SUMMARY REPORT

SERDP and ESTCP Workshop on Long Term Management of Contaminated Groundwater Sites

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ACRONYM LIST

AFFF	aqueous film-forming foam
BMAD	biologically mediated abiotic degradation
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CMRM	Chemical and Material Risk Management
CSIA	compound specific isotope analysis
CSM	conceptual site model
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
EA	enhanced attenuation
EACO	Enhanced Attenuation: Chlorinated Organics
EDB	ethylene dibromide
EI/EC	Emerging Issues and Emerging Contaminants
ESTCP	Environmental Security Technology Certification Program
IRIS	Integrated Risk Information System
ITRC	Interstate Technology & Regulatory Council
MCL	maximum contaminant level
MNA	monitored natural attenuation
NDMA	N-nitrosodimethylamine
NRC	National Research Council
ORP	oxidation reduction potential
PAH	polycyclic aromatic hydrocarbon
PFASs	per- and polyfluorinated substances
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PPBK	physiologically based pharmacokinetic
PPCP	pharmaceutical and personal care products
qPCR	quantitative polymerase chain reaction
RAO	remedial action objective
RPM	remedial program manager
SERDP	Strategic Environmental Research and Development Program
TBT	tributyltin
TCA	trichloroethane

TCE	trichloroethene
1,2,3-TCP	1,2,3- trichloropropane
TOP	total oxidizable precursor
USEPA	U.S Environmental Protection Agency
VI	vapor intrusion
VOI	value-of-information
WSN	wireless sensor networks

EXECUTIVE SUMMARY

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) are the Department of Defense's (DoD) environmental research programs (herein referred to as “The Programs”), harnessing the latest science and technology to improve DoD’s environmental performance, reduce costs, and enhance and sustain mission capabilities. The Programs fund basic and applied research as well as field demonstration and validation efforts. For additional information, refer to www.serdp-estcp.org.

This workshop focused on the research needed to more efficiently deal with the long term management and lengthy restoration of complex sites, with overall objectives to (1) review the current status of complex sites, expectations for restoration, and how they are managed, (2) identify options for achieving restoration goals more efficiently over longer periods of time, (3) prioritize the research and demonstrations needed to show that restoration goals can be achieved more efficiently over longer periods of time, and to develop the new technologies needed to support that paradigm, and (4) promote cooperation with other federal agencies to fund the needed work most efficiently.

Approximately 60 invited personnel representing DoD remedial program managers (RPMs), federal and state regulators, engineers, researchers, industry representatives, and consultants were in attendance. Two breakout sessions, each with four working groups, facilitated discussions of the current state of the science and ranking of research, demonstration and technology transfer needs for four areas: enhanced attenuation, long term monitoring, predictive modeling, and emerging contaminants.

The research, demonstration and technology transfer needs were prioritized in each work group (Table E-1). The needs identified by the expert panel for improving long term management of contaminated groundwater will guide the strategic plan for research and development in this area by SERDP and ESTCP over the next five to ten years.

Table E-1. Research, Demonstration and Technology Transfer Needs Identified

Research Needs	Demonstration Needs	Technology Transfer Needs
Enhanced Attenuation Working Group		
Understanding Understudied Processes (Critical)	Tools to Estimate Contaminant Transfer and Transformation Rates (Critical)	Technology Transfer of Cost Effective Methods for Amendment Delivery (Critical)
Understanding Chemical and Biological Processes that Impact Contaminant Mobility and or Transformation in Lower Contaminant Mobility Zones (Critical)	Innovative Methods to Accelerate Attenuation within Plumes (Critical)	Promote Use of CSIA to Determine Degradation Mechanisms and Track Enhanced Attenuation (High)
Development and Demonstration of High Resolution Characterization Techniques (High)	Develop and Demonstrate High Resolution Characterization Techniques (High)	
Predictive Modeling Workgroup		
Develop Practical Methods and Modeling Tools to Assess Site-Specific Effects of Matrix Diffusion and Sorption/ Degradation Low Permeability Zones (High)	Field Scale Estimates of Parameters Controlling Back Diffusion, Desorption and Degradation (Critical)	White Paper on Results of Ongoing VI Research and Data Collection (Critical)
Research on Long Term Subsurface Processes Important for Predictive Modeling (Critical)		Guidance and Training on Predictive Models for RPMs including Practical Management of Uncertainty (High)
Develop Practical Field-Scale Methods for Estimating Parameters Controlling Back Diffusion, Desorption and Degradation in Low Permeability Zones (Critical)		
Cost-Benefit Analysis of Site Management Decisions with Consideration of Uncertainty (Critical)		
Improved Vapor Intrusion Modeling (High)		
Long Term Monitoring Workgroup		
Development of Cost Effective Contaminant Sensors (High)	Coupling Modeling and Monitoring for Long Term Management (Critical)	Guidance on Matching Sample Frequency to System Dynamics (Critical)
Development of Sensor Networks for Operational or System Reliability Parameters (High)	Geophysical Monitoring of Biogeochemical Conditions (High)	
Improved Monitoring of Fractured Rock Systems (Critical)	Next-Generation Long Term Monitoring Systems (High)	
Development of Diagnostic Tools for Long Term Management (Critical)	Monitoring Strategies for Transitioning to Passive Management (Critical)	

Table E-2. Research, Demonstration and Technology Transfer Needs Identified (cont'd)

Emerging Contaminants Workgroup		
Transformation of Emerging Contaminants (Critical)	Demonstration and Validation of Technologies for Treatment of Emerging Contaminants Together with Contaminants of Historical Concern	Assessment of the Potential Impact of Changes in the Toxicity and Regulatory Standards of Chlorinated Solvents on Long Term Site Management, Remediation Efficiency and Cost (High)
Quantifying Emerging Contaminant Fate and Transport (High)		Standardization of DoD's Response to Emerging Contaminants at Legacy Restoration Sites (High)
Basic Research to Support Risk Assessment of PFASs (High)		Development of Standardized Methods by Contract Laboratories to Evaluate Presence of PFASs That Are Present in Military Sites (High)
		Wide Distribution of Brief Communications on Emerging Contaminants (High)

1.0 INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) are the Department of Defense's (DoD) environmental research programs (herein referred to as “The Programs”), harnessing the latest science and technology to improve DoD’s environmental performance, reduce costs, and enhance and sustain mission capabilities. The Programs fund basic and applied research as well as field demonstration and validation efforts. For additional information, refer to www.serdp-estcp.org.

SERDP and ESTCP must determine how their limited research, development, and demonstration funds can best be invested to improve DoD’s ability to effectively address its environmental requirements to manage and reduce the impacts of contaminated sites. The difficulties in completely restoring many complex sites contaminated with chloroethenes and related contaminants have led to the growing recognition that long term and lengthy restoration processes may be inevitable. This workshop focused on the research needed to more efficiently deal with the long term management and lengthy restoration of complex sites, with overall objectives to (1) review the current status of complex sites, expectations for restoration, and how they are managed, (2) identify options for achieving restoration goals more efficiently over longer periods of time, (3) prioritize the research and demonstrations needed to show that restoration goals can be achieved more efficiently over longer periods of time, and to develop the new technologies needed to support that paradigm, and (4) promote cooperation with other federal agencies to fund the needed work most efficiently.

2.0 METHOD

The SERDP and ESTCP Workshop on Long Term Management of Contaminated Groundwater Sites was held on 13-14 August 2013, in Arlington, Virginia. Approximately 60 invited personnel representing DoD remedial program managers (RPMs), federal and state regulators, engineers, researchers, industry representatives, and consultants were in attendance. The Agenda for the Workshop may be found in Appendix A; the Attendee list is provided in Appendix B. A steering committee composed of representatives from the various sectors assisted The Programs in defining the meeting’s scope and format. Members of the steering committee included Paul Johnson, Ph.D. (Arizona State University), Mike Kavanaugh, Ph.D. (Geosyntec Consultants), Jim Mercer, Ph.D. (Tetra Tech), and Hans Stroo, Ph.D. (Stroo Consulting LLC).

The agenda 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 (Appendix C) intended to summarize efforts supported to date to address research and demonstration needs at sites with contaminated groundwater as well as to provide an overview of the state of the science in four key areas. Attendees were provided with a summary of the SERDP Statements of Need released since FY00 that were relevant to the workshop topic, as well as a listing of ESTCP demonstration projects also relevant to the workshop topic. This summary is provided in Appendix D.

Two breakout sessions, each with four working groups, facilitated discussions of the current state of the science for four areas: enhanced attenuation, predictive modeling, long term monitoring, and emerging contaminants. In the first breakout session, participants reviewed the data gaps and technology needs where additional research and development or field demonstrations would improve the understanding and assessment of the long term management of contaminated groundwater sites.

The second breakout session built on the first session by focusing on the research, demonstration, and technology transfer needs for the long term management of contaminated groundwater sites. Research paths and demonstrations were prioritized as either critical or high priority, largely based on the sequence of events required to impact DoD site decisions within 3 to 5 years of research and demonstration initiation (Table 1).

A poster session was held in the evening of the first day of the workshop. This poster session highlighted key SERDP and ESTCP funded efforts that were focused on contaminated sediment issues.

The entire group participated in the final discussions and selection of the key issues and the critical and high-priority research, demonstration, and technology transfer needs. Several of the participants contributed to sections of this report describing specific issues and needs, and/or edited the draft versions.

Table 1. Definitions of Research, Demonstration and Technology Transfer Need Prioritization

	Critical	High
Research	Research that potentially could have a significant impact on cost-effective long term management of contaminated groundwater at DoD sites.	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 improve on cost-effective long term management of contaminated groundwater at DoD sites.	Field demonstrations or assessments that are of high priority but may not be able to be implemented until critical demonstrations or assessments are completed.
Technology Transfer	Specific actions or documents that could be undertaken immediately to promote technology transfer of key concepts or technologies.	Actions or documents that should be undertaken to promote technology transfer of key concepts or technologies once specific research and/or demonstrations have been completed.

3.0 RESEARCH ISSUES

As stated in Section 2, breakout sessions focused on four key technical areas: enhanced attenuation, long term monitoring, predictive modeling, and emerging contaminants. The following sections provide a summary of the questions posed to the workgroup in each technical area, as well as overarching issues discussed during the session.

3.1 Enhanced Attenuation

In some cases, natural attenuation of sources and dissolved plumes alone may not be acceptable or sufficient for transition to closure within reasonable timeframes, but low-cost enhancements to natural source depletion and dissolved plume attenuation may allow passive management. Such enhancements should have low capital costs, minimal ongoing operational and monitoring costs, and be capable of providing long term protection over large areas if necessary. Specific questions posed to the workgroup addressing enhanced attenuation included the following:

- What is the likely role of enhanced attenuation in long term site management?
- What are the most promising methods available to provide such enhancements?
- How can current and/or emerging diagnostic tools help define the need for enhanced attenuation or evaluate its performance?
- What are the highest priority research and development needs that will lead to effective enhanced attenuation technologies?
- What are the highest priorities for demonstration and technology transfer efforts to implement enhanced attenuation technologies?

As site characterization and remedial technologies have improved, it has become clear that many contaminated groundwater sites are too large or too complex to allow remediation within a reasonable timeframe. Because these sites have estimated remedial timeframes on the order of decades to centuries, their potential life-cycle costs are high. Recent research suggests that some natural processes, if augmented or enhanced, could decrease life-cycle costs by decreasing the remedial timeframe and/or providing a more sustainable approach to long term source and plume management. By developing methods to enhance these processes, the DoD may reduce the life-cycle costs for these large, complex groundwater sites.

3.1.1 Definition of Enhanced Attenuation and Potential Applications

Defining enhanced attenuation and how it differs from active remediation can be difficult. The Interstate Technology & Regulatory Council (ITRC) Enhanced Attenuation: Chlorinated Organics (EACO) Team (ITRC, 2008) defined enhanced attenuation (EA) as the use of low-energy, long acting (sustainable) technologies when monitored natural attenuation (MNA) is not sufficiently effective or acceptable. EA can provide an effective and efficient “bridge” from higher-energy remedies to MNA with technologies that either increase the attenuation of the contaminants within the affected aquifer or reduce contaminant loading to the downgradient aquifer.

There is no bright line distinguishing “active treatment” from “enhanced attenuation.” Instead, remediation may be viewed as a continuum, with enhanced attenuation bridging the gap between active remediation and natural attenuation. Both active remediation and enhanced attenuation may use the same physical, chemical, and biological processes, but these processes may be applied to varying degrees. For example, in a subsurface heating application, active remediation would heat to high temperatures to desorb or vaporize the organic contaminants, while enhanced attenuation may heat the subsurface just enough to increase the rate of microbial degradation while minimizing energy consumption. Depending on site conditions, active remedies could be characterized by high energy consumption, significant greenhouse gas emissions, negative impacts on worker and community, and high costs, without substantially reducing the remedy period.

The goal of all remediation approaches is to restore the entire site to unrestricted use. The difference between enhanced attenuation and traditional active remediation is the approach used to reach that goal (i.e., will a site manager have to decide whether to release greenhouse gases to meet an arbitrary time schedule or does he/she work with natural processes to minimize the total environmental impact of the site?)

With enhanced attenuation, the goal is to reduce consumption of natural resources and long term management costs while minimizing impacts on the local and global environment. This difference in approach between active treatment and enhanced attenuation results in different definitions of success. Where success for active remediation may be achieving the maximum contaminant levels (MCLs) by a certain date, success for enhanced remediation may be accelerating contaminant destruction rates to reduce total life-cycle energy consumption.

The differences between active remediation and enhanced attenuation identified above led the team to adopt the following definition of enhanced attenuation:

> *Modification of the groundwater system to provide incremental improvement in degradation rates that allows a site to transition from active remediation to monitored natural attenuation (MNA). These modifications include enhancing natural biological and chemical processes, hydrologic modifications to reduce further contamination of clean groundwater and acceleration of other degradation processes.*

The most appropriate candidates for use of enhanced attenuation include the following:

- Large, diffuse, and/or heterogeneous plumes that contain lower mobility zones which slowly release contaminants over long periods, thereby extending the remedial timeframes. Often these zones are identified as aquifer materials of lower hydraulic conductivity, or aquifer materials where contaminants are subject to sorption and desorption processes.
- Plumes with poorly defined source areas. These sources may include zones with lower contaminant mobility, or may reflect historical practices, such as random disposal of solvents over a large area.

- Plumes with depleted or contained sources, or low permeability layers that continue to release contaminants in amounts exceeding the natural attenuation capacity of the aquifer.
- Sites with ongoing natural processes that can potentially be accelerated.
- Sites that have been actively treated or have reached asymptotic levels, where enhanced attenuation can decrease the long term management costs.

Application of enhanced attenuation may facilitate regulatory and other stakeholder acceptance of less active remedial approaches at large, complex plumes. For example, if small modifications to the plume will accelerate the natural degradative processes, enhanced attenuation may satisfy the regulatory need to implement active remediation. If enhanced attenuation processes can demonstrate a stable or shrinking plume, it may be possible to pursue regulatory concurrence for no further active remedy. Finally, use of enhanced attenuation may allow a site to transition to a situation in which monitored natural attenuation is acceptable to the stakeholders.

Currently, the primary focus of remediation is to clean up the site within a reasonable time. As noted in the National Research Council's (NRC's) 2013 report (NRC, 2013), this goal is impractical for many large, complex plumes. Enhanced attenuation may facilitate changing the remedial paradigm to long term, sustainable, plume management. With this paradigm, it may be appropriate to incorporate risk-based remedial goals into the remedial action objectives, instead of defaulting to the MCLs.

In summary, enhanced attenuation may allow the DoD to decrease the long term costs associated with large, complex plumes through leveraging the site's ongoing natural processes. Enhanced attenuation may also support a paradigm shift from implementing high-cost, resource intensive technologies to more sustainable methods for long term plume management. By allowing remediation to proceed more slowly, the DoD may reduce consumption of natural resources, minimize impacts on the local and global environment, and realize significant cost savings.

3.1.2 Importance of the Conceptual Site Model

As discussed above, enhanced attenuation involves modifying the site to increase contaminant degradation rates or to reduce further contamination of clean groundwater. For these adjustments in site conditions to be effective, it is necessary to develop a thorough and reliable conceptual site model (CSM). Unfortunately, the CSMs for many sites are not well established. Multiple guidance documents on CSM development have been published by several organizations. Links to some of these documents are provided below. Practitioners are encouraged to follow the recommendations in these guidance documents and develop an accurate CSM before attempting to implement enhanced attenuation.

Conceptual Site Model Guidance Documents:

ASTM: www.astm.org/Standards/E2531.htm
ASTM: www.astm.org/Standards/E1689.htm
USEPA: http://www.epa.gov/superfund/health/contaminants/radiation/pdfs/sec_2clean.pdf
ITRC: www.itrcweb.org/ism-1/3_1_2_Conceptual_Site_Models.html.
TRIAD: http://www.triadcentral.org/mgmt/splan/sitemodel/

Army COE:
http://www.publications.usace.army.mil/Portals/76/Publications/EngineerManuals/EM_200-1-12.pdf

Specific State guidance:
Missouri: http://www.dnr.mo.gov/env/hwp/mrbca/docs/mrbcasection6.pdf
Alaska: http://dec.alaska.gov/spar/csp/guidance/csm05_draft.pdf
New Jersey: www.nj.gov/dep/srp/guidance/srra/csm_tech_guidance.pdf
Indiana: www.in.gov/idem/files/remediation_closure_guide_sect_02.pdf

3.2 Predictive Modeling

Credible predictive models are needed to determine when to transition to passive management and evaluate when residual contamination can be left in place with confidence that the risks are properly managed. Some processes affecting contaminant fate and transport are not adequately understood or adequately represented in current models. Specific questions posed to the workgroup addressing predictive modeling included the following:

- How can modeling tools be better used to guide management decisions such as transition assessments?
- If a site is too complex to use a numerical model, what tools should be used for decision making?
- Do the necessary tools already exist?
- What are the limitations and barriers to implementing these tools?
- What are the highest priority experimental and associated modeling efforts needed to improve predictions of remediation impacts and long term fate and transport?

Modeling is linked to other breakout sessions as demonstrated by the discussion on conceptual models (Section 3.1.1) and the connection with monitoring discussed in Section 3.3.3. In particular, the ongoing collection of necessary and sufficient data is necessary to develop, apply, and update accurate and useful predictive models.

3.3 Long Term Monitoring

Long term monitoring likely will be essential to ensure the protectiveness of passive remedies relying on slow processes. However, the cumulative costs using current approaches will be very high, and the temporal and spatial variability in monitoring results often requires relatively frequent monitoring at several locations. Improved techniques and technologies are needed to monitor remedies cost effectively. Specific questions posed to the workgroup addressing long term monitoring included the following:

- What will need to be monitored over long periods of time? (e.g., plume size, source depletion rate, impacts [i.e., indoor air])
- What are the most promising opportunities for more efficient monitoring technologies?

- Can revised sampling strategies reduce monitoring costs and/or increase the credibility and accuracy of long term monitoring results?
- Can current and/or emerging analytical methods or remote monitoring tools reduce long term monitoring costs?
- What are the highest-priority research and demonstration efforts needed to develop and deploy more efficient long term monitoring technologies and strategies?

The group identified several major themes that provide the foundation for the research, demonstration and technology transfer needs described in later sections. These themes are summarized in the following sections.

