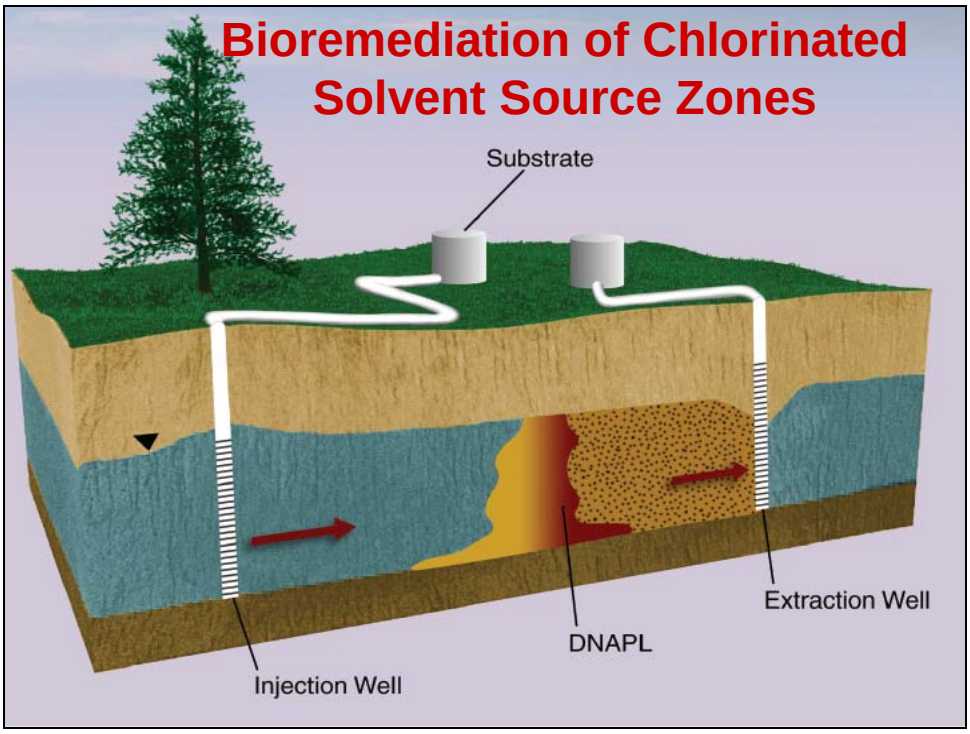
Biological Treatment Field Perspective

Hans Stroo, Ph.D.
HydroGeoLogic, Inc.

March 7, 2006

SERDP/ESTCP Workshop on Reducing the Uncertainty of DNAPL Source Zone Remediation

Baltimore, Maryland



Technology Background

- Innovative Technology – Rapidly Evolving
- Based on Enhancing Reductive Dechlorination
- Ability to Degrade Near-Solubility Conc. Recently Realized
- Used to increase flux, sequester, and/or degrade in place
- Three Proposed Mechanisms:
  - Increasing dissolution by degrading dissolved cmpds
  - Increasing solubility by partial degradation
  - Possibly increasing solubilization by “cosolvent” effects

Advantages

Possible complete destruction to innocuous products

Likely faster than baseline pump-and-treat

Less expensive than other remediation options

Can treat both dissolved and sorbed contaminants

Can move with the contaminant plume

Limitations

Residual toxic intermediates may accumulate

Some contaminants are resistant to biodegradation

Some contaminants are toxic to the microorganisms

May mobilize naturally occurring inorganics (As, Mn)

May reduce the effectiveness of natural bioattenuation

May cause biofouling of wells or clog the subsurface

Hydrogeology of a site may not be conducive to enhancing the microbial population

How Many Applications?

ESTIMATES - LITERATURE & VENDORS

Demonstrations:	**3**
Pilot-Scale Tests:	**30**
In Design Stage:	**10**
Full-Scale Cleanups:	**15**

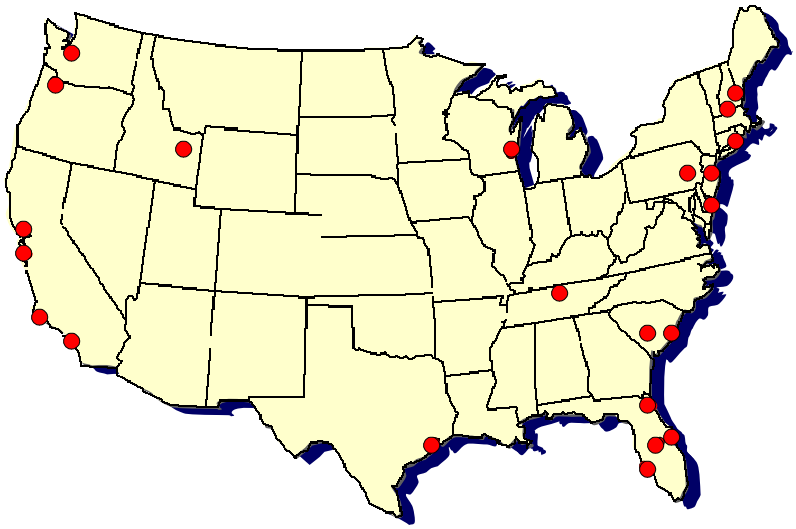
EVIDENCE OF RAPID ADOPTION

EPA (2003): "No Full-Scale Applications"

Navy (2004): 14 Pilot / 3 Full / 8 Uncertain

GSI (2005): 4 Pilot / 7 Full-Scale

SITES USING IN SITU BIOREMEDIATION TO TREAT DNAPL SOURCE ZONES



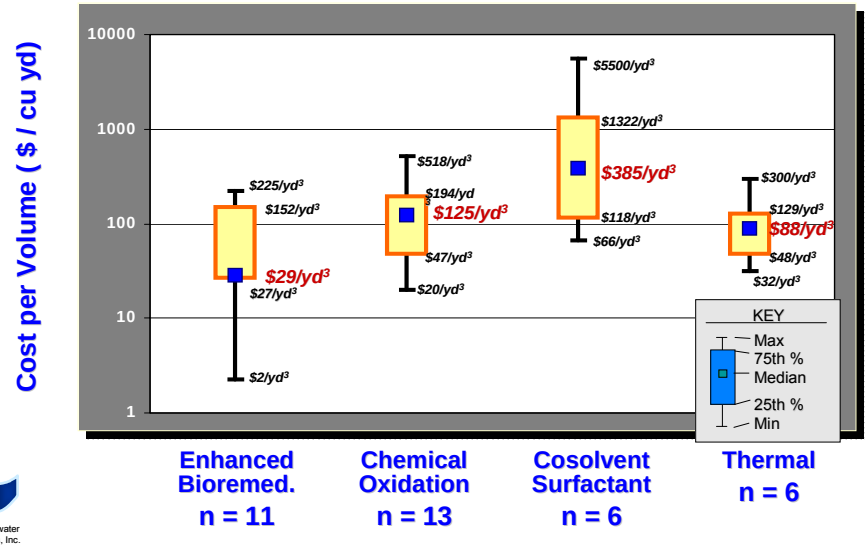
BioDNAPL Case Study Forum: Overview of Case Studies

Site	Scale	Cmax (ug/L)	Goal	Conditions	Operations	Results
Dover	Demo Test Cell	???	Flush + Contain	Fresh PCE Sandy 5-15' deep	Forced Recirc/ Bioaug./Lactate + Ethanol	**>50% removal (ca. 2 yr)** Complete Dechlorination
LC-34	Demo Test Plot	350,000	Remove Mass / Red. Flux	Older TCE Sandy, 0.75'/day 10-45' deep	Forced Recirc/ Bioaug. / Ethanol	Complete Dechlorination **99% Removal (ca. 1 yr)**
Arcadis	Demo Pilot 19K m^2	160,000	Remove Mass/ Red. Flux / Red. Costs	>20 yr PCE Silts/sand seams gw velocity? 5-30' deep	Forced Recirc/ 10% Molasses Every 8 weeks	Complete Dechlorination **Flushing of PCE (for 1 yr)** **Return to below baseline by year 3**
Oregon	Full-Scale 1200 ft2	7,000	Contain + Red. flux	Old PCE / Silty, 0.3'/day 4-12' deep	HRC injection	**99.9% Decrease in PCE Conc.** c-DCE Accumulation Low Ethene, 3 –Yr control
TAN-INEEL	Pilot - Full	ca. 500	Flush + Red. Size	Old Sludge Injection / Fract. basalt 210-300' deep	Injection of 30 to 60% Lactate (pilot) / whey powder (full)	Complete Dechlorination **Rapid Conc. Increases** **Plume Shrinkage** Some flux continues
TAMP	Pilo t	2,000	Reduce Conc. in Source	Aged TCE / Silt-Sand, 0.5'/day 7-20' deep	EOS Injection Temporary Recirculation	Complete Dechlorination **80-90% Conc. Decrease over 1 yr**

Other Reported Results

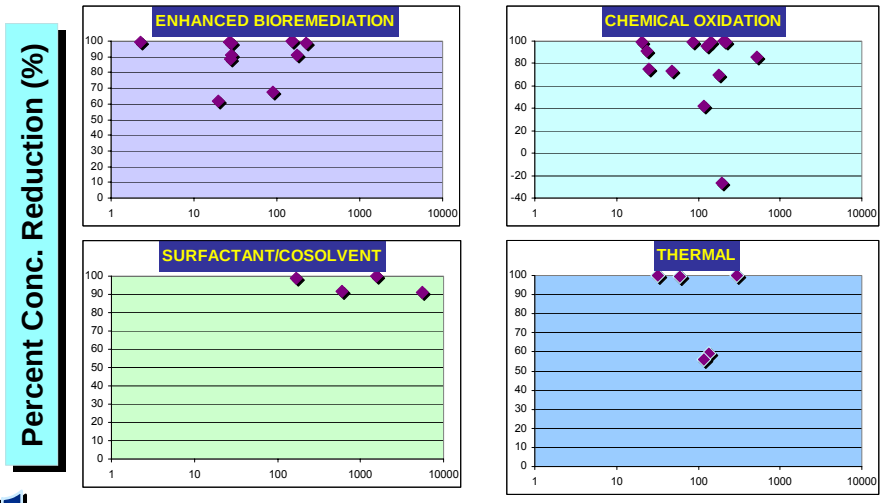
- **Treasure Island (22,500 ft^2):**
  - 20 mg/L PCE to below MCL
- **Field Pilot Test:**
  - 450 mg/L TCE to 7 mg/L VC in 22 weeks – One well
- **Hanscom AFB (ESTCP Demonstration):**
  - 97-99% Decreases in TCE, DCE, and VC Concentrations in Groundwater

ISB is Economically Attractive



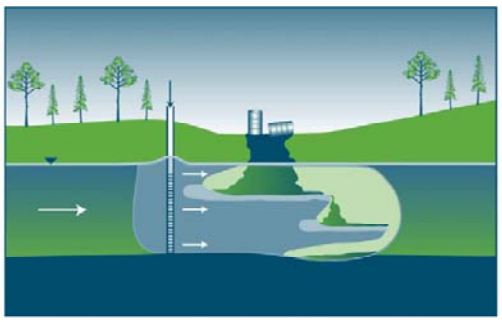
Groundwater Services, Inc.

Cost Evaluation – Performance vs. Cost



Groundwater Services, Inc.

Overview of In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones



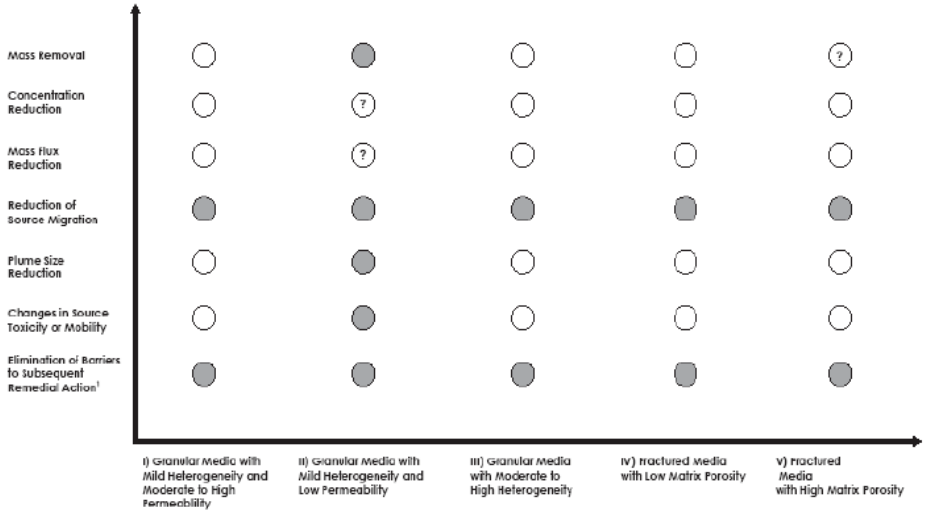
http://www.itrcweb.org/Documents/BioDNAPL-1.pdf

October 2005

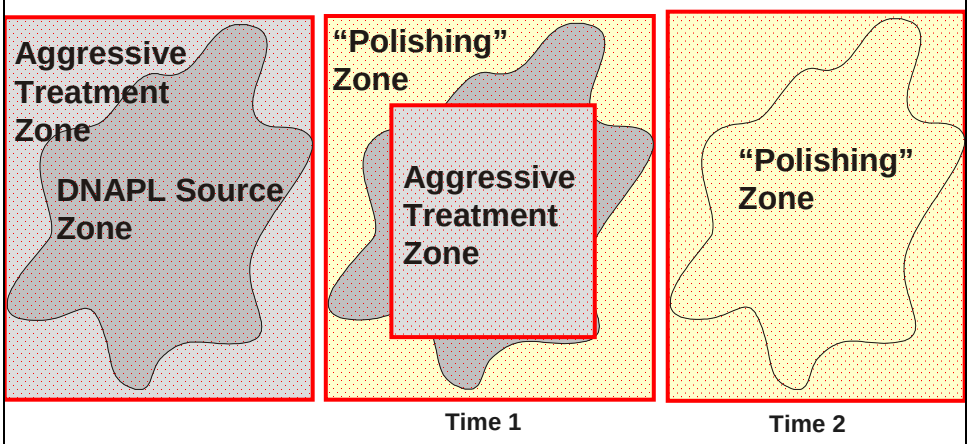
Prepared by
The Interstate Technology & Regulatory Council
Bioremediation of DNAPLs Team

Bioremediation:

"You Can't Always Get What You Want"



Bioremediation May Be Part of A Combined Treatment Strategy



Courtesy: Kent Sorenson

Data Needs

- Site conditions conducive to ISB?
- Conditions favoring different e^- donors?
- Achievable functional remedial objectives?
- Compatibility with other technologies?
- How much enhancement of dissolution can be achieved under field conditions?
- Ability to treat high-strength sources?
- Adverse Side Effects?
  (Gas Blockage/Secondary Water Quality)
- Can We Target DNAPL? (Partitioning Donors)

Key Decision Factors for Selecting and Implementing

- Available Time
- Accessibility of Contaminants
- Donors to Use
- Ability to control key environmental factors

Common Performance Metrics

- Dissolved Concentrations in Wells Within Or Immediately Down Gradient of the Source Zone (Real World)
- Flux (R&D Only)
- Mass Removal / Soil Cores (No Cases Found)

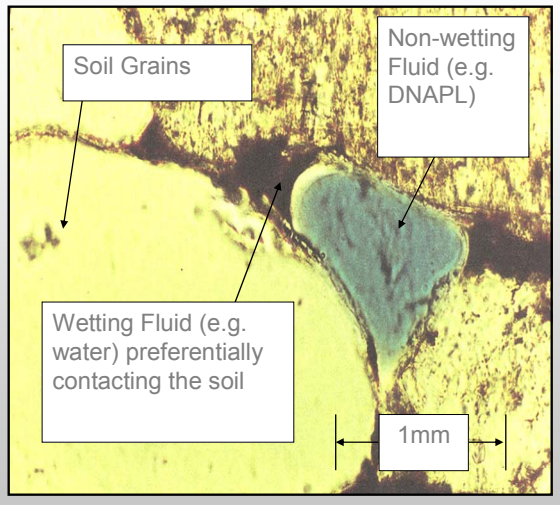
Surfactants

Status after 18 years of field studies

Tom Sale
Colorado State University

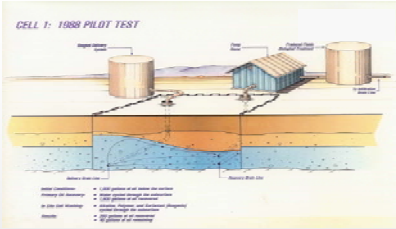
Presented to SERDP/ESTCP
DNAPL Workshop
Baltimore
March 7, 2006

Depletion of Entrapped NAPL



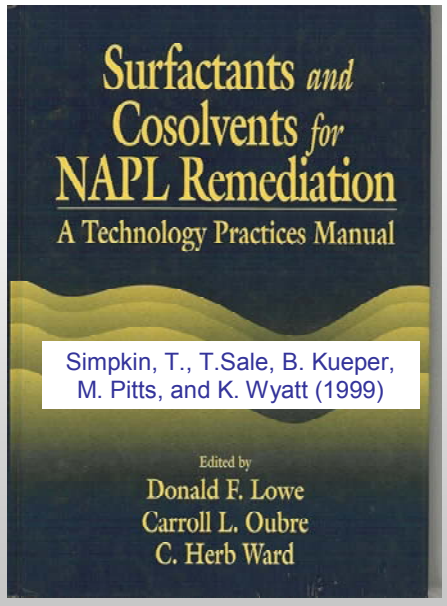
(From Wilson et al., (1990)

1. Chemical addition to enhance NAPL mobility and/or solubility
2. Beneficial reduction in site care requirements
   - Stand alone
   - Treatment train



1988 - Small Demonstration – 260 gallons post water-flood

1989 Main Pilot – 23,000 gallons post water-flood



Simpkin, T., T.Sale, B. Kueper, M. Pitts, and K. Wyatt (1999)

Status

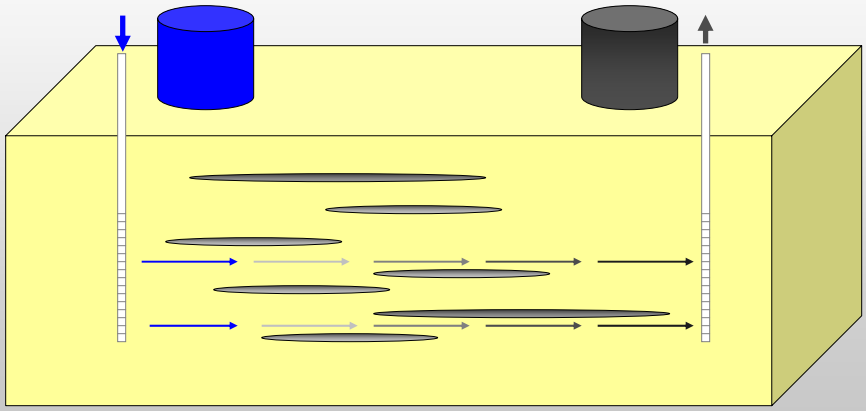
- 18 Years of field evaluations
- $100,000,000 Invested
- One? Full-Scale Application

- What does it all mean?

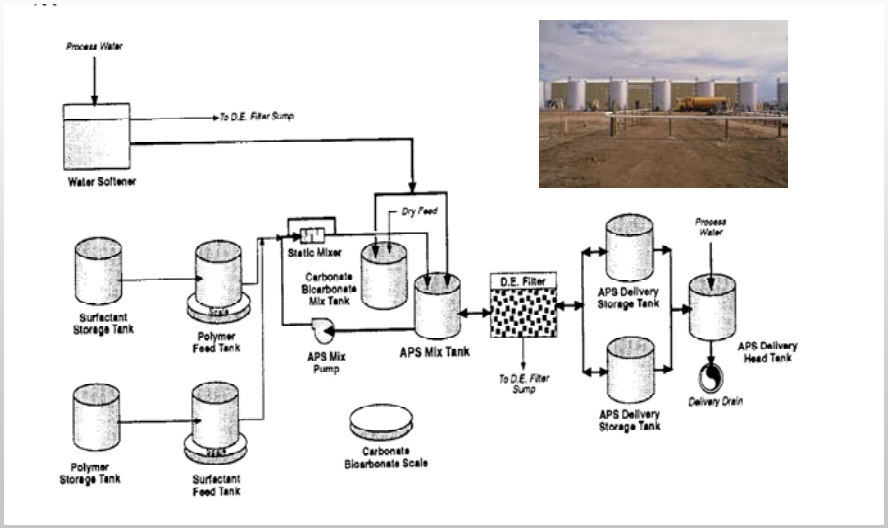
Presentation

- Process
- Performance
- Cost
- Constraints

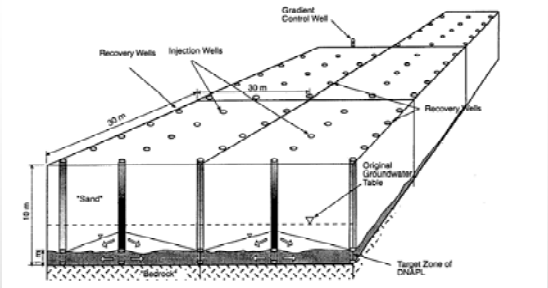
Process - Chemical Flushing

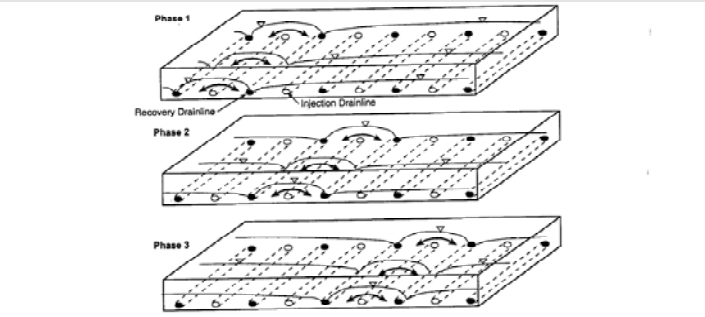


Process - Solution Generation

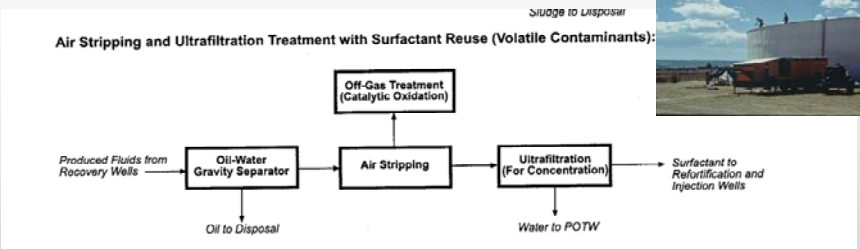


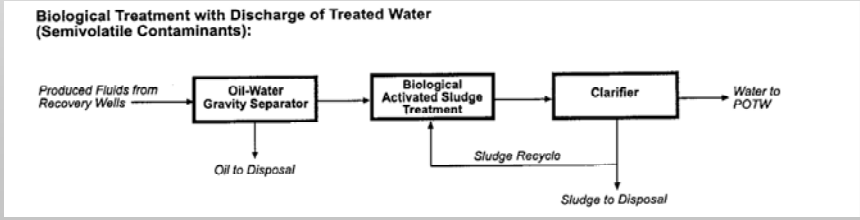
Solution Delivery– Recovery Systems





Process - Management of Produced Fluids





Performance and Cost - Key References

Simpkin T., T.C. Sale, B.H. Kueper M. Pitts, and K. Wyatt. (1999), **Surfactants and Cosolvents for NAPL Remediation: A Technology Practices Manual**, AATDF Editors. Lowe, D.F., K., Oubre, C.L., Ward, C.H., Lewis Publishers.

Naval Facilities Engineering Service Center (NFESC). 2002. **Surfactant-Enhanced Aquifer Remediation (SEAR) Design Manual**. NFESC Technical Report TR-2206-ENV. Battelle and Duke Engineering and Services.

NRC (2005), **Contaminants in the Subsurface: Source Zone Assessment and Remediation**, National Academy Press, Washington, D.C.

Fountain, J.C, , L. Abriola, L. Alvarez-Cohen, M. Baedecker, D. Ellis, T. Harmon, N . Hyaden, P. Kitanidis, J. Mintz, J. Phalean, G. Pope, D. Sabatini, T. Sale, B. Sleep, J. Wilson, J. Young, K. Yuracko

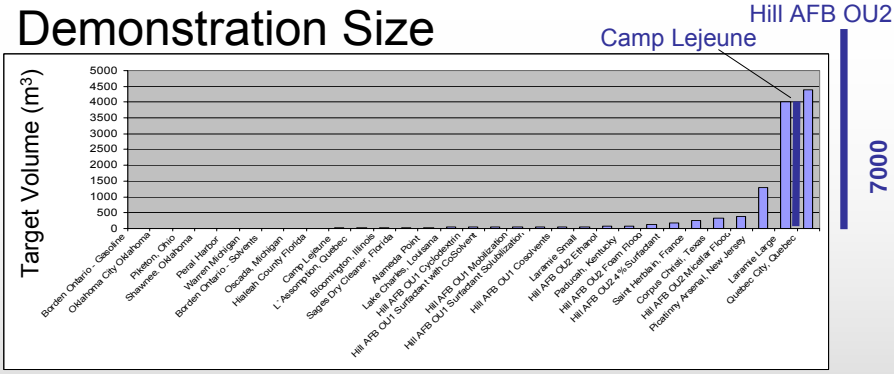
Performance and Cost - Demonstrations

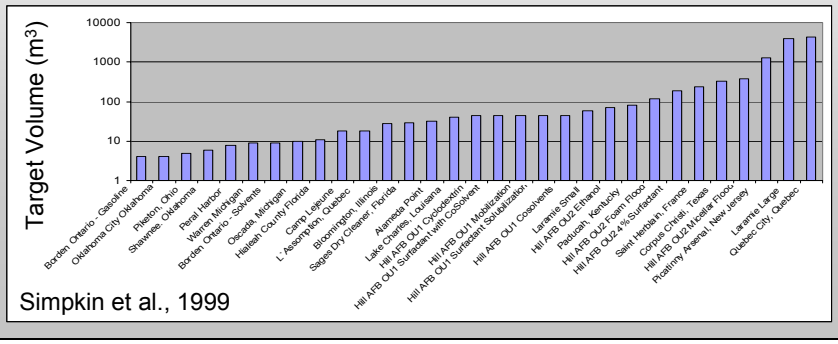
Project	*Field Completion Date*
Laramie, Wyoming—Small-Scale Field Demonstration	9/88
Warren, Michigan	7/89
Laramie, Wyoming—Large-Scale Field Demonstration	12/89
Hialeah County, Florida	2/90
Canadian Forces Base, Borden, Ontario—3-Meter Cell—PCE	11/90
Fredricksburg, Virginia	12/90
Corpus Christi, Texas	2/93
Paducah, Kentucky	8/94
Quebec City, Quebec	10/94
L'Assomption, Quebec	12/94
Commercial Site, New Jersey	1/95
Delmont Station, Pennsylvania	1/95
Hill AFB, Utah—Ethanol OU 1	8/95
Traverse City, Michigan	8/95
Picatinny Arsenal, New Jersey	8/95
Canadian Forces Base Borden, Ontario—Gasoline	12/95
Saint Herblain, France	1/96
Hill AFB, Utah—Surfactant with Cosolvent OU 1, Cell No. 8	8/96
Hill AFB, Utah—Complexing Sugar OU 1, Cell No. 4	8/96
Hill AFB, Utah—Surfactant Mobilization, OU 1, Cell No. 6	8/96
Hill AFB, Utah—Surfactant Solubilization, OU 1, Cell No. 5	8/96
Hill AFB, Utah—OU 1, Cell No. 3	9/96
Hill AFB, Utah—OU 2, Micellar Flood	9/96
Shawnee, Oklahoma	9/96
Piketon, Ohio	10/96
Lake Charles, Louisiana	3/97
Hill AFB, Utah—OU 2 Foam Flood	5/97
Canadian Forces Base Borden, Ontario—0.76 m Cylinder—PCE	9/97
Oklahoma City, Oklahoma	10/97

29 Sites

Simpkin et al., 1999

Demonstration Size





Simpkin et al., 1999

Performance

- Contaminant mass remaining in soil
- Fractional reduction of initial contaminant mass
- Concentrations in groundwater
- Flushing chemicals remaining in ground
- Redox state of the target

Estimated Mass Depletion and Soil Endpoints

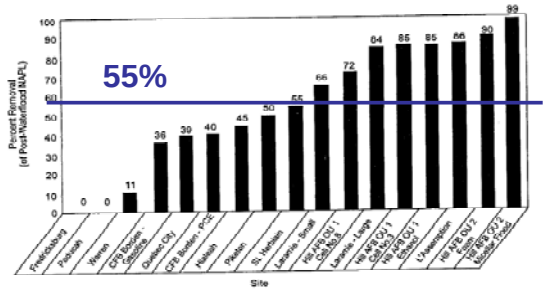


Figure 2.3. Summary of NAPL removals observed in field demonstrations.

