SERDP
Strategic Environmental Research and Development Program

ESTCP
Environmental Security Technology Certification Program

ANNUAL REPORT

DNAPL Source Zone Initiative

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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 (CAHs), continue to be difficult to remediate, particularly at sites containing CAH 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 reviews the technical basis for funding priorities, 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. In addition, links to relevant projects within the related Environmental Security Technology Certification Program (ESTCP) are included to provide an overview of the range of funded projects in this area. This report will be updated annually and is intended to meet SERDP's mandate to transfer science and technology emerging from these projects to regulators, cleanup specialists and the regulated community. A number of additional resources on the subject of DNAPL source zone remediation are available elsewhere on this website.

1.1 The DNAPL Challenge

Chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE) are found at approximately 80% of all Superfund sites with groundwater contamination and more than 3000 Department of Defense (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 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.

1.2.1 Science Needs

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.

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.

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.

Quantification of Uncertainty

Site-specific selection, design, and evaluation of remedial systems are necessarily based upon 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.

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.

1.2.2 Technology Needs

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.

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.

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

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.

Source Zone Bioremediation and Bioaugmentation
In situ bioremediation, including 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.

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.

1.2.3 Summary
Several SERDP and ESTCP projects are addressing the science and technology needs identified by the Expert Panel Workshop. Table 1 provides a summary of SERDP and ESTCP projects and the related science and/or technology need which a project addresses. Additional detail concerning these projects is provided in the following sections.

Table 1. Research Needs Addressed by Individual SERDP and ESTCP DNAPL Source Zone Projects

	SERDP				ESTCP					
Science Research Need	**CU-1292**	**CU-1293**	**CU-1294**	**CU-1295**	**CU-0008**	**CU-0116**	**CU-0218**	**CU-0314**	**CU-0318**	**CU-0319**
Assessment of Source Zone Treatment Technologies	✓	✓	✓	✓				✓	✓	
Physical/Chemical/Biological Interactions at NAPL Interface			✓							
Source Zone Delineation and Characterization		✓								
Quantification of Uncertainty		✓								
Effects of Treatment Amendments						✓				
Cost Effective Assessment Tools and Methodologies	✓	✓							✓	
Bioaugmentation					✓	✓				
Technology Research Needs										
Benefits of Partial Mass Removal from Sources				✓						
Source Zone Characterization and Flux Analysis				✓						
Diagnostic Tools to Measure Performance				✓					✓	
Assessment of Thermal Treatment								✓		
Source Zone Bioremediation and Bioaugmentation					✓	✓	✓			✓

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 (PIs) twice a year to review progress and make recommendations regarding future directions. To date, there have been four such meetings (December 2002, April 2003, December 2003, and April 2004).

This initiative has also led to several technology transfer opportunities. These include presentations on DNAPL source zone remediation at the annual AFCEE Tech Transfer conferences, and participation in ITRC's DNAPL Remediation team and the recently-formed ITRC team on Bioremediation of DNAPLs (see links section below).

3. SERDP PROJECTS

The projects included in this initiative consist of three ongoing projects started in 2002, and one project started in 2002 and concluding in 2004. Progress on these projects is summarized below.

3.1 Project CU-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.

Table 2 summarizes the findings from the database review. Well-monitored site demonstrations were reviewed and cost and performance data were tabulated on an equivalent basis for the major source treatment technologies. Of course, more costly and aggressive technologies are generally selected for the more difficult site conditions or remediation objectives, so these results should be viewed with some caution. In addition, performance is usually measured by the reduction in concentrations in key monitoring wells, generally located in or near the source area, and this method of performance assessment does not provide a complete evaluation of efficacy (percent mass removal was also estimated in most cases). Nevertheless, the data are a valuable summary of the real-world costs and performance achieved to date, and should provide project managers and researchers useful information on these technologies.

3.2 Project CU-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 pure cultures can biodegrade 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.

One of the more interesting results, summarized in Table 3, is a prediction of source longevity without treatment, with enhanced bioremediation alone, and with surfactant flushing (Surfactant Enhanced Aquifer Restoration or SEAR) followed by enhanced bioremediation. The results have demonstrated the importance of understanding the DNAPL architecture, expressed as the

Table 2. Summary of Costs and Performance of Key Source Zone Treatment Technologies (from CU-1292)