3.3.1 Appropriate Monitoring Methods for Site Goals and Conditions

The monitoring required during long term management may be determined by a variety of different objectives, phases of treatment, and site-specific conditions. Objectives for specific monitoring programs can include compliance, remedy optimization, failure warning, and performance assessment. Different sampling frequencies, analytes, and monitoring technologies will be appropriate at different locations and times. For example, relatively high resolution monitoring (e.g., multi-level samplers or use of geophysical sensors) may be appropriate to monitor responses of different regions to treatment, but lower resolution (e.g., broadly screened intervals in a few key wells) may be appropriate for subsequent long term MNA monitoring and early warning systems. An intermediate level of monitoring may be appropriate for enhanced attenuation. Also, recent findings suggest that many groundwater sites change slowly over time, albeit with considerable spatial and temporal variability, so long intervals between some monitoring events may be appropriate, but guidance on when and how monitoring programs should be altered over time is currently lacking.

3.3.2 The Potential Uses of Sensors

Sensor technologies continue to advance, and their use could reduce the costs and sustainability impacts associated with long term monitoring. Sensors may be applicable to passive or active remedies, and may be used for one-time monitoring events, or left in place for possibly automated and semi-continuous monitoring over long time periods. Use of sensors for subsurface restoration faces several difficulties, notably the need for frequent re-calibration of individual sensors, the potential for biological or chemical fouling over time, potential failure of sensor-electronics, and power failure (e.g. battery draining). Sensors may serve many functions in long term management including measuring contaminant concentrations, identifying changes in the hydrogeological or biogeochemical conditions that affect attenuation processes, and providing early warning of failures in containment systems. However it is critical that the development of sensors, or in fact any innovative monitoring method, be closely linked to a conceptual framework for interpreting the results. Some participants felt that the current conceptual framework is inadequate for determining what monitoring data are most useful for long term management, and for using the output in making management decisions.

Participants saw value in the development of relatively inexpensive sensors, which would be useful for decision making and not necessarily for regulatory compliance. For instance, sensors for hydraulic or biogeochemical data could provide useful information to interpret subsurface conditions related to plume behavior. Inexpensive sensors for contaminants or contaminant surrogates, even with low resolution, could be useful indicators of plume behavior and a useful bridge between more expensive groundwater sampling and analysis events. Low priced sensors could potentially be deployed in quantities sufficient to cover large areas at reasonable cost. A related topic was the potential uses for robotics in monitoring, (e.g., to sample inaccessible areas or to calibrate sensors).

3.3.3 Improved Modeling-Monitoring Linkages

The models used to predict performance of active or passive remediation often have considerable uncertainty, especially over long time periods. There is a perception that the models typically are not updated as monitoring results are obtained and that the monitoring programs are not designed to address the major uncertainties in the model predictions. In many cases, this situation happens because project managers do not perceive an added value in updating the models. Often after remediation commences, project managers use an observational approach for optimization. Improved linkages between the models and the monitoring results would allow continuous optimization of the monitoring program and iterative updating of the model predictions to support ongoing remedy management.

3.3.4 Appropriate Uses for Geophysical Tools

Geophysical techniques have often been oversold in the past, and currently they are under-utilized for monitoring. However, there have been significant advances over the last 10-20 years, including techniques that can infer fluid and rock properties at distances away from monitoring boreholes. There may be value in developing and demonstrating such techniques for monitoring hydrogeological or biogeochemical conditions. For example, geophysical signatures could be used to measure the responses to treatment or detect changes in factors affecting natural attenuation processes. Geophysical techniques are most likely to be used as part of an integrated monitoring system. They may also be valuable for identifying lithologic contrasts or preferential pathways, or for detecting breaches in confining units, physical containment systems, or permeable reactive barriers. It is important to realize that a single geophysical measurement alone is unlikely to provide reliable diagnostic information, and therefore integration of multiple methods is likely to be more successful.

3.3.5 Cost-Effective MNA Monitoring

MNA can continue for decades if not centuries, and as a result, the cumulative costs can be much higher than expected based on the "natural attenuation" terminology. Even small decreases in the annual monitoring costs can become significant over long time periods. However, there is a lack of scientifically credible guidance to define the minimum data set temporally and spatially needed to confirm that MNA is operating as intended and is fully protective. As sites transition to passive management strategies, which generally includes a reliance on natural attenuation, the cost of long term monitoring of these sites will become the major single cost item for DoD (and many other responsible parties), and this cost may continue for many decades. Reducing the economic and sustainability impacts of long term monitoring represents a major opportunity to decrease the future costs and liability associated with contaminated sites.

3.4 Emerging Contaminants

DoD defines emerging contaminants as a contaminant that has a reasonably possible pathway to enter the environment; presents a potential unacceptable human health or environmental risk; and does not have regulatory standards based on peer-reviewed science, or the regulatory standards are evolving due to new science, detection capabilities, or pathways (DoDI 4715.18). The group discussed the appropriate context of emerging contaminants with respect to the objectives of the Workshop and agreed that evolving regulatory standards, such as for trichloroethene (TCE), would be considered as an "emerging issue" rather than an emerging contaminant. In general, the group focused the discussion on emerging contaminants. However, given the significance of a changing TCE standard on the restoration of DoD contaminated sites relative to the workshop objectives, the group decided to include a statement of need on this topic as an emerging issue (see Sections 3.4.2 and 6.4.1).

There are numerous environmental contaminants that have evolving science and regulations. As such, these contaminants may not have previously been considered as site-related contaminants of concern (COCs). The identification of emerging contaminants at established restoration sites can significantly impact site objectives, schedule, cost, and ongoing remedial activities. Additionally, several contaminants are found in groundwater with chlorinated solvents, and some of these can complicate restoration. These co-contaminants may not degrade as easily or under similar conditions, and may require separate treatment. Specific questions posed to the workgroup addressing emerging contaminants included the following:

- Which contaminants and co-contaminants represent the most important targets for further research and demonstration projects and why are these targets for future research?
- What technologies are most promising for effective and cost-efficient treatment of these contaminants?
- What if any data gaps exist in the fundamental understanding of the fate and transport of these contaminants?
- Are improved diagnostic tools needed for any of these contaminants?
- What are the highest priority research and demonstration efforts needed to improve treatment of these co-contaminants?

3.4.1 Primary and Secondary Contaminants Identified

Following an in-depth discussion of which emerging contaminants represent the most important targets for further research and demonstration projects, the group agreed to group these contaminants into two categories, primary and secondary, based on the risk presented by the presence of these compounds in groundwater, in addition to their significance and occurrence at DoD sites, and their persistence in the environment.

The primary contaminants, in order of importance, were per- and polyfluoroalkyl substances (PFASs), 1,4-dioxane, 1,2,3-trichloropropane (1,2,3-TCP) and N-nitrosodimethylamine (NDMA). Although several SERDP and ESTCP projects specific to PFAS and 1,4-dioxane are currently on-going, many remaining data gaps were identified. Also, while 1,2,3-TCP is not a contaminant of concern at a large number of DoD sites, the intensity of contamination at a small number of sites is of significant concern. Similarly, SERDP and ESTCP have funded several studies on NDMA, but recently released reports have revealed new data on NDMA occurrence and updated information on its environmental impacts (Krasner et al., 2013).

Secondary contaminants identified by the group included pharmaceutical and personal care products (PPCPs) from treated wastewater that may be reused at DoD facilities; tungsten; tributyltin (TBT, an organotin compound used primarily as a biocide in antifouling paints); ethylene dibromide (EDB, which is used as a scavenger for lead in anti-knock gasoline mixtures and aviation fuel, in addition to uses as a solvent, in waterproofing preparations, as a chemical intermediate in the synthesis of dyes and pharmaceuticals, and as a fumigant, insecticide and nematicide); nitro-polycyclic aromatic hydrocarbons (nitro-PAHs); oxy-polycyclic aromatic hydrocarbons (oxy-PAHs); and 1-bromopropane (which is used as a solvent for cleaning metal surfaces and adhesives, and has also been deployed as a replacement for tetrachloroethene as a dry cleaning solvent).

3.4.2 Emerging Issues (Potential Change in Regulatory Standard of TCE)

On September 28, 2011, the U.S. Environmental Protection Agency (USEPA) released its final health assessment for TCE to the Integrated Risk Information System (IRIS) database. The final health assessment may have significant implications for corrective action activities at chemical release sites where TCE is a contaminant of concern. The toxicity assessment may lead to increases in risk estimates by a factor of 2 to 9 depending on the assumptions used. These increased risk estimates may have important regulatory implications for ongoing and future site remediation, and may lead to some formerly closed DoD sites being re-opened due to exceedence of a lower MCL (Ettinger and Strohbehn, 2011). The more stringent risk-based screening levels for TCE (compared to the current regulatory standard; the drinking water MCL) implicates protectiveness measures in final decision documents and remedial action objectives, may result in new pathways of concern (i.e., inhalation via vapor intrusion), and may result in significantly higher cost to complete with impact to schedule, cost, and remedial design.

4.0 RESEARCH NEEDS

The research needs identified during the workshop are described below. The needs are grouped by the technical areas posed to the workshop attendees and are then broken out as critical or high priority research needs.

4.1 Enhanced Attenuation

During the workshop, several specific research topics were identified and discussed that fell under three general topics: 1) understanding understudied processes that impact contaminant mobility and or transformation in plumes; 2) chemical and or biological processes impacting contaminant mobility and/or transformation in lower contaminant mobility zones; and 3) development and demonstration of high resolution characterization techniques to identify the lateral and vertical extent of lower mobility zones. These topics are presented below in more detail.

4.1.1 Understanding Understudied Processes (Critical)

Several processes can impact the mobility and/or the transformation of contaminants in plumes, and these processes may provide adequate attenuation and protection after source control is implemented. However, a more thorough understanding of the kinetics and spatial extent of these processes is needed, both for previously considered processes and particularly for processes that have not been studied in detail before. These latter processes can include, but are not limited to, contaminant destruction, contaminant mass transfer, and geochemical manipulation of the aquifer. For example, biotic reductive dechlorination of chlorinated solvents has been extensively researched, but it is still very difficult to predict and quantify in situ reaction kinetics in a heterogeneous aquifer. Similarly, the potential role of natural organic matter in aerobic cometabolism of TCE and the extent to which this process can contribute to overall plume remediation has been little investigated. The importance of contaminant back diffusion has been demonstrated, but the kinetics of this process and the potential degradation processes that can occur at the interface between the lower mobility zones and transmissive zones require additional research.

Ultimately the goal of research to be conducted under this topic is to gain the ability to quantify the long term impacts of natural processes on the aquifer. Areas of particular interest include:

- Microbial ecology
  - Identifying genes and linking those genes to function was identified as a need by the researchers in the group. With high throughput, quantitative polymerase chain reaction (qPCR), it is possible to obtain a large amount of information concerning which genes are present in a given sample. However, we have limited understanding of what these genes do, nor do we have a good understanding of the extent to which these genes are expressed and result in contaminant degradation. By understanding the functions of these genes, we can use the qPCR data more effectively and develop a greater understanding of which processes are occurring. The concept of linking gene numbers and gene expression to degradation rates in an aquifer also was considered to be a key research need.

    - Finding new organisms. This specific topic may be of particular importance for addressing emerging contaminants.
    - Identifying rate limiting aspects of microbial processes.
- Aerobic cometabolism of TCE as supported by natural organic matter (i.e., no need for additional substrates) was also considered as an important topic of study by the group. If aerobic conditions prevail, this natural process may play an important role in long term plume management. It may be possible to enhance this process through low rate oxygen addition. Of particular interest is the validation of enzyme activity probes that currently allow a qualitative determination of whether aerobic cometabolism is occurring. These tools need to go beyond the qualitative capability and provide quantification of impact on the degradation rate.
- Formation of reactive mineral phases, such as magnetite and iron sulfides, provides a potentially viable alternative to enhance attenuation and reduce long term management cost. It is important to understand the role that microbes, groundwater chemistry, and solid-phase chemistry play in forming these reactive mineral phases, a process known as biologically mediated abiotic degradation (BMAD). To date, most research has focused on direct degradation of contaminants by microbes. The potential indirect effects, such as their role in forming reactive minerals in various environments, have not been extensively studied, although BMAD has been identified as a key process in "sustained treatment" that appears to go on for years after many electron donor addition processes.
- Effects of temperature and pH on reaction rates need to be understood so as to exploit their roles in enhancing attenuation. Increasing the groundwater temperature by a few degrees may significantly accelerate the rates of degradation processes that are already occurring. Reactions such as microbial reductive dechlorination are often inhibited by low pH, which could be adjusted to accelerate degradation.
- Understanding the kinetics governing commingled contaminant plumes will likely result in optimized long term management. However, the group recognized that it may be difficult to enhance the attenuation of commingled contaminant plumes; therefore there is a need for research and development leading to that understanding. Of particular interest were the following issues:
    - What are the mechanisms and conditions that lead to preferential versus simultaneous degradation of mixed contaminants?
    - What are the interactions among abiotic and biotic processes in commingled contaminant plumes?
- Estimating the natural assimilative capacity of an aquifer is critical for efficient design of active remediation systems and for identifying when to transition to enhanced attenuation and eventually monitored natural attenuation. Research on how to quantify an aquifer's assimilative capacity will support better estimates of remedial timeframes and cost-benefit analyses for use of enhanced attenuation. Better understanding of sustained treatment processes associated with bioremediation electron donor addition can make enhanced attenuation more robust and reliable.

4.1.2 Understanding Chemical and Biological Processes that Impact Contaminant Mobility and or Transformation in Lower Contaminant Mobility Zones (Critical)

The purpose of this research topic is to gain a greater understanding of chemical and/or biological processes that control contaminant storage and release from lower contaminant mobility zones and the extent to which these low mobility zones sustain groundwater plumes. The literature demonstrates that zones of lower contaminant mobility can extend the remedial timeframe of a plume by providing a long term release of contaminants into transmissive zones. The contaminant storage and release processes are slow and can occur over the course of decades, perhaps centuries. A greater understanding of chemical and biological processes in lower mobility zones and their rates will support improved predictive modeling of plume behavior. In addition, the information may allow adjusting these processes to decrease the contaminant release rate to less than the aquifer’s assimilative capacity.

4.1.3 Development and Demonstration of High Resolution Characterization Techniques (High)

Recent research has demonstrated that lower mobility zones can provide a long term release of contaminants, which can significantly extend the time required to achieve site closure. Although these zones may represent only a small fraction of the plume volume, they can sustain the plume for decades or even centuries at some sites. Targeted treatment of the lower mobility zones could potentially decrease the remedial timeframe at a site without active remediation of the entire plume footprint. Implementation of this approach, however, requires a detailed understanding of the lateral and vertical extent of these zones. The purpose of this topic is to develop and/or demonstrate cost-effective methods for characterizing these lower mobility zones. Although there are existing site characterization methods that may provide useful data, the development of novel techniques was listed as both a research and a demonstration need, depending on whether the methods currently exist (in which case it would be a demonstration need) or will require significant development.

4.2 Predictive Modeling

As discussed previously, predictive modeling can be a valuable tool to support long term management of contaminated groundwater. In addition to modeling groundwater flow, these models need to be able to predict important fate and transport processes with sufficient accuracy and precision to enable sites to be managed better such that cleanup objectives can be more reliably met at lower net cost. The following research areas were identified as being needed to improve predictive modeling for long term management of contaminated groundwater. The research areas below are listed in the sequence they were discussed at the breakout session and are not meant to imply an order of importance.

4.2.1 Develop Practical Methods and Modeling Tools to Assess Site-Specific Effects of Matrix Diffusion and Sorption/Degradation Low Permeability Zones (High)

SERDP has supported the development of complex numerical models for dense nonaqueous phase liquid (DNAPL) source areas (e.g., SERDP Projects ER-1293 and ER-1294) and simpler analytical models for addressing remediation (e.g., SERDP Project ER-1295 and ESTCP Projects ER-200704, ER-200436, and ER-201126). A number of existing models also exist for modeling groundwater flow and contaminant fate and transport in the subsurface (e.g., MT3D and related variants). For sites being transitioned into long term management, the processes of back diffusion and desorption and degradation within low permeability zones may significantly affect the long term behavior of dissolved plumes. These processes are currently not adequately accounted for in commonly used models. Therefore, development of modeling approaches that can be incorporated into commonly-used models is deemed a high priority. These models should be capable of simulating matrix diffusion in and out of low permeability zones and sorption /degradation within these regions. These models could be modules attached to existing groundwater models.

It is important not only that these models be able to capture aquifer responses to mass transfer limitations, but that they be computationally efficient and sufficiently simple to facilitate calibration from realistically attainable field data with reasonably available resources, and that they be capable of being used to evaluate prediction uncertainty.

4.2.2 Research on Long Term Subsurface Processes Important for Predictive Modeling (Critical)

Important factors for reducing the uncertainty in predictive models for long term management of contaminated groundwater include better estimates of the parameters in the models that describe processes such as matrix diffusion, sorption, and degradation (both biotic and abiotic) in and around low permeability zones. To foster better estimates of these parameters, a more comprehensive understanding of the fundamentals of these processes is needed. The degradation and diffusion that occur in and around the interfaces of low and high permeability layers is likely to be especially important. Additional research on the slower, long term degradation that might be occurring in the subsurface is also of importance. Either laboratory studies or field studies might be applicable to support this work. The modeling tools discussed above should be used to assist with the evaluation of data generated from these efforts.

4.2.3 Develop Practical Field-Scale Methods for Estimating Parameters Controlling Back Diffusion, Desorption and Degradation in Low Permeability Zones (Critical)

Site-specific data are needed to reduce prediction uncertainty using modeling tools discussed above that incorporate matrix diffusion, sorption, and degradation. Field-scale methods for estimating parameters associated with these processes would likely provide the greatest degree of reliability, but such tests currently do not exist. Similarly, hydraulic characterization of field sites is rarely done at a scale that is relevant for estimating the contribution of these processes, particularly, back diffusion. Consequently, research is needed to develop and validate field-scale methods for estimating the impacts of these processes. These tests may include (but are not limited to) stressing the subsurface systems via activities such as push-pull tests or shut-down tests, if active remediation systems are currently in place. The stress imposed on the subsurface system by the field test must be large enough to allow for unambiguous interpretation of the results. At the same time, the new field tests must be practical to allow for widespread adoption at active sites. The field-scale methods developed need to take into account the likely spatial and temporal variability in the critical parameters. The modeling tools discussed above should be used to assist with the evaluation of the data generated from these efforts.

4.2.4 Cost-Benefit Analysis of Site Management Decisions with Consideration of Uncertainty (Critical)

Having adequate data is important to manage the uncertainty in predictive model output. But the collection of data can be costly, and there is a reluctance to collect too much data. Data collection approaches that provide enough information to minimize uncertainty while also maintaining reasonable sampling costs have not been addressed systematically. Practical methods are needed to evaluate the value-of-information (VOI) of various data collection options. These methods should consider the costs as well as the benefits in terms of reduced prediction uncertainty. The development of practical and efficient methods for evaluating VOI is deemed a high priority to facilitate optimization of characterization and monitoring efforts and minimize total cost.

4.2.5 Improved Vapor Intrusion Modeling (High)

Vapor intrusion (VI) is one of the most important risk pathways for groundwater contaminants that potentially impact humans. Understanding the potential for risk from this pathway is important for long term management of groundwater contamination. Ideally, groundwater predictive models could be linked to VI models so that potential VI risks could be estimated within an acceptable degree of uncertainty (without being overly conservative). Screening level models currently exist for VI, but the general consensus is that they do not accurately represent all of the processes occurring and are often overly conservative.