TABLE 2.3. ACHIEVED ENDPOINT SOILS CONCENTRATIONS

Project	Soil Concentrations
Laramie, Wyoming–Small-Scale Field Demonstration	Average 5,100 mg/kg
Laramie, Wyoming–Large-Scale Field Demonstration	Average 4,000 mg/kg Range 300 to 11,000 mg/kg
Quebec City, Quebec	Average 19,000 mg/kg
L'Assomption, Quebec	Average 4,500 mg/kg Range 10 to 10,000 mg/kg
Hill AFB, Utah: OU 2 Foam	Average 2,800 mg/kg Range 100 to 31,000 mg/kg
Hill AFB, Utah: OU 1 Ethanol	Average ~ 100 mg/kg[a]
Hill AFB, Utah: OU 1 Cosolvents, Cell No. 3	Average ~ 1,000 mg/kg[a]
Hill AFB, Utah: OU 1 Surfactant Mobilization, Cell No. 6	Average ~ 100 mg/kg[a]
Hill AFB, Utah: OU 1 Surfactant Solubilization, Cell No. 5	Average ~ 1,000 mg/kg[a]
Hill AFB, Utah: OU 1 Surfactant with Cosolvent, Cell No. 8	Average ~ 100 mg/kg[a]

5,000 mg/kg

[a] Total concentrations were estimated using measurements of select analytes in soil and their overall mass fraction in the NAPL.

Simpkin et al., 1999

NRC, 2005 – Well Designed Field Tests

TABLE 5-2 Summary of Well-Designed Field Tests of Surfactant and Cosolvent Flooding

198

Year	Location/Additive	Geology	NAPL	Swept Pore Volume (m^3)	Reduction in NAPL Mass (%)	Post-NAPL Saturation (%)	Reference
1991	Borden, Ontario 14 PV, 2% Surf.	Sand	PCE	9.1	77	0.2	Fountain et al., 1996
1994	L'Assomption, Quebec 0.9 PV, Surf./Alcohol/Solvent	Sandy Gravel	DNAPL	6.1	86	0.45	Martel et al., 1998
1995	Hill AFB, UT, OU1 9 PV, 82% Alcohol	Sandy Gravel	LNAPL[a]	4.5	85	0.9	Rao et al., 1997
1996	Hill AFB, UT, OU1 9.5 PV, 3% Surf. / 2.5% Alcohol	Sandy Gravel	LNAPL[a]	4.5	78	0.8	Jawitz et al., 1998
1996	Hill AFB, UT, OU1 6.5 PV, 4.3% Surf.	Sandy Gravel	LNAPL[a]	4.5	86	0.4	Knox et al., 1999
1996	Hill AFB, UT, OU2 2.4 PV, 8% Surf.	Sand	DNAPL	57	99	0.03	Brown et al., 1999
1996	Hill AFB, UT, OU1 4 PV, 95% Alcohol	Sandy Gravel	LNAPL[a]	4.5	80	0.4	Falta et al., 1999
1997	Hill AFB, UT, OU2 4% Surf. & Foam	Sand	DNAPL	31	90	0.03	Szafranski et al., 1998
1999	Camp Lejeune, NC 5 PV, 4% Surf.	Silt	PCE	18	72	0.5	Holzmer etal., 2000
1999	Alameda Point, CA 6 PV, 7% Surf.	Sand	DNAPL	32	98	0.03	Hasegawa et al., 2000
1999	Pearl Harbor, HI 10 PV, 8% Surf.	Volcanic Tuff	Fuel Oil	7.5	86	0.35	Dwarakanath et al., 2000
2000	Hill AFB, UT, OU2 2.4 PV, 4% Surf.	Sand	DNAPL	188	94	0.07	Meinardus et al., 2002

NOTE: PV = pore volume; Surf = surfactant

[a]LNAPL means an LNAPL with sufficient DNAPL components present, such that in the ... e waste

85%

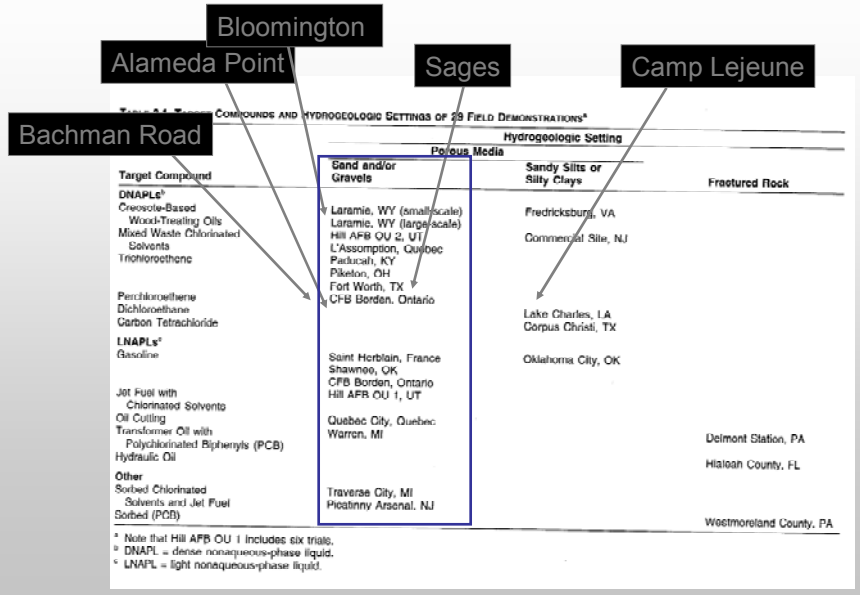
15%

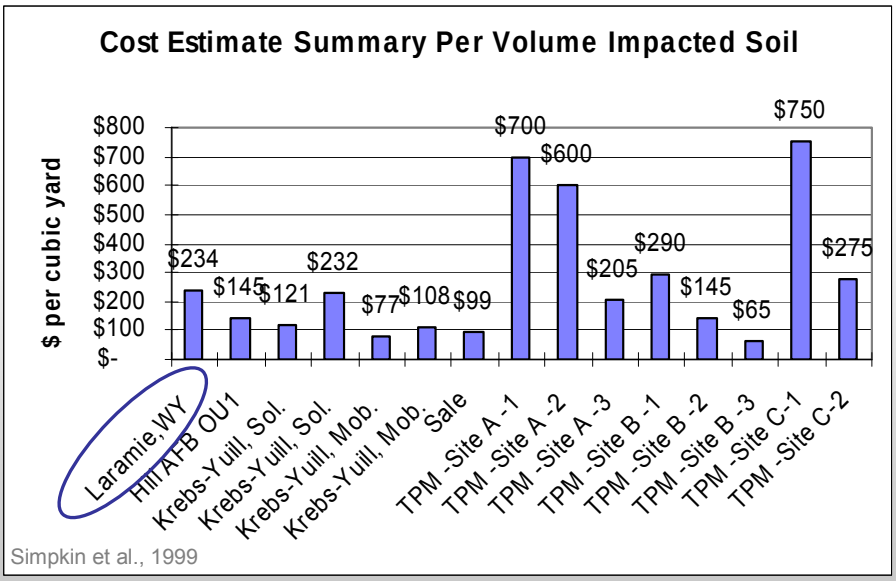
Additional Sites

Year	Site	NAPL	yd^3	Reference
1997	Sages Dry Cleaner Site, FL	PCE	30	Kavanaugh et al., (2003)
2000?	Bachman Road, MI	PCE	10	Kavanaugh et al., (2003)
2002?	Virginia Beach, VA, Cyclodextrin	TCA	Small	ESTCP CU-0113
2001?	Bloomington IL	MGP	30	Young et al. 2002

Total to date 37 sites

Technology Niche



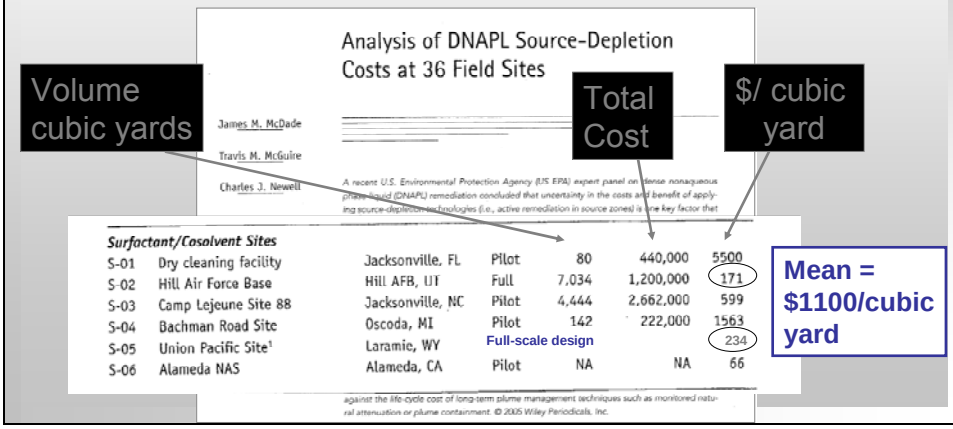


Mean = $270 / cubic yard Range = $77-750 / cubic yard

Other Cost Estimates

Camp Lejeune $500, and $165 /yd^3 ESTCP CU9714 C&P

Virginia Beach +$1000/ yd^3 ESTCP CU0113 C&P



Constraints to use

- Cost
- Mass Depletion
- Complexity
- Ambiguity as to benefits
- Perceived adverse impacts
- Scalability
- Competition from other technologies

Constraints to use – Perceived potential adverse impacts

Vertical Mobilization of DNAPL

Borings
Lower IFT

Adverse Impacts of Residual Flushing Solution

Mobilized contaminant
Competition for electron acceptors
Mobilization of metals (e.g. Arsenic)

Depletion of Financial Resources

Residual contamination - site care requirements may be unchanged

Constraints to use – Scalability

(10-acre hypothetical application)

Basis Calculations

Inputs Values refect Bloomington Site (Young et al., 2002)

$SurfactantFrac := 0.04$ $BuytlAlcoholFrac := 0.08$ $PolymerFrac := 0.0013$ $CaCl2Frac := 0.0008$

$PreflushPV := 10$ $TreatmentPV := 3$ $PostTreatmentPV := 10$

Site characteristics reflect TRS (2005)

$\phi := 0.25$ $K := 7 \cdot 10^{-3} \cdot \frac{cm}{sec}$ $TargetVolume := 440000 \cdot yd^3$ $\rho_w := 1 \cdot \frac{gm}{cm^3}$

Calculations

$PoreVolume := TargetVolume \cdot \phi$ $PoreVolume = 22 \times 10^6\ gal$

$WtSurfactant := TreatmentPV \cdot PoreVolume \cdot \rho_w \cdot SurfactantFrac$ $WtSurfactant = 11 \times 10^3\ ton$

$WtBuytlAlcohol := TreatmentPV \cdot PoreVolume \cdot \rho_w \cdot BuytlAlcoholFrac$ $WtBuytlAlcohol = 22 \times 10^3\ ton$

$WtPolymer := TreatmentPV \cdot PoreVolume \cdot \rho_w \cdot PolymerFrac$ $WtPolymer = 362\ ton$

$WtCaCl2 := TreatmentPV \cdot PoreVolume \cdot \rho_w \cdot CaCl2Frac$ $WtCaCl2 = 222\ ton$

$WtTotal := WtSurfactant + WtBuytlAlcohol \ldots + WtPolymer + WtCaCl2$ $WtTotal = 34 \times 10^3\ ton$

$ProducedFluidsVol := PoreVolume \cdot (TreatmentPV + PostTreatmentPV)$ $ProducedFluidsVol = 289 \times 10^6\ gal$

1mgd ~ Service for 10,000 people

It is not just DNAPL in Transmissive Zones - Significant source mass can reside in layers of low hydraulic conductivity

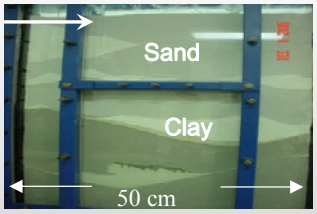


Figure 1.1: Setup - Sand and Clay

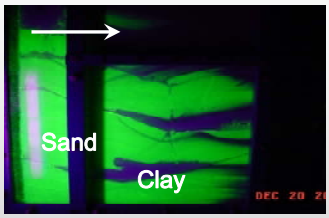


Figure 1.2: Fluorescein Inflow (Matrix Storage)

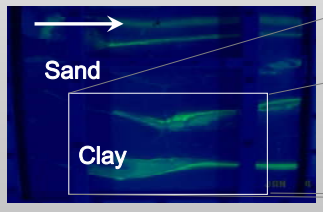


Figure 1.3: Source Off – Back Diffusion

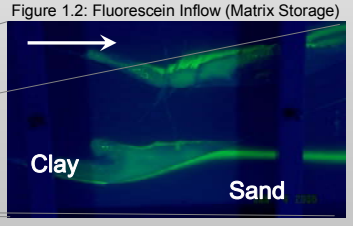
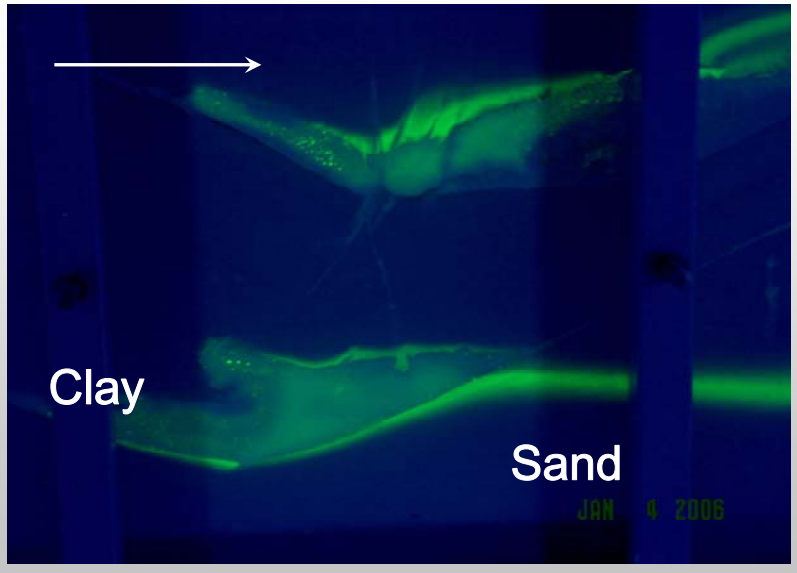


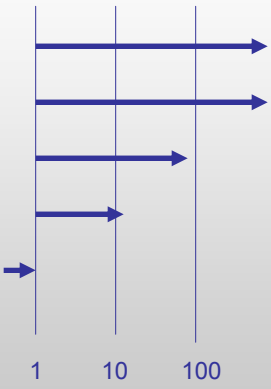
Figure 1.4: Close-up of Back Diffusion

Contaminant Storage and Release from Layers of Low Hydraulic Conductivity



Constraints to use - Other options

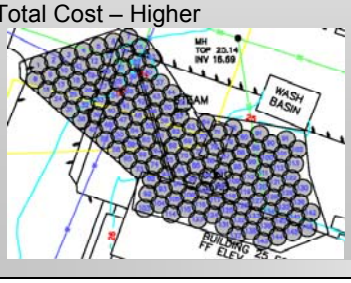
- Thermal
- *In Situ* Chemical Oxidation
- Biological Treatment
- *In Situ* Chemical Reduction
- Surfactant - Cosolvent



Other Options

ZVI-Clay -Admixing Iron and Clay

Construction Cost - $71/cubic yard
Total Cost – Higher



	Surfactant Flushing	ZVI-Clay
Cost	○	●
Mass depletion	○	●
Complexity	○	●
Ambiguity as to benefits	○	●
Perceived adverse impacts	○	●

Data Courtesy of CH2M HILL and the US Navy

What does it all mean?

- The market is expressing a preference for other technologies
- Shift from a petroleum like production paradigm to in situ destruction

  Why?

  No above ground treatment
  Less sensitivity to heterogeneity
  Treatment of more than DNAPL

- Treatment trains?

Use of ISCO and ISCR for DNAPL

In Situ Chemical Oxidation
In Situ Chemical Reduction

Richard A. Brown, Ph.D.

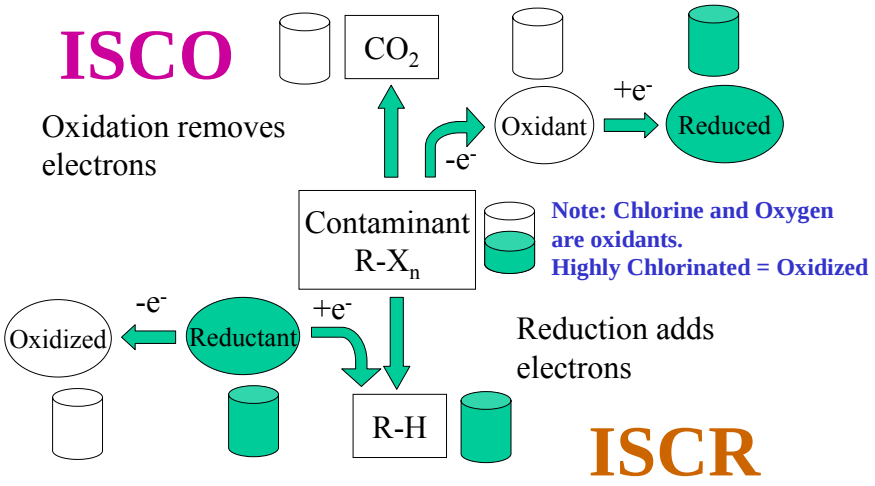
ERM.

In Situ Chemical Treatment

- Two keys to success
  - Does the reaction take place?
    - Competing reactions
  - Can the reagent contact the contaminant?
    - In sufficient quantity for sufficient time
    - The most critical part of the application

ERM.

Oxidation & Reduction Principles



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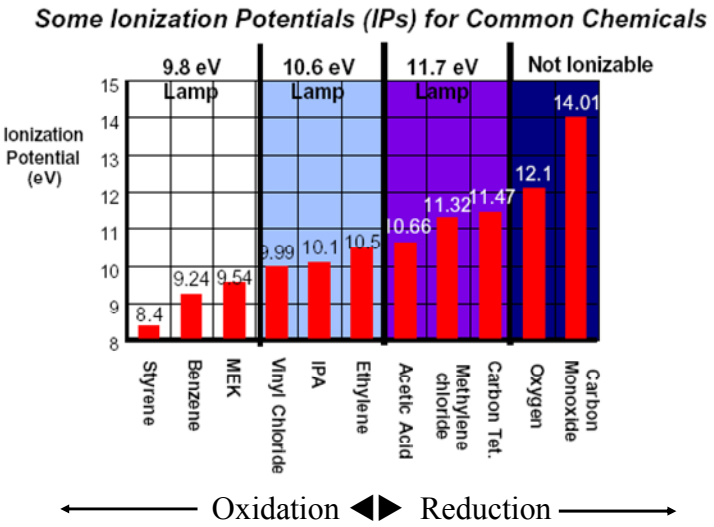
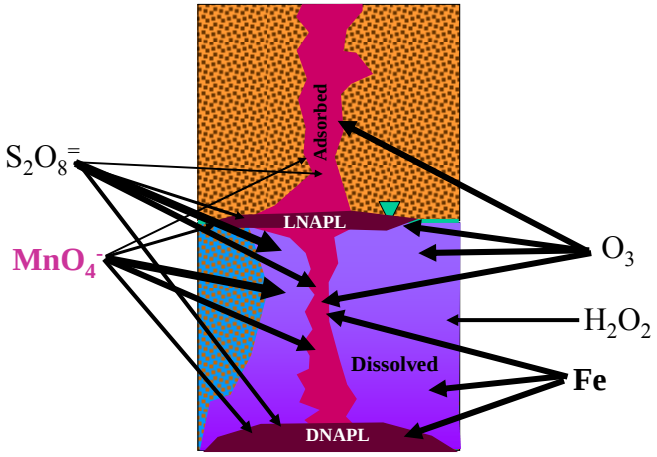


ERM.

Applicability of ISCO/ISCR



Available Oxidants for ISCO

- Hydrogen Peroxide
- Potassium Permanganate
- Sodium Permanganate
- Sodium Persulfate
- Ozone

Available Oxidants

- Ozone (no Activator)
  - $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ E_o 2.07v
  - Hydroxyl Radical
    - $O_3 + H_2O \rightarrow O_2 + 2OH^{\cdot}$
    - $2O_3 + 3H_2O_2 \rightarrow 4O_2 + 2OH^{\cdot} + 2H_2O$
    - $2OH^{\cdot} + 2H^+ + 2e^- \rightarrow 2H_2O$ E_o 2.76v
- Persulfates (Requires Activation)
  - $S_2O_8^{=} + 2e^- \rightarrow 2SO_4^{=}$ E_o 2.01v
  - $S_2O_8^{=} \rightarrow 2(SO_4^-)^{\cdot}$
  - $(SO_4^-)^{\cdot} + e^- \rightarrow \mathbf{SO_4^{=}}$ Eo 2.5v
- Hydrogen Peroxide (Requires Activation)
  - $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ E_o 1.77v
  - $H_2O_2 \rightarrow 2OH^{\cdot}$; $2OH^{\cdot} + 2H^+ + 2e^- \rightarrow 2H_2O$ E_o 2.76v

ERM.

Available Oxidants

- Permanganate (No Activator)
  - $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ E_o 1.695v
    - K^+, Na^+

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Properties of Oxidants

- Hydrogen peroxide
  - Clear solution
    - Miscible
  - 15, 30 & 50% solutions sold
    - 3-20% solutions used
  - Needs catalyst
- Potassium Permanganate
  - Purple crystalline solid
  - Soluble to 4-6%
    - Depends on temperature
  - Generally dissolved on site
- Sodium Permanganate
  - 40% Purple solution
  - Dense
- Sodium Persulfate
  - White crystalline solid
  - Soluble to 56%
  - Needs catalyst
    - Iron/heat
- Ozone
  - Gas generated on site
    - 3-5% from air
    - 5-10% from O_2

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Performance of Oxidants with CVOCs

Oxidant	Amenable CVOC's	Slow to React CVOCs	Recalcitrant CVOCs
Peroxide, Old Fenton's	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2	TCA, CT, $CHCl_3$
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2	TCA, CT, $CHCl_3$
Calcium Peroxide	PCE,TCE, DCE, VC, CB	TCA, CH_2Cl_2	CT, $CHCl_3$
Potassium Permanganate	PCE, TCE, DCE, VC,		TCA, CT, $CHCl_3$, DCA, CB, CH_2Cl_2
Sodium Permanganate	PCE, TCE, DCE, VC,		TCA, CT, $CHCl_3$, DCA, CB, CH_2Cl_2
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2, $CHCl_3$	TCA, CT
Sodium Persulfate, Heat	All CVOCs		
Ozone	PCE, TCE, DCE, VC,		TCA, CT, $CHCl_3$, DCA, CB, CH_2Cl_2

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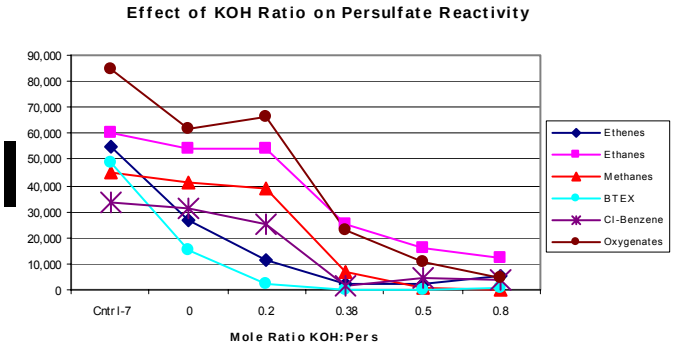
Advanced Persulfate Activation

- Chelated Iron
- Peroxide
- KOH
- Heat

Novel Persulfate Activation

Alkaline Activation

- **pH > 10**



Room temperature
Aqueous solutions
7 days
Analyzed by GC-MS

25 g/L sodium persulfate
KOH as pH modifier

Heated Persulfate

ug/L	45° C	
Analyte	**Control Ave.**	**Persulfate Ave.**
Chloromethane	<100	ND
1,1-Dichloroethene	6,731	ND
Methylene Chloride	16,506	ND
t-1,2-Dichloroethene	686	ND
1,1-Dichloroethane	15,684	ND
c-1,2-Dichloroethene	22,212	ND
Chloroform	17,094	ND
1,1,1-Trichloroethane	7,225	ND
1,2-Dichloroethane	38,010	ND
Benzene	11,084	ND
Carbon Tetrachloride	17,152	ND
Trichloroethene	7,500	ND
Toluene	9,321	ND
1,1,2-Trichloroethane	26,386	ND
Tetrachloroethene	3,036	ND
Chlorobenzene	10,868	ND
Ethylbenzene	8,716	ND
m,p-Xylene	4,519	ND
o-Xylene	1,749	ND
1,3-Dichlorobenzene	5,908	ND
1,2-Dichlorobenzene	13,241	ND
1,2,4-Trichlorobenzene	2,328	ND

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Oxidant Usage (& Cost!)