Location	Performance (% reduction in groundwater concentration)	Cost ($/yd^3)
	Bioremediation	
Orlando	99.8	9
Germantown	99.7	NA
Duluth	99.5	27
Idaho Falls	99.8	10
Largo	95.6	178
Rochester	81.9	16
	In Situ Chemical Oxidation	
Framingham	98.9	NA
Aiken	99.5	216
Hutchinson	91.2	13
Piketon	70.1	28
Camden County	99.8	36
Rockville	83.6	NA
	In Situ Thermal Treatment	
Skokie	99.3	32
Pinellas	83.7	77
PCP Site	88.9	133
Savannah River	NA	44
Visalia	NA	39
Cape Canaveral	54.2	116
	Surfactants/Cosolvents	
Hill AFB	99.3	170
Camp Lejeune	NA	6,975
Ontario	90.3	NA
Laramie	NA	79
Quebec	91.8	NA
Jacksonville	70.7	156
Alameda	NA	66
NA – not available		

Table 3. Modeled Source Longevity with and without Source Zone Treatment in Varying DNAPL Architectures

Scenario	Natural Dissolution	Source Zone Bioremediation	SEAR + Bioremediation
High G:P	**54**	**11**	**<1**
Low G:P	**245**	**50**	**24**
Pool Only	**817**	**163**	**157**

G:P = Ganglia to pool ratio
From Christ et al. (in press)

ganglia:pool ratio (i.e., the relative volumes present in dispersed ganglia or in concentrated DNAPL pools).

Another 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.

3.3 Project CU-1294: Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (Tissa Illangesekare, 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 up-scaling methods to estimate mass transfer at field scales.

Significant progress has been made on the development of models and on the use of partitioning tracers as a method to estimate mass. Results have shown that partitioning behavior changes significantly as a result of biological or oxidation treatments, although the partitioning is not changed by surfactant treatment (see Table 4). Progress has also been made on the measurements of mass transfer coefficients at point scales, particularly with the measurements of coefficients following surfactant treatment.

The point-scale results will then be used in very large-scale tank experiments to validate the up-scaling methods and model predictions. Different remediation methods can be simulated at a large scale under carefully controlled conditions. This work has just been started. The up-scaling methodology has been developed, and is based on the so-called Gilland-Sherwood relationship, in which an experimentally determined mass transfer coefficient (the Sherwood number). The Sherwood number can the be up-scaled based on measured relationships with the

Table 4. Summary of residual DNAPL volumes estimated by tracers and compared with the initial and final volumes in the columns

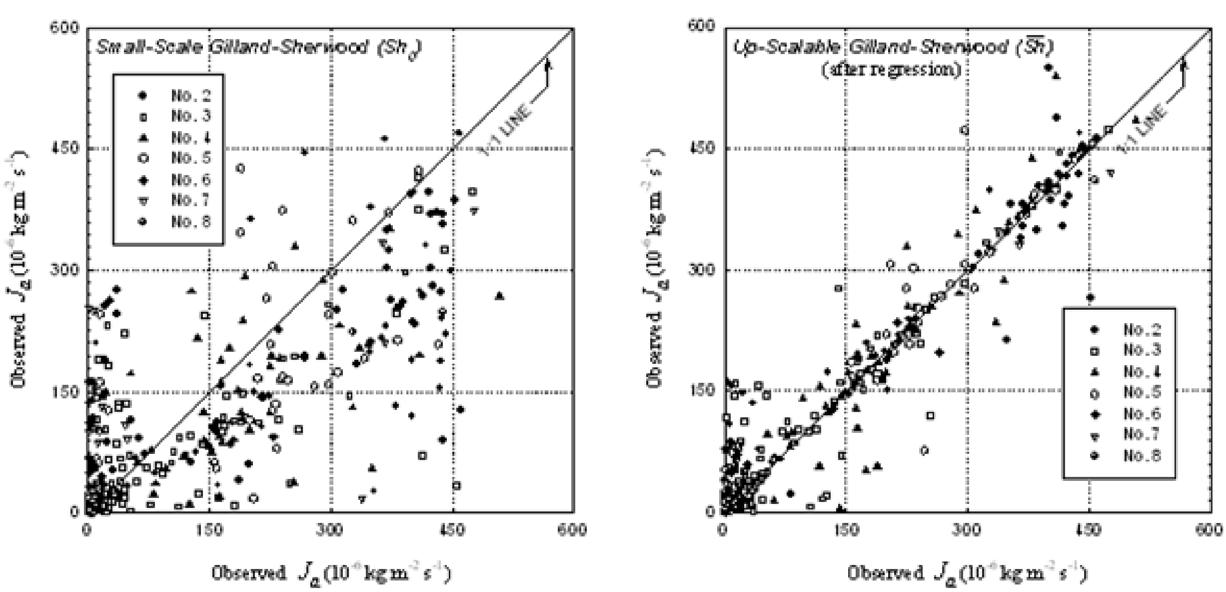
DNAPL Type	Initial DNAPL Volumes (mL)	Pre-surfactant				Post - surfactant				Final DNAPL Volumes
		Hexanol		DMP		Hexanol		DMP		
		V	%	V	%	V	%	V	%	
Dyed TCE	16	13.58	84.9	11.75	73.4	4.44	103	2.96	69	4.3
Field DNAPL	16	13.88	86.7	12.64	79.0	2.07 (5.10)[1]	28 (69)	5.11 (8.05)[1]	69 (109)	7.4