Short term temporal changes in VI behavior are known to occur and are one of the most difficult aspects of VI modeling. Factors that might induce these temporal changes include weather conditions, subsurface conditions, and building dynamics. But quantitative cause-effect relationships describing these processes are not well known. Better VI models are needed to better understand and quantify these relationships and interpret data sets currently being collected under SERDP, ESTCP, and other projects. Until these cause-effect relationships are better defined, it will not be possible to make reliable predictions that can be used with confidence at specific sites where long term management of contamination is being considered. These improved VI models need to consider transient conditions, be three dimensional, and incorporate all mechanisms that substantially contribute to transient VI behavior. The models also should be able to address and evaluate uncertainty. Finally, there is a need for a modeling approach that allows for coupling of groundwater, atmosphere, and potentially-impacted buildings. These VI models may need to be at the research level at this time. Once the processes impacting VI are better understood, more simplistic models that can be used routinely can be developed and linked to predictive groundwater models.

4.3 Long Term Monitoring

4.3.1 Development of Cost Effective Contaminant Sensors (High)

Development of sensors capable of rapidly and accurately measuring the concentrations of target contaminants within a well could save considerable time and resources. Currently, samples must be collected in the field, often by people who must spend considerable time traveling to the site and sampling each well, and in most cases those samples must then be shipped to an analytical laboratory with results available 1 – 3 weeks later. Deployable sensors could provide near-instantaneous results for far less cost and energy use. Such sensors will require development, with a need for minimal recalibration. However, development of cost-effective contaminant sensors would significantly reduce costs and increase the sustainability of monitoring. More sustainable monitoring is one of the goals specifically mentioned in the DoD Green and Sustainable Remediation policy.

4.3.2 Development of Sensor Networks for Operational or System Reliability Parameters (High)

Sensors may be useful for both active and passive long term management strategies. A significant opportunity may be the development, demonstration and deployment of inexpensive data-dense sensors or sensor networks that may monitor groundwater parameters that are correlated with the contaminant of concern or conditions controlling attenuation processes. The emerging technology of wireless sensor networks (WSN) has potential applications in real-time and long term monitoring of large plumes. The sensors in the network transmit data wirelessly to a central computer to remotely monitor the development/expansion of a plume or to assess remedial effectiveness. Properly designed WSNs will allow for conservation of power in the sensor nodes (sensor operation and data transmission) so that the network can operate with minimal access for maintenance for automated long term monitoring. This sensor-based technology could be deployed in dedicated continuous sampling mode or as a rapid snapshot site assessment. Such sensors would not be used for compliance monitoring, but could be useful for ensuring attenuation processes operate as expected, or barrier systems are still functioning. The sensors could provide early warning of operational problems or system failures (breaches, changes in regional hydrogeology, or problematic geochemical conditions such as redox or pH changes). Sensor results also may be useful for determining when more costly traditional groundwater sampling is needed, and for ensuring reliable performance between infrequent compliance monitoring events.

This type of sensor-based monitoring technology may well lead to a new paradigm in data collection and utilization, with far more information available even though each individual measurement may not be as accurate as laboratory analyses of grab samples collected at a few monitoring points. The data collected from sensor networks can provide useful information on the plume configuration and the environmental conditions controlling attenuation, presumably for less cost and environmental impact than current methods. Also, the WSN data can be assimilated with more accurate data from grab sampling to make more informed decisions based on real-time and expected long term plume behavior.

The participants specifically recommended research and eventual demonstration of networks of relatively inexpensive sensors for operational or system reliability parameters. These could include standard sensors such as pH, dissolved oxygen (DO) and other dissolved gases, oxidation reduction potential (ORP), conductivity, water levels, temperature, or pressure, as well as geophysical sensors or innovative sensors, potentially capable of measuring key parameters such as groundwater velocity or electron acceptor flux. The objective is to reduce costs and sustainability impacts of long term monitoring by deploying sensor networks to reduce the risks of system failures due to physical or geochemical changes and to allow remote monitoring of the key conditions affecting the performance of natural or enhanced attenuation processes.

4.3.3 Improved Monitoring of Fractured Rock Systems (Critical)

Fractured rock sites are generally complex, and at many sites there will be contaminants remaining in inaccessible fractures and within the rock matrix, even after aggressive source zone treatment has been completed. Long term monitoring is a likely outcome at the majority of fractured rock sites, but there are significant technical and economic challenges in monitoring these sites because of the extreme spatial heterogeneity, the difficulties involved in drilling and identifying suitable monitoring locations, and the problem of identifying groundwater flow paths. Improving monitoring of fractured rock sites with attention to the fact that monitoring will likely extend over multiple decades could reduce the overall costs significantly because of the number of these sites and the longevity of residual contaminants within fractured rock aquifers.

In particular, cost-effective methods to estimate the mass stored within the matrix, within both the source and plume, would be helpful. Critically, methods to measure the flux of contaminants from the rock matrix into the fracture network (i.e., the back diffusion rates) as well as reactive processes within the rock matrix are needed. These measurements could help managers better understand the long term risks and evaluate the need for continued management of remaining contaminants. Quantifying the mass stored, slow reactive processes, and mass flux is critical to evaluate the performance of aggressive source treatment and to monitor the progress of natural or enhanced attenuation. Finally, "surgical monitoring" of problematic regions within a fractured rock aquifer could lead to reduced overall costs of long term monitoring and allow more timely and focused additional treatment if needed.

4.3.4 Development of Diagnostic Tools for Long Term Management (Critical)

It may be important at sites relying on enhanced or natural attenuation to ensure that biological activity or other degradative processes persist over time. Cost-effective techniques are needed to provide ancillary diagnostic evidence during the long NA phase, when contaminant concentration monitoring may occur infrequently. For instance, field-scale diagnostic evaluations, such as push-pull tests or tracer tests, could be performed at intervals to determine whether the natural attenuation processes are still occurring and to estimate the associated attenuation rate.

In particular, cost-effective methods are needed to verify that specific degradation processes are occurring, and to estimate the in situ degradation rates over time. Different tools will likely be needed for anaerobic or aerobic treatment systems, for evaluating biotic or abiotic processes and for reducing or oxidizing conditions. These diagnostic tools may be useful to assess initial rates, to determine whether NA mechanisms are still operating at original or predicted rates, and to determine whether degradation rates are equal to or greater than back diffusion rates so that the plume is contained. Similarly, diagnostic tests and data analysis methods are needed to determine whether degradation rates in a downgradient plume are in line with mass flux rates from a source area following source area remediation. Such data could be used to verify or modify the rates used in the original attenuation modeling or remedy decision basis.

4.4 Emerging Contaminants

4.4.1 Transformation of Emerging Contaminants (Critical)

DoD regularly tracks emerging contaminants based on their prevalence and potential impacts to DoD's operations and the fact that they may be reasonably expected to enter the environment and have real or perceived threats to human health or the environment. Understanding the transformation of emerging contaminants such as PFASs, 1,4-dioxane and 1,2,3-TCP in the environment will aid in both understanding their fate and transport in the subsurface, as well as the design and application of remedies including MNA, enhanced bioremediation or biologically enhanced abiotic degradation process (e.g., reactive mineral phases).

Specific research needs identified included the following:

- Elucidation of abiotic and biotic (metabolic and cometabolic) degradation mechanisms under a realistic range of concentrations and mixtures of contaminants
- Elucidation of biotic degradation pathways
- Identification of natural microorganisms that can metabolize PFASs, 1,4-dioxane and 1,2,3-TCP
- Quantification of abiotic and biotic degradation rates
- Identification and potential accumulation of degradation byproducts
- Development of diagnostic tools to identify and monitor abiotic and biotic degradation mechanisms (e.g., for 1,4-dioxane, improved biological markers with a focus on kinetics, in relevance to any new discovery of biological degradation)

4.4.2 Quantifying Emerging Contaminant Fate and Transport (High)

Emerging contaminants of particular interest to DoD include PFASs such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), 1,4-dioxane, 1,2,3-TCP, and NDMA. Knowledge of emerging contaminant fate and transport in the unsaturated and saturated zones is critical for effective remedy selection, implementation and long term management of impacted sites.

Quantification of sorption-desorption processes, diffusion coefficients, and mass transfer rate (e.g., from low to high permeability media and regions of mobile-immobile water) parameters are needed to accurately simulate emerging contaminant transport in the subsurface. Research on these parameters should encompass a range of natural soils and aquifer materials, performed under both water-saturated and unsaturated conditions, to provide parameter information that can support decision processes over a range of site conditions.

Specifically for PFASs, the following research issues are of particular importance:

- Primary factors/basic mechanisms responsible for migration into groundwater;
- Mechanisms of soil interactions, impact on source zones, bioavailability, and treatment consequences;
- Speciation as a function of pH and ionic strength;
- Impact of co-contaminant treatment technologies on PFASs fate and transport.

For 1,4-dioxane, evaluating the transport characteristics of 1,4-dioxane in highly diverse soils and its role in sustaining large dilute plumes is an important research need given the magnitude of 1,4-dioxane plumes at some DoD sites. For NDMA, the in situ formation due to well materials construction or natural geological formations should also be evaluated, together with the behavior of NDMA in low permeability materials.

4.4.3 Basic Research to Support Risk Assessment of PFASs (High)

DoD has identified PFASs as an emerging contaminant group with potentially significant environmental liability at legacy restoration sites. Recent investigations have observed highly complex mixtures of PFASs in groundwater at select DoD sites. Although toxicity data currently exist for PFOA and PFOS, strategic studies are still needed to address the quantitative dose-response assessment for these contaminants, and the hazard identification and dose-response assessment for other prevalent PFASs for regulatory human health risk assessments. Specifically, particular emphasis is needed to support quantitative dose-response, physiologically based pharmacokinetic (PBPK) modeling (including human and comparative toxicokinetics and toxicodynamics), and/or mixture toxicity for the suite of PFASs found at DoD sites at environmentally relevant concentrations.

5.0 DEMONSTRATION NEEDS

The demonstration needs identified during the workshop are described below. The needs are grouped by the technical areas posed to the workshop and are then broken out as critical or high priority demonstration needs.

5.1 Enhanced Attenuation

A number of existing remedial and site characterization technologies may be appropriate for use in enhanced attenuation. However, in some cases, application of these technologies to enhance contaminant attenuation still must be validated. The topics listed below were determined to be the most critical demonstration needs identified during the workshop.

5.1.1 Tools to Estimate Contaminant Transfer and Transformation Rates (Critical)

The purpose of this demonstration need is to develop and demonstrate tools that show the occurrence of and quantify the rates of long term, sustainable attenuation processes. The focus is on developing tools for assessing and monitoring the effectiveness of long term attenuation processes. This information will be needed to accomplish the following:

- Obtain regulatory and other stakeholder concurrence that enhanced attenuation is a viable, protective long term remedial option.
- Support cost-benefit analyses of different methods for enhancing attenuation at a given plume.
- Track the progress of enhanced attenuation.

Topics of particular interest include the following:

- Tools to predict reaction rate(s), including molecular biological tools.
- Understanding hydrogen fractionation rates to allow use of compound specific isotope analysis (CSIA) for aerobic reactions. This topic includes 2D and 3D (different isotopes and different elements) CSIA.
- Tools to estimate abiotic reaction rates.

5.1.2 Innovative Methods to Accelerate Attenuation within Plumes (Critical)

The purpose of this topic is to demonstrate field-scale implementation of innovative uses of existing technologies to accelerate the plume attenuation rate in a cost effective and sustainable manner. Field-scale demonstrations and/or analyses of data from existing sites may provide valuable information concerning long term effects of various technologies used in combination or applied in an innovative manner. Specific examples include the following:

- Hydraulic manipulation to prevent influx of clean groundwater through a contaminated zone, thereby eliminating further generation of contaminated groundwater. This approach may include low cost, sustainable hydraulic methods to divert upgradient, clean groundwater around the contaminated zone. Alternatively, an amendment, such as iron or clay, could be injected to decrease the permeability of the contaminated zone and divert clean, upgradient groundwater around it. The iron and clay may also promote natural attenuation processes within the contaminated zone. Regardless of the specific method used, isolation of the contaminated groundwater is expected to provide additional contact time for natural attenuation processes to proceed. The focus should be on low cost, sustainable methods to achieve diversion of clean groundwater. An example of this is ESTCP project ER-201328 *"Contaminant Flux Reduction Barriers for Managing Difficult-to-Treat Source Zones in Unconsolidated Media."*

- Use of passive, sustainable techniques to deliver amendments in a cost effective manner. For example, amendments could be distributed in transects that divide the plume into a series of segments, minimizing the level of effort needed to maintain the treatment zone and enhancing natural attenuation processes between each treatment zone. Sustainable technologies, such as solar-powered pumps, could be used for amendment injection.
- Innovative combinations of existing technologies. For examples, amendments could be applied in a series of reactive zones to allow sequential degradation reactions.

Largely, the focus of this demonstration topic is on innovative application of existing remedial technologies to enhance contaminant attenuation in a more cost effective and sustainable manner.

5.1.3 Develop and Demonstrate High Resolution Characterization Techniques (High)

This demonstration topic was identified as both a research need and demonstration need, and was discussed in Section 4.1.3.

5.2 Predictive Modeling

5.2.1 Field Scale Estimates of Parameters Controlling Back Diffusion, Desorption and Degradation (Critical)

The need for field scale tests to estimate parameters in predictive models was discussed previously in Section 4.2. These tests need to be demonstrated and validated in the field.

5.3 Long Term Monitoring

5.3.1 Coupling Modeling and Monitoring for Long Term Management (Critical)

Long term management of contaminated groundwater sites poses unique challenges for the DoD. Management decisions include the following: a) transition assessment to long term management with either active or passive strategies, b) establishing a long term monitoring program, c) selecting institutional controls including the scope of regular reviews of the site status, such as five year reviews at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites, and d) providing updated estimates of time to achieve closure or no further action status. To inform these decisions, there is a clear interdependency between monitoring programs and the use of fate and transport models for predictions of long term performance regardless of whether a site is under active or passive long term management.

Over the past decade, several consensus reports have documented the limitations of existing groundwater modeling tools in providing accurate estimates of times to achieve site remedial action objectives (RAOs) (USEPA, 2003; NRC, 2005; NRC, 2013). Predicting the trajectory of any remediation activity at complex sites (including natural attenuation) will require further research to clarify the conditions under which non-ideal processes such as back diffusion and non-equilibrium desorption are likely to be contributing factors in the remediation of the plume zone. An additional challenge is the development of better characterization tools to establish the necessary initial conditions for modeling, and incorporating the limiting non-ideal processes into applicable contaminant transport models.

The appropriate design of field studies to evaluate the resulting predictive capability of models represents an additional technical challenge. While significant progress has been made in the development of new numerical tools for multi-phase contaminated sites in both the saturated and unsaturated zones, these models are not widely used in practice, and are still in need of further verification/validation at the field scale. Before these tools will become as common in use as MODFLOW and other numerical tools, further demonstration and validation are needed, along with appropriate technology transfer. Matching data needs for accurate modeling development with monitoring or diagnostic tools represents a significant demonstration need. Both the target analytes and the spatial and temporal scales of monitoring programs must be linked with the scales used in model development for both fate and transport of contaminants as well as for performance assessment modeling tools. Innovative demonstration projects linking monitoring strategies with application of fate and transport or performance assessment models of in situ remediation technologies could reduce the costs of long term monitoring and increase confidence in the monitoring results.

Key inputs to predictive models include appropriate biotic and abiotic degradation rate constants, retardation constants, and descriptions of potentially important processes such as matrix diffusion. Degradation parameters typically have significant influence on model predictions. Techniques for quantifying degradation rates in ways that can be incorporated as modeling parameters are therefore needed. Techniques, especially field scale methods, should be applicable for determining model parameter values and process descriptions, especially in light of issues with scaling of laboratory–derived parameter values to the field. Likewise, consideration of spatial and temporal changes in plumes and subsurface conditions over time may require periodic verification of conditions and associated model descriptions. Monitoring techniques that provide this information and enable iterative application of monitoring and model updates are needed to support effective long term remedy management.

5.3.2 Geophysical Monitoring of Biogeochemical Conditions (High)

The use of geophysical tools can be a valuable part of an integrated long term monitoring program or transition assessment. Geophysical sensors deployed within existing boreholes can evaluate conditions beyond the borehole and increase understanding of the rates and sustainability of enhanced or natural attenuation. For example, geophysical signals might be used to identify and study low-permeability regions within the subsurface, to track the spread of injected amendments, or to detect biogeochemical changes impacting attenuation (changes in redox, pH, or electron acceptor influx, for example). Geophysical techniques could detect signatures of important degradation pathways, such as magnetite formation, and analyses of geophysical measurements taken at intervals could detect important trends in the biological or geochemical attenuation processes.

Adapting existing techniques to biogeochemical monitoring could improve the 4-dimensional understanding of complex sites and provide early warnings of important changes in the subsurface environment. Geophysical methods may also be useful at interfaces (e.g., groundwater-surface water interfaces) to help quantify locations and rates of water and solute exchange that may be important in quantifying fluxes across these interfaces. A key demonstration need is the integration of geophysical data and interpretations into remedy design, monitoring, and management decisions. It is difficult, however, to interpret and infer hydrogeologic and biogeochemical conditions from geophysical measurements alone. A degree of "ground truthing" with measurements of contaminant concentrations or other chemical and biological indicators is needed for confirmation. Thus, there needs to be consideration given to the nominal long term monitoring schemes that are to be integrated with geophysical monitoring.

5.3.3 Next-Generation Long Term Monitoring Systems (High)

Recent research suggests that changes in subsurface conditions and contaminant concentrations are usually slow, albeit with high temporal and spatial variability. These conditions support a transition to very infrequent compliance monitoring in many cases, with perhaps a more targeted spatial effort at each interval. More efficient monitoring could reduce costs for both active and passive management systems, and could improve the value of the monitoring data for a range of management decisions. Transferring this knowledge into practice will require demonstrations, data mining, and the development of technically credible guidance on optimizing monitoring programs for both spatial and temporal density. Comparisons of current and innovative targeted approaches, preferably at relatively complex sites, would allow evaluations of the costs and reliability of different strategies. Developing data-driven, technically credible monitoring guidance could reduce costs and improve long term management by linking the monitoring programs to the overall system dynamics (i.e., the subsurface groundwater velocity and heterogeneity, as well as the biogeochemical conditions and attenuation rates).

5.3.4 Monitoring Strategies for Transitioning to Passive Management (Critical)

Most complex sites will transition over time to increasingly passive management, whether it involves a gradual "winding down" or a formal transition to MNA or a No Further Action determination. Transition decisions will also involve determination of how much source treatment or removal is sufficient. Such decisions may happen for the whole site or for individual operating units or portions of sites. These decisions will require different types of monitoring, and monitoring plans that should be designed to collect the types of data needed for transition assessments. Examples include trend analyses for key parameters, estimates of matrix diffusion within the source and plume, prediction of how much source treatment or removal will affect contaminant mass flux out of the source area, estimates of the assimilative capacity (e.g., based on organic carbon or reactive mineral abundance), mass balances of both the mass flux out of the post-remediation source area and the assimilative capacity of the downgradient aquifer, and mass balances of electron donors and acceptors. Such an approach would likely be based on time-concentration data analyses to identify asymptotic performance, but other lines of evidence are needed to ensure that an asymptote is not due to poor design or operation, and that concentrations are likely to remain stable after the transition. Demonstrations and resulting guidance on technically credible approaches for making transition decisions would be helpful to both site managers and regulators, and should improve the design and acceptance of more cost-effective monitoring plans.