$[\text{Oxidant}]_{\text{Required}} =$

$[\text{Stoichiometric Demand}]_{\text{Contaminant}} +$

$[\text{Soil Oxidant Demand}] +$

$[\text{Metals}]_{\text{Red}}$

$[\text{Organic Carbon}]_{\text{Oxidizable}}$

$\mathbf{[Decomposition]_{Oxidant}}$

Decomposition and SOD are critical and often overlooked factors that drive the cost.

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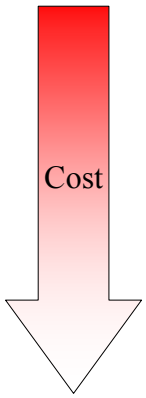
ISCR – In Situ Chemical Reduction

- Zero Valent Metals
  - Iron
  - Aluminum
  - Bi metals
- Reduced Iron
  - IRZM
- Bio-Iron

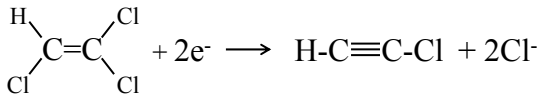
Evolution of ISCR

- Iron Walls/Funnel & Gate
- Iron-Sand Walls
- Hydraulic Fracturing with iron-sand
- Injectable iron
- Iron/Bio
- Reduced iron

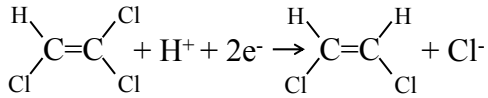


Zero Valent Iron

- Removal Processes ($Fe^{o} \rightarrow Fe^{+2} + 2e^{-}$)
  - ß-elimination:

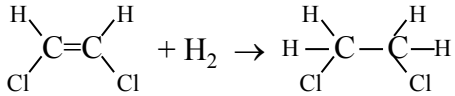


  - Hydrogenolysis



  - Hydrogenation

$Fe^{o} + H_2O \rightarrow H_2 + FeO$

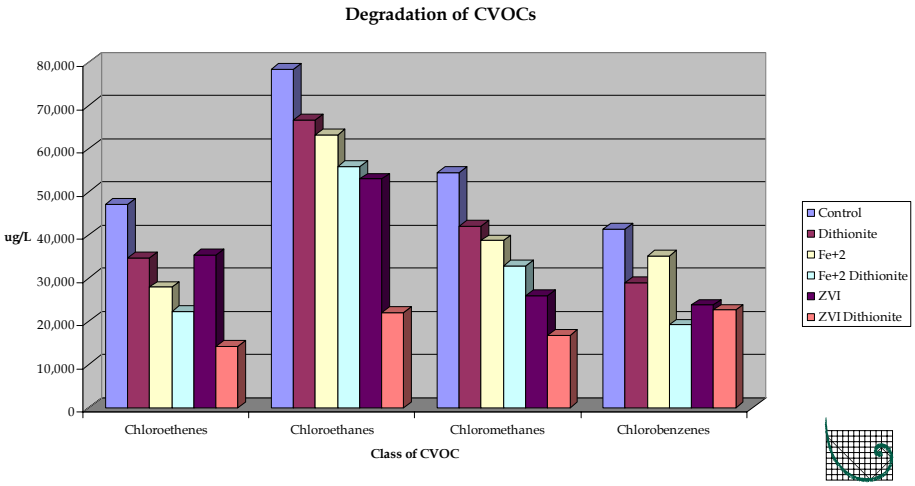


Injectable Iron

- Micro-Scale Iron
  - 1 to 5 µ
  - $15-50/Kg
- Nano-Scale Iron
  - 10 nM
  - $100-300/Kg

Iron II has many of the same Reactions as ZVI

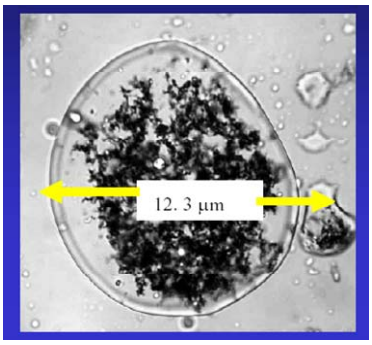
Reduced Iron Systems

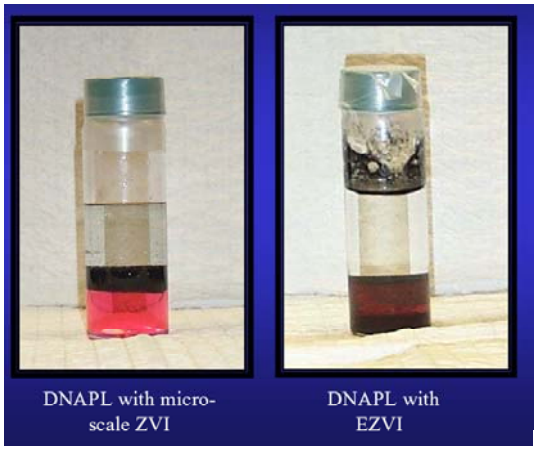


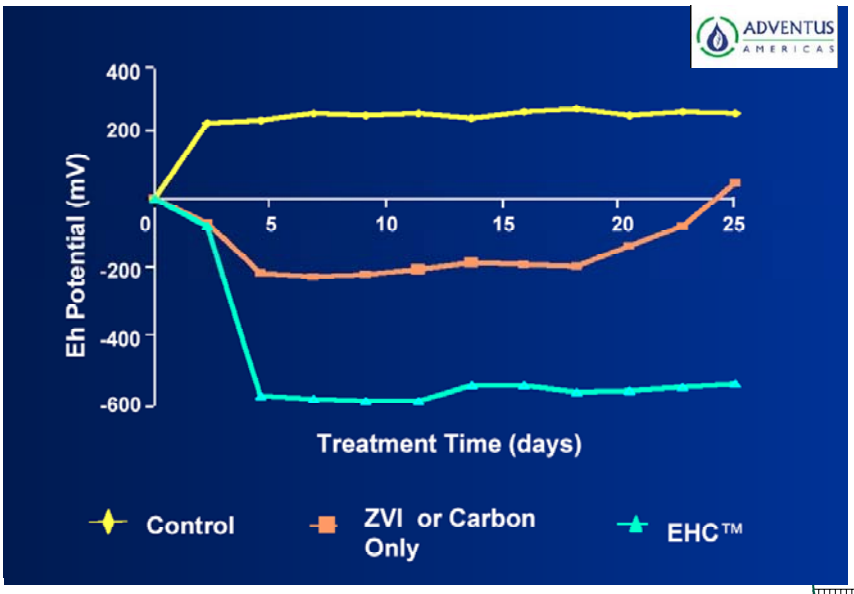
Bio-Iron Combinations

- EHC
- EZVI

EZVI







EHC

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Applications of ISCR

- Source Area
  - EHC, EZVI
  - Pneumatic/ZVI
  - Nano Scale
- Groundwater
  - PRBs
  - IRZM
  - Abiotic MNA

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Delivery is Key to ISCO/ISCR

- Conventional
  - Wells
  - Geoprobe
- Pneumatic Fracturing
- Hydraulic Fracturing
- Pressure Pulse

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The Key to ISCO(R) Performance:

Success is achieved when enough Oxidant/Reductant is in contact with the contaminant for a long enough period of time to react effectively

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Dosage/ Loading

Distribution

Success is *enough Agent* *in contact* with the contaminant for a *long enough period of time* to *react effectively*

Persistence

Contaminant Destruction

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Issues With DNAPL Chemical Treatment

- Does the DNAPL have to dissolve first?
  - Will oxidants react with DNAPL Liquid?
  - Is the crust impermeable?
- Will the oxidant penetrate the soil column to the DNAPL?
- Will the oxidant last long enough to react with DNAPL?
- Will Permanganate form a crust?
- Can Iron treat DNAPL?

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Soil Core Boring B-6, 21 to 23 ft bls

Courtesy of the IT Group

Answers??!!

- Does the DNAPL have to dissolve first?
  - Depends on NAPL saturation (residual vs recoverable)
  - Oxidants will react with DNAPL Liquid
  - Some promote dissolution
- Will the oxidant penetrate to the DNAPL?
  - Sodium permanganate and persulfate can be made into dense solutions
  - All will treat distributed residual NAPL
- Will the oxidant last long enough to react with DNAPL?
- Will Permanganate form a crust?
  - Is the crust impermeable?
- Can Iron treat DNAPL?

Permanganate "Crusting"

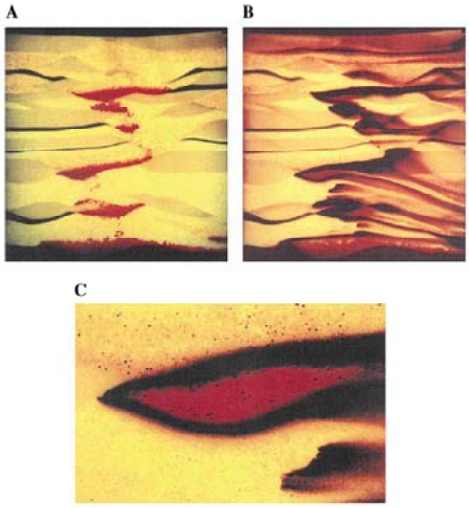

Fig. 9. Photographs from the potassium permanganate experiment: (A) a photograph showing the configuration of the TCE prior to the permanganate flood; (B) a photograph after the 1/3 pore volume slug of potassium permanganate solution had traversed the chamber (~1.2 pore volumes)—dark rinds around the pools are precipitated MnO_2; (C) a close-up photograph showing the MnO_2 rind surrounding pool #5.

S.H. Conrad et al. / Journal of Contaminant Hydrology 58 (2002) 13–49

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Answers??!!

- Will the oxidant last long enough to react with DNAPL?
  - Permanganate yes, Persulfate maybe, Peroxide no (current state-of-practice)
  - Ozone will but also strips NAPL
- Will Permanganate form a crust?
  - Permanganate forms a limited permeability crust
- Can Iron treat DNAPL?
  - If the proper size or in conjunction with carbon

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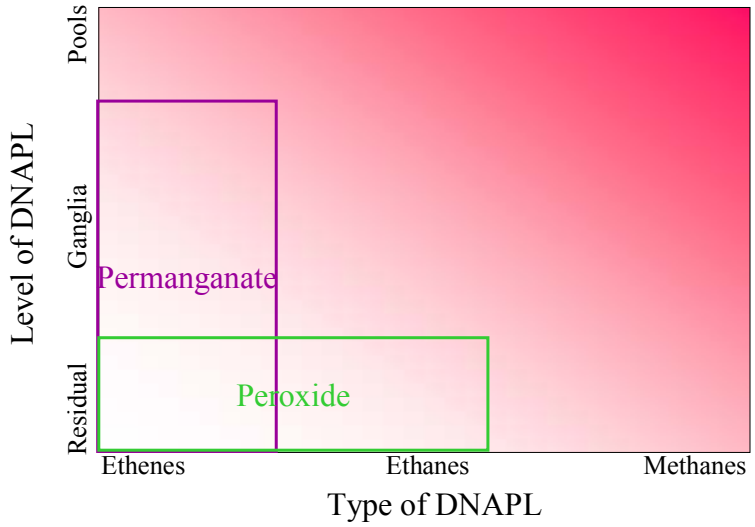
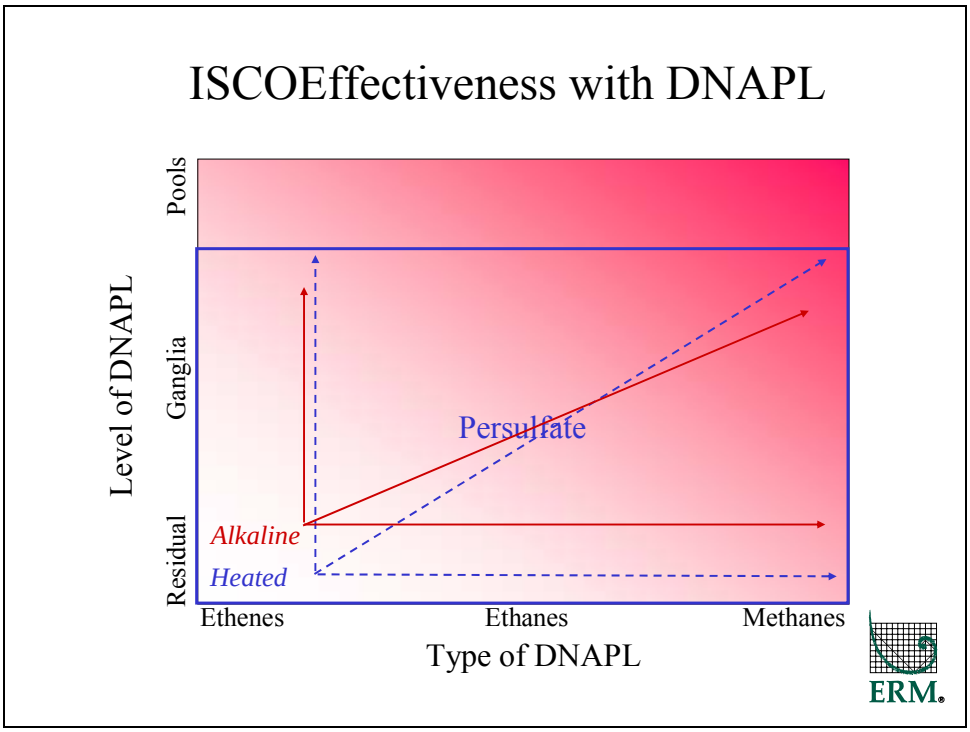
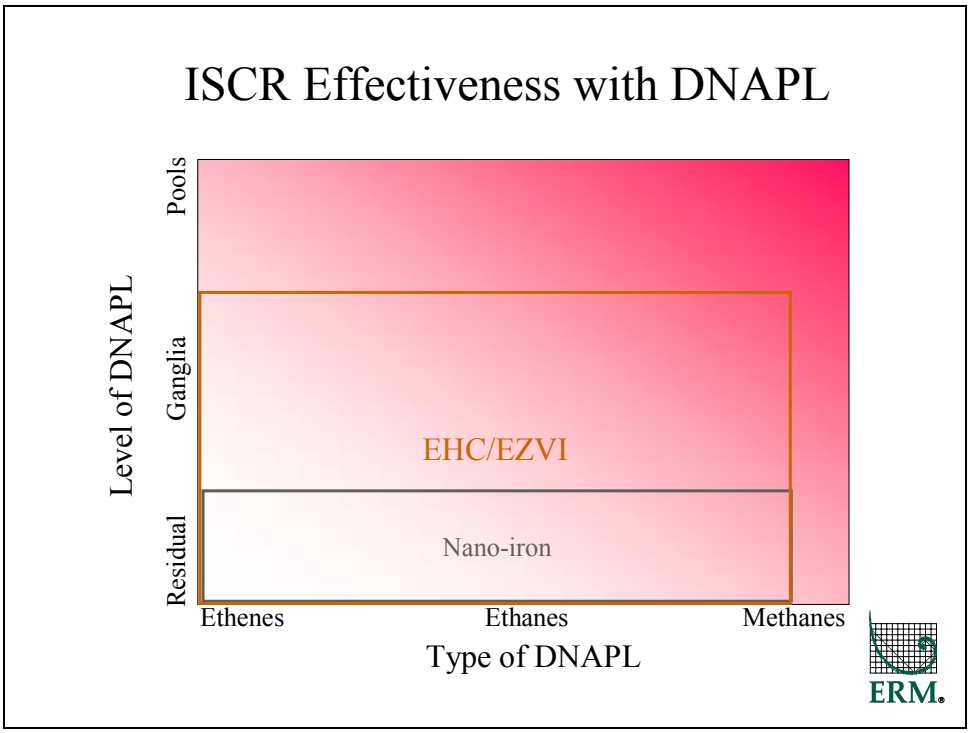
Questions on Usage/Applicability

- How much is the technology really used for DNAPL remediation and at what scale?
- What are the key decision processes for determining whether and how to implement the technology?
- What are the data gaps/needs for more effective implementation of the technology?
- What are the metrics most commonly used in the field to assess effectiveness of the technology?

ISCO Effectiveness with DNAPL




ISCOEffectiveness with DNAPL
Pools
Ganglia
Residual
Level of DNAPL
Persulfate
Alkaline
Heated
Ethenes
Ethanes
Methanes
Type of DNAPL
ERM.


ISCR Effectiveness with DNAPL
Pools
Ganglia
Residual
Level of DNAPL
EHC/EZVI
Nano-iron
Ethenes
Ethanes
Methanes
Type of DNAPL
ERM.

Questions on Usage/Applicability

- What are the key decision processes for determining whether and how to implement the technology?
  - DNAPL Quantity, DNAPL Type, Geology
- What are the data gaps/needs for more effective implementation of the technology?
  - Where is it? How much is there?
- What are the metrics most commonly used in the field to assess effectiveness of the technology?
  - Reduction in GW concentrations/Rebound

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Thermal Treatment Issues

March 2006

Michael D. Basel, Ph.D., P.E.

Haley & Aldrich, Inc.

Overview of Technology Development

- Evolved from Enhanced Oil Recovery Techniques
- Steam Injection was first pilot tested for environmental remediation at Solvent Services Site in San Jose, CA in 1987 - 1988
- Steam Injection "blended" with electrical resistance heating at Lawrence Livermore National Labs in CA; 1990 – 1991
- Three Main Categories of Thermal Technologies
  - In Situ Thermal Desorption (ISTD)
  - Electrical Resistance Heating (ERH)
  - Steam Injection

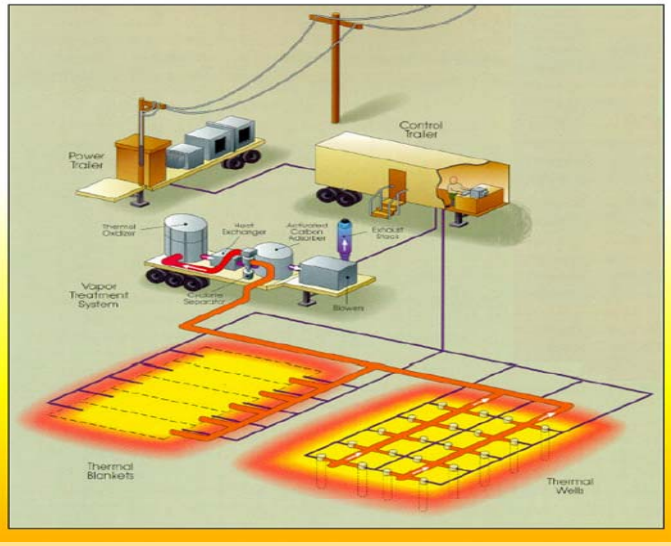
Common Themes for Thermal Technologies

- Thermal Technologies Enhance Mass Removal But Do Not Achieve "Full Cleanup" of Large-Scale Areas
- Case Studies Have Identified Most Favorable Conditions
  - Concentrated or Confined Source Areas
  - Cap at Ground Surface
  - Moderate Permeabilities
  - Higher Volatility compounds
  - Contaminants within Layer-Cake Stratigraphy
  - Limited groundwater influx
- Small vendor list has limited developments
- Full-Scale Cleanup Effectiveness Cannot Be Predicted From Bench or Pilot Tests
- Potential for Unintended Migration Is "The Challenge"

Summary of Thermal Technologies

- In Situ Thermal Desorption (ISTD)
- Electrical Resistance Heating (ERH)
- Steam Injection (Steam Enhanced Extraction
  - Description
  - Prevalence of Use
  - Data Gaps / Challenges

In Situ Thermal Desorption (ISTD) Uses Conductive Heating



Technology Overview

- Patented by Shell Oil Company - US. Terratherm is exclusive license holder in U.S.
- Heats soil by conduction (like an oven element)
  - For shallow soils (2'-3'): Heating blanket
  - For deeper soils: Electrical heaters in wells, typical well spacing is 5 – 10'. Accommodates asymmetric heaters.
- Treatment Mechanisms Dependent on Temp
  - Steam Drive (100C): Vaporize contaminants, Possibly in-situ pyrolysis/oxidation
  - High Temp (>100C): In Situ Destruction

Status of Technology

- Best for Small, Highly Concentrated Source Zones.
- Has been postulated that treatment of low permeability soils enhanced by microfractures
- Costs are Proportional to Volume of Soil Being Heated and Duration of Heating Required.
- Most Effective for Unsaturated Soils or Low Groundwater Yields.
- Most Historical Environmental Applications Have Been Shallow Soils (0-90 feet BGS)
- Best treatment of high boiling point compounds such as coal tars requires high temperatures (~300 C)

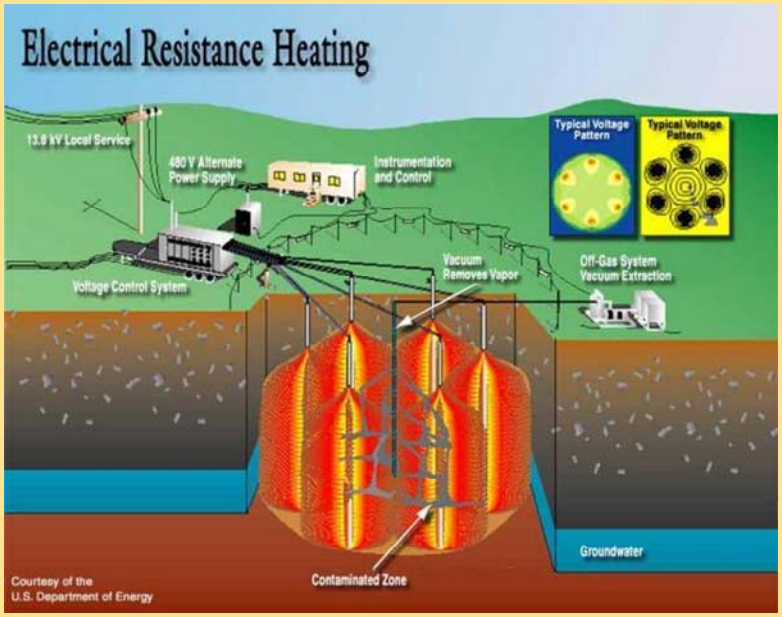
ISTD Has Numerous Applications

- Missouri Electric Works/BADCAT Demos (1996-97)
  - 12 wells; 2-12 feet BGS; PCBs
- Portland, IN – Vadose Zone Soils Remediation (1997)
  - ~ 100 wells; 2-19 feet BGS; Solvents
- Eugene, OR – Soils and GW Remediation (1998)
  - ~ 700 wells; 1-11 feet BGS; Petroleum Products
- Centerville Beach, CA – Full Scale Remediation (1999)
  - ~ 60 wells; 5-16 feet BGS; PCBs
- Alhambra, CA – Vadose Zone Soils Remediation (2002-4)
  - ~ 600 wells; 2-90 feet BGS; PCP, PAHs
- North Adams, MA – Tar Holder Remediation (2003-5)
  - ~ 25 Wells; 2-20 feet BGS w/in Former Gas Holder

Alhambra CA – Wood Treating Site (during construction)

Challenges For ISTD

- Large Treatment Areas Pose Many Challenges (Energy Requirements, Heating Balance, Treatment Monitoring, Fugitive Vapor Control).
- Water Influx Must Be Minimized.
- DNAPLs Within Water Table Create Challenge to Address.
- Treatment of high boiling point compounds such as coal tars require high temperatures for definitive treatment.
- Enhancements to Process Being Developed



Technology Overview

- Uses electromagnetic waves to heat up soil and groundwater
- Electrodes in symmetric patterns are required to transmit energy
- All subsurface features receive energy. Water is <u>required</u> to uniformly transmit energy.
- Large subsurface features (tank, foundations, etc.) act as energy sinks
- Requires careful control of energy input to provide heating without causing dryout
- Effective yet balanced removal of energy and contaminants is design concern

Status Of Technology

- Commercially Available. 3 Phase or 6 Phase
- Multiple field applications have been completed
- Current developments are focused on mechanisms of recovery for low boiling point contaminants in low permeability soils with 3-phase heating
- Focusing on lowering energy requirements by just heating to reduce viscosity or enhance biodegradation (Would still require collection of fluids)
- Most applicable for concentrated source areas

Well Field Layout - Portland, OR

Partial Summary of ERH Projects

Site	Type	Phases Used
Savannah River Site	single array pilot	six-phase
Niagara Falls AFB	single array pilot	six-phase
Dover AFB	single array pilot	six-phase
Chicago, IL	full-scale (failure)	six-phase
Fort Richardson Pilot	single array pilots	six-phase
Fort Wainwright	single array pilot	six-phase
Petroleum Refinery	single array pilot	six-phase
Skokie, IL	full-scale	six-phase, then three-phase
Western Washington	full-scale	three-phase
Fort Richardson Full Scale	full-scale	three-phase
Georgia Manufacturer	full-scale	three-phase
Pesticide Manufacturer	single array pilot	six-phase
Launch Complex 34	rectangular pilot	mostly three-phase
USAF Plant Four	single array pilot	six-phase
Waukegan, IL	full-scale	three-phase
Portland, OR	full-scale	three-phase

Challenges of ERH

- Extraction/Treatment Equipment Cost
- Electrical Costs
- Electrode Failures/Ineffectiveness
- Incomplete heating of less conductive zones

  (i.e., sands, silts)
- Insufficient temperature to address high boiling point constituents

3) Steam Injection

- Steam Enhanced Extraction (UC Berkeley Patent)
- Dynamic Underground Stripping (LLNL Patent)

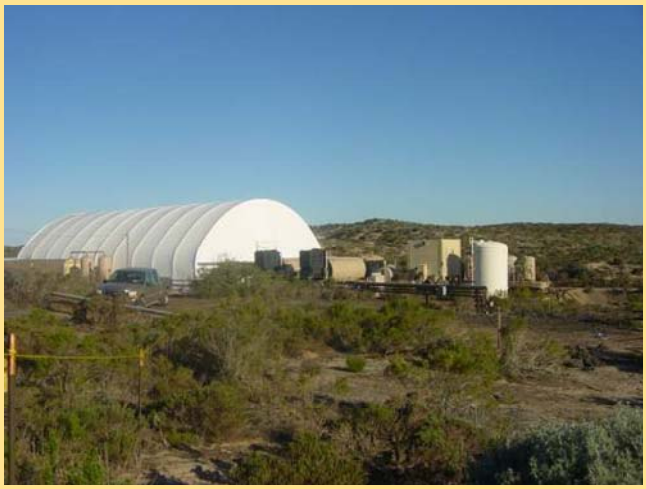
Design Issues For Steam Injection

- Design of Injection Rates / Injection Well Spacing / Injection Depth
- Design of Recovery System, Wells, Pumps, and Treatment Train
- Temperature Monitoring
- Cost Effective Pilot Test
- Incorporating complementary technologies like 3 Phase Heating and ERT
- Safety requires close supervision
- Scale-up