[1]The volumes estimated using the partitioning coefficient determined after treating the field DNAPL with surfactant.

groundwater velocity, chemical properties, amount of NAPL present in the system, soil heterogeneity, and the entrapment architecture. This up-scaling allowed excellent correlations between simulated and observed mass fluxes (example in Figure 1).

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.

Figure 1. Comparisons of observed and modeled mass fluxes using experimentally-derived (left) and proposed up-scalable Gilland-Sherwood correlations (right)



3.4 Project CU-1295: Impacts of DNAPL Source Zone Treatment, Dr. Lynn Wood, U.S. EPA

This project is designed to develop a scientifically defensible approach to evaluating the benefits of DNAPL source depletion. The fundamental premise is that mass flux should be the basis for assessing the long-term impacts of treatment. Specifically, the research seeks to characterize the relationships between DNAPL architecture, mass removal, and mass flux through both modeling and mass flux measurements at several field sites undergoing different remediation approaches.

The first field measurements have been done at Hill AFB, before and after surfactant-enhanced remediation. Initial results show impressive reductions in mass flux at all transect sites (Figure 2), and the results will allow a comparison of different methods of measuring mass flux (i.e., mass flux meters and integrated pump tests – see Figure 3). Monitoring will continue, to establish the long-term plume response. Initial measurements have also been performed at Ft. Lewis, before in situ thermal treatment was started. Thermal treatment is ongoing, and post-treatment measurements will be made soon. Mass flux measurements will also be made at two other sites (Borden CFB and the Sages Dry Cleaner site in Jacksonville, FL).

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 an analytical model that predicts source zone behavior with and without remediation, and in linking this source zone model with transport equations to predict plume response.

Figure 2. Comparison of pre- and post-contaminant mass discharge at Hill AFB OU2

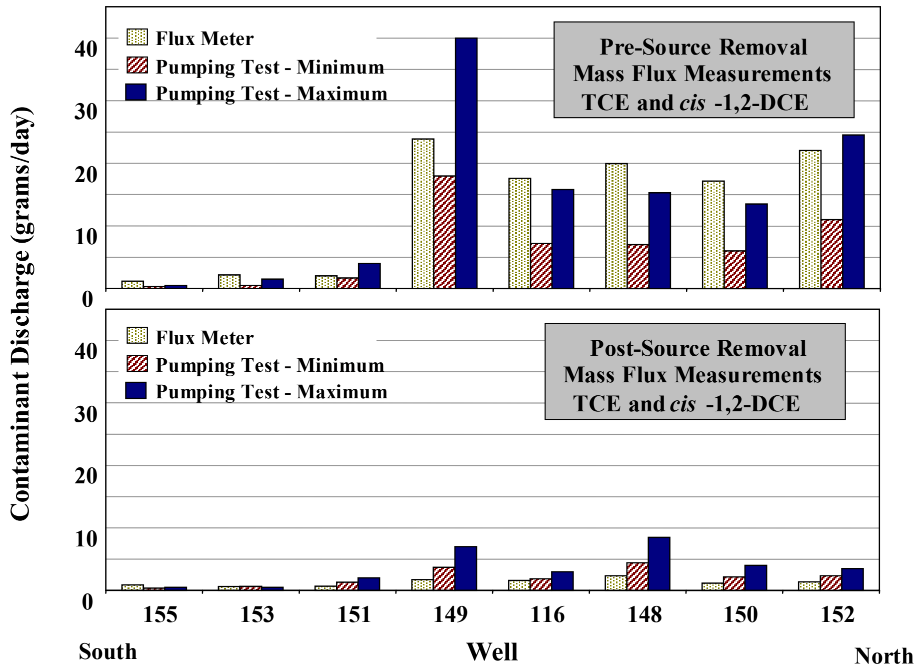
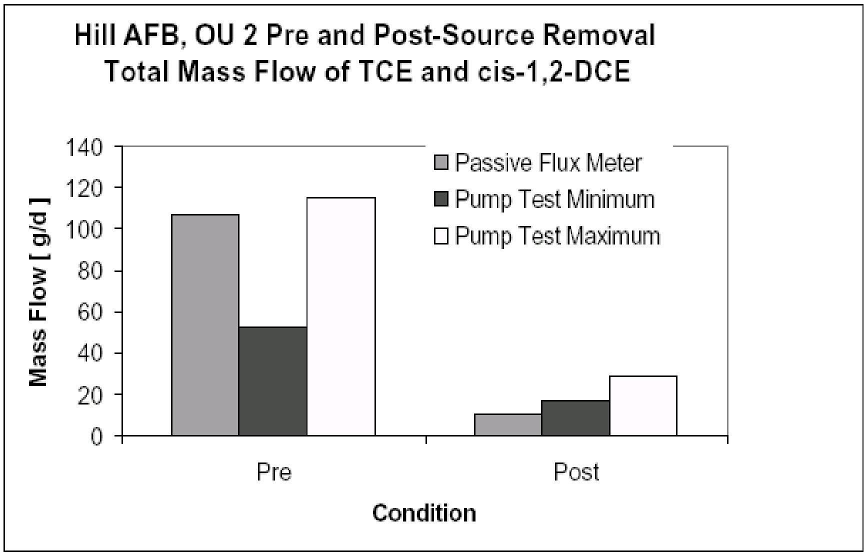