5.4 Emerging Contaminants

5.4.1 Demonstration and Validation of Technologies for Treatment of Emerging Contaminants Together with Contaminants of Historical Concern (Critical)

Many emerging contaminants occur in soil and groundwater together with contaminants of historical concern for DoD. For example, 1,4-dioxane is known to co-occur with chlorinated solvents (Mohr, 2010; Anderson et al. 2012). Similarly, PFASs often co-occur with petroleum hydrocarbons and/or chlorinated solvents at fire training areas and crash sites. While remediation technologies are readily available and highly successful for petroleum hydrocarbons and chlorinated solvents, remediation technologies for emerging contaminants are not as well documented. Moreover, individual treatment technologies are usually suboptimal in treating contaminant mixtures consisting of compounds with variable chemical and physical properties. Comprehensive strategies will likely be needed in many circumstances to effectively treat key emerging contaminants together with co-contaminants. These strategies could be based on treatment processes that are sufficiently non-specific to apply to a wide range of contaminant types, or they could involve combinations of compatible treatment processes, or sequential (in time or space) applications of treatment processes. In situ and ex situ implementations have to be considered.

Specific areas of research needs around key contaminant classes include the following:

- Assessing the impact of petroleum hydrocarbons and chlorinated solvents on the treatment efficacy of emerging contaminants in groundwater;
- Developing cost-effective remedial strategies to address contaminant mixtures at contaminated sites;
- In the case of PFASs, minimizing the formation of PFOA from precursors present in aqueous film-forming foam (AFFF) during groundwater treatment directed at co-contaminants.

6.0 TECHNOLOGY TRANSFER NEEDS

One common theme which emerged from discussions of the four key technical areas (enhanced attenuation, long term monitoring, predictive modeling, and emerging contaminants) was an urgent need for SERDP and ESTCP to expand upon its existing technology transfer program. Participants consistently cited the need for targeted technology transfer efforts, and several felt the transfer of existing ESTCP products had not been sufficiently effective. Support for conferences and travel to training opportunities continues to decline, especially within the public sector, yet the need for targeted information increases. Remediation managers and their consultants need trustworthy, practical information that is easily accessible via the internet. In particular, credible, well-advertised, and well-managed webinars are appreciated, especially if they can be combined with continuing education credits needed by many professionals. Of particular value are archived webinars that can be accessed on-demand and optionally linked to continuing education credits. An overarching technology transfer need is therefore to continue and expand the current efforts to develop useful and web-based tools and training opportunities, and to make these resources as accessible as possible to managers, consultants, and regulators.

Specific suggestions resulting from the formal and informal workshop discussions amongst workshop participants are provided below.

- During the first breakout session, and following a group exercise to identify data gaps and technology needs to improve the understanding and assessment of the long term management of contaminated groundwater sites, it became very clear to the diverse group of participants that there is an existing body of knowledge on enhanced attenuation, long term monitoring, predictive modeling, and emerging contaminants that has not been fully synthesized. The recommendations of many of the breakout groups revolved around developing “white papers” that summarize prior SERDP, ESTCP, other DoD, USEPA and private sector efforts around long term management of contaminated sites. The development of these white papers would not only serve as a technology transfer activity, but also would support SERDP and ESTCP in making better decisions on funding future research and demonstration efforts.
- Following both the first and second breakout sessions, a clear recommendation from the participants included SERDP and ESTCP’s consideration of other methodologies for technology transfer. Given the current travel restrictions imposed on DoD personnel, traditional in-person methods for communicating SERDP and ESTCP project results are no longer viable options for many DoD and other federal and state employees. As a result, workshop participants recommended that SERDP and ESTCP explore other approaches for communicating the wealth of knowledge generated by ongoing and completed research and demonstration projects.
- One option that was discussed in some detail is a webinar program coordinated and presented by SERDP and ESTCP. The goal of this program would be to communicate the results of SERDP and ESTCP projects. The webinars would be offered regularly by SERDP and ESTCP (e.g., once or twice a month, at lunchtime, on the same day of the week for continuity and branding purposes). The presentations would be archived and made available for download via a SERDP and ESTCP technology transfer portal. Because the primary goal of these webinars is effective communication of

project results, SERDP and ESTCP would provide clear guidance to its principal investigators regarding the development of the presentation materials and would request the following:

- Webinar presentations would be limited to 35 or 40 minutes in length in order to allow sufficient time for interaction with DoD site managers via phone or online;
- The content would include an overview of project objectives, methodology, results and costs, with a focus on what the results mean and how the research can help advance progress in the field.

In order to facilitate access to any white papers or alternative approaches for technology transfer such as the webinar program, limited discussions recommended that SERDP and ESTCP develop a centralized webpage where DoD personnel can readily access and download relevant documents and archived webinar content. A calendar listing dates for future technology transfer activities would also be available on this website.

Specific technology transfer needs identified during the workshop are described in the following sections. The needs are grouped by the technical areas posed to the workshop and in some cases are then broken out as critical or high priority technology transfer needs.

6.1 Enhanced Attenuation

Although enhanced attenuation is a novel concept, many existing remedial and site characterization technologies are directly applicable to this remedial approach. Workshop participants identified technology transfer as a critical need with respect to implementing more cost effective solutions for large, complex plumes. The specific technology transfer topics are presented below.

6.1.1 Technology Transfer of Cost Effective Methods for Amendment Delivery (Critical)

The cost associated with amendment delivery is often a limiting factor to full-scale implementation of in situ techniques that can promote long term enhanced attenuation of natural processes. The effectiveness of various in situ amendment delivery techniques has been demonstrated and compared in the literature. However, it appears that the findings of these studies have not been disseminated throughout the environmental industry. The goal of this topic is to develop guidance, manuals, or other training methods of facilitating implementation of effective approaches for amendment delivery.

6.1.2 Promote Use of CSIA to Determine Degradation Mechanisms and Track Enhanced Attenuation (High)

Research has demonstrated that CSIA can be a powerful tool for determining which processes are occurring in situ. To obtain regulatory concurrence for implementation of enhanced attenuation and to track enhanced attenuation's progress, it will be necessary to identify the different degradation processes and their relative extents of occurrence for a given plume. Thus, use of CSIA during site characterization and CSM development could be an important tool in ensuring effective implementation of enhanced attenuation. Although CSIA's usefulness has been demonstrated by prior investigations, this tool is seldom used in the environmental industry. The goal of this topic is to disseminate information and capitalize on existing training methods for promoting use of CSIA as a cost effective technique for identifying and tracking enhanced attenuation.

6.2 Predictive Modeling

6.2.1 White Paper on Results of Ongoing VI Research and Data Collection (Critical)

As discussed previously, SERDP and ESTCP funded research on VI is currently ongoing through a number of projects. Prior to implementing the VI modeling efforts discussed previously, it is prudent to prepare a white paper that summarizes the status of the ongoing VI research, especially as related to its impacts on VI modeling. Based on the white paper, better decisions can be made on how to proceed with any further VI model development.

6.2.2 Guidance and Training on Predictive Models for RPMs including Practical Management of Uncertainty (High)

Guidance and training is needed for remedial project managers and other high level users of information on the best application of predictive models. In addition, other guidance and training is need for those who are actually performing the modeling. These two levels of guidance are related, but somewhat different in their level of detail and focus.

The types of guidance and training material prepared could vary and needs to be evaluated in more detail so that the most benefit can be obtained from the expenditures.

The guidance for RPM should cover the following topics:

- A summary of the modeling tools currently available and who should perform modeling.
- Evaluating/understanding uncertainty in model predictions and tradeoffs with data collection.
- How model uncertainty impacts decisions.
- VOI guidance on how much data collection is needed to cost-effectively minimize model uncertainty.
- Re-calibration frequency of models, using long term monitoring results.
- Communication of modeling results.

The guidance for modelers should cover the following topics:

- A summary of the modeling tools currently available and where to find them.
- Evaluating/understanding model prediction uncertainty. How to use uncertainty evaluation tools.
- Re-calibration frequency of models, using long term monitoring results.
- Communication of modeling results.

6.3 Long Term Monitoring

6.3.1 Guidance on Matching Sample Frequency to System Dynamics (Critical)

Changes within the subsurface often occur very slowly, due to the generally slow groundwater velocities, low temperatures, and slow attenuation processes. As a result, sites may require only very infrequent monitoring to evaluate trends and ensure continued protectiveness, and in many cases only a few targeted monitoring locations may be needed to track progress and ensure remedial objectives continue to be met. More efficient monitoring could significantly reduce costs for both active and passive management systems, but there is little guidance on what monitoring schedule and spatial intensity is appropriate for different site conditions. A data-driven protocol is needed for optimizing long term monitoring systems to reduce costs and maintain confidence in the long term reliability and sustainability of the remedy. While sites often have unique and challenging characteristics, some guidance would be useful for different types of sites based on hydrogeologic conditions and the age of the contaminant source which is often determined by natural dissolution and remediation applied. This guidance is considered a technology transfer need, but it may also require some related development and demonstration.

6.4 Emerging Contaminants

6.4.1 Assessment of the Potential Impact of Changes in the Toxicity and Regulatory Standards of Chlorinated Solvents on Long Term Site Management, Remediation Efficiency and Cost (High)

As mentioned previously, on September 28, 2011, the USEPA released its final health assessment for TCE to the IRIS database. This assessment likely has significant implications for risk-based corrective action activities at chemical release sites where TCE is a chemical of concern and is expected to lead to increases in risk estimates by a factor of 2 to 9 depending on the assumptions used. These increased risk estimates may have important regulatory implications for on-going and future site remediation in addition to potentially reopening closed sites. This is of particular significance for DoD since a large fraction of DoD's environmental cleanup liabilities are the result of TCE contamination.

This proposed effort involves a white paper study that summarizes the new toxicity information (e.g., reference dose, etc.) and the prospective change to regulatory standards (i.e., MCLs). This study will present and summarize information that site managers can use to ascertain how the revised risk levels will affect their specific cleanup program. Specifically, the white paper will include information on the effectiveness of treatment technologies on environmental media characterized by low TCE concentrations, impacts on treatment timeframes, and costs. Finally, this white paper should quantify, to the extent practical, resulting impacts on long term site management strategies, cleanup timeframes, and ultimately, cleanup costs at DoD sites.

6.4.2 Standardization of DoD's Response to Emerging Contaminants at Legacy Restoration Sites (High)

In the actuality of limited resources, federal and state agencies are struggling with how to identify, prioritize and manage emerging contaminants. Many emerging contaminant initiatives must rely heavily on either preliminary studies, or existing guidance and processes established by others. A consistent DoD process for managing emerging contaminants is missing. Thus, standardized best practices are needed to respond to emerging contaminants at a programmatic level within DoD. Currently, the Air Force Emerging Issues and Emerging Contaminants Program (EI/EC) has developed programmatic guidance for field responses to PFASs and 1,4-dioxane at legacy restoration sites.

This proposed effort involves a white paper study that evaluates how each of the DoD services tracks, prioritizes and addresses emerging contaminants in groundwater. DoD-wide programs, such as the Chemical and Material Risk Management (CMRM) Program, will also be evaluated. General adoption of best practices within DoD will be explored.

6.4.3 Development of Standardized Methods by Contract Laboratories to Evaluate Presence of Per- and Polyfluoralkyl Substances That Are Present in Military Sites (High)

Analytical methodology for the quantification of individual per- and polyfluorinated chemicals that occur at military sites in groundwater, sediment and soil are now available in the peer-reviewed literature for adoption/modification by commercial laboratories that support execution of the DoD Environmental Restoration program. Analytical methodology is applicable to perfluorinated PFOS/PFOA and related homologs, precursors to PFOS/PFOA (and their homologs) that occur in AFFF formulations used to fight hydrocarbon-fuel fires, polyfluorinated chemicals found in fluorotelomer-based AFFF, and other polyfluorinated chemicals that are likely degradation products of polyfluorinated chemicals (precursors) found in AFFF formulations. In addition, analytical methodology that determines the total oxidizable precursors (TOP) content of groundwater, sediment, and soil also is available in the peer-reviewed literature. The TOP assay provides information on the quantity and fluorocarbon chain length of precursors in the sample that form perfluorocarboxylates under the thermally-activated persulfate conditions of the TOP assay. The TOP assay generates quantitative information on the concentrations and chain-lengths of precursors that cannot yet be quantified as discrete chemical species.

This proposed effort involves a white paper study that summarizes available analytical methodologies for individual PFAS and for TOP, and the potential for their modification and subsequent adoption by commercial laboratories that support execution of the DoD environmental restoration programs.

6.4.4 Wide Distribution of Brief Communications on Emerging Contaminants (High)

In addition to the technology transfer and communication efforts detailed above, the group discussed several other white paper studies that may be informative for site managers in their efforts to plan for and respond to the presence of emerging contaminants at DoD sites. Brief fact sheets or white papers were discussed by the group with the objective of compiling state of knowledge information and presenting it in a summary format on each of the following topics:

- Identification of PFASs precursors and the development of standardized methods to evaluate PFOS/PFOA formation from these precursors;
- Evaluation of impacts of water reuse and irrigation practices on future groundwater quality;
- From a field perspective, development of a toolbox and screening methodologies to evaluate the potential significance of emerging contaminants at an individual site.

7.0 CONCLUSION

The workshop highlighted the progress that the DoD has made in addressing remediation and management of contaminated groundwater. However, it was clear that there remain many challenges in managing the most complex contaminated groundwater sites. Research and demonstrations have contributed to the past success, but still are needed to address future challenges.

Discussions during the workshop focused on four key technical areas: enhanced attenuation, predictive modeling, long term monitoring, and emerging contaminants. One common theme which emerged from discussions within the four technical areas was an urgent need for SERDP and ESTCP to expand upon its existing technology transfer program. Several recommendations were made for products that could be developed in the short term that would greatly benefit the end user community.

Over 30 different research, demonstration, or technology transfer needs were identified during the workshop. Identification of these research and demonstration needs will directly impact the direction of SERDP and ESTCP investments over the next 3 to 5 years.

8.0 REFERENCES

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APPENDIX A

Agenda

SERDP/ESTCP WORKSHOP:
LONG TERM MANAGEMENT OF CONTAMINATED GROUNDWATER SITES

TUESDAY, AUGUST 13, 2013		
0800	**Registration/Breakfast**	
0830	**Welcome and Introduction** **Workshop Objectives and Structure**	Andrea Leeson SERDP and ESTCP
0835	SERDP and ESTCP Summary of Contaminated Groundwater Research and Demonstrations	Andrea Leeson SERDP and ESTCP
0850	Overview of NRC Report	Michael Kavanaugh Geosyntec
0920	Defense Environmental Restoration Program Study	Catherine Vogel Noblis
0940	DoD RPM Perspective	Michael Pound U.S. Navy
1000	**Break**	
1015	Predictive Modeling	Ron Falta Clemson University
1040	Long Term Monitoring	Chuck Newell GSI Environmental
1105	Enhanced Attenuation	Bob Borden Solutions IES
1130	Emerging Contaminants	Charles Schaefer CB&I
1155	**Lunch**	
1300	**Breakout Session I Discussions: Data Gaps** • Predictive modeling • Long term monitoring • Enhanced attenuation • Emerging contaminants	Session Chairs
1530	**Afternoon Break**	
1600	Reception with Poster Session	
1730	**Adjourn**	

Wednesday, August 14, 2013		
0800	**Breakfast**	
0830	Regulatory Perspective	John Wilson U.S. EPA
0900	Reports from Breakout Session I	Breakout Session Chairs
1000	Open Discussion	
1015	**Morning Break**	
1030	**Breakout Session II Discussions: Development and Prioritization Research Needs and Technology Transfer Opportunities**	Breakout Groups
1200	**Lunch**	
1230	**Breakout Session II Discussion** (cont'd)	Breakout Groups
1430	**Afternoon Break**	
1515	Breakout Session II Reports	Breakout Session Chairs
1645	Closing Remarks	Andrea Leeson
1700	**Workshop Adjourn**	

Thursday, August 15, 2013		
0900	Report Outline and Assignments	Session Chairs and Authors
1200	**Adjourn**	

APPENDIX B

Attendee List

Workshop Attendees

Linda Abriola, Ph.D.
Tufts University

Michael Adam
U.S. EPA

Richelle Allen-King, Ph.D.
University at Buffalo SUNY

Hunter Anderson, Ph.D.
AFCEC

Michael Annable, Ph.D.
University of Florida

Michael Basel, Ph.D.
Haley & Aldrich Inc.

Robert Borden, Ph.D.
Solutions-IES

Sandy Britt
ProHydro Inc.

Richard Brown, Ph.D.
ERM Inc.

Kim Parker Brown
NAVFAC HQ

Chuck Coyle
U.S. Army Corps of Engineers

Cindy Crane, Ph.D.
HydroGeoLogic, Inc.

James Cummings, Ph.D.
U.S. EPA

Kathy Davies
U.S. EPA

Rula Deeb, Ph.D.
Geosyntec Consultants

Patrick Evans, Ph.D.
CDM Smith

Ronald Falta, Ph.D.
Clemson University

Jennifer Field, Ph.D.
Oregon State University

Gregory Gervais
U.S. EPA

Laurie Haines-Eklund
U.S. Army Environmental Command

David Haldeman
Nebraska DEQ

Paul Hatzinger, Ph.D.
CB&I

Tissa Illangasekare, Ph.D.
Colorado School of Mines

Richard Johnson, Ph.D.
Oregon Health & Science University

Matthew Penning
HydroGeoLogic, Inc.

Mike Kavanaugh, Ph.D.
Geosyntec Consultants

Carmen Lebrón
NAVFAC EXWC

Hope Lee, Ph.D.
Pacific Northwest National Laboratory

Andrea Leeson, Ph.D.
SERDP and ESTCP

Frank Löffler, Ph.D.
University of Tennessee

Kira Lynch
U.S. EPA

David Major, Ph.D.
Geosyntec Consultants

James Mercer, Ph.D.
Tetra Tech

Timothy Mott
U.S. EPA

Charles Newell, Ph.D.
GSI Environmental Inc.

Katie O'Toole
HydroGeoLogic, Inc.

Jack Parker, Ph.D.
University of Tennessee

Randy Parker
U.S. EPA

Kurt Pennell, Ph.D.
Tufts University

Michael Pound
NAVFAC Southwest

Deanne Rider
HydroGeoLogic, Inc.

Thomas Sale, Ph.D.
Colorado State University

Charles Schaefer, Ph.D.
CB&I

Yasmin Shafiq
HydroGeoLogic, Inc.

Allen Shapiro, Ph.D.
U.S. Geological Survey

Thomas Simpkin, Ph.D.
CH2M HILL

Mike Singletary
NAVFAC Southeast

Lee Slater, Ph.D.
Rutgers University

Kent Sorenson, Ph.D.
CDM Smith

Clint Sperry
U.S. EPA

Robert Steffan, Ph.D.
CB&I

Hans Stroo, Ph.D.
Stroo Consulting LLC

Paul Tratnyek, Ph.D.
Oregon Health & Science University

Michael Truex
Pacific Northwest National Laboratory

Catherine Vogel
Noblis

Mark Widdowson, Ph.D.
Virginia Tech

John Wilson, Ph.D.
U.S. EPA

APPENDIX C

Presentations

Environmental Restoration Workshop

Long Term Management of Contaminated Groundwater Sites

13 August 2013

SERDP DOD • EPA • DOE | ESTCP

Objectives of the Workshop

1. Review the current status of complex sites, expectations for restoration, and how they are managed,
2. Identify options for achieving restoration goals more efficiently over longer periods of time,
3. Prioritize the research and demonstrations needed to show that restoration goals can confidently be achieved more efficiently over longer periods of time, and the new technologies needed to support that paradigm, and
4. Promote cooperation with other federal agencies to fund the needed work most efficiently.