Ideal Features for Steam Injection

- Easy access to utilities and monitoring
- Available experienced O&M staff
- Moderate permeability or layer-cake geology with contaminants in high K zone
- Limited heterogeneities
- Impermeable cover at ground surface
- Contaminants that are
  - highly volatile,
  - low viscosity,
  - single component, or
  - confined

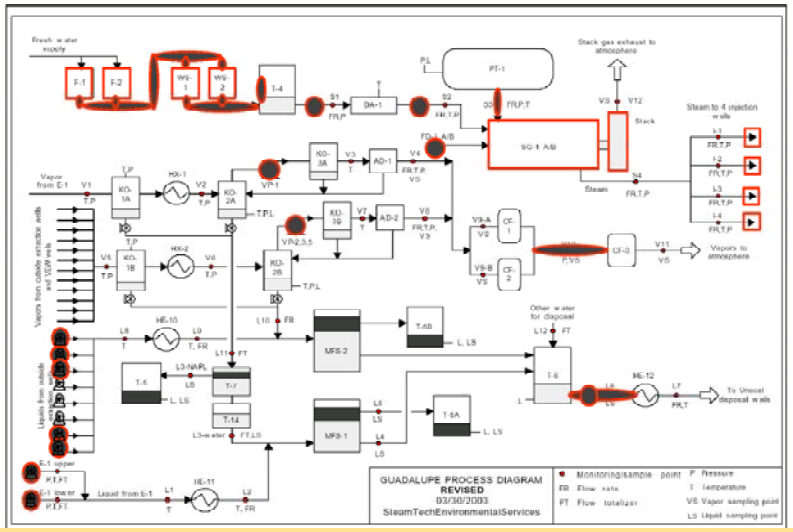
Pilot Test Near Guadalupe, CA



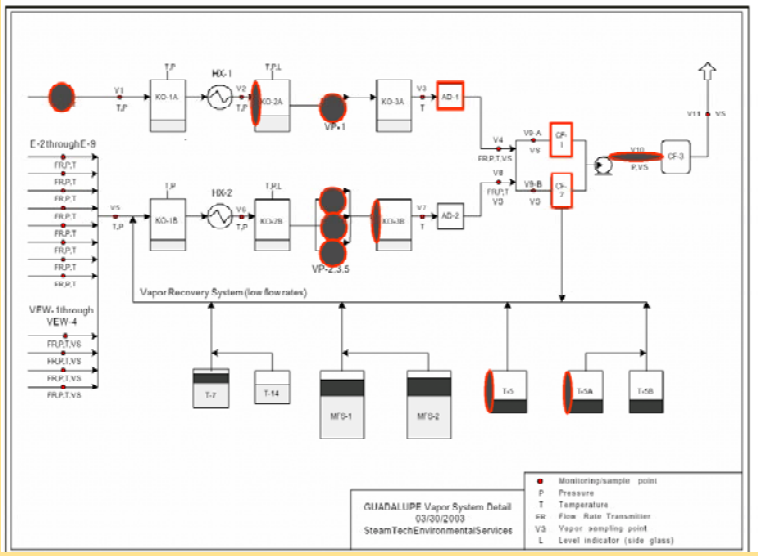
Overview of Pilot Test

- 100’ x 100’ Treatment Cell
- 4 Injection Wells, 9 Extraction Wells
- Fear of Redoing Pilot Test led to “Belts and Suspenders Approach”
- Detailed Data Collection Program
- Results Demonstrated Sizable Mass Removal but Not Reduction to Target Cleanup Level

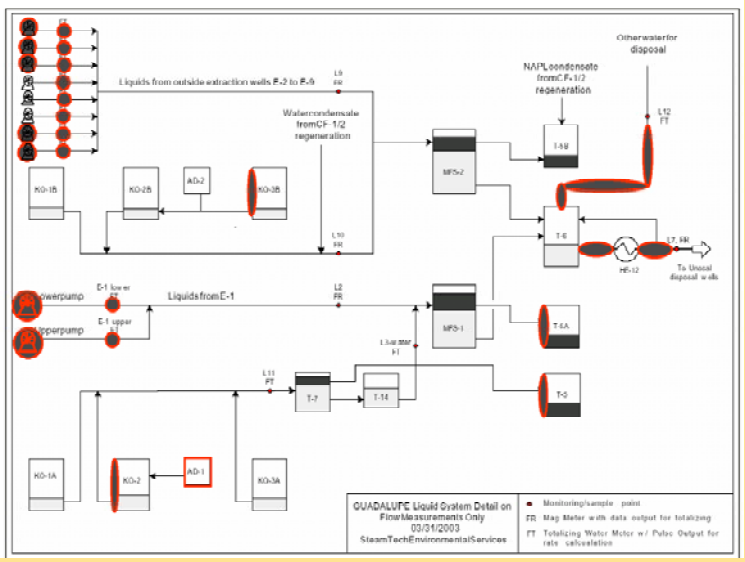
Multiple Components Were Replaced During Pilot Test



Vapor System Modifications



Liquid System Modifications



Thermal Technologies Data Gaps (Barriers to Implementation)

- Regulatory expectations of performance standards specified by target cleanup concentration
- Lack of Best Practices Manual (Equipment, practices, compendium of lessons learned)
- Unique Equipment Needs for High Temp Environment
- Templates for Design and Contracting (Performance Based Contracting)
- Critical Number of Full Scale Applications

Decision Process For Implementation

- Bench Testing (When, Why, How)
- Pilot Testing
  - Design equipment
  - Simple tests can optimize "bang for buck"
- Performance Metric
- Full Scale Design
  - Energy delivery system
  - Fluid recovery, treatment, discharge system
  - Phased application methodology
- Construction

Commonly-Used Performance Metrics

Easy to Define – Process Based

- Development of Specified Temperature Field (Steam Zone) for Specified Duration
- Percent Run Time
- Applied energy (i.e. pore volumes of injected steam)

More Difficult – Benefit Based

- Recovery of Specified Mass
- Percent reduction in mass removal rate

Problematic – Subsurface Based

- Attainment of specified subsurface concentrations

Summary of SERDP & ESTCP Projects Focused on Characterization & Remediation of DNAPL Source Zones

Andrea Leeson

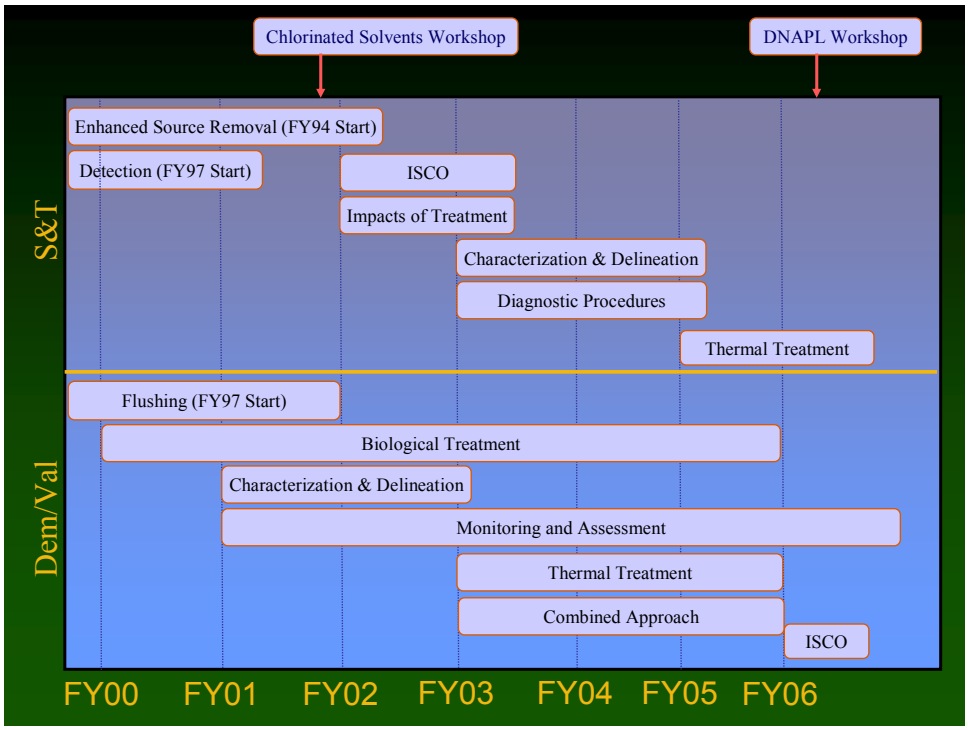
SERDP & ESTCP DNAPL Workshop

7 March 2006

Overview

- SERDP Research
  - DNAPL research initiated in 1994
  - Discussion organized by Statement of Need
- ESTCP Demonstration/Validation
  - First demonstration in 1997
  - Technologies selected as became available
  - Discussion organized by technology
    - Treatment
    - Characterization/Delineation
    - Monitoring and Assessment

SERDP & ESTCP DNAPL Overview 2



Project Presentations

- Tuesday, March 7, 11 AM - Noon
- Charge
  - Provide a brief overview of the project objectives at the initiation of the project.
  - Provide an update on the status of meeting those objectives
  - Discuss any challenges/issues encountered throughout the project towards meeting the objectives
  - Provide your thoughts on the key workshop questions

SERDP & ESTCP DNAPL Overview 4

Project Presentations (cont'd)

- FY02 SERDP SON: Impacts of Treatment
  - ER-1293: Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment (Linda Abriola, Tufts University)
  - ER-1294: Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (Tissa Illangasekare, CSM)
  - ER-1295: Impacts of DNAPL Source Zone Treatment: Experimental and Modeling Assessment of the Benefits of Partial Source Removal (Lynn Wood, U.S. EPA)

SERDP & ESTCP DNAPL Overview 5

Poster Presentations

- Tuesday, March 7, 12 – 1 PM and 5 – 7 PM
- Charge
  - Provide a brief overview of the project objectives at the initiation of the project.
  - Provide a summary of results and conclusions to date.
  - Provide an update on the status of meeting the project objectives.
  - Discuss any challenges/issues encountered throughout the project towards meeting the project objectives.

SERDP & ESTCP DNAPL Overview 6

Poster Presentations (cont'd)

- FY02 SERDP SON: Impacts of Treatment
  - ER-1292: Decision Support System to Evaluate Effectiveness and Cost of Source Zone Treatment (Chuck Newell, GSI)
  - ER-1293: Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment (Linda Abriola, Tufts University)
  - ER-1294: Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (Tissa Illangasekare, CSM)
  - ER-1295: Impacts of DNAPL Source Zone Treatment: Experimental and Modeling Assessment of the Benefits of Partial Source Removal (Lynn Wood, U.S. EPA)

SERDP & ESTCP DNAPL Overview 7

Poster Presentations (cont'd)

- SERDP Related Projects
  - ER-1349: A Field-Scale Model for DNAPL Source Depletion with Time: Model Development, Calibration, and Uncertainty (Jack Parker, ORNL)
- ESTCP Biological Treatment
  - ER-0008: Biodegradation of DNAPLs through Bioaugmentation of Source Areas (Carmen Lebrón, NFESC and Dave Major, GeoSyntec)
  - ER-0218: In Situ Bioremediation of Chlorinated Solvent Source Areas with Enhanced Mass Transfer (Kent Sorenson, CDM and Tamzen MacBeth, North Wind)

SERDP & ESTCP DNAPL Overview 8

Poster Presentations (cont'd)

- ESTCP Monitoring & Assessment
  - ER-0318: Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent-Contaminated Sites (Rula Deeb, Malcolm Pirnie)
  - ER-0424: Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (Carmen Lebrón, NFESC and Bernie Kueper, Queens University)

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Poster Presentations (cont'd)

- ESTCP Thermal Treatment
  - ER-0314: Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment (Paul Johnson, Arizona State University)

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Additional Resources

- Project Specific Links
  - www.serdp.org or www.estcp.org
- On-Line Library
  - http://docs.serdp-estcp.org/
- 2001 Chlorinated Solvents Workshop Report
  - http://www.estcp.org/documents/techdocs/chlorsolvcleanup.pdf
- SERDP/ESTCP DNAPL Source Zone Initiative Web Site
  - http://www.serdp-estcp.org/DNAPL.cfm

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DEVELOPMENT OF ASSESSMENT TOOLS FOR EVALUATION OF THE BENEFITS OF DNAPL SOURCE ZONE TREATMENT

ER-1293

Dr. Linda M. Abriola
Tufts University

Presented at SERDP/ESTCP DNAPL Source Zone Workshop
March 7, 2006

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DoD EPA DOE SERDP
Strategic Environmental Research and Development Program

Technical Objectives

- To provide a more comprehensive understanding of the impacts of DNAPL source zone treatment on contaminant mass fluxes in heterogeneous field settings.
- To develop tools and protocols for field monitoring and cost/benefit remediation analyses for such DNAPL sites.

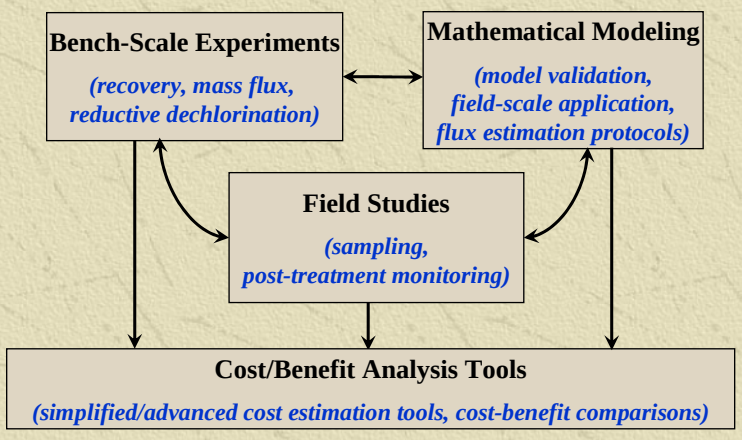
FOCUS:

(a) unconsolidated media and environments favorable for microbial attenuation

(b) near source mass fluxes and plume development under natural gradient conditions

TECHNICAL APPROACH:

A Multidisciplinary Integration of Laboratory, Modeling, and Field Studies



Project Tasks

(I) Bench-scale assessment of DNAPL recovery and contaminant fluxes

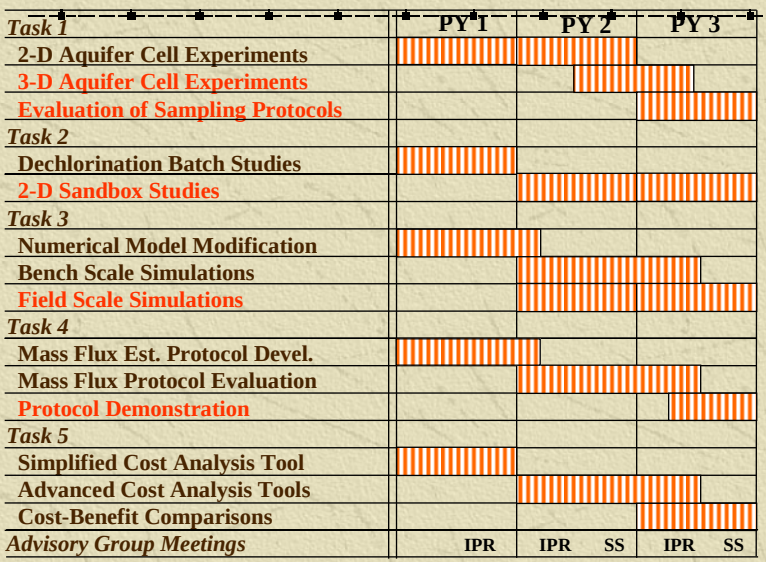
(II) Evaluation of the potential for microbial reductive dechlorination following source zone treatment

(III) Refinement, validation, and application of a numerical model for source zone remediation

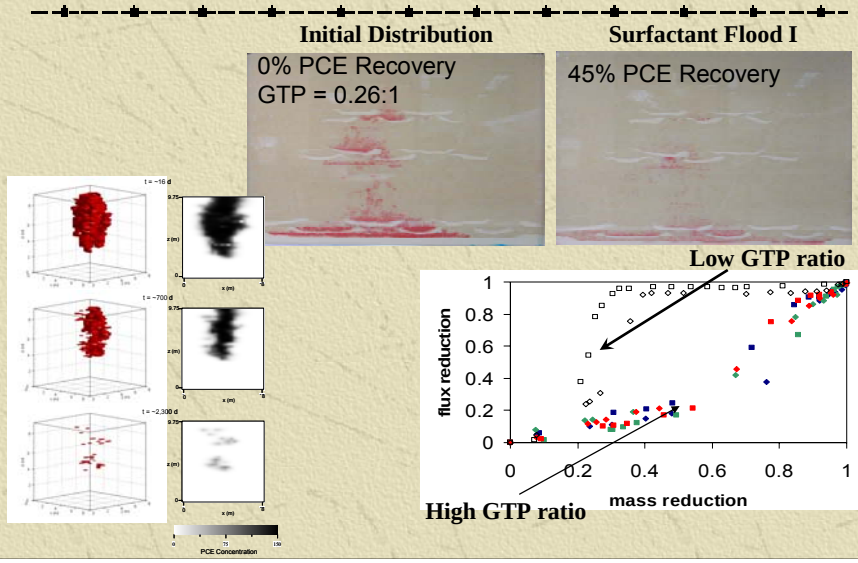
(IV) Mass flux estimation protocol development and evaluation

(V) Cost-benefit analysis tools development

SCHEDULE OF TASKS



Mass Flux vs Mass Removal



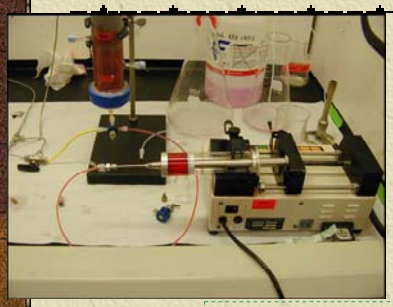
Lessons Learned: Mass flux v. mass removal

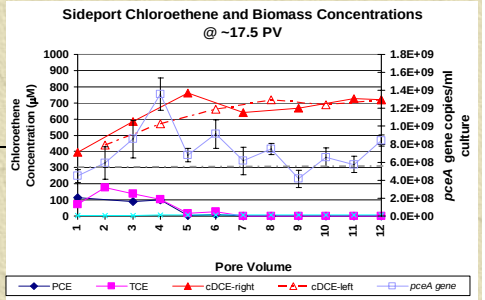
- Significant reductions in contaminant mass flux (2 orders of magnitude) can be realized with only moderate mass removal (e.g., 50%) for *in situ* surfactant flushing technologies in sandy, unconsolidated, porous media.
- DNAPL architecture and composition govern cumulative mass recovery performance and the relationship between recovery and mass flux reduction – architecture can be described quantitatively by the DNAPL ganglia-to-pool (GTP) ratio.
- The GTP ratio may be estimated *a priori* at sites with extensive knowledge of the DNAPL volume, rate of release, and spatial variability in subsurface hydraulic and capillary (pressure-saturation) parameters.
- Following aggressive DNAPL source zone treatment, significant contaminant mass may persist, which can result in locally-high aqueous phase concentrations.

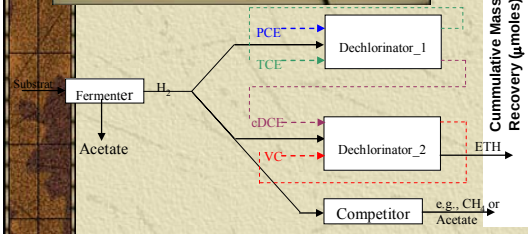
Implications:

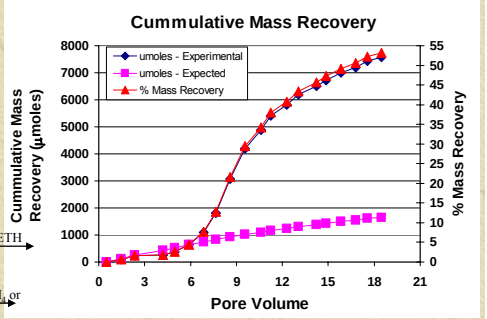
- Mass flux levels or mass flux reduction may be useful metrics for quantification of efficiency of remediation
- Mass recovery (as a percentage of initial mass) may be another useful remediation metric but recovery goals must be site-specific, varying with source zone characteristics
- DNAPL architecture at a site should influence remedial technology selection and design

Source Zone Dechlorination









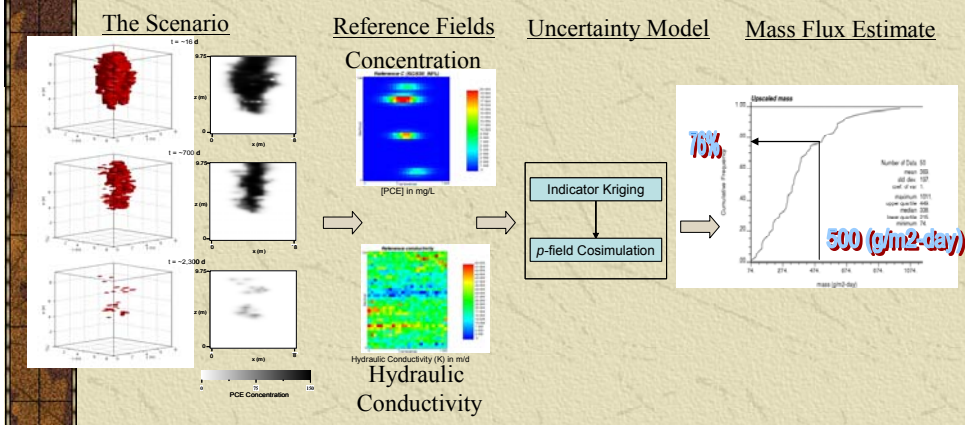
Lessons Learned: Source zone dechlorination

- Under appropriate conditions, reductive dechlorination can be achieved within a DNAPL source zone; chlororespiring bacteria exist, dechlorinate, and grow in the presence of pure and mixed DNAPLs.
- Without aggressive mass removal, bioenhanced DNAPL dissolution is unlikely to reduce source longevity substantially or lead to source zone treatment times that are acceptable within a regulatory framework.
- Polyoxyethylene (20) sorbitan monooleate, a nonionic surfactant, has negligible effects on most PCE-to-*cis*-DCE dechlorinating bacteria. In contrast, it inhibits chloroethene-dechlorination by *Dehalococcoides* spp. The inhibition however, is reversible, and dechlorination resumes following the removal (e.g., sorption, dilution, microbial degradation) of the surfactant.

Implications

- Use of aggressive mass removal technologies that can be readily coupled with in situ bioremediation approaches offer considerable promise for DNAPL source zone restoration and long-term plume management.
- Bioenhancement of dissolution can increase risk – unless complete dechlorination is achieved
- Delivery and maintenance of electron donor levels in DNAPL zone will be an important factor in remedial design

Estimating Mass Flux



Lessons Learned: Estimating mass flux

- Geostatistical models can be used successfully to estimate downgradient contaminant mass flux and uncertainties arising from multi-level transect measurements.
- For transects that have large contaminated regions, corresponding to low levels of source mass removal, mass fluxes and the associated uncertainty can be quantified with realistic sampling densities (1%)
- For transects associated with high levels of mass removal (98% in this study) that feature only a few hot spots and a large near-zero concentration region, a minimum sampling density of 6-7% is required to obtain accurate estimates of uncertainty. Such densities are not economically feasible for most field-scale applications.