Figure 3. Mass flux measurements by flux meters and integrated pump tests at Hill AFB



From: Hatfield et al., 2003 (http://www.diffusionsampler.org/Documents/Hatfield_&_Annable_2003_Monterey_Passive%20Flux%20Meter.pdf)

4. ESTCP PROJECTS

Although this initiative is focused on the SERDP projects, several technology demonstration and validation projects address DNAPL source zone remediation. Specifically, three projects seek to demonstrate the efficacy of bioremediation of source zones. One is designed to demonstrate bioremediation through enhanced mass flushing, using only biostimulation (CU-0218), and the others address the use of bioaugmentation, either alone (CU-0008) or in conjunction with chemical oxidation (CU-0116).

Another project is designed to provide a critical evaluation of the state of the art of in situ thermal treatment (CU-0314). Another large project will evaluate the use of several innovative diagnostic tools at several sites undergoing different remediation technologies (CU-0318). Finally, one project is investigating 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 (CU-0319).

In FY04, a project was initiated to develop a user-friendly screening tool to reduce the uncertainty of estimating and predicting remedial outcomes when evaluating source zone treatment (CU-0424). The project developed from a Navy survey of well over 100 sites that had attempted source zone remediation. Based on this survey, the most common technologies selected were in situ thermal (28%), chemical oxidation (21%), and bioremediation (20%). Of the thermal sites, most had used electrical resistance heating, and of the chemical oxidation sites, most had used permanganate. No sites had met MCL values throughout the site, but over half claimed they had met their remedial goals. The database developed during this project has allowed further evaluation of the potential performance and costs of source treatment. 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 too 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.

Finally, one project worth brief mention is ESTCP CU-9920, intended to demonstrate the use of enhanced anaerobic bioremediation by addition of soluble carbohydrates such as molasses. One of the sites (Hanscom AFB) apparently had a residual TCE DNAPL source. Molasses was injected for approximately 2 years in and near this source area. Dissolved TCE, cis-DCE and VC concentrations were reduced by approximately 99% (to below 5 ppb), 50% and 75% (to approximately 1 mg/L each). Concentrations 18 months after active treatment stopped were <5 ppb, 9 ppb and 6 ppb, respectively (99% reductions). Secondary water quality impacts included elevated levels of BOD and COD, several ketones that were well above applicable criteria, and concentrations of dissolved iron, lead, manganese and arsenic that exceeded drinking water criteria. The final report is currently in preparation.

5. WEB RESOURCES

Dry Cleaners Coalition: Documents on field applications of remediation technologies: www.drycleancoalition.org/profiles.

Phase 1 Report: Survey of Chlorinated Solvent Remediation Projects
http://www.estcp.org/documents/techdocs/Phase%20I%20Site%20Survey-Final%20Version%20(3).pdf

EPA Document, "DNAPL Remediation: Is There a Case for Source Depletion?":
http://www.epa.gov/ada/download/reports/600R03143/600R03143.pdf

EPA Document: Appropriate Goals for DNAPL Source Zone Remediation:
http://gwtf.cluin.org/docs/options/dnapl_goals_paper.pdf

ITRC Documents on DNAPL remediation:
http://www.itrcweb.org/user/DNAPL-2.pdf
http://www.itrcweb.org/user/DNAPL-2.pdf
http://www.itrcweb.org//DNAPL-3.pdf

ITRC Bioremediation of DNAPLs Team:
http://www.itrcweb.org/common/content.asp?en=PU830961&sea=Yes&set=Both&sca=Yes&sct=Long&ead=tb&sad=lt&vw=reset