SERDP/ESTCP WORKSHOP:
LONG TERM MANAGEMENT OF CONTAMINATED GROUNDWATER SITES

TUESDAY, AUGUST 13, 2013		
0800	**Registration/Breakfast**	
0830	**Welcome and Introduction** **Workshop Objectives and Structure**	Andrea Leeson SERDP and ESTCP
0835	SERDP and ESTCP Summary of Contaminated Groundwater Research and Demonstrations	Andrea Leeson SERDP and ESTCP
0850	Overview of NRC Report	Michael Kavanaugh Geosyntec
0920	Defense Environmental Restoration Program Study	Catherine Vogel Noblis
0940	A RPM's Roadmap for Remedial Technology Selection	Michael Pound U.S. Navy
1000	**Break**	
1015	Challenges in Modeling Long Term Behavior at Contaminated Sites	Ronald Falta Clemson University
1040	How Monitoring Fits Into Long Term Management of Contaminated Groundwater Sites	Charles Newell GSI Environmental
1105	Enhanced Attenuation	Robert Borden Solutions-IES
1130	Emerging Contaminants	Charles Schaefer CB&I
1155	**Lunch**	
1300	**Breakout Session I Discussions: Data Gaps** • Predictive modeling • Long term monitoring • Enhanced attenuation • Emerging contaminants	Session Chairs
1530	**Afternoon Break**	
1600	Reception with Poster Session	
1730	**Adjourn**	

WEDNESDAY, AUGUST 14, 2013		
0800	**Breakfast**	
0830	Regulatory Perspective	John Wilson U.S. EPA
0900	Reports from Breakout Session I	Breakout Session Chairs
1000	Open Discussion	
1015	**Morning Break**	
1030	**Breakout Session II Discussions: Development and Prioritization Research Needs and Technology Transfer Opportunities**	Breakout Groups
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1230	**Breakout Session II Discussion** (cont'd)	Breakout Groups
1430	**Afternoon Break**	
1515	Breakout Session II Reports	Breakout Session Chairs
1645	Closing Remarks	Andrea Leeson
1700	**Workshop Adjourn**	

Breakout Session 2

- Identify research, development, demonstration, and technology transfer needs and opportunities for the long-term management of contaminated groundwater sites building on the results of Breakout Session I.
- Needs and opportunities identified should be able to have research completed and provide potential valuable information that could impact DoD site management decisions within 3 to 5 years of research & demonstration initiation.

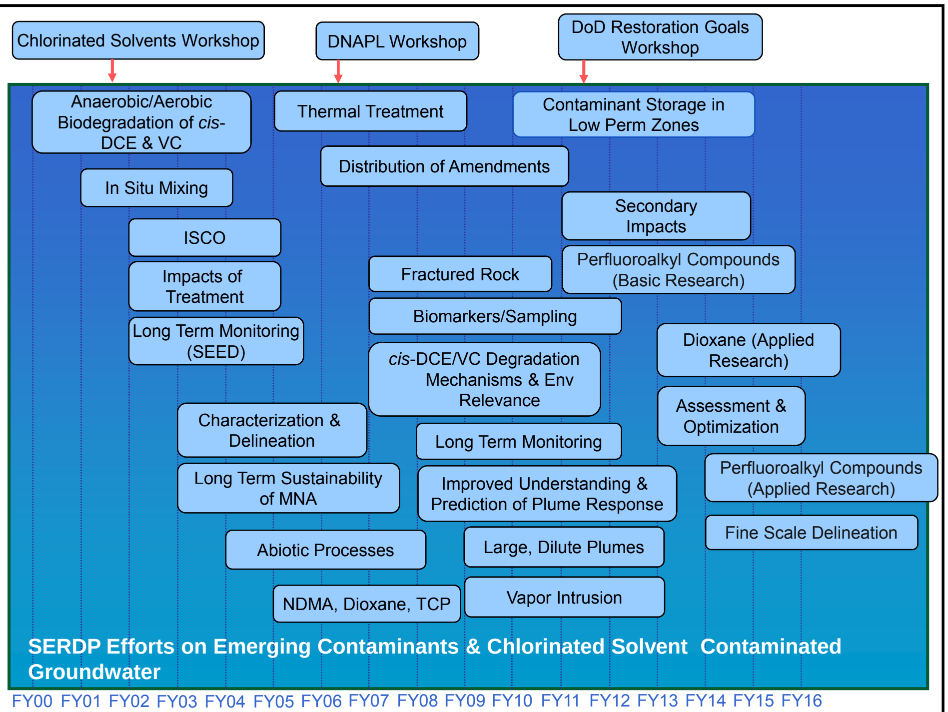
Criteria for Prioritizing RDT&E Needs

	Critical	High
Research	Research that potentially could have a significant impact on cost-effective long-term management of contaminated groundwater at DoD sites.	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 improve on cost-effective long-term management of contaminated groundwater at DoD sites.	Field demonstrations or assessments that are of high priority but may not be able to be implemented until critical demonstrations or assessments are completed.
Technology Transfer	Specific actions or documents that could be undertaken immediately to promote technology transfer of key concepts or technologies.	Actions or documents that should be undertaken to promote technology transfer of key concepts or technologies once specific research and/or demonstrations have been completed.

Generate paragraph descript for each need identified.

Summary of SERDP & ESTCP Projects

- Provided links to projects working on issues associated with contaminated groundwater
- Limited to those addressing chlorinated solvents and emerging contaminants
- SERDP SONs from FY00 to present
- ESTCP project from about FY03 to present



DNAPL Source Zones

- Contaminant Flux Reduction Barriers for Managing Difficult-to-Treat Source Zones in Unconsolidated Media (ER-201328)
- Determining Source Attenuation History to Support Closure by Natural Attenuation (ER-201032)
- Assessment of the Natural Attenuation of NAPL Source Zones and Post-Treatment NAPL Source Zone Residuals (ER-200705)
- Combining Low-Energy Electrical Resistance Heating with Biotic and Abiotic Reactions for Treatment of Chlorinated Solvent DNAPL Source Areas (ER-200719) (completed)

Fractured Rock

- Rapid Assessment of Remedial Effectiveness and Rebound in Fractured Bedrock (ER-201330)
- Designing, Assessing, and Demonstrating Sustainable Bioaugmentation for Treatment of DNAPL Sources in Fractured Bedrock (ER-201210)
- Demonstration of a Fractured Rock Geophysical Toolbox (FRGT) for Characterization and Monitoring of DNAPL Biodegradation in Fractured Rock Aquifers (ER-201118)
- Demonstration and Validation of a Fractured Rock Passive Flux Meter (ER-200831)
- DNAPL Removal from Fractured Rock Using Thermal Conductive Heating (ER-200715) (completed)

Low Permeability Issues

- Electrokinetic-Enhanced (EK-Enhanced) Amendment Delivery for Remediation of Low Permeability and Heterogeneous Materials (ER-201325)
- Enhanced Amendment Delivery to Low Permeability Zones for Chlorinated Solvent Source Area Bioremediation (ER-200913)
- Cooperative Technology Demonstration: Polymer-Enhanced Subsurface Delivery and Distribution of Permanganate (ER-200912) (completed)

Emerging Contaminants

- Natural Attenuation and Biostimulation for In Situ Treatment of 1,2-Dibromoethane (EDB) (ER-201331)
- 1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE) (ER-201326)
- Sustained In Situ Chemical Oxidation (ISCO) of 1,4-Dioxane Using Slow Release Chemical Oxidant Candles (ER-201324)
- Treatment of N-Nitrosodimethylamine (NDMA) in Groundwater Using a Fluidized Bed Bioreactor (ER-200829)
- Field Demonstration of Propane Biosparging for In Situ Remediation of N-Nitrosodimethylamine (NDMA) in Groundwater (ER-200828)

Subsurface Characterization

- Cost-Effective and High-Resolution Subsurface Characterization Using Hydraulic Tomography (ER-201212)
- Direct Push Optical Screening Tool for High Resolution, Real Time Mapping of Chlorinated Solvent DNAPL Architecture (ER-201121)
- Parallel In Situ Screening of Remediation Strategies for Improved Decision Making, Remedial Design, and Cost Savings (ER-200914)
- Verification of Methods for Assessing the Sustainability of Monitored Natural Attenuation (ER-200824) (completed)

Guidance & Tools

- Frequently Asked Questions about Monitored Natural Attenuation in the 21st Century (ER-201211)
- Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites (ER-201129)
- Development of an Expanded, High-Reliability Cost and Performance Database for In-Situ Remediation Technologies (ER-201120)
- Decision Support System for Matrix Diffusion Modeling (ER-201126) (completed)
- Decision and Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty (ER-200704) (completed)
- In Situ Chemical Oxidation for Groundwater Remediation: Technology Practices Manual (ER-200623) (completed)

Guidance & Tools (cont'd)

- Protocol for Selecting Remedies for Chlorinated Solvent Releases (ER-200530) (completed)
- Application of Nucleic Acid-Based Tools for Monitoring MNA, Biostimulation and Bioaugmentation at Chlorinated Solvent Sites (ER-200518) (completed)
- Develop a Mass Flux Toolkit to Quickly Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives (ER-200430) (completed)
- Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (ER-200424) (completed)
- Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent-Contaminated Sites (ER-200318) (completed)
- Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment (ER-200314) (completed)

Remediation Technologies

- In Situ Biogeochemical Transformation of Chlorinated Solvents (ER-201124)
- Solar-Powered Remediation and pH Control (ER-201033)

Long Term Monitoring

- Methods for Minimization and Management of Variability in Long-Term Groundwater Monitoring Results (ER-201209)

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"Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites"
Summary of a NRC Committee Report

Michael Kavanaugh,
Senior Principal
Geosyntec Consultants, Inc.

LONG TERM SITE MANAGEMENT WORKSHOP
SERDP/ESTCP
AUGUST 13-15, 2013

Arlington, VA

Geosyntec.com
engineers | scientists | innovators

Groundwater Contamination Issues and Technology Performance have been Discussed in Several National Reports

NRC Reports – 1994, 1999,2003, 2005,2012

EPA, 2004, DNAPL Remediation: Selected Projects Approaching Regulatory Closure

EPA, 2003, The DNAPL Remediation Challenge: Is There a Case for Source Depletion?

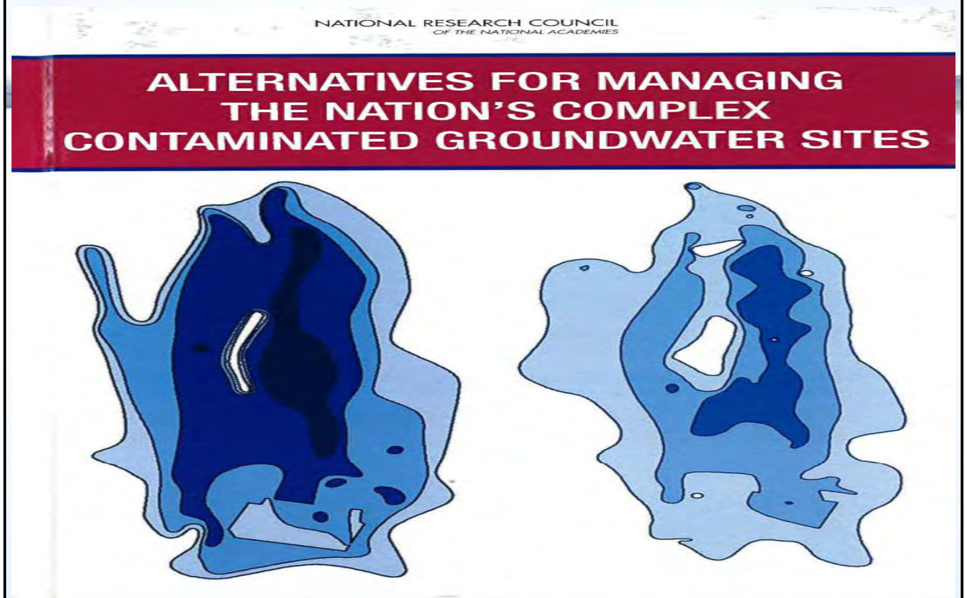
Environment Agency, 2003, Illustrated Handbook of DNAPL Transport and Fate in the Subsurface

ITRC, 2002. DNAPL Source Reduction: Facing the Challenge

ITRC, 2011, Integrated DNAPL Site Strategy

Numerous SERDP/ESTCP Reports and Books

Geosyntec consultants

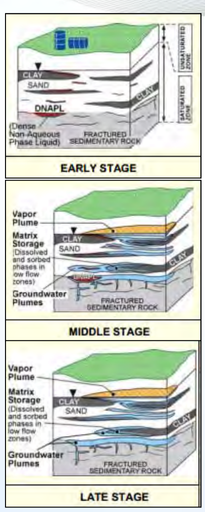


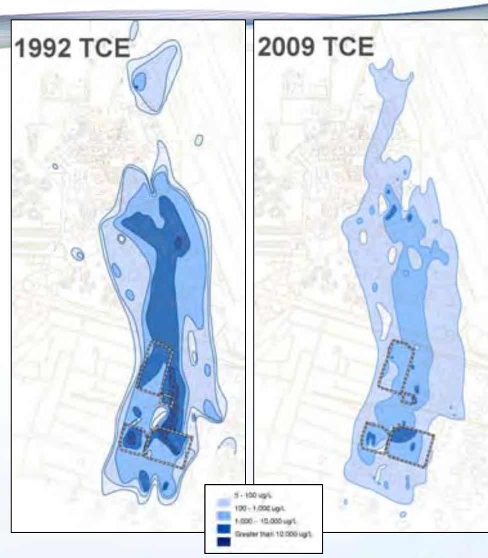
National Academy Press, 2013

Geosyntec consultants

Evolution of a Plume at a Contaminated Site
Matrix Diffusion and Vapor Intrusion Risk

From Sale et al., 2008





Persistent, low concentration plume due to matrix effects: MEW Site, CA

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Statement of Task

- **What is the size of the nation's current (2010) hazardous waste site problem?**
- **What are the capabilities of current technologies to restore contaminated groundwater?**
- **What is the future of treatment technologies**?
- **Can mass removal be better correlated with site-specific risks?**
- **How can the decision process be improved?**

Geosyntec consultants

Committee Membership

MICHAEL KAVANAUGH, NAE, *Chair*, Geosyntec
WILLIAM ARNOLD, University of Minnesota
BARBARA BECK, Gradient Corporation
YU-PING CHIN, The Ohio State University
ZAID CHOWDHURY, Malcolm Pirnie/ARCADIS
DAVID ELLIS, DuPont Engineering
TISSA ILLANGASEKARE, Colorado School of Mines
PAUL JOHNSON, Arizona State University
MOHSEN MEHRAN, Rubicon Engineering Corporation
JAMES MERCER, Tetra Tech GEO
KURT PENNEL, Tufts University
ALAN RABIDEAU, State University of New York, Buffalo
ALLEN SHAPIRO, U.S. Geological Survey
LENNY SIEGEL, Center for Public Environmental Oversight
WILLIAM WALSH, Pepper Hamilton LLP

Geosyntec consultants

Presenters at Committee Meetings

- Laurie Haines-Eklund, Army Environmental Command
- Jim Cummings, US EPA Superfund Office;
- Adam Klinger, EPA Underground Storage Tank Office;
- Jeff Marquesee and Andrea Leeson, SERDP;
- Brian Looney, DOE Environmental Management;
- John Gillespie, Air Force Center for Environmental Excellence;
- Anna Willett, Interstate Technology and Regulatory Council;
- Alan Robeson, American Water Works Association; Jill Van Dyke, National
- Groundwater Association; Ira May, May Geoenvironmental Services;
- Roy Herndon, Orange County Water District
- Milad Taghavi, LADWP; Carol Williams, San Gabriel Supply;
- Gil Borboa, City of Santa Monica;
- David Lazerwitz, Farella Braun + Martel, LLP;
- James Giannopoulos, California State Water Quality Control Board;
- Herb Levine, EPA Region 9;
- Alec Naugle, CA Region 2 Water Board;
- David Sweeney, New Jersey DEP.
- Rula Deeb, ARCADIS;
- Amy Edwards, Holland & Knight LLP;
- Brian Lynch, Marsh Environmental Practice;
- Richard Davies, Chartis;
- Henry Schuver and Helen Dawson, EPA;
- Tushar Talele, ARCADIS;
- Anura Jayasumana, Colorado School of Mines;
- Deborah Morefield, Office of the Deputy Undersecretary of Defense;
- Alana Lee, EPA Region 9; Betsy
- Southerland and Matt Charsky, EPA;
- Mike Truex, Pacific National Lab;
- Jim Gillie,Versar/Joint Base Lewis McChord.

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Report Peer Reviewers

- Lisa Alvarez-Cohen, University of California, Berkeley;
- Linda Lee, Purdue University;
- Jacqueline MacDonald Gibson, University of North Carolina, Chapel Hill;
- David Nakles, Carnegie Mellon University;
- Stavros Papadopulos, S.S. Papadopulos & Associates, Inc.;
- Tom Sale, Colorado State University;
- Rosalind Schoof, Environ International Corporation;
- Hans Stroo, HydroGeoLogic, Inc.
- Marcia E. Williams, Gnarus Advisors, LLC.

The review of this report was overseen by Susan L. Brantley, Pennsylvania State University; and Mitchell Small, Carnegie Mellon.

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Statement of Task

- **What is the size of the nation's current (2010) hazardous waste site problem?**
- What are the capabilities of current technologies to restore contaminated groundwater?
- What is the future of treatment technologies?
- Can mass removal be better correlated with site-specific risks?
- How can the decision process be improved?

Estimated Number of Sites/Facilities with Conditions not allowing for Closure and Costs to Complete

Program/Agency	Number of Facilities	Number of Sites	Estimated Cost to Complete ($B)
DoD		4,329	$12.8
CERCLA	1,364		$16 -23
RCRA	2,844		$32.4
UST		87,983	$11
DOE		3,650	$17.3 – 20.9
Other Federal Sites		>3,000	$15 - 22
State Sites		>23,000	$5
TOTALS		>126,000	$110 - 127

See Table 2-6 in report

Conclusions – Size of the Problem

- **126,000** sites that have not yet reached closure is likely an *underestimate.*
- Could not determine the total number of sites with residual contamination above levels allowing for UU/UE (must be > 126,000).
- Estimated future cost of **$110-127** billion likely an *underestimate.*
- More than **12,000** sites are "complex".

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Attributes of Highly "Complex Sites"

- Large releases of contaminants over long time frames.
- Highly heterogeneous subsurface geologic environments.
- Some contaminants recalcitrant and persistent.
- Levels of contaminants several orders of magnitude above levels allowing for UU/UE (e.g. MCLs).
- Several years of remedial efforts with an indication of asymptotic behavior – multiple 5-year reviews.
- Costs to achieve restoration exceeding $20 - $50 million.