Implications

- Sampling protocols will be key to remedial assessments
- Multi-stage sampling strategies that identify the locations of follow-on samples from initial measurements may improve flux estimates at lower sampling densities (research is ongoing)
- Remedial design and evaluation must include consideration of performance measurement uncertainty
- From a regulatory standpoint, mass flux limits will likely need to be prescribed in terms of mean values and acceptable levels of uncertainty

Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools

Project Number: ER-1294

Tissa Illangasekare, Junko Marr, Bob Siegrist
Center for the Experimental Study of Subsurface Environmental Processes (CESEP)
Colorado School of Mines

Kenichi Soga
Cambridge University, UK

SERDP/ESTCP Workshop on Reducing the Uncertainty of DNAPL Source Zone Remediation

March 7, 2006

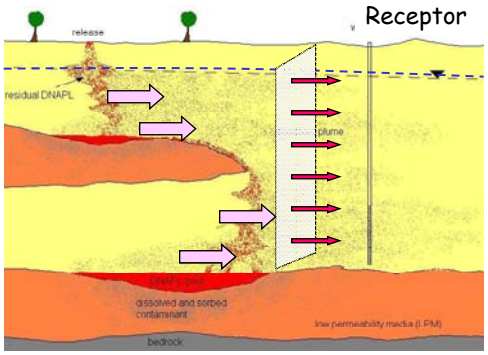
1

PROJECT OBJECTIVES

ADVANCE THE KNOWLEDGE TO DEVELOP TOOLS TO PREDICT CONCENTRATIONS OF DISSOLVED FLUX FROM ENTRAPPED DNAPLS, PRIOR TO AND POST REMEDIATION

Source Zone Treatment Technologies

1. Surfactant
2. Biological
3. Chemical oxidation
4. Thermal treatment



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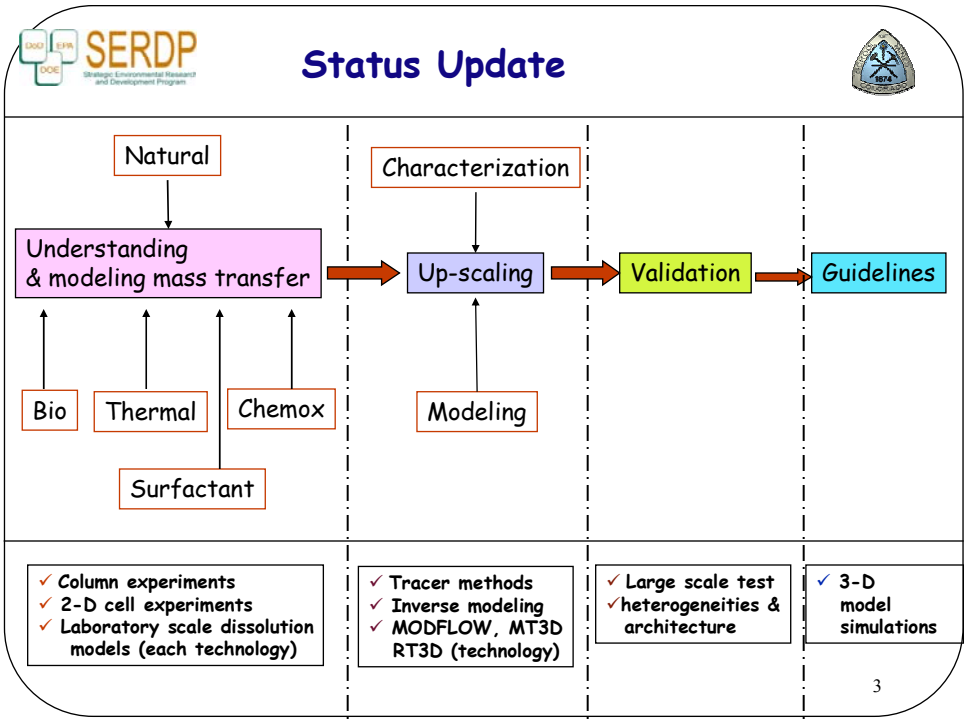
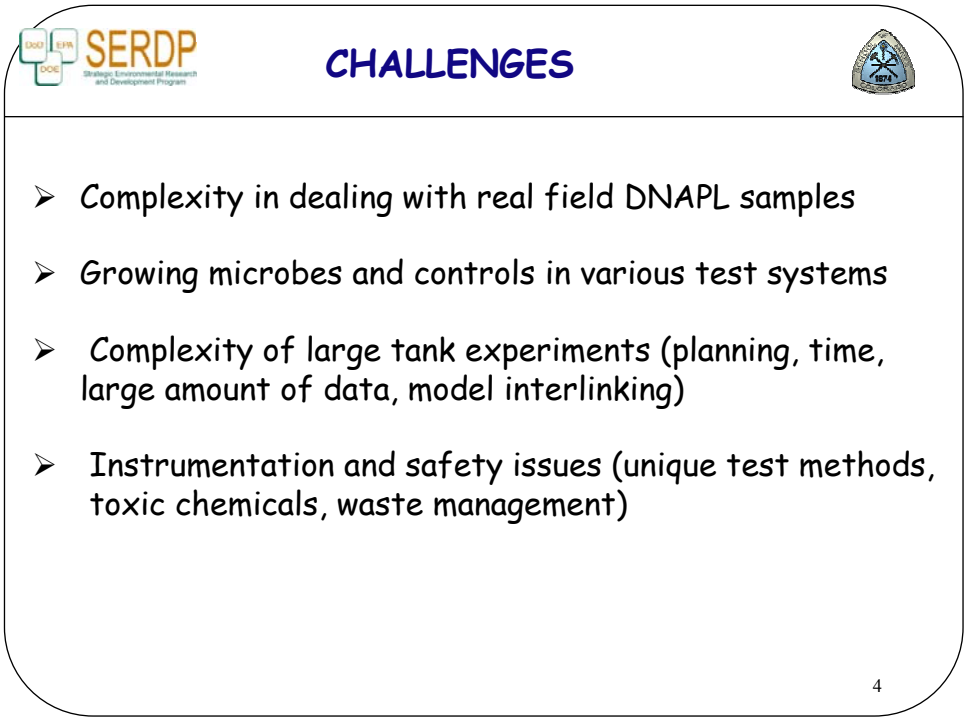

SERDP
Status Update
Natural
Characterization
Understanding
& modeling mass transfer
Up-scaling
Validation
Guidelines
Bio
Thermal
Chemox
Modeling
Surfactant
✓ Column experiments
✓ 2-D cell experiments
✓ Laboratory scale dissolution models (each technology)
✓ Tracer methods
✓ Inverse modeling
✓ MODFLOW, MT3D RT3D (technology)
✓ Large scale test
✓heterogeneities & architecture
✓ 3-D model simulations
3

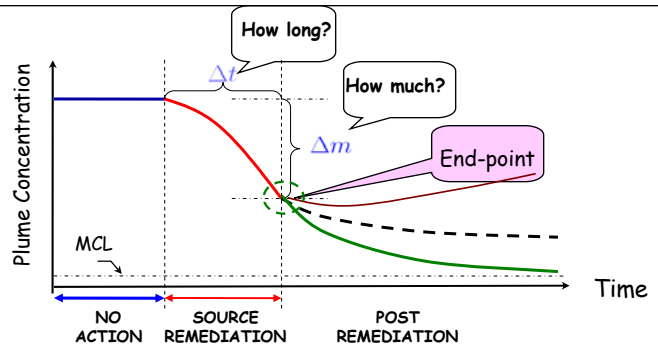

SERDP
CHALLENGES
➢ Complexity in dealing with real field DNAPL samples
➢ Growing microbes and controls in various test systems
➢ Complexity of large tank experiments (planning, time, large amount of data, model interlinking)
➢ Instrumentation and safety issues (unique test methods, toxic chemicals, waste management)
4

ISSUES

- Necessity to monitor NAPL source depletion required 2-d test systems- How close to reality in 3-d?
- With all the controls we have in laboratory settings, it is not possible to fully understand processes and accurately characterize the system- How can we understand field?
- For accuracy and convenience, well-characterized silica sand was used- How to deal with field with complex soils?
- Geostatistical methods used to create heterogeneities in tank tests- How well does this capture real field heterogeneity?

5

Knowledge Base/Tools



- Goal was to study relation between source zone mass and flux.
- Practical questions applicable to field, but field data not available to answer the questions.
- Even though the test scales do not match field, processes are captured to "validate" models, methods and tools.
- How long should treatment be performed to reach "acceptable" end points?

6

Question 1

Whether, and under what circumstances, source zone remediation should be attempted?

- ✓ Sufficient data to understand and quantify heterogeneity and entrapment architecture (existing methods are not adequate).
- ✓ Knowledge on source morphology (residuals, pools, rebound).
- ✓ Adequate understanding of hydrodynamics in the source zone (estimate mass flux, effective delivery of treating agents).
- ✓ Good appreciation of the limitations of the specific technology for site specific conditions.

7

Question 2

What objectives are reasonable for DNAPL source zone remediation at specific sites?

- ✓ Objectives should be tailored to site conditions.
- ✓ Complete mass removal should not be an objective, as it is not feasible.
- ✓ Make decisions based on mass flux emission from source zone rather than concentrations (no direct relation with mass entrapment and flux).
- ✓ Highly heterogeneous sites with potentially less vertical spread, mass reduction should not be an objective (low ganglia/pool)
- ✓ Homogeneous (high ganglia/pool)- mass reduction may be a reasonable objective (still recognize the limitations of the specific technology to site conditions)

8

Question 3

How progress towards achieving those objectives should be measured?

✓ **Progress should be measured based on mass flux emissions (not concentrations or mass removal from source zone)**

- Quantity of mass removal can not be estimated
- No direct relation between mass and flux

✓ **Assessment of expected end points and projection of post-treatment behavior (plume longevity and expected risk at receptor).**

- Depends on the specific technology
- Post remediation processes

9

Project Team

Investigators: Illangasekare, Marr, Saenton, Kim, Soga, and Siegrist

Students: Ann Kaplan- MS- Bio batch and column
Kent Glover- PhD- Bio cell, large tanks and modeling
Jeff Heiderscheidt- PhD-Chem oxidation, large tanks and modeling
Jose Gago- PhD-Thermal Treatment
Derrick Rodroguez- PhD- Rebound
Casey Ramey-BS-Bio batch and column (undergraduate)

Post-doc: Satawat Saenton- Post-Doc- Modeling and up-scaling
Yongcheol Kim - Post Doc- Large tank experiments
Mini Mathew - Post Doc- Modeling, decision tool

Cambridge Students:
Inudu Kulasuriya- PhD- - Surfactants batch and column
John Page- PhD- Surfactants

Related Projects:
NSF- Tracer methods
AFCEE- Source zone conceptual model at FB Warren and Caswell
- Vegoil treatment
Army- Model Calibration
NSF- DNAPL migration

10

Field Demonstrations

Impacts of DNAPL Source Zone Treatment: Experimental and Modeling Assessment of Benefits of Partial Source Removal

…assess the benefits of aggressive in situ DNAPL source-zone remediation

Laboratory Experiments

Mathematical Modeling

1

PROJECT OBJECTIVES

Goal:

Develop a scientifically defensible approach for assessing the benefits of aggressive in situ DNAPL source-zone remediation

Specific Objectives:

- **Assess response to DNAPL mass removal through mass flux and plume behavior at several field sites**
- **Characterize relationship between DNAPL architecture, mass removal and contaminant mass flux in laboratory aquifer models**
- **Conduct mathematical simulations to describe relationship between DNAPL removal, mass flux and subsequent plume response**
- **Compile statistics on relationship between partial DNAPL removal and contaminant flux behavior for several hydrogeologic templates of actual field sites**

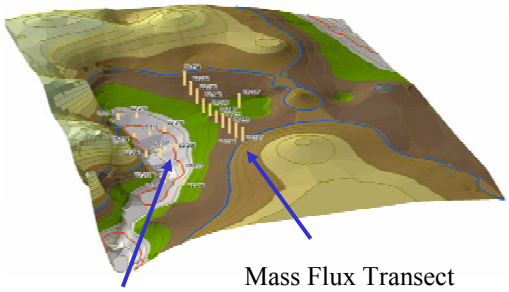
2

Field Measurements of Contaminant Flux

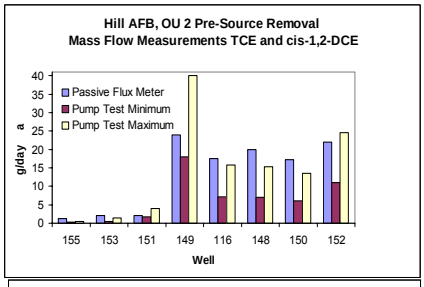
Pre & Post Remedial Measurements will be made at four DNAPL Field Sites.

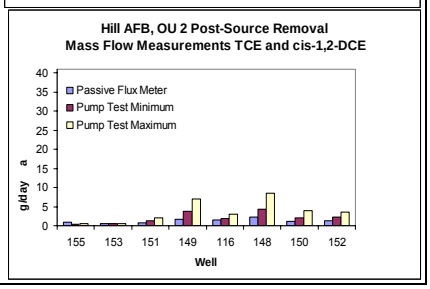
3

Hill AFB Flux Measurements

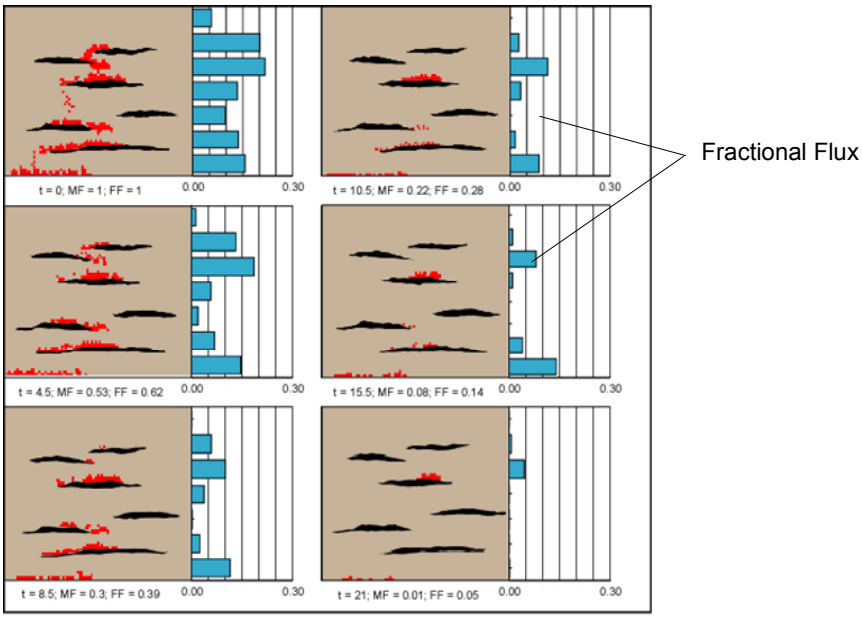


- June 2002 First Flux Measurement
- July 2002 Surfactant Flood
- June 2003 Second Flux Measurement

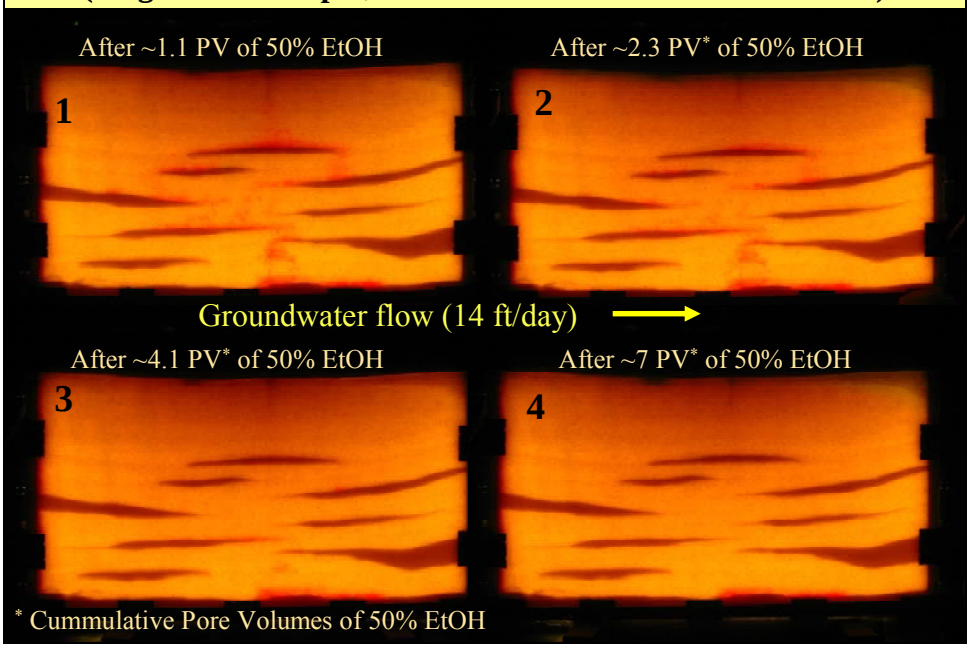


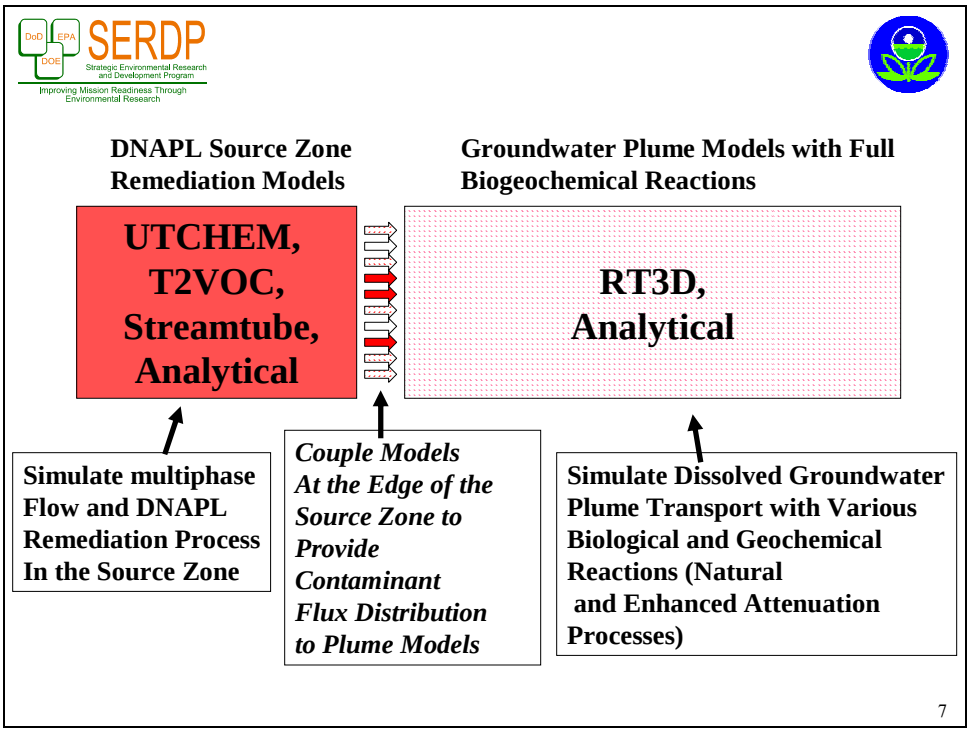


Laboratory experiment showing flux plane response to changes in DNAPL architecture



Cosolvent Remediation of DNAPL in a Laboratory Aquifer Model (Single DNAPL Spill, Four Consecutive Cosolvent Flushes)





Objective 1 (Field)

- Pre-remedial flux measurements have been completed (five sites).
- All post-remedial flux measurements will be completed this year (with the exception of NA3 at Fort Lewis).
- Delays in remedial schedules have likewise delayed post remedial flux measurements.

Objective 2 (Laboratory)

- Two-dimensional experiments are approximately 60% complete, and should be finished by late summer.
- Results to date support power-law applications to describe DNAPL mass-flux relationships.

Objective 3 (Modeling)

- Analytical screening model developed to assess flux and plume responses to DNAPL mass depletion.
- Objective is effectively complete, additional work will be conducted to evaluate plume response and development of GUI.

Objective 4 (Discharge Response for Different Systems)

- This objective has been modified to assess uncertainty in site characterization through Monte Carlo simulations using analytical models.
- Work will be complete by fall of this year.

8

Key Workshop Questions:

1. **What objectives are reasonable for DNAPL source zone remediation?**
   Removal of most of the DNAPL mass leading to an order of magnitude reduction in discharge, and a shorter source life

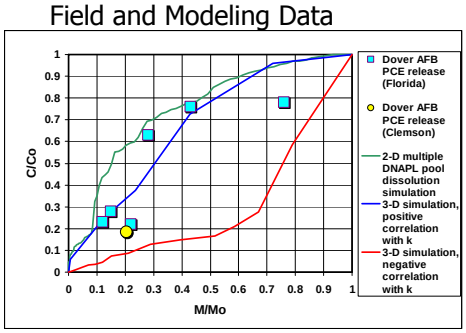
2. **When should DNAPL source zone remediation be attempted?**
   Simple answer – when it makes a significant difference in the plume behavior (length, mass, longevity, risk)
   This is actually a very complex question that depends on site conditions as well as regulatory, financial, and moral considerations.

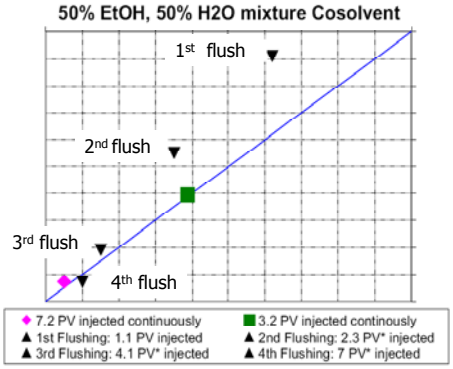
3. **How should source remediation progress be measured?**
   Pre- and post-remediation mass in source zone; pre- and post-remediation discharge from source (over a long time!)

9

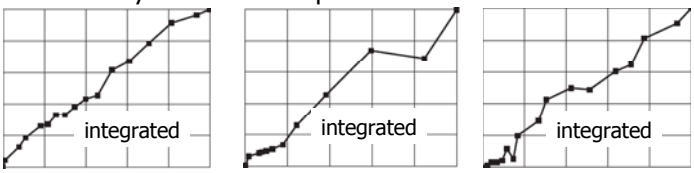
Source reduction leads to discharge reduction

Field and Modeling Data





Laboratory dissolution experiments



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Discharge reduction may or may not be enough to meet site goals

Example: Objective is to reduce maximum plume extent

Analysis of leading order behavior: Assume linear response of discharge to source mass reduction and neglect dispersion. With prompt removal of "X" of the DNAPL, maximum plume length is

$$x = \frac{-v}{\lambda_p} \ln\left(\frac{C_m}{C_0(1-X)} \right)$$

Percent reduction in maximum plume length	20%	50%	70%	80%	90%
$C_m/C_0=10^{-2}$	0.60	0.90	0.96	0.975	0.984
$C_m/C_0=10^{-3}$	0.75	0.968	0.992	0.996	0.998
$C_m/C_0=10^{-4}$	0.84	0.990	0.998	0.9994	0.9997

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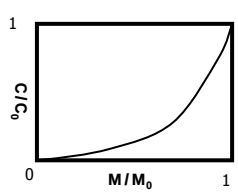
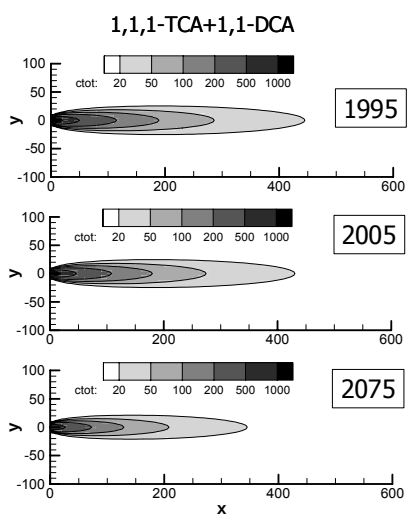
Example: 300 kg release of 1,1,1-TCA in 1975

- DNAPL source has Γ=2.0, C_0=2 mg/l; water flow through source zone is 600 m^3 per year
- The TCA is assumed to undergo reductive dechlorination in the plume to 1,1-DCA with a first order rate of 0.8/yr (very low).
- 1,1-DCA degrades to chloroethane with a first order rate of 0.2/yr (very low)





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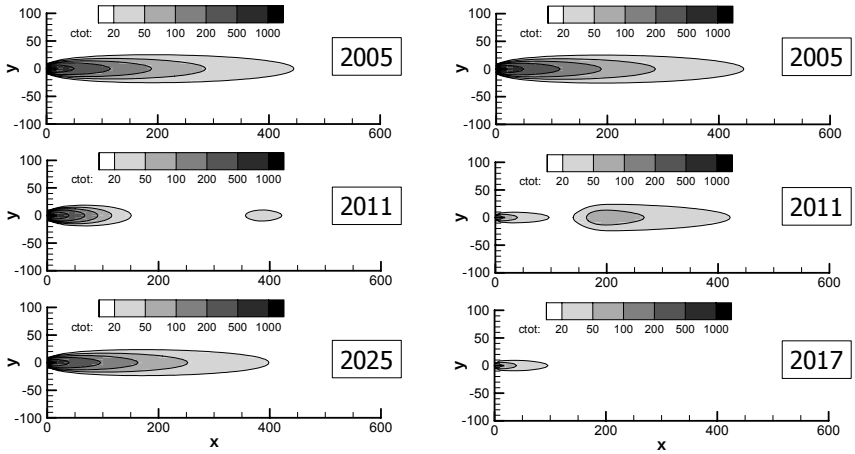
Compare source and plume remediation

Enhance reductive dechlorination in the plume from 0-200 m, during the period of 2005 to 2010

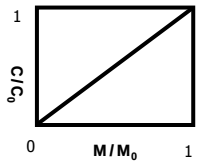
Remove 70% of source mass Between 2005 and 2006

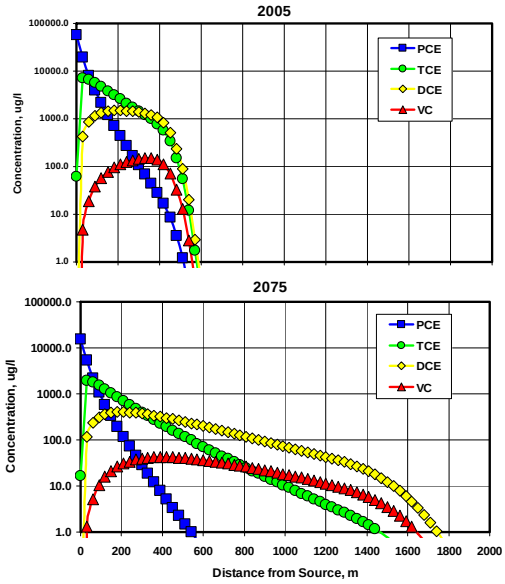


3

Harder Case: 1620 kg release of PCE in 1975

- DNAPL source has Γ=1.0, C_0=100 mg/l; water flow through source zone is 300 m^3 per year
- Assume reductive dechlorination from PCE→TCE →DCE →VC
- Ground water pore velocity is 30 m/yr, R=2, decay rates are low: PCE, 0.4/yr; TCE, 0.15/yr; DCE, 0.1/yr; VC, 0.2/yr





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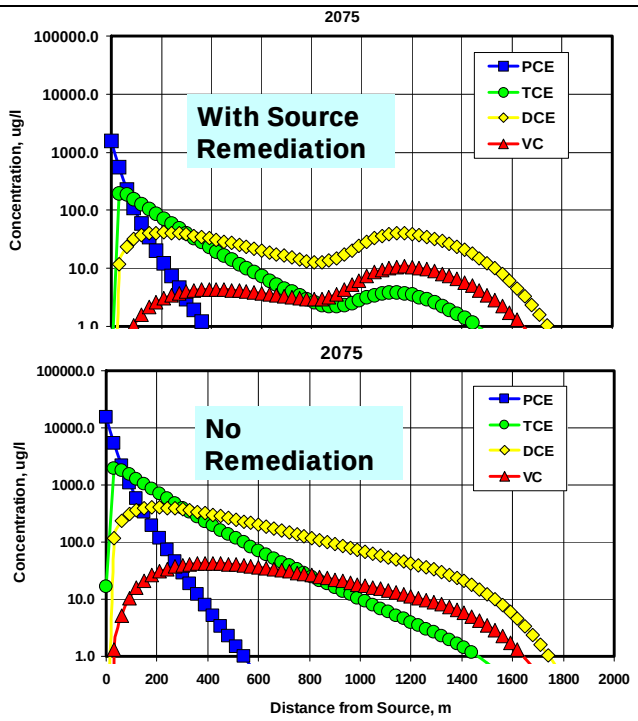
Improving Mission Readiness Through Environmental Research

Remove 90% of source mass in 2005

Concentrations drop by factor of 10 out to ~800m

Leading edge of plume is not affected

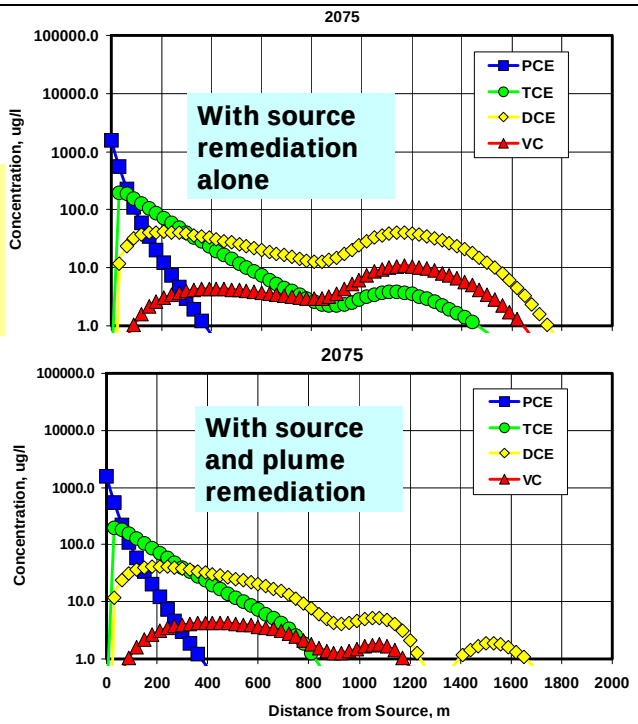


SERDP
Strategic Environmental Research and Development Program
Improving Mission Readiness Through Environmental Research

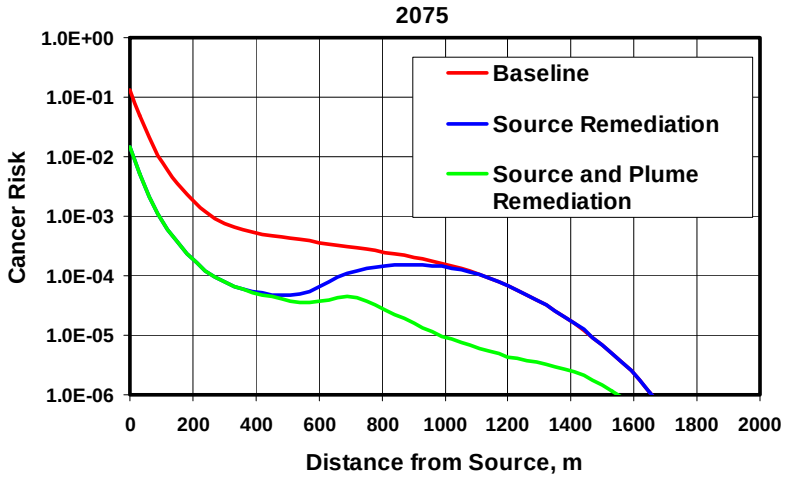
Remove 90% of source mass in 2005

Enhance reductive Dechlorination of PCE and DCE from 0-400m, years 2005-2025

Enhance aerobic Degradation of DCE and VC from 400 to 700m, Years 2005-2025



Change in lifetime cancer risk from contaminated well water



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Appendix D

Background Information

TECHNICAL REPORT

Summary of SERDP and ESTCP Projects Focused on Characterization and Remediation of Dense Nonaqueous Phase Liquid (DNAPL) Source Zones

February 2006

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Acronyms and Abbreviations

CAH	chlorinated aliphatic hydrocarbon
CDEF	cyclodextrin-enhanced flushing
DCE	dichloroethene
DNAPL	dense nonaqueous phase liquid
DoD	Department of Defense
DOE	Department of Energy
ECRS	experimental controlled release system
EPA	Environmental Protection Agency
ERH	electrical resistance heating
ESTCP	Environmental Security Technology Certification Program
EZVI	emulsified, zero-valent, nanoscale iron
GRFL	Groundwater Remediation Field Laboratory
ISCO	in situ chemical oxidation
ITRC	Interstate Technology and Regulatory Council
MIP	membrane interface probe
MNA	monitored natural attenuation
NETTS	National Environmental Technology Test Site
NFESC	Naval Facilities Engineering Service Center
ORNL	Oak Ridge National Laboratory
PCE	tetrachloroethene
R&D	research and development
RTF	remediation time frame
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
TCA	trichloroethane
TCE	trichloroethene
VC	vinyl chloride
VOC	volatile organic compound
XSD	halogen specific detector

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) are Department of Defense (DoD) programs designed to develop and transition innovative research and technology to help DoD perform its mission in several environmental areas, including cleanup of contaminated sites. These programs are executed in full partnership with the Department of Energy (DOE) and the Environmental Protection Agency (EPA).

SERDP is a research and development program aimed at the development and application of innovative environmental technologies that will reduce the costs, environmental risks, and/or the time required to resolve environmental problems while simultaneously enhancing safety and health. ESTCP is an applied program that seeks to promote innovative, cost-effective environmental technologies through demonstration and validation at DoD sites. Further information on these programs is available on the program web sites at http://www.serdp.org/ and http://www.estcp.org.

While DoD facilities have numerous types of contaminants, chlorinated solvents are by far the most prevalent, particularly the chlorinated ethenes such as trichloroethene (TCE) and tetrachloroethene (PCE), as well as related compounds such as trichloroethane (TCA), vinyl chloride (VC), and dichloroethene (DCE). These compounds, collectively categorized as chlorinated aliphatic hydrocarbons (CAH), continue to be difficult to remediate, particularly at sites containing CAHs as dense nonaqueous phase liquid (DNAPL), where the DNAPL serves as a continuing long-term source of dissolved-phase groundwater contamination.

Since 1994, a number of projects have been funded by SERDP and ESTCP in the area of DNAPL source zone characterization and remediation. This report reviews the current technical basis for funding priorities, provides the scope and objectives of areas of research in DNAPL source zone characterization and remediation over the past several years, and also provides a summary of specific SERDP and ESTCP projects, summarizing their objectives in advancing the understanding of key issues related to source zone cleanup.

2. THE DNAPL CHALLENGE

Chlorinated solvents such as TCE and PCE are found at approximately 80% of all Superfund sites with groundwater contamination and more than 3,000 DoD sites in the United States. (This discussion is excerpted from the SERDP Expert Panel Report on research and development [R&D] needs for chlorinated solvent cleanup.) The life-cycle costs to remediate these sites are uncertain but are likely to exceed several billions of dollars nationally. DoD alone could spend more than $100 million annually for hydraulic containment at these sites using pump-and-treat technologies, and estimates of life-cycle costs exceed $2 billion.

CAHs are also among the most difficult contaminants to clean up, particularly when their DNAPL sources remain in the subsurface. Both the U.S. EPA and the National Academy of Sciences have concluded that DNAPL sources may be contained, but remediation to typical cleanup levels for most DNAPL sites is often "technically impracticable." Other DNAPL sources, such as coal tar and creosote, pose similar problems. Although these other DNAPLs tend to have significantly different properties than the CAH ones, notably lower solubilities and higher boiling points, much of the following discussion is relevant to them as well.

Over the past 10 to 15 years, pump-and-treat processes have not fully remediated sites with DNAPL occurrence. However, recent tests of innovative source remediation technologies, such as surfactant or alcohol flooding and in situ thermal treatment, suggest that significant mass removal and reductions in mass discharge from sources is possible at some DNAPL sites. These results have led to increasing regulatory and public pressure to remediate sources. However, source remediation can be extremely expensive in the short term, and we can rarely predict with confidence whether it will be effective. Innovative technologies have not been thoroughly evaluated, and therefore, research and development is clearly needed in several areas to better understand whether and how to attempt source remediation. Prioritizing the most urgent research is essential, given limited funds and the large number of potential projects.

SERDP convened an expert panel workshop in August 2001 to evaluate the needs for research and development in the general area of chlorinated solvent site cleanup. The workshop identified R&D priorities and made specific recommendations for guiding research and technology development for a 5- to 10-year period.

An overall objective of the workshop was to determine how these programs can optimize investment of their limited research, development, and demonstration funds to improve DoD's ability to effectively address CAH-contaminated sites. Workshop participants were asked to identify the major basic and applied research, development, and demonstration needs; the specific technical issues that must be addressed to meet regulatory and other stakeholder concerns; and the major gaps in our scientific understanding of CAH contamination and cleanup. Further, the participants were asked to prioritize these research and development needs and identify those areas with the greatest promise to help DoD accomplish its goals.

Following are brief descriptions of the highest priority research needs identified during the workshop.

2.1 Science Needs

2.1.1 Assessment of Source Zone Treatment Technologies

Better use of existing technologies is a more valuable pursuit than the development of still newer technologies. The field has matured to the point that the fundamental technology-based approaches to cleanup of CAH source zones exists and improvements will come from better implementation of these existing approaches.

2.1.2 Physical/Chemical/Biological Processes at NAPL Interfaces

Research is needed on the fundamental physical, chemical, and biological processes at the interface between NAPL and the aqueous phase. Currently, the nature, rate, and extent of interactions that occur at the interface are poorly understood. Further research is needed on the fundamental processes controlling interactions at the interface, including the effects of NAPL architecture and composition, aqueous phase water chemistry and microbiology, and flow regime characteristics.

2.1.3 Source Zone Delineation and Characterization

Research and development of source treatment technologies is more important than improved plume treatment. Plume remediation technologies are generally well understood and sufficiently mature. Recent development of more aggressive source-zone treatment technologies has caused a reevaluation of the previous conventional wisdom that source removal is "technically impracticable" and long-term containment is the most practicable remedial strategy. Consequently, there is increasing regulatory and public pressure to remediate source zones, despite significant scientific uncertainties about the value of source zone remediation, or even the appropriate methods to measure or define the "success" of such efforts.

2.1.4 Quantification of Uncertainty

Site-specific selection, design, and evaluation of remedial systems are necessarily based on imperfect knowledge of site characteristics and properties. The significant heterogeneity of most subsurface environments dictates that critical site parameters, such as hydraulic conductivity, groundwater velocity, microbial activity, contaminant concentration, and sorption/desorption rates can vary over orders of magnitude within relatively short spatial distances. Complete characterization of a site is essentially an unobtainable goal. Thus, predictions and decisions needed for remediation are often subject to a high degree of uncertainty. Thus, there is an urgent need for the development of tools and methodologies to both quantify and reduce the uncertainty associated with parameter estimation and model predictions.

2.1.5 Effects of Treatment Amendments

The in situ treatment of soil and groundwater contaminated by chlorinated solvents may negatively affect subsurface conditions. Remediation technologies may alter site physical, chemical, and microbiological parameters that impact flow and transport, thereby affecting contaminant behavior and treatability in situ. Treatment may change NAPL distribution and composition (e.g., due to solubilization and mobilization). Geochemical and microbial changes are a concern within the treated source area as are the potential these changes have to degrade downgradient water quality. The potential for occurrence of these and related effects as well as their relative impacts (positive or negative) are highly dependent on the complex interactions between treatment process design and pretreatment environmental conditions. We do not currently have sufficient understanding or guidance available to assist remedial project managers in adequately predicting or monitoring these potential side effects.

2.2 Technology Needs

2.2.1 Benefits of Partial Mass Removal

In the majority of cases, source treatment will result in only partial mass removal. The inability to remove all of the mass is partly a result of the inability to find and access all of the DNAPL in the source areas, and partly a result of the technical difficulties involved in removing DNAPLs from the subsurface. Although meeting current cleanup criteria for groundwater (in the low part-per-billion range) may require removal of well over 99% of the total mass, partial mass removal may reduce plume longevity, plume size, and/or the future costs for site management. Predicting and demonstrating that these benefits will result from treatment, and quantifying the reductions in risk, concentrations, flux, and life-cycle costs has proven controversial and difficult. Better methods of predicting and measuring the benefits are needed in order to determine when source removal should be attempted, and how such removal efforts should be evaluated.

2.2.2 Develop Better Performance Assessment Tools

Several promising source zone cleanup technologies are available and efforts are better spent now to understand the promise of these technologies as opposed to developing newer ones. In many instances, the tools needed to measure performance are inadequate. The development of better diagnostic tools, and guidance on the use of existing tools, are critical needs.

2.2.3 Source Zone Characterization and Flux Analysis

Better tools and techniques are needed to estimate both the total contaminant mass in source zones, and the mass release rates from those sources. To measure the impacts of source treatment, or to understand the risks posed by a residual source, it is essential to have accurate estimates of the total mass and the mass release rates before and after treatment. Combining mass release rates with estimates of natural attenuation capacity or fate and transport models can allow us to develop meaningful risk-based plume management strategies and regulatory approaches. The current state of the science does not satisfy these needs. Consequently, setting performance goals and determining the potential for “success” from source treatment is difficult and controversial.

2.2.4 Assessment of Thermal Treatment

Thermal treatment is a very promising area for future investments of research funding. This conclusion reflects both the potential for in situ thermal treatment, and the current state of its development.

2.2.5 Source Zone Bioremediation and Bioaugmentation

In situ bioremediation, including monitored natural attenuation (MNA), biostimulation, and bioaugmentation is another technology deemed worthy of focused funding. This emphasis reflects the potential cost-effectiveness of both passive and active bioremediation approaches. Further, both MNA and enhanced bioremediation may be significant elements of treatment trains for source zone remediation, in many cases following more aggressive treatment using, for example, thermal or surfactant flushing technologies.

2.2.6 Diagnostic Tools to Evaluate Remediation Performance

The performance of existing and developing source zone reduction technologies needs to be better understood. Evaluating performance may require new diagnostic tools. Technical guidance is needed on the use of diagnostic tools to improve conceptual models of remediation performance.

2.3 Summary

Several SERDP and ESTCP projects are addressing the science and technology needs identified by the 2001 Chlorinated Solvents Workshop. At the conclusion of the 2006 DNAPL Workshop, these needs will be revisited and updated based on new knowledge gained in the last 5 years.

3. OVERVIEW OF SERDP DNAPL RESEARCH

An overview of the research areas that have been investigated by the SERDP and ESTCP programs is provided in Figure 1. This figure illustrates the initiation year of the specific research area as well as the occurrence of key strategic workshops: the Chlorinated Solvents Workshop (2001) and the DNAPL Workshop (2006).

Prior to 2001, investment in DNAPL source zone characterization and remediation was limited. Two areas of research were investigated: enhanced source zone removal, and detection and monitoring of source zones. These programs are described in detail in Sections 3.1 and 3.2, respectively.

In 2001, the SERDP and ESTCP programs reached a point at which it was necessary to refine and redefine their overall strategic plans for remediation of chlorinated solvent contaminated sites. The overarching question was how these programs could best invest their limited research, development, and demonstration funds to improve DoD's ability to effectively address its chlorinated solvent-contaminated sites. A workshop was held with experts in the field of chlorinated solvent remediation to solicit input on three key areas: the major basic and applied research needs, the specific technical issues that must be addressed to meet regulatory and other stakeholder concerns, and the major gaps in our scientific understanding of CAH contamination and cleanup. Results from this workshop are summarized in Section 2 of this document and were published in a summary report. These findings have been used to guide the selection of areas of research in the SERDP and ESTCP programs.

Five areas of research have been pursued since the 2001 Chlorinated Solvents Workshop: in situ chemical oxidation; impact of partial DNAPL source zone removal on the plume; characterization and delineation of DNAPL source zones; development of diagnostic procedures for the evaluation of technology performance; and thermal treatment. These research areas are described in more detail in the following sections.

3.1 Enhanced Source Zone Removal

SERDP research into environmental restoration issues associated with DNAPLs began in 1994 with the initiation of a project by the U.S. EPA Robert S. Kerr Environmental Research Laboratory (ER-368). This project was led by Dr. Carl Enfield and focused on evaluating enhanced source removal technologies for their effectiveness at removing nonaqueous phase contaminants from the source zone. The technologies were tested in controlled release test cells at the Groundwater Remediation Field Laboratory (GRFL) at Dover Air Force Base, Delaware. Five different technologies were tested:

- **Cosolvent Solubilization** flushes the contaminated soils with a cosolvent such as ethanol. The cosolvent dissolves the contaminants as it is flushed through the soil and then is pumped and treated aboveground.

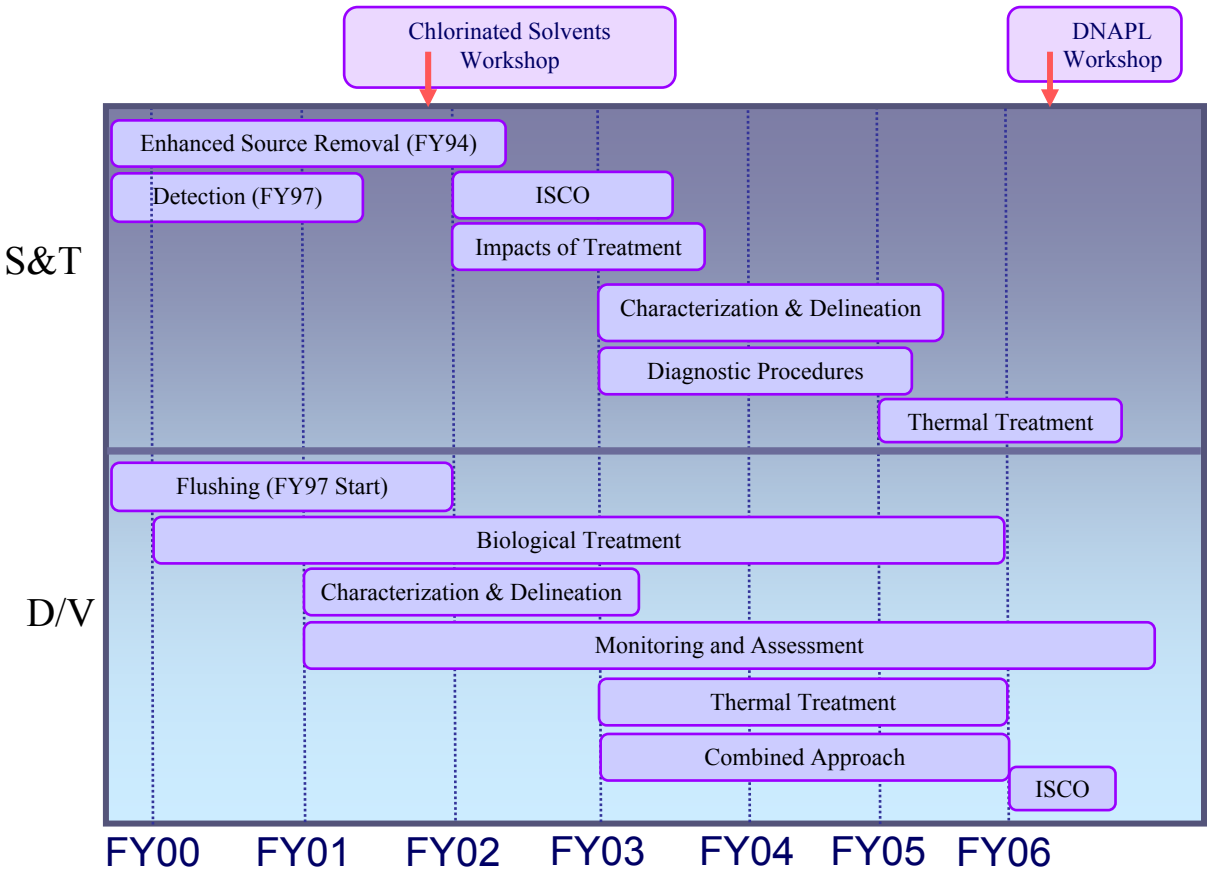

Figure 1. Overview of SERDP and ESTCP Efforts on DNAPL Source Zone Characterization and Remediation

- **Cosolvent Mobilization** flushes the contaminated soils with a cosolvent such as tert-butyl alcohol enabling the contaminant to flow through the soil, at which point it then is pumped aboveground and treated.
- **Macromolecular Solubilization** is similar to surfactant solubilization, but sugars are used in place of surfactants.
- **Surfactant Solubilization** combines the effects of a cosolvent and a surfactant to solubilize PCE, which then is flushed out of the test cell.
- **Air Sparging/Soil Vapor Extraction** uses air as the remedial fluid. Air is forced into the contaminated zone to volatilize the PCE. The vapors then are withdrawn and treated at the surface.

Results from this project demonstrated that enhanced source removal technologies can be used to rapidly remove DNAPL from unconsolidated porous media. However, none of the technologies removed all DNAPL mass under the conditions of the test. Technology effectiveness ranged from approximately 45% to 90% removal of the total DNAPL mass. A statistically based Lagrangian model has been developed and used to forecast performance of source remediation technologies. Data suggests that partial DNAPL removal can result in substantial decreases in

contaminant concentrations in groundwater emitted from a treated source zone. The researchers concluded that additional research was required to determine the extent to which contaminant mass discharge from source zones is influenced by DNAPL mass depletion. The Final Report for this project is available in the SERDP and ESTCP Online Library.

3.2 Detection, Monitoring, and Modeling of DNAPLs

Additional SERDP research into environmental restoration issues associated with DNAPLs was initiated in 1997 when a request for proposals was released requesting proposals on the treatment of DNAPLs and on the detection, monitoring, and modeling of DNAPLs (Figure 1). Projects selected were focused on the location and characterization of DNAPL source zones (ER-1089, ER-1090, and ER-1128); however, results from these studies were relatively inconclusive and did not lead to a robust technology for the characterization of DNAPL source zones.

3.3 In Situ Chemical Oxidation

In FY02, research on in situ chemical oxidation (ISCO) was initiated to improve our understanding of (1) the mode of action of oxidants on free phase and residual DNAPLs, including the associated chemical reactions, reaction kinetics, and other effects that can impact overall destruction efficiency; (2) the stability and reactivity of oxidants in an aquifer matrix with varying soil conditions (pH, iron content, etc.); and (3) the impact of varying soil parameters on oxidant fate and overall destruction efficiency. Three projects were selected in this area: ER-1288, ER-1289, and ER-1290. These projects focused on understanding the mechanism of action and kinetics of various oxidants, including permanganate, persulfate, and modified Fenton's reagent. These projects addressed one of the critical science needs identified at the 2001 Chlorinated Solvents Workshop, assessment of source zone treatment technologies, which called for better use of existing technologies, such as ISCO. A more detailed summary of the projects can be found on the ISCO Initiative Web Page.

Under ER-1288, Dr. Rick Watts (Washington State University) is leading an effort to develop a better understanding of modified Fenton's reagent. Specific objectives of the study focus on the generation of transient oxygen species from the catalytic decomposition of hydrogen peroxide by the different minerals contained in aquifer solids, the generation of transient oxygen species by soluble iron-catalyzed Fenton-like reactions, the role of different oxygen species in the degradation of common organic contaminants, the potential for the treatment of contaminants in sorbed and DNAPL states, and the use of process chemistry to optimize reagent delivery. This project is scheduled for completion by June 2006.

Dr. Eric Hood (GeoSyntec) is heading ER-1289, which focuses on providing a better understanding of the site-specific applicability of permanganate and Fenton's ISCO and the potential post-treatment impacts of the technology. Specific objectives include: (1) develop a comprehensive perspective on the kinetics of oxidation of common groundwater contaminants by the most commonly used oxidants (permanganate [MnO_4^-] and Fenton's reagent [H_2O_2/Fe^{2+}]); (2) evaluate the effect of the aquifer matrix on oxidant mobility and stability using standardized oxidant demand measurement protocols; and (3) identify significant secondary impacts of ISCO

on groundwater geochemistry and microbial activity at the field-scale. This project is scheduled for completion by June 2006.

Under ER-1290, Dr. Bob Siegrist (Colorado School of Mines) is seeking to quantify the pore/interfacial scale DNAPL reactions and porous media transport processes that govern delivery of oxidant to a DNAPL-water interface and degradation of the DNAPL. Specific objectives are to (1) determine the interphase mass transfer rates and degradation of DNAPLs as a function of oxidant type and concentration, interfacial cross-flow velocity, and system properties; (2) determine the effects of porous media of varying properties on DNAPL degradation; (3) determine the effects of DNAPL entrapment morphology on mass reduction and changes in mobile contaminants after ISCO; (4) assess coupling of ISCO with mass recovery and/or natural attenuation; (5) determine if partitioning tracer test methods can be used for performance assessment at ISCO treated sites; and (6) develop decision support aids to enable cost-effective implementation of ISCO for a given site and performance goals. This project is scheduled for completion by June 2006.

3.4 Impact of Partial Source Removal

Also in FY02, research was initiated on the impact of partial DNAPL source zone removal on the plume. Specifically, research was sought that would result in or lead to assessment tools or approaches to evaluate the site specific appropriateness of DNAPL source zone removal/destruction technologies and/or an ability to predict the effect of source zone removal/destruction on the dissolved phase plume. The focus of this research area was not on specific innovative technologies for source removal but rather on the development of a fundamental understanding of the long-term impact of source zone removal technologies to allow rational selection, design, and assessment of such technologies. Four projects were selected in this area: ER-1292, ER-1293, ER-1294, and ER-1295. These projects are scheduled to complete in FY06 through FY07 and are described in detail in Section 4 (DNAPL Research Initiative).

3.5 Characterization and Delineation of DNAPL Source Zones

In FY03, an additional area of research was initiated into the characterization and delineation of DNAPL source zone. Although proposals were also requested in FY03 for the development of diagnostic procedures to evaluate the performance of chlorinated solvent source zone and/or groundwater plume in-situ remedial technologies, no projects were selected under this topic. Proposals under the characterization and delineation of DNAPL source zones Statement of Need (SON) were specifically requested to develop better tools and procedures to delineate and characterize DNAPL source zones, as well as develop protocols and guidance for cost-effectively characterizing source zones using existing and/or new technologies to aid in the selection and design of remediation options. Two projects were selected under this research area: ER-1347 and ER-1365.

Dr. George Pinder (University of Vermont) is the principal investigator under ER-1347, and the objective of this project is to develop, test, and evaluate a computer-assisted analysis algorithm to identify the location and geometry of a DNAPL source. The technical approach exploits the

concept that DNAPL is indicated by the presence of a DNAPL species concentration in excess of a specified value attributable to dissolution as described by formulae based on Raoult's law. Development of a computer-based search strategy that uses groundwater flow and transport modeling under uncertainty, a linear Kalman filter to combine modeling information and field data, and an optimization algorithm will assist in defining the DNAPL source. The algorithm will indicate where, and if necessary when, to sample groundwater quality in order to define the location of the DNAPL containing area identified with the prespecified concentration of the target compound. This project is scheduled to complete in FY07.

Under ER-1365, Dr. Walter Illman (University of Iowa) is leading the project to develop algorithms that fuse different types of information using a stochastic approach to provide a characterization, monitoring, and predictive technology for the DNAPL source zone. The information to be used in the characterization program includes hydraulic and pneumatic tomography, conservative tracer tomography, and partitioning tracer tomography. Algorithms have been developed to handle the large amounts of data generated during cross-hole testing, in which conservative and partitioning tracers are injected between several wells to locate and map DNAPL accumulations. Current work is focused on validating the algorithms in synthetic aquifers. This project is scheduled to complete in FY06.

3.6 Thermal Treatment of DNAPL Source Zones

In FY05, research on thermal treatment of DNAPL source zones was initiated to improve our understanding of (1) the mechanisms of removal and destruction of free phase and residual DNAPLs during in situ thermal treatment, including the reductions in plume loading and plume longevity and (2) the impact of varying subsurface conditions on overall removal and destruction efficiency during thermal treatment. Three projects were selected in this area—ER-1419, ER-1423, and ER-1458—and are briefly described in the following paragraphs. These projects addressed one of the critical science needs identified at the 2001 Chlorinated Solvents Workshop, assessment of thermal treatment. These projects are scheduled to complete and submit final reports in FY07 through FY08.