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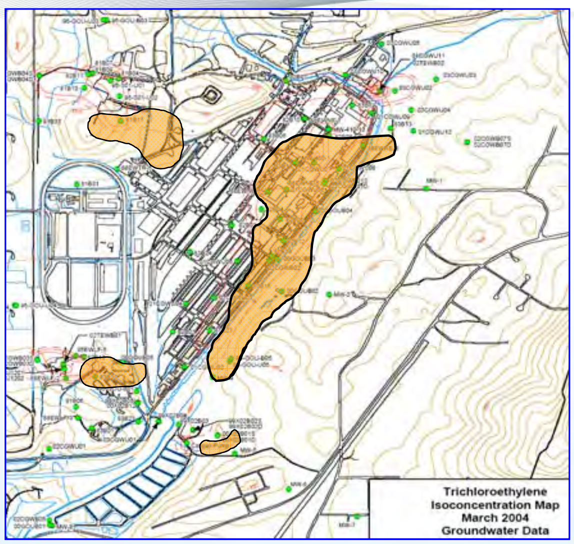
OU1 SIA Ground Water TCE Plume: Anniston Army Depot



TCE > MCL

(5 ppb)

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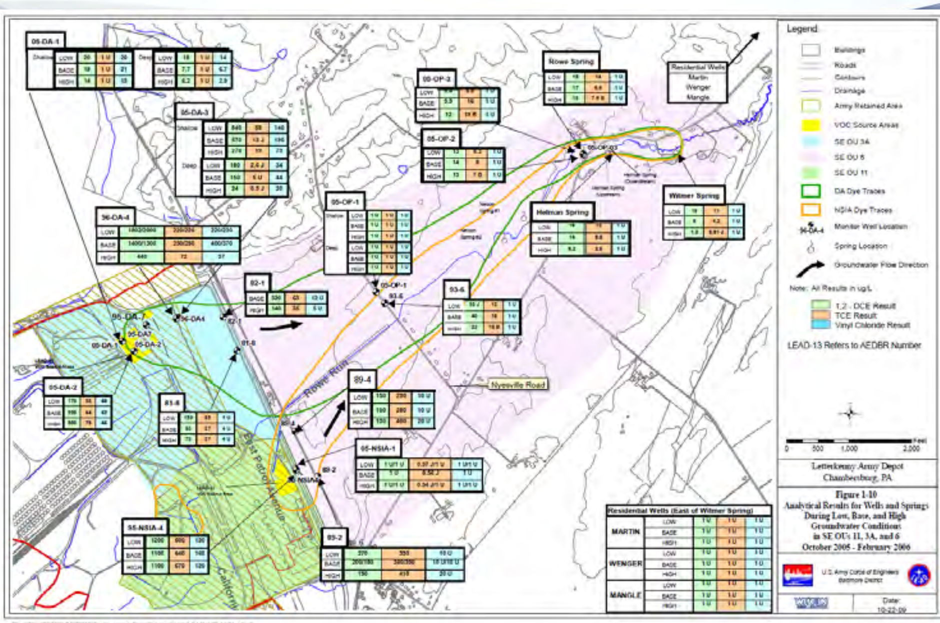
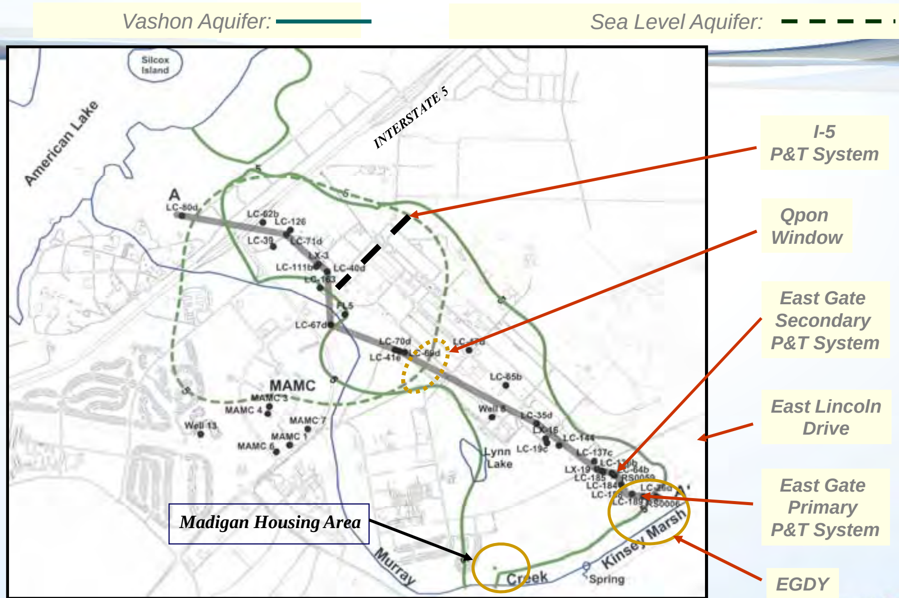
Site Map – OU3A, OU11, and OU6



Extent of TCE Plume/Site Features: Ft. Lewis



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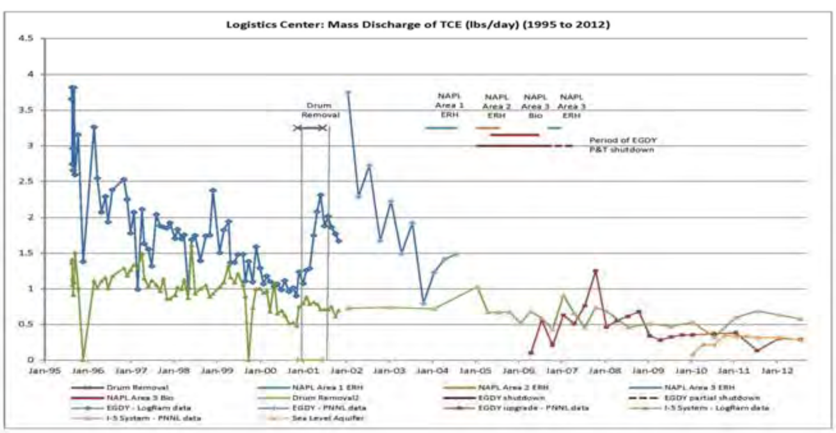
Source Mass Discharge Reduction at Ft. Lewis



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These Sites are Characteristic of Highly Complex Groundwater Contaminated Sites in Army Portfolio

- Highly heterogeneous geologic settings.
- High Cost of Site Characterization.
- Multiple five year reviews.
- Uncertain benefits of source depletion compared to active LTM (i.e. containment).
- Reluctance to use of TI waivers.
- No clear exit strategy.
- Exposure pathways controlled – low risks of failure.
- LTM most likely outcome.

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Historical Capabilities of Current Technologies for Groundwater Restoration

Source Removal

- Thermal Treatment
- *In Situ* Chemical Oxidation
- Surfactant and Co-solvent Flushing
- *In Situ* Bioremediation
- Combined Remedies

Plume Remediation / Containment

- Pump and Treat - hydraulic containment
- Physical Containment
- Permeable Reactive Barriers
- Monitored Natural Attenuation
- Natural Attenuation
- Combined Remedies

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Historical Performance – Source and Plume Remedial Technologies – Case Study Summaries thru 2010

Technology (No. of Sites with "sufficient" data)	Order of Magnitude Concentration Reduction	Order of Magnitude Mass Discharge Reduction
Thermal (14)	<10x - 10^4	<10x - 10^3
ISCO (~140)	<10x - 10^2	NR
In-Situ Bio (unk)	<10x - 10^3	NR
Surfactant – Cosolvent (<10)	<10x - 10^2	NR
Pump & Treat (>100)	<10x - 10^3	NR
Combined Remedies (unk)	Not reported (NR)	NR

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Key Finding: Current Capabilities to Achieve UU/UE

"Based on what is known about the effectiveness of remediation technologies (as described in this chapter [4]), the Committee concluded that regardless of the technology used, the complete removal (i.e. restoration) of contaminant mass at complex sites is unlikely. Furthermore, the Committee discovered no transformational remedial technology or combination of technologies that can overcome the current challenges associated with restoring contaminated groundwater at complex sites. At these sites, some amount of residual contamination will remain in the subsurface after active remedial actions cease, requiring long-term management." (pg 114, NRC,2013)

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Statement of Task

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- What is the future of treatment technologies?
- Can mass removal be better correlated with site-specific risks?
- **How can the decision process be improved?**

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Better Decision Making: Post-Remedy Phase of Groundwater Remediation

- Focus on decision making at most complex sites that are in remedy operation and maintenance phase with UU/UE remedial action objectives, often throughout the impacted aquifer.
- Goal: Consensus on path forward in face of challenges posed by technical, financial and sustainability constraints on achieving UU/UE.

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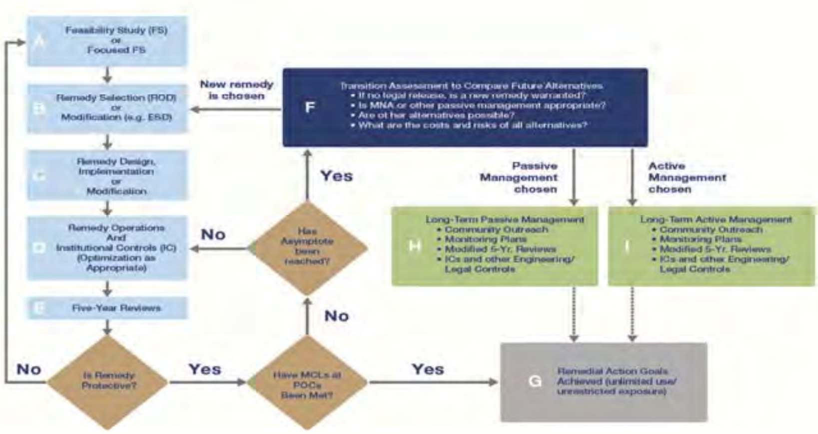
Alternative Decision Making Process



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Statement of Task

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- **What is the future of treatment technologies**?
- Can mass removal be better correlated with site-specific risks?
- How can the decision process be improved?

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Technical Challenges for LTM of Complex Sites

- More quantitative CSMs – pathways, distribution of contaminants.
- Advanced diagnostic tools to quantify attenuation mechanisms (abiotic, biotic).
- Enhanced removal through combined remedial technologies.
- Improved monitoring technologies and use of sensors.
- Modeling tools to improve prediction of time to achieve objectives under optimum remedial strategies.
- Research support to address these challenges.

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The Future: LTM as an Infrastructure Problem

- Goal of long-term management "end states": minimize probability of failure and consequences of same.
- A Geotechnical Engineering Perspective: Applying appropriate "best design practices" with "safety factors."

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Geotechnical Engineers Methodology for Risk Analysis of Dams: Design Assumptions and Safety Factors

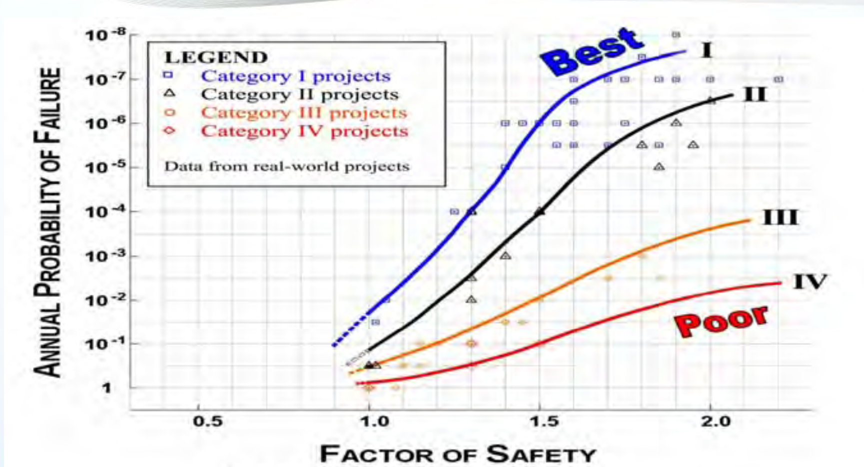

Fig. 1. Factor of safety versus annual probability of failure

F. Silva;T. Lamb; W. Marr, JOURNAL OF GEOTECHNICAL AND GEOENVIRONMENTAL ENGINEERING, Dec. 2008

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The Future: LTM as an Infrastructure Problem (cont.)

- Importance of advanced diagnostic tools and modeling capabilities for transition assessment decisions and addressing risks of residual contamination.
- An increasing role of optimization, monitoring, real time decision making, sensors, mobile technologies, visualization tools, "The Internet of Things."

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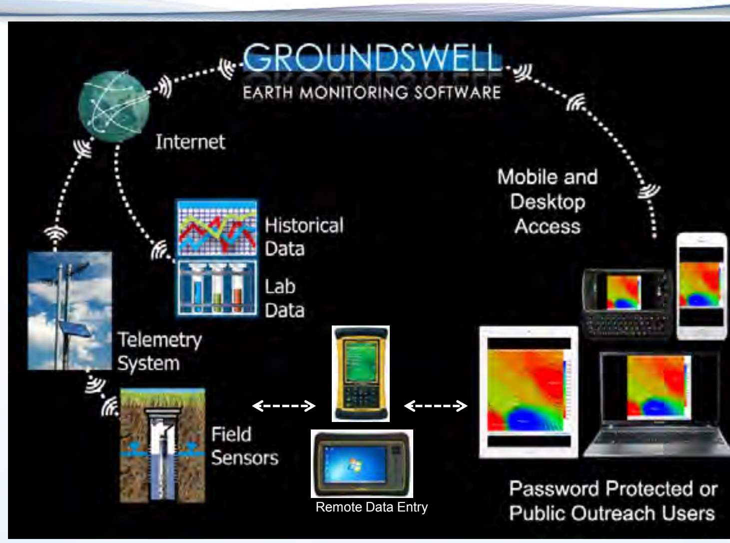
Conceptual Model of Integrated Monitor and Control System



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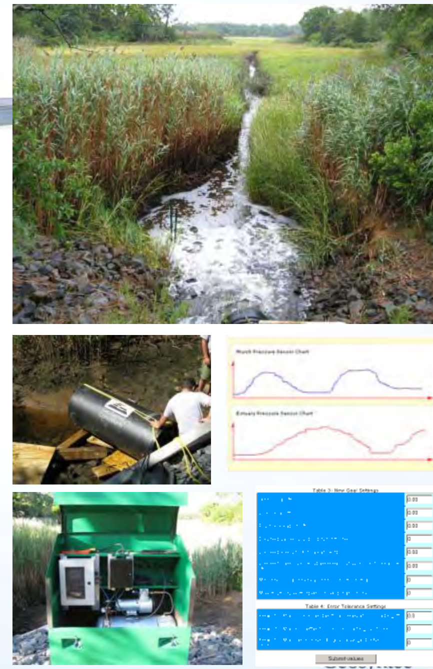
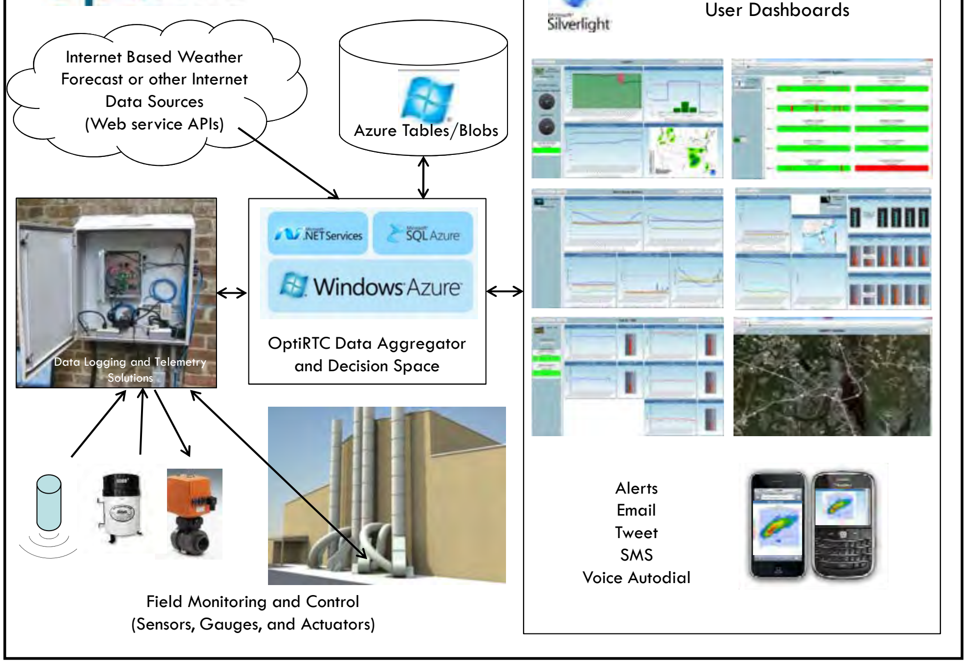
Initial Research Problem

- Find the least expensive most flexible means for monitoring and controlling the physical environment with integrated dynamic data streams.



OptiRTC Platform



NAVFAC Naval Facilities Engineering Command
Southwest Division

An RPM's Roadmap for Remedial Technology Selection

Naval Air Station North Island
Coronado, California

Michael Pound, Lead RPM

RPM Responsibilities

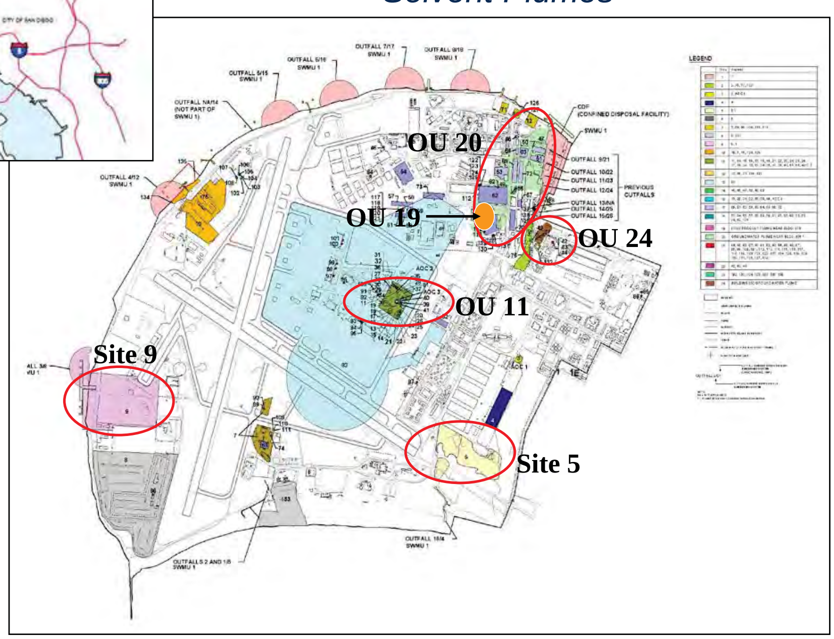
- **Budgeting**
  - Programming funding
- **Execution**
  - Developing SOWs/GE
  - Technical evaluations of contractors proposals
  - Negotiating new awards
- **Project Management**
  - Managing schedule and budget of awarded projects
  - Interfacing with stakeholders
  - Reviewing and approving invoices
  - Data calls
  - Setting technical direction for projects

What Guides Technology Selection?

- CERCLA Feasibility Study 7 criteria
- DOD/DON Policy (P&T, GSR, Eco Risk)
- RPM/Peer experience
- Contractor experience
- Technical guidance documents/literature
- Training classes
- What's hot
- Funding availability
- Site infrastructure constraints
- Current and future land use
- Conference presentations
- Vendor presentations
- Regulatory Agencies
- Local community input

NAS North Island Overview

NAS North Island Sites with Chlorinated Solvent Plumes



NAS North Island Overview

- **Natural Reductive Dechlorination of Chlorinated Solvents in NAS North Island Groundwater Plumes**
  - **Some sites showed evidence of complete transformation**
  - **Some site exhibited only partial transformation**
    - geochemical interferences?
    - lack of suitable electron donor?
    - microbiological limitations?