Under ER-1419, Dr. Kurt Pennell (Georgia Institute of Technology) is investigating the fundamental physical, chemical, and biological processes that govern thermal remediation of DNAPL source zones. Project plans include (1) quantifying temperature dependence of chloroethene physico-chemical properties, phase behavior, and sorption-desorption parameters; (2) elucidating chloroethene chemical reaction pathways and byproduct formation as a function of temperature and system conditions; (3) assessing activity and resilience of dechlorinating species during and after thermal treatment; and (4) evaluating thermal treatment performance in laboratory-scale systems.

Dr. Ralph Baker (TerraTherm) is leading ER-1423 and will be determining the relative significance of the various contaminant removal mechanisms below the water table (stream stripping, volatilization, in situ destruction, enhanced solubilization) during thermal conductive heating as well as assessing the percentage of DNAPL source removal and accompanying change in water saturation at various treatment temperatures/durations through boiling. In addition, project plans include evaluating the potential for DNAPL mobilization, either through

volatilization and recondensation, and/or pool mobilization outside the treatment zone during heating.

In project ER-1458, Dr. Rick Johnson (Oregon Health and Science University) is leading an effort to improve our understanding of the processes that lead to successful remediation of DNAPL source zones using electrical resistance heating (ERH) and to translate results into practical in situ thermal remediation guidelines. To achieve this objective, researchers will use well-controlled, very large-scale experimental aquifers coupled with numerical modeling. DNAPL will be introduced into the aquifer both as uncontrolled releases of 200 to 400 L of PCE or TCE and as strategically placed local source zones containing other DNAPL tracer with a range of physical properties. Performance of the ERH will be monitored using temperature, and voltage experiments (including degradation products) will be monitored using continuous online capillary gas chromatography.

3.7 Related Efforts

A related effort is being conducted under project ER-1349. This project is led by Dr. Mark Widdowson and is focused on developing methods to assess the long-term effectiveness of MNA. A component of this project is led by Dr. Jack Parker from the Oak Ridge National Laboratory (ORNL). Dr. Parker is working to develop a field-scale model for DNAPL source depletion with time. They have proposed a simple parametric model for field-scale DNAPL dissolution kinetics as a function of gross source zone geometry, mean groundwater velocity, and DNAPL mass remaining. High resolution numerical experiments of field-scale DNAPL dissolution in heterogeneous aquifer materials have been performed for a variety of statistical aquifer properties, DNAPL release scenarios, and groundwater flow regimes to assess the accuracy and limitations of the model and to develop practical calibration protocols. This project is scheduled to be completed by December 2006.

4. OVERVIEW OF ESTCP DEMONSTRATION AND VALIDATION EFFORTS

ESTCP demonstration and validation efforts on DNAPL source zone remediation have been underway since FY97 (Figure 1). Several projects have been initiated since then, each focusing on a specific innovative technology for DNAPL source zone remediation, characterization, or assessment. In the following sections, a summary of the ESTCP demonstration/validation efforts to date is provided.

4.1 Treatment Technologies

Under ESTCP, several types of DNAPL source zone remediation technologies have been investigated over the past several years, including biological treatment, flushing technologies, thermal treatment, and ISCO. In addition, two projects have focused on technologies for which the mechanism of action is a combination of biological as well as abiotic modes of action. The majority of these projects are currently underway and are expected to be completed within one or two years. In the following sections, a summary of the projects funded to date is provided that discusses project objectives, current status, and estimated completion date.

4.1.1 Biological Treatment

Four projects seek to demonstrate the efficacy of bioremediation of source zones. One is designed to demonstrate bioremediation through enhanced mass flushing, using only biostimulation (ER-0218), and the others address the use of bioaugmentation, either alone (ER-0008 and ER-0438) or in conjunction with chemical oxidation (ER-0116).

Under ER-0218, Dr. Kent Sorenson (CDM) and Ms. Tamzen MacBeth (North Wind Inc.) are leading an effort in which enhanced mass transfer effects through bioremediation will be demonstrated in a DNAPL source area. Two different scenarios will be evaluated. Under Scenario 1, an electron donor will be added in a "conventional" concentration range. The resulting reductive dechlorination is expected to enhance mass transfer by maintaining a steep concentration gradient along the entire water/DNAPL interface and by generating products of increasing solubility. In Scenario 2, the electron donor is added at concentrations or in specific mixtures to increase the effective solubility of the contaminants in addition to the benefits of the first scenario. This demonstration is being conducted at Fort Lewis, Washington, and is scheduled to be completed in late 2006.

Under ER-0008, Ms. Carmen Lebrón (Naval Facilities Engineering Service Center [NFESC]) is leading an effort together with investigators from GeoSyntec to demonstrate a bioaugmentation methodology using natural consortia of dechlorinating microorganisms to stimulate the biodegradation of contaminants at the DNAPL interphase. The goal of this bioaugmentation approach is to contain the source area by rapidly degrading the high concentrations of dissolved phase contaminants that emanate from the DNAPL source area and/or substantially increase the dissolution rate of DNAPL, leading to accelerated source cleanup. This project is being conducted at the Dover National Environmental Technology Test Site (NETTS) in Delaware and is scheduled to be completed by late 2006.

Dr. Herb Ward (Rice University) is leading project ER-0438. This project will conduct a demonstration of DNAPL source zone bioremediation with a known initial DNAPL mass and composition. This project is utilizing the experimental controlled release system (ECRS) at Rice University to avoid many of the difficulties inherent in field-scale work. This project is scheduled to be completed by late 2006.

In ER-0116, Dr. Eric Hood (GeoSyntec) is investigating the impacts of permanganate and reduced manganese-oxides on the activity of dehalorespiring microorganisms. Investigations have been conducted in the laboratory as well as at a field site at Cape Canaveral, Florida, at which an ISCO demonstration had previously been conducted. Results to date indicate that a sequential treatment approach consisting of permanganate flushing followed by biostimulation and bioaugmentation is feasible for treatment of TCE contamination, although microbial recolonization may be required. This project is scheduled to be completed by late 2006.

4.1.2 Flushing Technologies

Two ESTCP projects have investigated the use of flushing techniques for remediation of DNAPL source zones: ER-9714 and ER-0113. Both projects have completed the demonstration, and final documents are available on the ESTCP web site. A brief summary of the projects is provided below.

Under ER-9714, the cost and performance of in situ surfactant flooding for DNAPL removal, and the feasibility and benefits of surfactant regeneration and reuse was evaluated. The demonstration was conducted at a former dry cleaning facility located at the Marine Corps Base Camp Lejeune, North Carolina. During the field demonstration, 110 yd^3 of a low permeability (5×10^{-4} to 5×10^{-5} cm/sec) shallow aquifer contaminated by residual and free-phase PCE was treated using a surfactant formulation that was tailored for high PCE solubilization, injection into a high clay content aquifer, and amenability to surfactant recovery. The removal of PCE DNAPL in the bottom 5 ft of the shallow aquifer was targeted. The extracted surfactant solution was treated at the surface using pervaporation to separate the organic contaminants and concentrated using micellar-enhanced ultrafiltration to reinject surfactants at their original concentration. Post-treatment soil samples showed the DNAPL removal efficiency to be approximately 72%. Results of this demonstration can be found in detail in the Final Report or in the Cost and Performance Report.

The use of cyclodextrin as the flushing agent was investigated under project ER-0113. Cyclodextrin-enhanced flushing (CDEF) begins with the injection of a water-based cyclodextrin solution. This solution is flushed through the contaminated aquifer and then extracted. The performance targets for this demonstration were to remove more than 90% of the DNAPL mass and to reduce the initial aqueous TCE concentration by 99%. The overall duration of the demonstration was 4 months, during which approximately 32.5 kg of TCE and TCA were removed. The decrease in DNAPL saturation was approximately 70 to 81%. TCE concentrations in the reference wells declined between 38.5 to 99.4% (average of 77.3%) from their pre-CDEF levels. The highest aqueous TCE concentrations measured during the CDEF demonstration were up to 9 times higher than the average pretreatment TCE concentrations. Even higher solubility enhancements (up to 19 times) were observed for 1,1,1-TCA. These values demonstrate that CDEF significantly enhanced the contaminant removal rates. Results of

this demonstration can be found in detail in the Final Report or in the Cost and Performance Report.

4.1.3 Thermal Treatment

One ESTCP project is focused on thermal treatment for DNAPL source zone remediation. The project is designed to provide a critical evaluation of the state of the art of in situ thermal treatment (ER-0314). To date, the investigators (Dr. Bruce Alleman of Battelle and Dr. Paul Johnson of Arizona State University) have identified approximately 100 sites where in situ thermal treatment has been implemented, and several of these sites have sufficiently detailed monitoring records to allow useful evaluation of the performance achieved. In addition, a workshop is tentatively planned to bring together leading vendors to assess the current state of the art in this rapidly evolving field. Currently, this project is scheduled to be completed by late 2007.

4.1.4 In Situ Chemical Oxidation

Two projects are being initiated in FY06 to investigate the use of ISCO for treatment of DNAPL source zones: ER-0623 and ER-0632. A brief summary of the two projects is provided below.

Dr. Robert Siegrist (Colorado School of Mines) is leading project ER-0623 with a team of collaborators from the Colorado School of Mines, CH2M Hill, and the Navy. The overall goal of this project is to generate a knowledge-base along with engineering know-how that facilitates a standard-of-practice that enables more predictable, cost-effective application of ISCO alone or coupled with other remedial options. The specific objectives are to (1) develop an integrated ISCO protocol built on a framework of decision-support tools for determining ISCO viability and best practices for site-specific conditions, (2) evaluate case studies of ISCO technology application and compare the protocol-generated best practices against case study results to determine the ability to predict performance of site-specific ISCO applications, (3) test the integrated protocol at a selected number of DoD field sites, (4) make appropriate refinements to the protocol based on field study results and technical panel review, and (5) document recommended practices in a Frequently Asked Questions guide and a comprehensive ISCO Technology Practices Manual.

Under ER-0632, Dr. Rick Watts (Washington State University) is leading an effort with Dr. Dick Brown (ERM) to conduct a rigorous demonstration of peroxygen-based ISCO at a DNAPL source zone site. The specific objectives of the demonstration are to 1) apply rational process chemistry to improve the design and implementation of peroxygen ISCO at the demonstration level, including maximizing hydrogen peroxide and persulfate distribution, evaluating hydrogen peroxide/persulfate stabilization procedures, and comparing increased hydrogen peroxide stability to the stability of persulfate; 2) to validate the effectiveness of peroxygen ISCO in the field by detailed assessment of contaminant loss, fate, and product formation, including the potential for concurrent and subsequent biological degradation of contaminants; and 3) to implement and document an ISCO optimization approach that involves multiple phases ranging from bench-scale treatability studies to full-scale application.

4.1.5 Enhanced Biodegradation Combined with Abiotic Approach

Two projects are addressing the issue of DNAPL source zone remediation through approaches that enhance biodegradation, while also affecting an abiotic mechanism: ER-0319 and ER-0431.

Under ER-0319, Mr. Arun Gavaskar (Battelle) and Dr. Rob Hinchee (IST) are leading an effort to investigate the use of vegetable oil to sequester the DNAPL within a source zone, thereby reducing mass flux from the source and slowly biodegrading the chlorinated solvents in place. A demonstration site has been selected, and the project is scheduled to be initiated during 2006 and completed by late 2007.

Dr. Tom Krug (GeoSyntec) is investigating the use of emulsified, zero-valent, nanoscale iron (EZVI) in project ER-0431. The investigators intend to evaluate in the laboratory the proportion of the chlorinated solvent mass destruction that is occurring due to abiotic dehalogenation versus enhanced biodegradation as a result of the addition of electron donor in the form of an oil emulsion, then inject EZVI into two pilot test areas within a DNAPL source zone using the two most promising EZVI injection technologies. Laboratory studies are nearing completion and the field effort is scheduled to begin in 2006.

4.2 Characterization and Delineation of Source Zones

To date, only one project has been conducted in ESTCP to demonstrate a technology to characterize DNAPLs. Under ER-0109, a suite of sensor technologies was demonstrated for real-time in situ characterization of DNAPL. The sensors consist of a halogen-specific detector (XSD) designed to operate downhole behind a membrane interface probe (MIP) that samples the soil formation for volatile organic compounds (VOC). Moving the detector downhole and measuring while the direct push probe is continuously advanced provides an order of magnitude increase (from feet to inches) in the spatial resolution when compared to previous methods that use an MIP coupled to an uphole detector. A second sensor system that makes use of a very high repetition rate microchip laser to detect small-scale spatial variability in fluorescence from petroleum products or humic substances that may be dissolved in DNAPL is intended to provide greater spatial resolution (tenths of inches). Finally, a third sensor system that employs a video imaging system integrated into a push probe provides direct visual verification of DNAPL source zones indicated by the XSD and fluorescence measurements. This project was scheduled for completion in 2005. The lead investigators are currently completing the final documentation.

4.3 Monitoring and Assessment

Several projects are examining some aspect of the monitoring and assessment of DNAPL source zones, including ER-0114, ER-0318, ER-0424, ER-0436, and ER-0530. These projects include issues such as measurement of mass flux, as well as improved decision making. A brief summary of these projects is provided below.

Dr. Kirk Hatfield (University of Florida) is demonstrating a "flux meter" in project ER-0114. The flux meter is a self-contained permeable unit that is inserted into a well or boring such that it intercepts groundwater flow but does not retain it. The interior composition of the meter is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and inorganic contaminants present in fluid intercepted by the unit. The sorbent matrix is also impregnated with known amounts of one or more fluid soluble "resident tracers." These tracers are leached from the sorbent at rates proportional to the fluid flux. Following exposure to groundwater flow for a period ranging from days to months, the meter is removed and the sorbent carefully extracted to quantify the mass of all contaminants intercepted and the residual masses of all resident tracers. The contaminants' masses are used to calculate time-averaged contaminant mass fluxes, while residual resident tracer's masses are used to calculate cumulative fluid flux. This flux meter was demonstrated at several sites. Currently, final documentation is being prepared and should be posted to the ESTCP web site within the next few months.

Under ER-0318, Dr. Mike Kavanaugh and Dr. Rula Deeb (Malcolm Pirnie) are evaluating a variety of innovative diagnostic tools at several sites undergoing different remediation technologies. The tools to be investigated include side-by-side assessments of different mass flux measurement techniques, stable compound isotopes to assess degradation of contaminants, molecular biological evaluations of biodegradation, and rock core analyses to evaluate matrix diffusion. This project has conducted demonstrations at three sites: Fort Lewis, Washington, Watervliet Arsenal, New York, and Vandenberg Air Force Base, California. This project is currently scheduled to complete final documentation by early 2007.

One of the key integrating projects for the DNAPL work funded by SERDP and ESTCP is the development of a user-friendly screening tool to reduce the uncertainty of estimating and predicting remedial outcomes when evaluating source zone treatment (ER-0424). The project is managed by Ms. Carmen Lebrón (NFESC), and the lead investigators are Dr. Bernie Kueper of Queens University and scientists from GeoSyntec. By integrating field experience and state-of-the-art numerical modeling, the researchers expect to develop the screening tool, along with guidance on its use. The screening tool should provide a valuable decision framework for determining when source treatment should be attempted and which technologies are most appropriate, as well as for selecting appropriate remediation and performance objectives.

Dr. Mark Kram (NFESC) and Dr. Mark Widdowson (Virginia Tech) are leading project ER-0436. The objective of this demonstration is to evaluate the capabilities of the Natural Attenuation Software to provide reasonable estimates of cleanup times associated with combining source-area remediation with MNA. The tool will be evaluated using data from six to eight sites throughout the United States that encompass diverse geologic and hydrogeochemical environments. By comparing the predictions from early data sets to empirical data during the

predicted period, the utility of the estimates will be assessed. A performance report will then be developed to document the conditions and metrics for these sites. This project is currently scheduled to be complete by June 2006.

Under ER-0530, Dr. Tom Sale (Colorado State University) is leading an effort to develop a document that highlights current knowledge regarding best practices for management of chlorinated solvent releases. This is intended to be accomplished through the development of an ESTCP Protocol for Selecting Remedies for Chlorinated Solvents Releases at DoD Facilities. Inclusive to the protocol will be a quick access guide to Frequently Asked Questions. These documents are scheduled to be completed by June 2007.

5. SUMMARY

This document was intended to provide a general overview of the history of the research and development efforts on DNAPL source zone characterization and remediation under SERDP, and to provide an overview of the demonstration and validation projects focused on DNAPL source zone remediation funded through ESTCP. Throughout the document, web links have been provided to guide the reader to additional resources providing information on specific projects. Additional resources may be found by accessing the SERDP and ESTCP Online Library.

2005 ANNUAL REPORT

DNAPL Source Zone Initiative

February 2006

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Acronyms and Abbreviations

AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
CAH	chlorinated aliphatic hydrocarbon
DNAPL	dense nonaqueous phase liquid
DoD	Department of Defense
ITRC	Interstate Technology and Regulatory Council
NAPL	nonaqueous phase liquid
PCE	tetrachloroethene
PI	principal investigator
RTF	remediation time frame
SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethene

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) is designed to develop and transition innovative research and technology to help the Department of Defense (DoD) perform its mission in several environmental areas, including cleanup of contaminated sites. While DoD facilities may have several contaminants, chlorinated solvents are by far the most prevalent. These compounds, collectively categorized as chlorinated aliphatic hydrocarbons (CAH), continue to be difficult to remediate, particularly at sites containing CAHs as dense nonaqueous phase liquid (DNAPL), where the DNAPL serves as a continuing long-term source of dissolved-phase groundwater contamination.

SERDP is currently funding a number of projects in the area of DNAPL source zone characterization and remediation. A Technical Review Panel of experts from academia and the consulting industry provides SERDP with objective professional evaluations of progress made on these projects, identifies knowledge gaps in DNAPL research and development, and recommends potential areas of funding. This technical oversight format is unique in the field of cleanup technology research and development, and ensures continuity and cross-fertilization in this focused effort to elucidate the benefits of source zone characterization and remediation.

This report highlights the scope and objectives of the individual SERDP projects, and summarizes their progress in advancing the understanding of key issues related to source zone cleanup. It serves as a follow-up to the initial 2004 Annual Report.

2. PROGRAM OVERVIEW

SERDP's DNAPL initiative was formed in 2002 with the initiation of several projects and the formation of an Expert Panel to advise SERDP and assist in coordinating efforts in this area. The panel members include Dr. Hans Stroo (chair), Dr. Paul Johnson (Arizona State University), Dr. James Mercer (TetraTech), Dr. Michael Kavanaugh (Malcolm Pirnie), and Dr. Robert Hinchee (IST). The panel meets with the principal investigators (PI) twice a year to review progress and make recommendations regarding future directions. To date, there have been six such meetings (December 2002, April 2003, December 2003, April 2004, December 2004, and April 2005).

This initiative has also led to several technology transfer opportunities. These include presentations on DNAPL source zone remediation at the annual Air Force Center for Environmental Excellence (AFCEE) Tech Transfer conferences, and participation in Interstate Technology and Regulatory Council's (ITRC's) DNAPL Remediation Team and the recently-formed ITRC team on Bioremediation of DNAPLs.

The projects included in this initiative consist of three ongoing projects started in 2002 (ER-1293, ER-1294, and ER-1295), and one project started in 2002 and concluding in 2005 (ER-1292). Progress on these projects is summarized below.

2.1 Project ER-1292: Decision Support System to Evaluate Effectiveness and Cost of Source Zone Treatment (Charles Newell, Groundwater Services, Inc.)

The initial overall goals of this project were: 1) to develop a source evaluation methodology, based on generic "source settings" for different types of DNAPL sources; 2) to generate source concentration versus time curves for each source setting, based on modeling and literature reviews; and 3) to develop a source remediation cost and performance database. The final report for this project is currently being completed before its original scheduled completion, largely because of concerns that the information available was not yet sufficient to allow a technically defensible decision support system. The project has made excellent progress on the cost and performance database, and the final report will focus primarily on these findings.

The 2004 report summarized the database review, which used well-monitored site cleanups willing to share cost and performance data for the major source treatment technologies. The project has been completed, and valuable cost and performance data have been published (see Figures 1 and 2). The project also attempted to estimate the potential for source depletion projects to reduce the remediation time frame, showing that if concentration reductions show typical first-order kinetics, the impact of typical source depletion technologies (roughly 80 to 90% reductions in source zone concentrations) on remediation time frames will be far less impressive (Figure 3). In addition, a decision support system was developed based on the results from the project. A draft version of the support system has been prepared and the final version should be available soon.

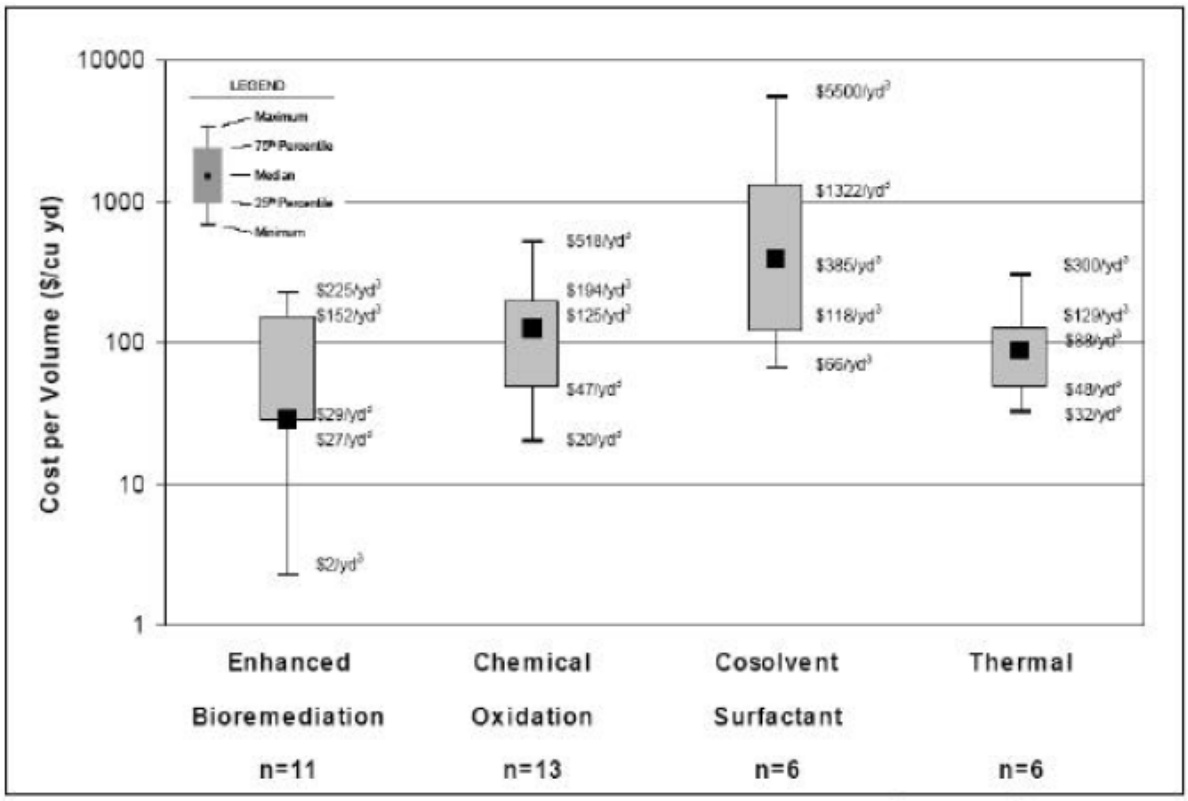

Figure 1. Summary of Costs for Source Depletion Projects by Technology

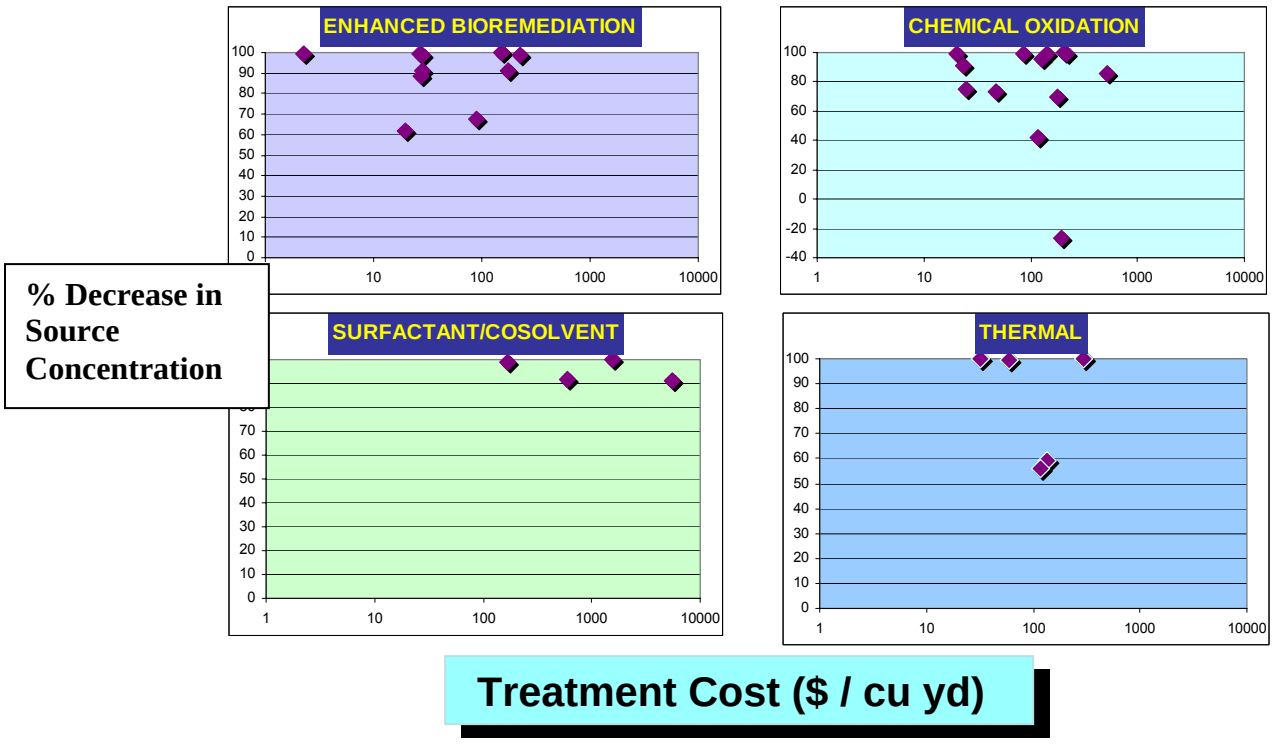

Figure 2. Summary of Costs and Performance by Technology

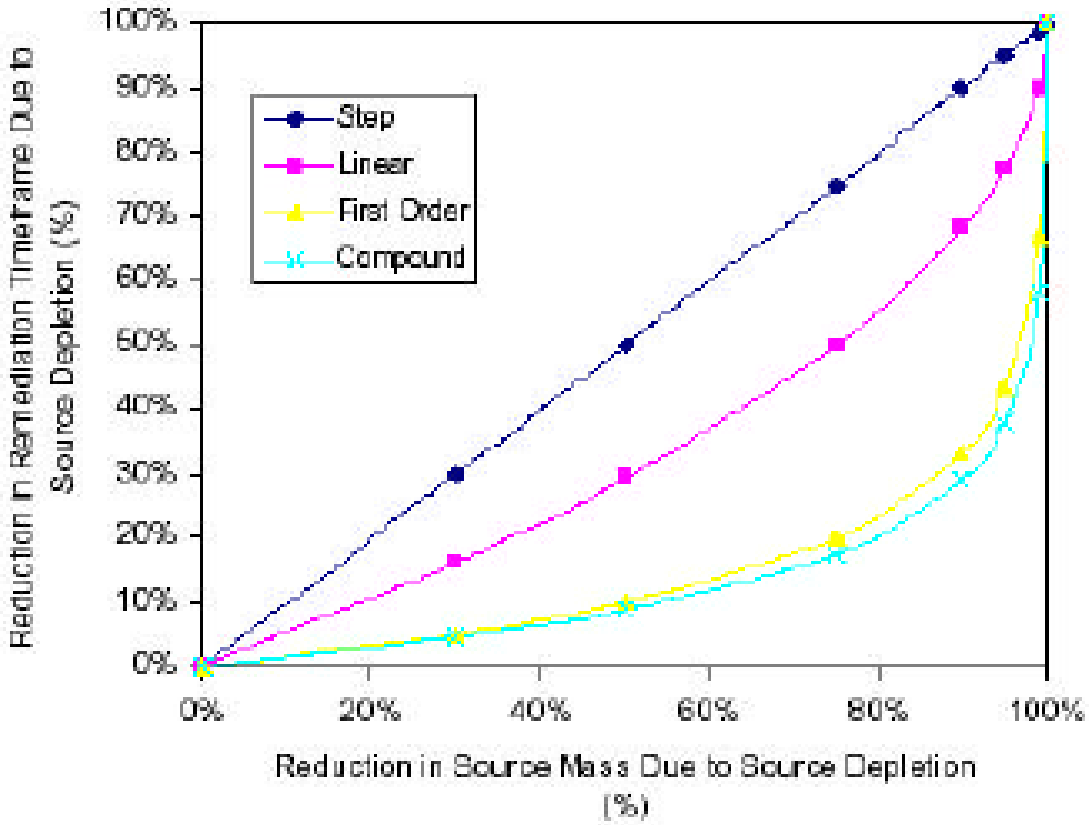

Figure 3. Impact of Source Reduction on Remediation Time Frame (RTF). (Assuming kinetics are first order, a typical 80% reduction in the source mass will yield only a 17% decrease in the time needed for complete cleanup.)

2.2 Project ER-1293: Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment (Linda Abriola, Tufts University)

This project is designed to develop tools that can be used 1) to predict and monitor plume responses to source treatment and 2) to perform cost/benefit analyses of source zone treatment. The project includes bench- and field-scale studies, as well as mathematical modeling, with emphasis on surfactant treatment and bioremediation, individually and in conjunction. Progress has included studies demonstrating that pure cultures can biodegrade tetrachloroethene (PCE) when present as a DNAPL and measurement of the dechlorination kinetics, development and validation of a mathematical model of plume development with and without treatment, and development of methods to perform uncertainty analyses of mass flux predictions.

The project has shown that significant reductions in contaminant mass flux can be achieved with only moderate mass removal by surfactant flushing in sandy media, although significant mass may persist following aggressive source zone treatment. As part of this surfactant flushing research, they have also evaluated a potential improvement in the technology known as Density-Modified Displacement (Figure 4). They have also proposed that the mass removal achievable, and the relationship between mass flux and mass removal, is highly dependent on the DNAPL architecture. The investigators have focused on describing DNAPL architecture by a ganglia-to-pool ratio.

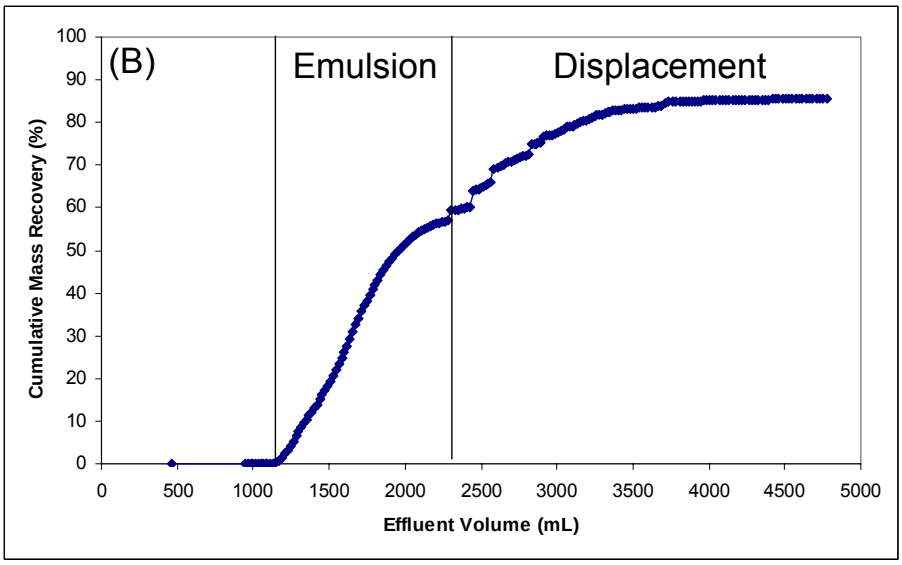

Figure 4. Cumulative Mass Recovery During Density-Modified Displacement

One key result has been development of an uncertainty analysis model that evaluates the uncertainty in conductivity and concentrations separately. The output then estimates the uncertainty in a mass flux estimate. Such a model can be useful in determining how many samples are needed, where more sampling is needed, and how the uncertainty can be most efficiently reduced. This model has undergone extensive development and testing, and future plans include using the model to evaluate the uncertainty in real-world field measurements of mass flux. For example, the model has been used to estimate that accurate estimates of mass flux in areas that have experienced high levels of mass removal may require measuring 6 to 7% of the total groundwater volume along a transect. Such a sampling density is far in excess of the amounts typically analyzed during a groundwater sampling program and may be economically prohibitive in many cases.

The project has also focused on the combination of surfactant flushing and bioremediation. Bioremediation was shown to enhance flushing in column studies by a factor of approximately 4.7 (Figure 5). Modeling studies have suggested that the combination can significantly reduce plume longevity, particularly at sites with a favorable DNAPL architecture (i.e., DNAPL primarily located in ganglia as opposed to

pools). Lab testing has shown that dechlorinating bacteria can remain active in the presence of high PCE and moderate surfactant (Tween-80) concentrations. The project has also developed a cost analysis tool for surfactant-enhanced remediation and is extending this tool to other in situ remediation technologies.

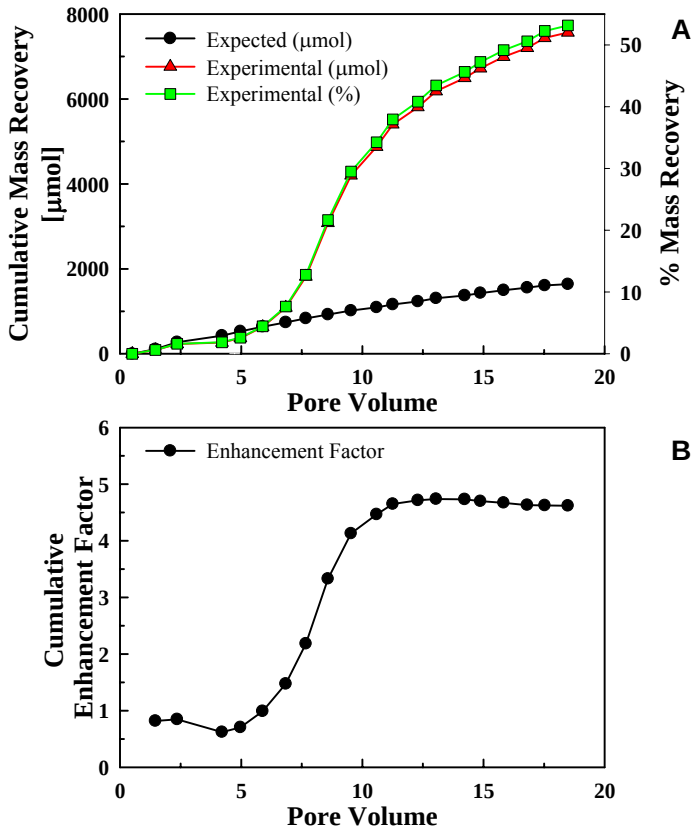

Figure 5. Mass Recovery and Flux Enhancement During Bioremediation Testing

2.3 Project ER-1294: Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (Tissa Illangasekare, Colorado School of Mines)

This project is designed to understand, quantify, and model mass transfer from source zones before and after remediation. Thermal, biological, and chemical (surfactants and oxidants) remediation methods are all being simulated in laboratory tests. The lab tests yield measurements of the mass transfer coefficients at small scales, and these measurements will then be used in models, relying on upscaling methods to estimate mass transfer at field scales. One of the key observations made in the laboratory experiments in small test cells is that in the case of bio treatment, the mass transfer rates increased significantly during source zone bioremediation. The increase depends on the entrapment morphology (Figure 6). Upscaling these processes to larger scales is in progress. Similar upscaling studies are performed for the other treatment technologies.

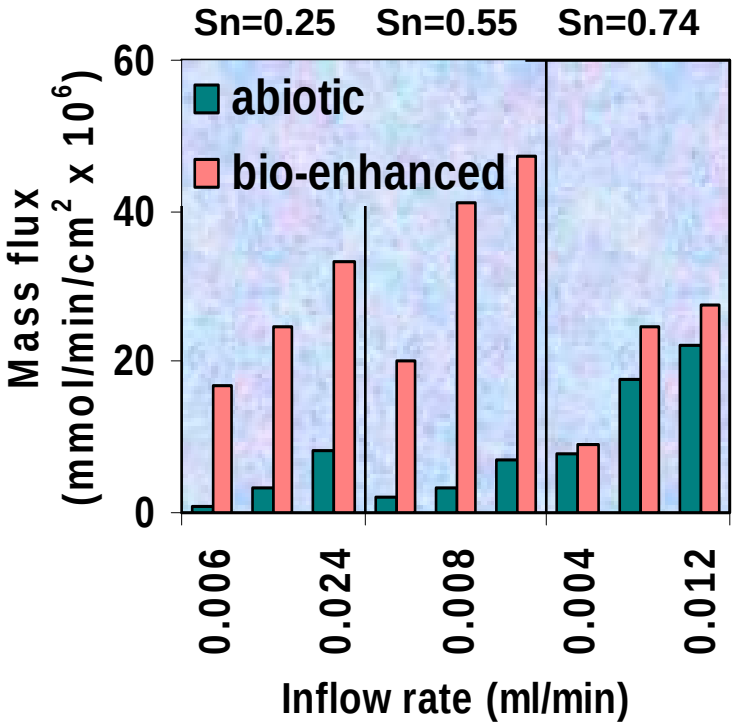

Figure 6. Change in Mass Transfer during Biotreatment for DNAPL Morphologies in Pools with Different Average Saturations. (Biological activity enhanced the mass transfer rates by factors of 4 to 13 in average pool saturations of 0.55 or less. When the saturation was high [0.74], the mass transfer enhanced by a factor less than 1.5.)

Significant progress has been made on the development and experimental validation of models and evaluation of the feasibility of using partitioning tracers as a method to characterize DNAPL source zones with complex entrapment architecture. Improved methods of analysis to determine the DNAPL architecture using numerical models have been developed. Batch and column studies have shown that partitioning behavior changes significantly as a result of biological or oxidation treatments although the partitioning is not changed by surfactant treatment. However, for the partitioning test to be feasible to determine mass removal after treatment, a sufficient volume has to be removed to change the DNAPL entrapment architecture. Methods to use observed flux to determine source zone architecture that contributes to plume emission have been researched. Progress has also been made on the measurements of mass transfer coefficients at point scales. The modeling tools for mass flux prediction based on point-scale characterization information are based on popularly used three-dimensional groundwater flow code MODFLOW and transport code MT3D. Technology specific mass transfer simulators have been developed based on reaction package RT3D. These simulators are coupled to the flow and transport simulators to predict both pre- and post-treatment mass flux and plume development. The parameter estimation methods are based on popularly used inversion codes PEST and UCODE.

As the methods and tools that have been developed cannot be validated in the field under conditions of natural flow and complex DNAPL architecture resulting from geologic heterogeneity, a series of controlled experiments were conducted in intermediate scale test tanks to generate a comprehensive data set for validation. The instrumentation used allows for the accurate monitoring of the source zone mass depletion during treatment. By observing the downstream concentrations, it is possible to evaluate the effect of source zone mass depletion on pre- and post-treatment mass flux down gradient from the source zone.

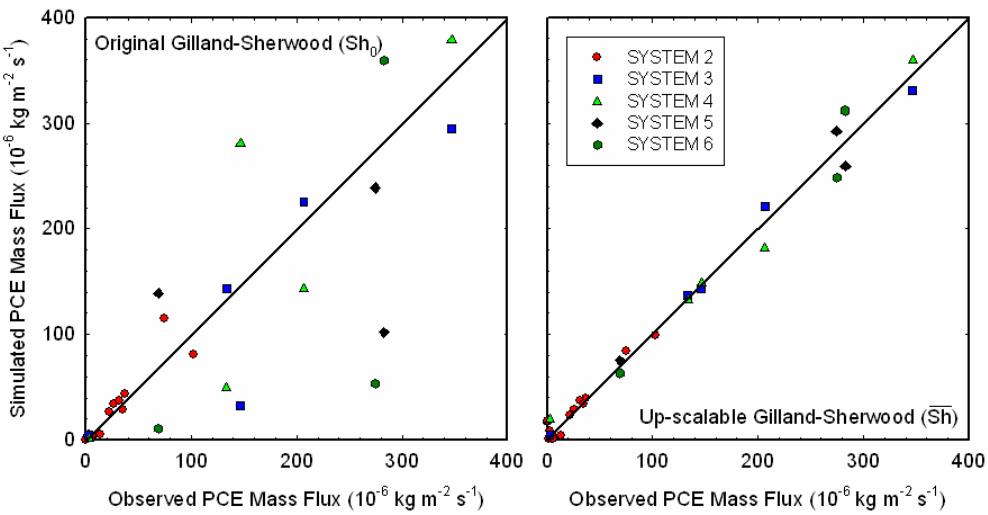

Figure 7. Validation of Upscaling Methodology Developed for NAPL Dissolution in an Intermediate Scale Tank Experiment (In the left graph, the simulated mass flux emission from a source zone without upscaling is compared with the experimentally observed flux. The right graph shows good match between the upscaled flux using the developed method and the observations. The "system" refers to different grid sizes used in mass flux interpretation from observations and model-simulated concentrations.)

Different remediation methods have been simulated at in these tanks under carefully controlled conditions. The work has indicated that the upscaling methods used to simulate mass flux yielded close agreement with measured mass flux values (Figure 7). The researchers have cooperated closely with investigators leading another project on in situ chemical oxidation, as well as with other DNAPL SERDP projects. Figure 8 shows the results from one of the large tank experiments where chemical oxidation was used to treat a source zone with a low heterogeneity packing. Similar results are available for the other treatment technologies to evaluate and model the effects of source zone mass removal on mass flux.

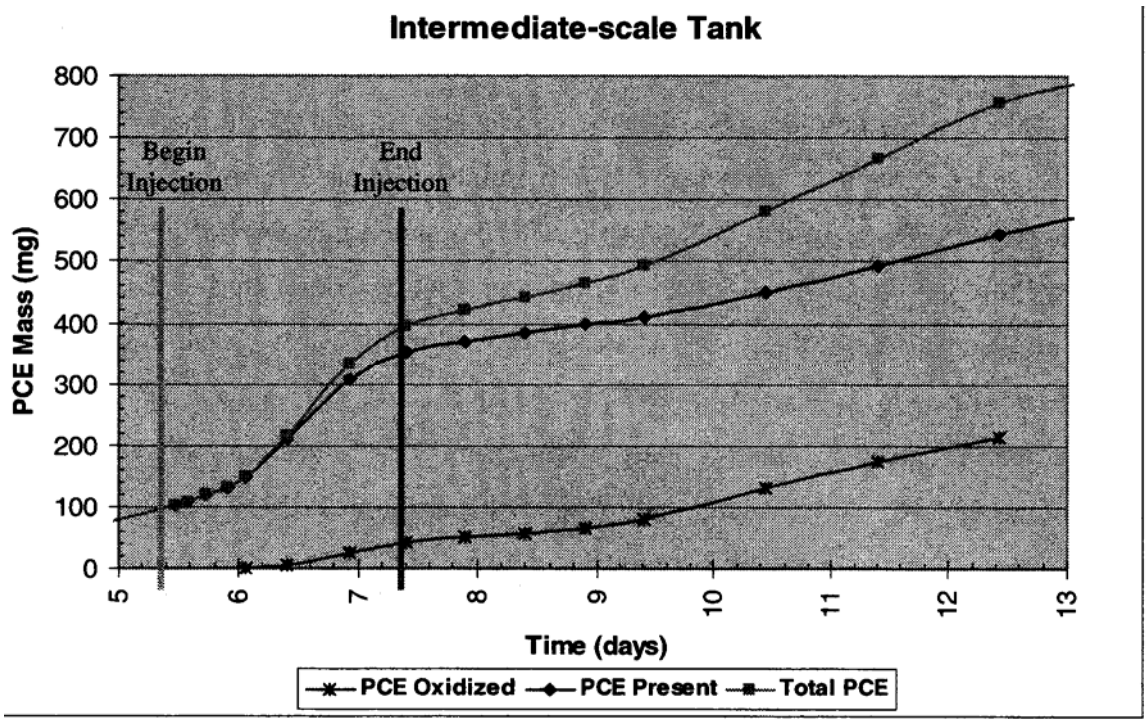

Figure 8. Results of an Intermediate Scale Tank Study with a Low Heterogeneity Packing. (Dissolution increased as expected during the injection of the oxidant. The slope of the total PCE line becomes greater than the slope of the dissolved PCE line prior to the oxidant arrival, indicating the mass transfer from DNAPL was enhanced by the presence of oxidant. Similar results are available for high heterogeneity packing.)

For field application of this methodology, it will be necessary to develop field characterization techniques to obtain information on the DNAPL entrapment architecture. Preliminary analysis suggests that down gradient concentration and mass flux data can be used to determine entrapment architecture (i.e., by identifying the hot spots producing significant solute mass) using inverse modeling tools. Numerical simulations in three-dimensional settings are underway to develop guidelines on field characterization techniques to obtain the information needed to use the tools developed in this research.

The project has been extended, but should be completed by late 2006. The original focus on development of a decision tool has been deferred in favor of continued investigation of the fundamental processes occurring during partial source remediation.

2.4 Project ER-1295: Impacts of DNAPL Source Zone Treatment (Lynn Wood, U.S. EPA)

This project is designed to develop a scientifically defensible approach to evaluating the benefits of DNAPL source depletion. The project's overall goal is to determine the impacts of partial DNAPL source removal from heterogeneous aquifers on the extent of

migration and the longevity of the contaminant plume. Specifically, the research seeks to characterize the relationships between DNAPL architecture, mass removal, and mass flux through laboratory testing, numerical modeling, and mass flux measurements at several field sites undergoing different remediation approaches.

Field measurements have been done at Hill Air Force Base (AFB) before and after surfactant-enhanced remediation. In addition, measurements have been made at the Sages Dry Cleaner site in Jacksonville, Florida, and the Borden site in Ontario, Canada, where permanganate was injected into a DNAPL source zone. Data is also being assimilated from five source zone remediation tests performed at the Dover National Environmental Technology Test Site. Initial results showed impressive reductions in mass flux at the Hill AFB transect sites (2004 report). Measurements have also been performed at Fort Lewis before in situ thermal treatment was started. Post-treatment measurements will be made as soon as the site has cooled sufficiently to allow sampling and analysis. The combination of all of these mass flux measurements will not only allow an assessment of the impacts of partial mass removal on mass flux but also should provide an opportunity to compare different methods of measuring mass flux and to determine the level of uncertainty accompanying such measurements.

The project also includes a substantial modeling effort to better understand and predict the relationship between mass removal and mass flux. Significant progress has been made in developing "Lagrangian streamtube models" (published in 2005) that predict mass flux reductions due to nonaqueous phase liquid (NAPL) mass removal. One of the key findings of this work is that, as the heterogeneity in aquifer properties and NAPL spatial distribution increases, less mass reduction is required to achieve a given flux reduction. However, for a similar flux reduction, the source longevity will be greater in the more heterogeneous system.

Data from a laboratory study of cosolvent flushing is shown in Figure 9, illustrating the relationship between source mass reduction and mass flux. Such data, or more likely predictions from the modeling efforts, can then be used to evaluate the amount of mass removal needed to achieve performance goals, such as the flux reduction needed to ensure that natural attenuation can be protective (see conceptual depiction in Figure 10).

The project has been delayed due to difficulties in sampling the field sites. However, the work has generated several publications, notably on the modeling efforts and on the measurement and use of mass flux to characterize sources and assess performance.

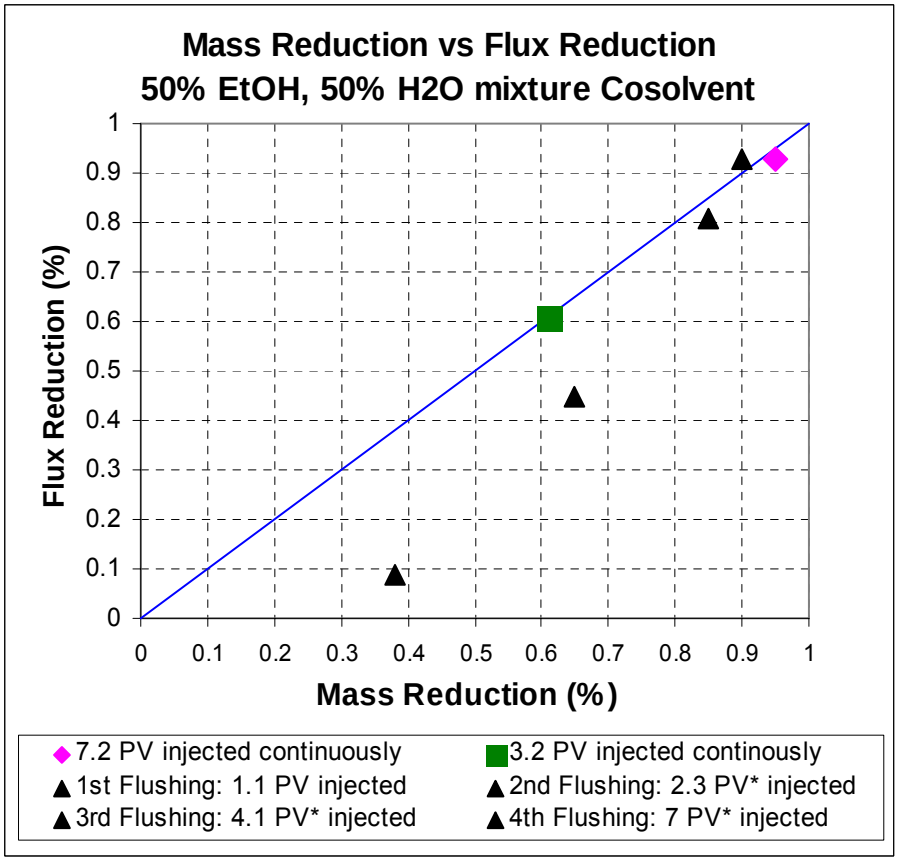

Figure 9. Mass and Flux Reductions Measured During Cosolvent Flushing Studies (50% ethanol/50% water mixture)

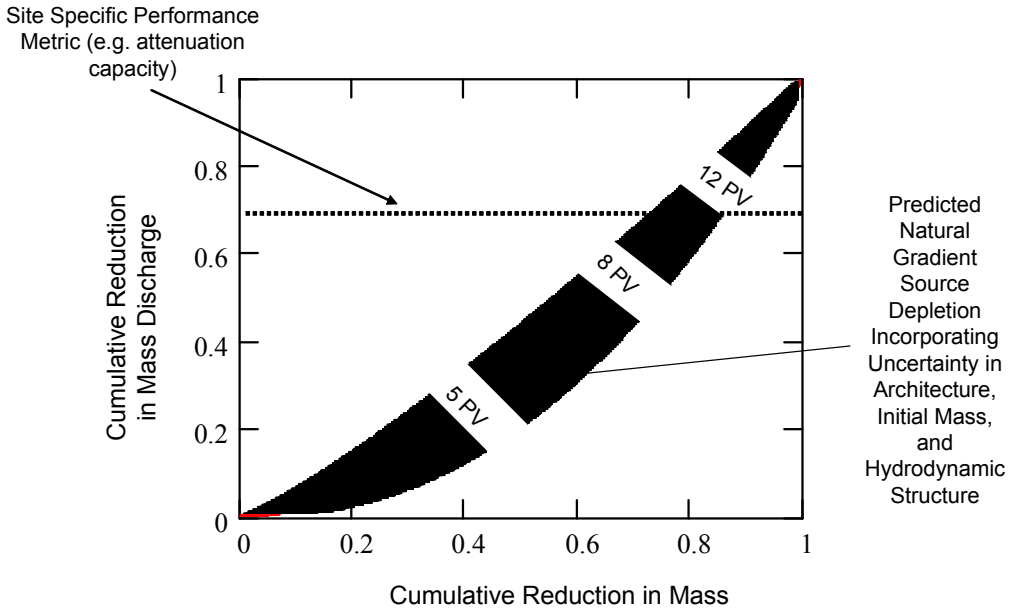

Figure 10. Relationship Between Reductions in NAPL Mass and Contaminant Flux Relative to Performance Metrics

3. SUMMARY

The SERDP projects involved in the DNAPL Initiative are scheduled to be completed in 2006, with one project (ER-1293) extended to 2007. All final documents from these projects will be posted on the SERDP web site. Numerous journal articles have resulted from these projects, and a publication list for each project will be available at the conclusion of the projects.