- **Navy policy to minimize/eliminate the use of P&T**
  - *Navy/Marine Corps Policy for Optimizing Remedial and Removal Actions Under the Environmental Restoration Program* (Ser N45C/ N4U732343, 23 Apr. 2004)

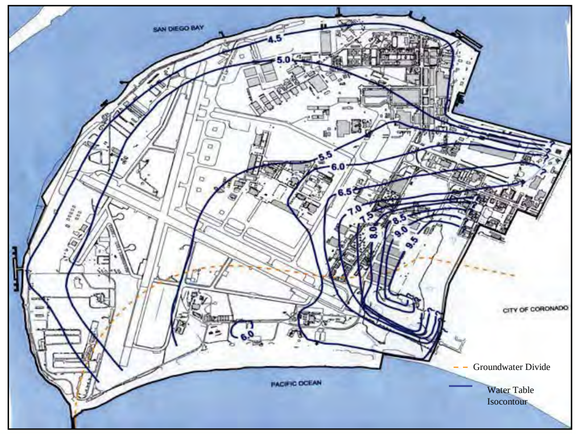
- **What remedial technologies should be considered?**

Background

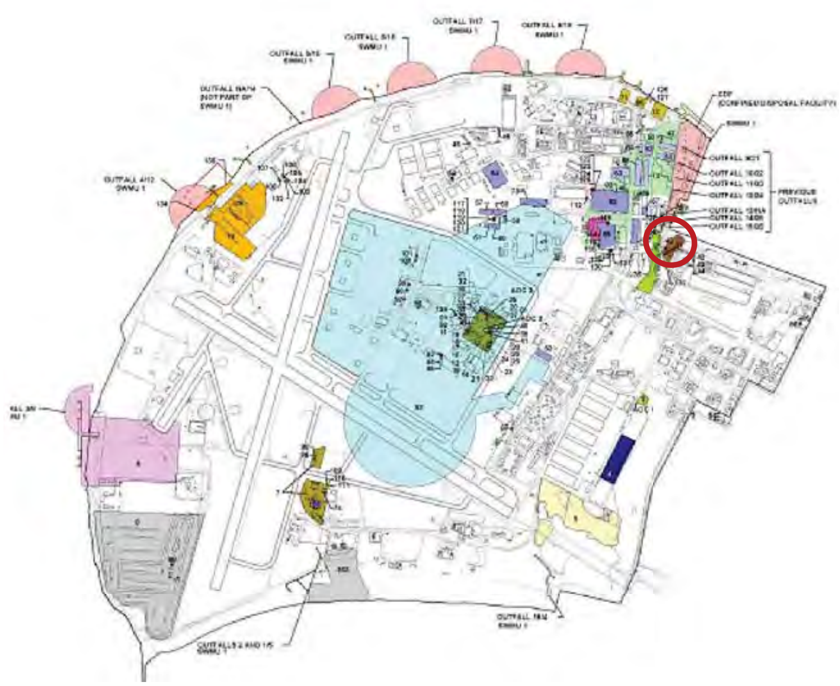
- **Geology**
  - **Pleistocene Bay Point Formation**
    - Sands, silts and clays
  - **Holocene beach sand**
  - **Artificial fill**
  - **Lower permeability layers within Bay Point Formation**
    - A silt
    - B clay
  - **Localized faulting**

Background

- **Groundwater**
  - –**Shallow unconfined aquifer**
    - Depth to water ranges from 7 to 28 ft bgs
    - Communicates hydraulically with saline waters of San Diego Bay
    - Freshwater lens recharged by irrigation water (golf course)
  - –**Not designated for municipal beneficial use**
  - –**Deeper groundwater semi-confined by low-permeability layers**

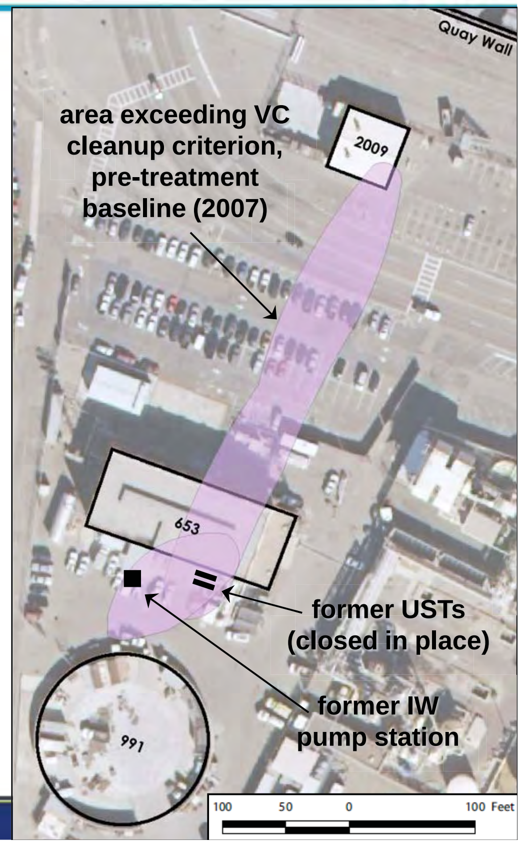


Operable Unit 24



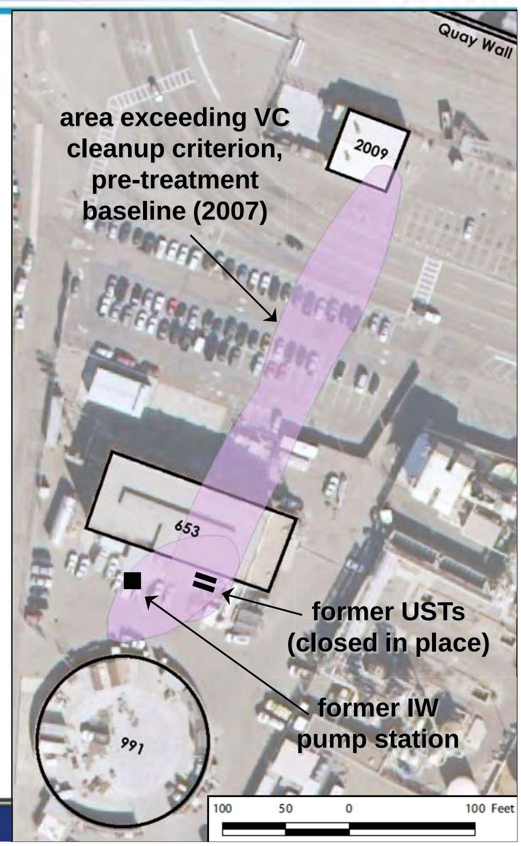
OU 24 Overview

- **Shallow groundwater contamination**
  - ~5 to 38 ft bgs
  - predominantly cDCE and VC
  - total CVOCs as VC exceeding 525 µg/L action level for VC
- **Suspected parent products:** PCE, TCE
- **Suspected source:** Industrial Waste Pipeline
- **Contaminants migrating toward San Diego Bay**
- **Aqueous phase CVOC mass within target treatment area:** ~15 kg



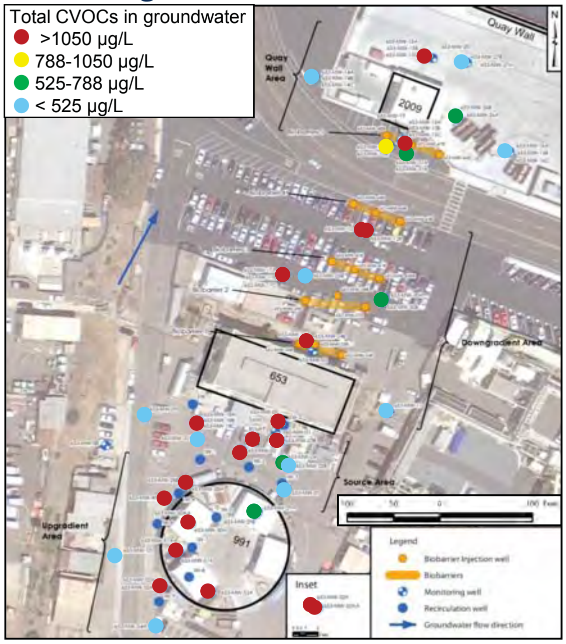
OU 24 Technology Selection

- **2005 Evaluating Remedial Strategy**
  - Lots of bioremediation being discussed in the literature/Battelle conferences
  - Biodegradation appears to have occurred and stopped
  - No pump and treat
  - No site work since 1999
  - High traffic area/lots of utility infrastructure
  - Appears to be low hanging fruit
  - Navy contractors unfamiliar with implementing an in-situ biodegradation approach
- **2006 Strategy Selection/Implementation**
  - Decided to take an in-situ approach
  - Evaluated contractors for the project and implemented contracting approach

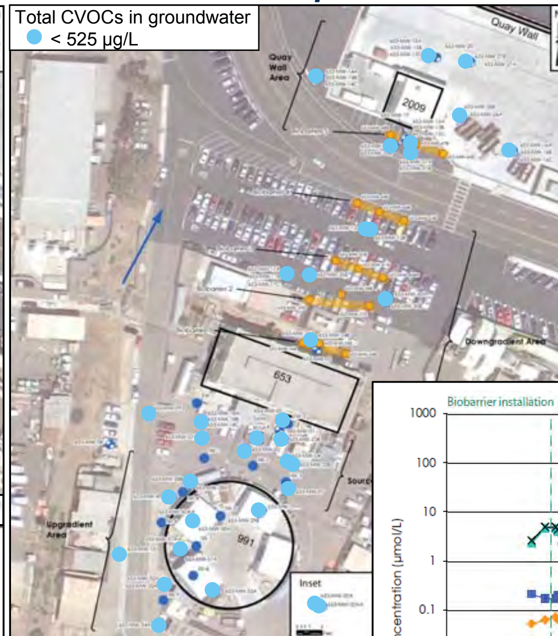


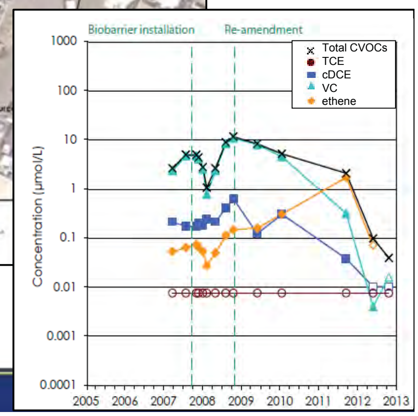
OU 24 EISB Results

Highest concentration



2013 or last sample collected





- Increase in *Dhc vcrA* and DOC, sulfate reduction
- Ethene & ethane production with VOC decreases

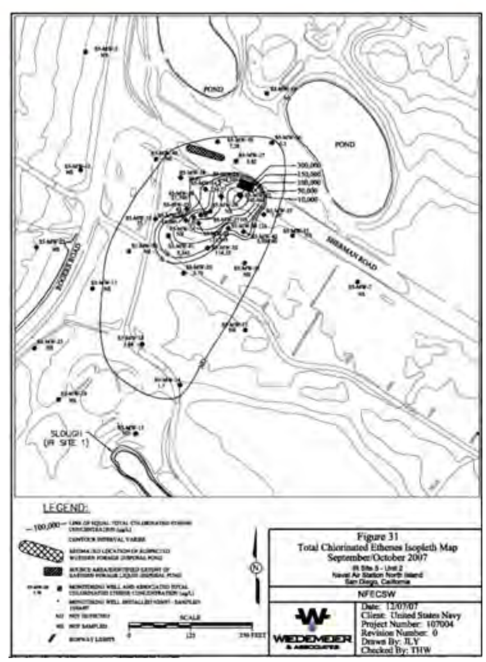
Installation Restoration Site 5 Unit 2

Site 5 Unit 2 Overview

- **Suspected source:** Liquid Waste Disposal Pits – part of landfill operated from mid-1940s to mid-1960s and converted into a golf course in 1984
- **Groundwater Contamination**
  - ~1 to 9 ft bgs
  - Mixture of Chlorinated Ethenes and Petroleum hydrocarbons
  - Total CVOCs > 600,000 μg/L, mostly *cis*-DCE
- **Parent Compounds:** PCE/TCE

Site 5 Unit 2 Technology Selection

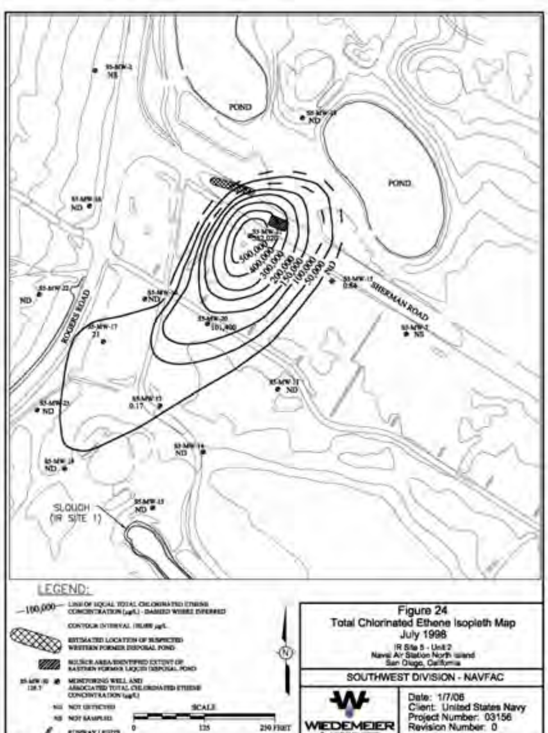
- **Mid 1990s site characterization conducted**
- **1998 Monitored Natural Attenuation study predicted it would be >100 years for the site to achieve remedial goals; source removal recommended**
- **1999-2001**
  - **Push to spend $$$ on cleanup**
  - **ISCO becoming popular; RPM wanted to use it**
  - **TCRA for source reduction with excavation and ISCO initiated**

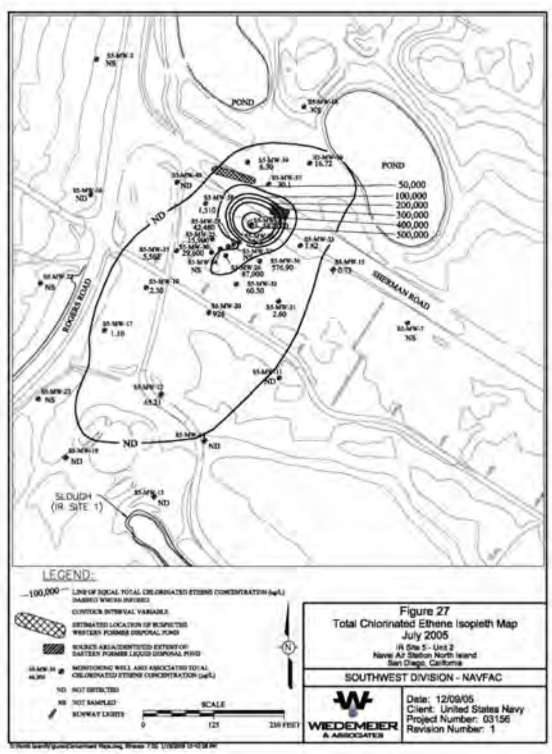


Remedy Selection – ISCO, Excavation, & MNA

- 2002 TCRA using ISCO (Fenton's reagent) followed excavation and then by more ISCO using $KMnO_4$

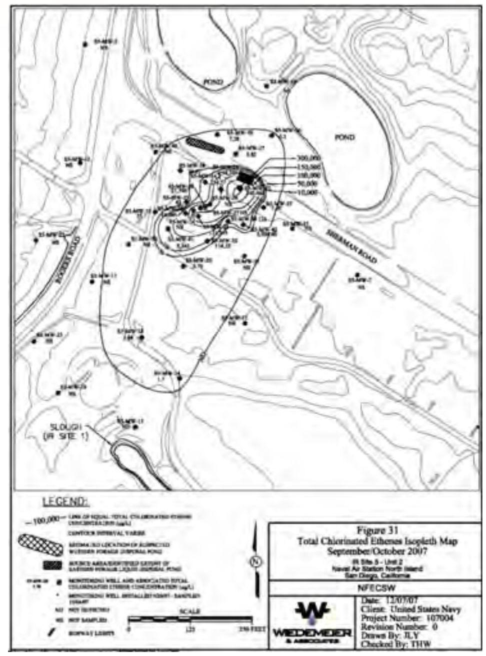
Total Chlorinated Ethene Concentrations July 1998 and July 2005





Site 5 Unit 2 Post-TCRA Conditions

- **2005**
  - **Groundwater monitoring showed the TCRA had reduced the contaminant mass but the plume footprint is relatively unchanged**
  - **Initiated study to determine where the remaining contaminate mass is and evaluate the biological degradation rate**
- **2007**
  - **Mass in place evaluation found 2000+ kg of VOC mass remains at the site**
  - **MNA evaluation found extremely rapid degradation rates**
    - Total VOC concentrations are reduced from 700,000 ug/L to <1 ug/L over a <200 feet flowpath distance

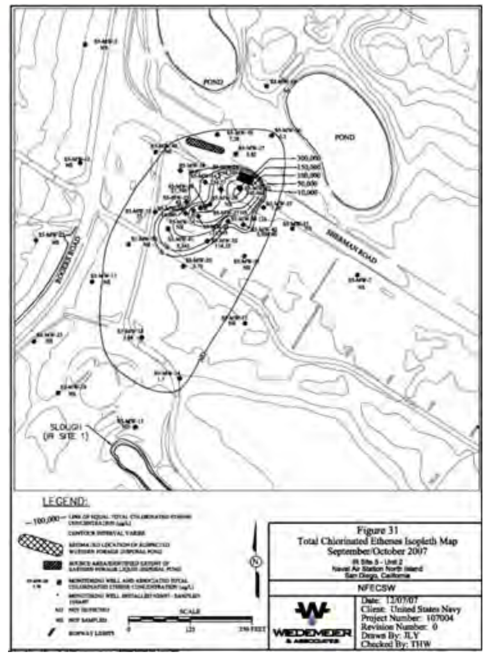


Site 5 Unit 2 Final Remedy Evaluation

- **No Action**
- **Institutional Controls**
- **Monitored Natural Attenuation**
  - **Soil and Groundwater**
- **Source Area 75% and 95% mass removal with Monitored Natural Attenuation**
  - **Excavation of Contaminated Soil**
  - **Monitored Natural Attenuation for Groundwater and Residual Contamination in Soil**

Site 5 Unit 2 Final Remedy Evaluation

- Natural Attenuation Software used to evaluate various remedial approaches to reach remedial goals
  - No mass removal 85 years
  - 75% mass removal 35 years
  - 95% mass removal 25 years
  - No source reduction to meet remedial goals at POC
- GSR evaluation with SiteWise
  - MNA had highest energy use and NO_x, SO_x, and GHG gas emissions, water usage, and accident fatality
  - Increasing mass removal had higher PM_{10} and accident injury



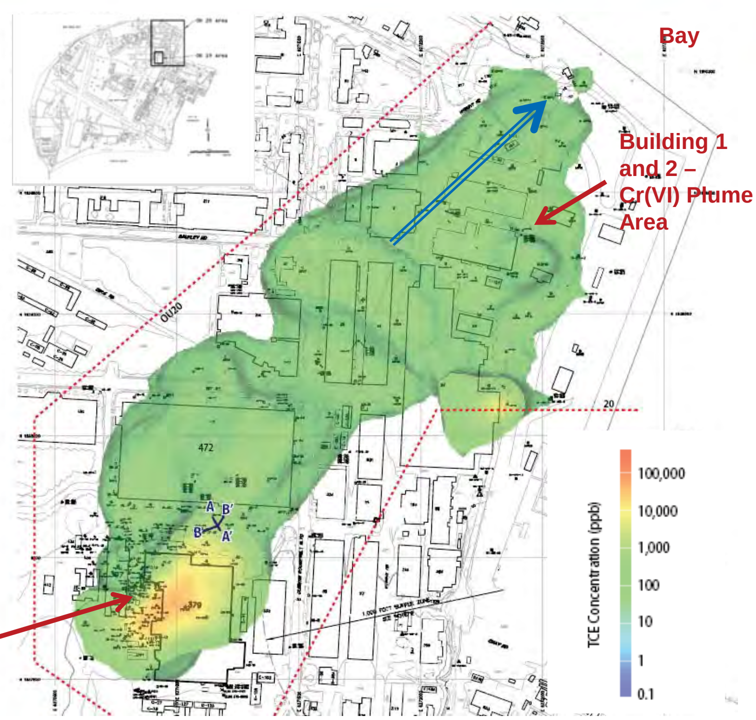
Bright and Shiny Object Detour

- Ran into a vendor conducting a brown bag/parking lot demonstration of a portable ozone remediation system at a contractor's office
  - Like the portability of the system and ease of system step
  - Considered conducting a large scale pilot
  - But it was likely to cost $500K+ after adding of the cost of work plans, equipment, utilities, etc.
  - And mother nature is keeping the plume from reaching the Pacific Ocean and slowly decreasing the contaminant mass over time
  - Funding better used addressing other sites at NASNI

Operable Unit 19/20

OU 19/20 Groundwater Plume

- OU-19/20 covers the LNAPL plume(s) in vicinity of Buildings 379/397/472 and dissolved CEs extending up to Buildings 1 and 2
- Catastrophic release
- Cr(VI) plume located near Building 1 and 2
- Cr(VI) being addressed first (as a TCRA), due to proximity to the Bay



Building 379/397/472 - LNAPL Plume Area

OU19/20 Overview

- Over 4,000 feet long, leading edge close to Bay
- LNAPL/DNAPL at Building 379/397/472 source area
  - LNAPL: JP-5, Stoddard solvent, TCE mixture
  - DNAPL: TCE source of dissolved plume
  - Dissolved Plume: TCE (there may be sources other than the DNAPL)
  - Dissolved Plume (Leading Edge) : Cr (VI) > 100 mg/L, also includes TCE > 80 mg/L (TCE likely from sources other than DNAPL at Building 379/397/472)
- Hexavalent Chromium plume with a second TCE source area in the Buildings 1 and 2 area which is in the toe of the OU20 plume
- The plume flows through the heavily industrialized portion of the base to the carrier piers

OU19/20 Technology Selection

- 2007 Evaluating Remedial Strategy
  - Plume characterized by CPT; completed in 1999
  - High traffic area/lots of buildings and utility infrastructure
  - Conducted pilot studies with ZVI and ISCO (persulfate); ISCO pilot study identified a major hexavalent chromium plume in the Building 2 area
  - Large plume; technically challenging and $$$ to tackle everything at once
  - Divide plume into segments (source area, dissolved, and leading edge with a phased approach
  - Phase 1 is to address the leading edge because of the potential for discharge to San Diego Bay

Phase I: OU 20 Leading Edge

- A commingled groundwater plume (~ 3 acres) with elevated levels of chloroethenes [mainly (TCE); up to 79 mg/L and Cr(VI); up to 174 mg/L] in the vicinity of Buildings 1 and 2
- TCE and VC exceeded limits of 81 and 525 μg/L, respectively (California Toxics Rule)
- Vertical migration likely inhibited by silty and clayey deposits
- Plating operations within Building 2 identified as primary source of contamination

Original plume configuration

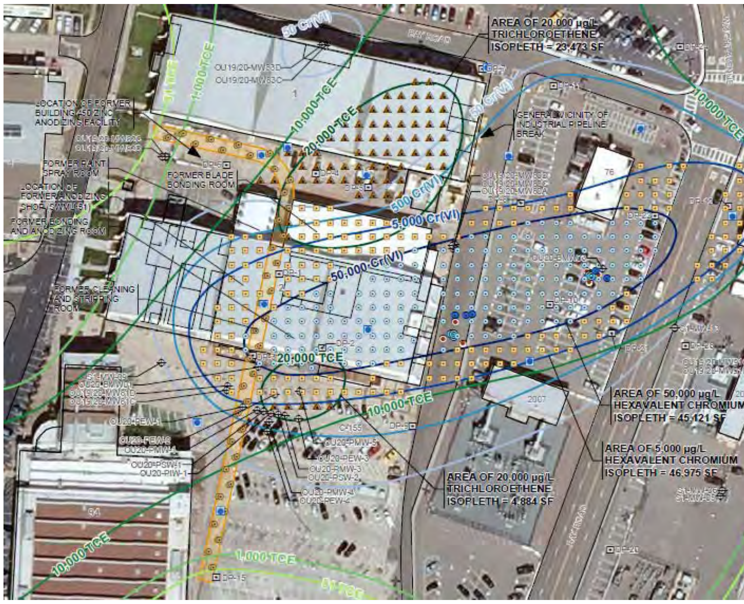
100 50 0 100 Feet

OU 20 Phase I Implementation Approach

- **Because of site characteristics and use, an in-situ approached is preferred**
  - **Step 1: Due to the age of the characterization data supplemental characterization is required to determine the current plume configuration for remedy design and bench scale treatability study conducted**
  - **Step 2: Pilot study – Injectability evaluation, substrate application, performance monitoring and assessment**
  - **Step 3: Full-scale implementation via a Time Critical Removal Action**

EISB Time Critical Removal Action

Application



Phase II: Implementation Approach LNAPL/DNAPL and Dissolved Plume

OVERALL TECHNICAL APPROACH (THREE STEPS)

1. **Assess Data Gaps**

2. **Conduct Feasibility Study to Evaluate Remedial Alternatives; Bench/Pilot Scale Treatability Studies as needed**

3. **Implement Full Scale**

Phase II: Implementation Approach LNAPL/DNAPL and Dissolved Plume

NAVFAC

Data Gap Approach

LEGEND

- MONITORING WELL
- PRODUCT WELL
- PRODUCT MONITORING WELL
- PROPOSED DATA GAP WELLS
- WELLS PROPOSED FOR LNAPL SAMPLING
- EXISTING WELLS PROPOSED FOR MONITORING
- VAPOR DEGREASER
- PROPOSED WELL - SEALASKA
- OU 19/20 BOUNDARY
- NASNI BOUNDARY
- IR SITE 1
- TCE ISOCONCENTRATION (µg/L)

- Baseline Sampling
  - Gaging 80 Wells (water/product)
  - Redevelop 50 Wells
  - Sample 72 Wells
- 10 CPT, 10 DPT Locations
- 40 wells at 10 locations (4 zones)
- Sample 40 newly installed wells

Phase II: Implementation Approach LNAPL/DNAPL and Dissolved Plume

NAVFAC

Feasibility Study: Potential Technologies

DNAPL and groundwater dissolved phase

- ICs
- MNA
- Vertical barriers (slurry walls/sheet pile walls/grout curtains)
- Air sparging/soil vapor extraction (AS/SVE)
- Groundwater extraction and *ex situ* treatment
- Surfactant/Cosolvent flushing
- Dual/Multi-phase extraction
- In situ chemical oxidation (ISCO)
- *In situ* bioremediation
- Thermal treatment (electrical resistance heating [ERH]/steam flushing/conductive heating)
- ISCR
- Permeable reactive zone (PRZ)

Additional vadose zone soil and soil gas, LNAPL (OU 19/20)

- Capping
- Excavation
- SVE
- Free product recovery

Technologies for OU 9 Bench Tests (as Applicable to OU 19/20)

- MNA
- *In situ* bioremediation
- ISCO
- Self-Sustaining Treatment for Active Remediation (STAR)

Full-scale implementation based on FS results

Conclusion

- Technology evaluation and selection are done within the framework of CERCLA
- The level at which a technology is considered is driven by the RPM's and Contractor's knowledge and experience
- Other stakeholder can influence remedy selection
- Other key factors are
  - Site constraints
  - Current and future land use
  - Availability of funding

Questions?

CHALLENGES IN MODELING LONG TERM BEHAVIOR AT CONTAMINATED SITES

Ronald W. Falta
Clemson University
Clemson, SC

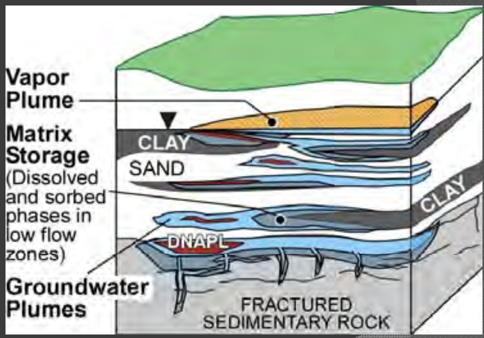
8/13/13

Outline

- DNAPL Source Zones
- Vapor Intrusion
- Dissolved groundwater plumes

DNAPL source zones

- Highly contaminated, may or may not still contain DNAPL
- Relatively small footprint compared to plume
- Transport is multiphase – gas/water/DNAPL
- Aggressive remediation often performed
- Long-term behavior controlled by contaminants in low K zones (diffusive sinks)



Source: Chlorinated Solvent FAQs

Source zone modeling capabilities

- Comprehensive 3-D multiphase models have long been available (>20 yrs)
- Models account for multiphase advection, dispersion, adsorption, diffusion, heat transfer, reactions
- Handle fully heterogeneous porous and fractured media

Partial listing:

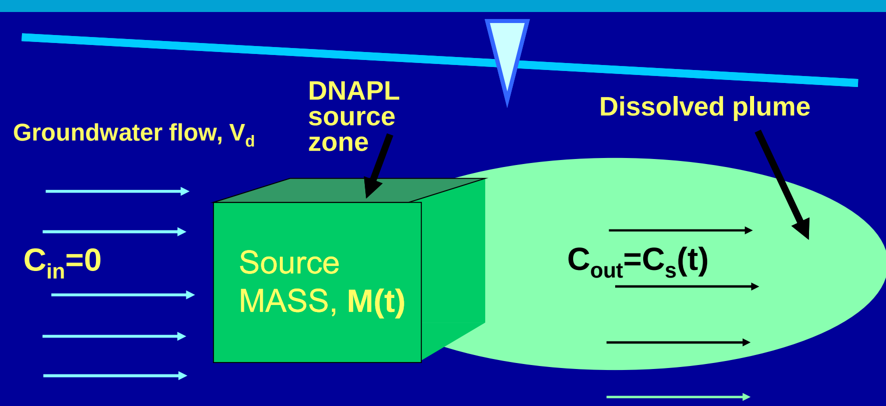
UTCHEM (Delshad et al., 1996)
STOMP (White et al., 1995)
NUFT (Nitao, 1996),
MUFTE (Helmig et al., 1994)
MAGNAS (Panday et al., 1994),
T2VOC (Falta et al., 1995),
COMPFLOW (Unger et al., 1996),
MISER (Abriola et al., 1997)
TMVOC (Pruess and Battistelli, 2002)
DNAPL3D-RX (West et al. 2008)
TMVOC-MP (Zhang et al., 2007)

and various commercial petroleum reservoir simulators

These advanced simulators are widely used in research, but are rarely used in practice

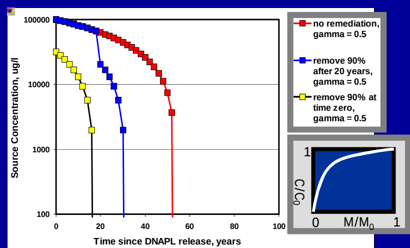
- Require extensive background and training to use
- Training is not readily available compared to groundwater modeling
- Computationally intensive (run times of hours)
- Models may be “touchy” to run
- Few Graphical User Interfaces (PetraSim for TOUGH; GMS for UTCHEM)
- Site characterization is rarely detailed enough for true predictive capability -- 3D distribution of multiphase hydrogeological parameters and contaminant distribution

Opposite End of the Spectrum: Black Box Model. The Discharging Concentration (C_s) Depends on the Mass Remaining in the Source Zone, (M)

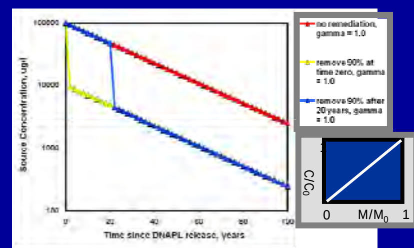


$$\frac{dM}{dt} = -Q(t)C_s(t) - \lambda_s M \qquad \frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma}$$

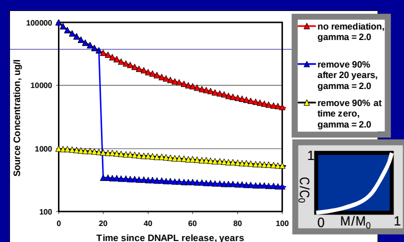
Source Behavior – Black Box Model



Γ = 0.5



Γ = 1.0

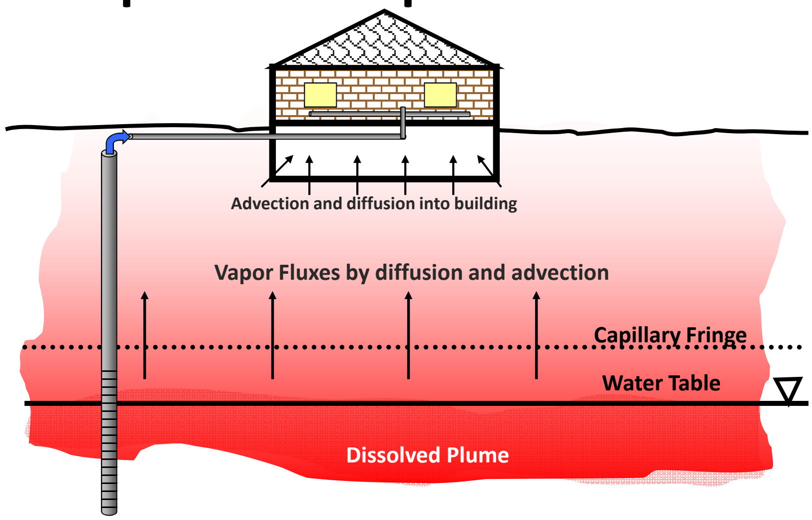


Γ = 2.0

Possible research needs

- Intermediate-level source zone models that are easier to apply than the multiphase flow models, but include the important physical processes
- Different models probably needed for different types of remediation: thermal, ISCO, ERD, surfactants, etc.

Vapor Intrusion – many complex multiphase transport mechanisms



Vapor Intrusion – Orders of Magnitude Lower Concentrations are of Concern Compared to Groundwater

- Example: ***TCE***
- Regulatory thresholds vary but are low, on the order of ~2 ug/m^3 or .002 ug/L
- Dimensionless Henry's constant ~ 0.37
- Groundwater with 5 ug/L can produce equilibrium vapor concentrations of (0.37)x(5)=1.85 ug/L or 1850 ug/m^3
- ***Vapor standards are ~1000 times lower than equivalent groundwater standards***

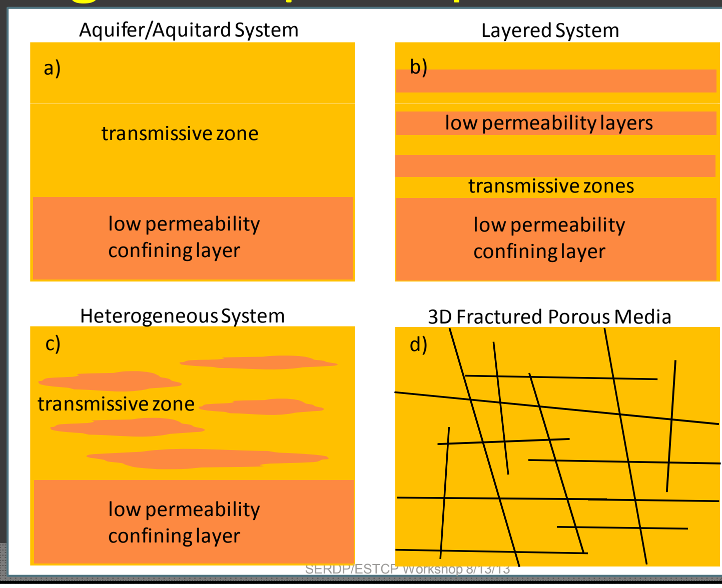
Some Observations

- Existing multiphase flow models have advanced capability for simulating vapor intrusion – but appear to be rarely used
- Prediction of vapor intrusion remains elusive – perhaps due to subtle transport issues
- Dynamics of vapor movement in vadose zone are complex (atmospheric pressure, rainfall, pressure in the building, water table fluctuations, capillary rise etc.)
- *How does transport across the capillary fringe occur?*

Groundwater Plume Modeling

- Modeling is very commonly done at contaminated sites
- Several powerful models available: **MODFLOW/MT3DMS** (Zheng and Wang, 1999); **FEFLOW** (Trefry and Muffels, 2007); **HydroGeoSphere** (Therrien and Sudicky, 1996) and others
- Excellent Graphical User Interfaces (GMS, Groundwater Vistas, Visual MODFLOW, etc…)
- Model training readily available
- ***GW transport models work "OK" in some settings***

However, sites where matrix diffusion is significant pose a problem

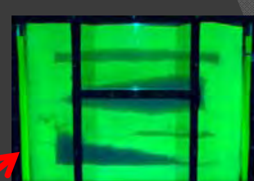


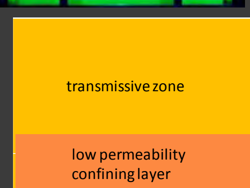
Numerical models can simulate matrix diffusion using high resolution grids

- If all of the heterogeneity is represented in the model (with very fine grids) only advection and diffusion are needed

Examples of 2D models:

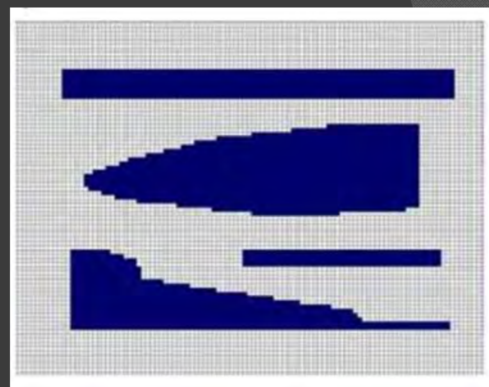
- Chapman et al., 2012
- Parker et al., 2008
- Chapman et al., 2012





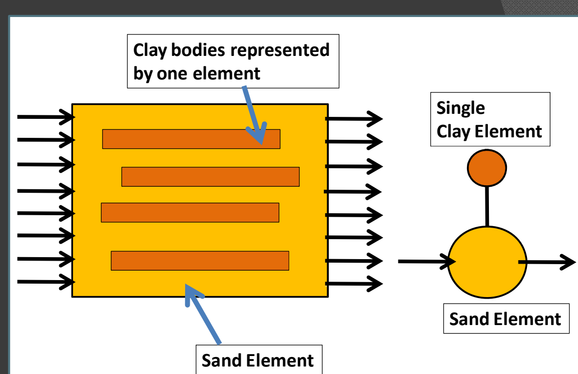
The “high resolution” method is probably not practical for 3-D field scale simulations

- Matrix diffusion is controlled by gradients at the millimeter to centimeter range
- Field scale gridblock sizes are on the order of tens of centimeters to several meters
- **The key matrix diffusion processes occur at the subgridblock scale**



Dual porosity models are a step in the right direction….

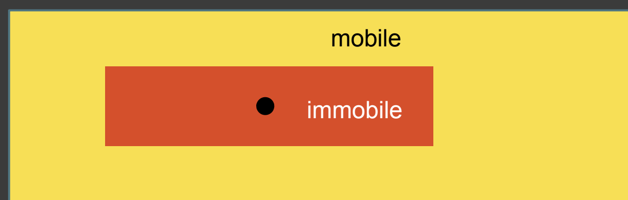
- Each gridblock is subdivided into two volumes, one for the high K part, and one for the low K part
- Matrix diffusion is represented by first order mass transfer equation between the mobile and immobile zones



conceptual model **mathematical model**

Dual porosity models cannot resolve the concentration gradients accurately enough

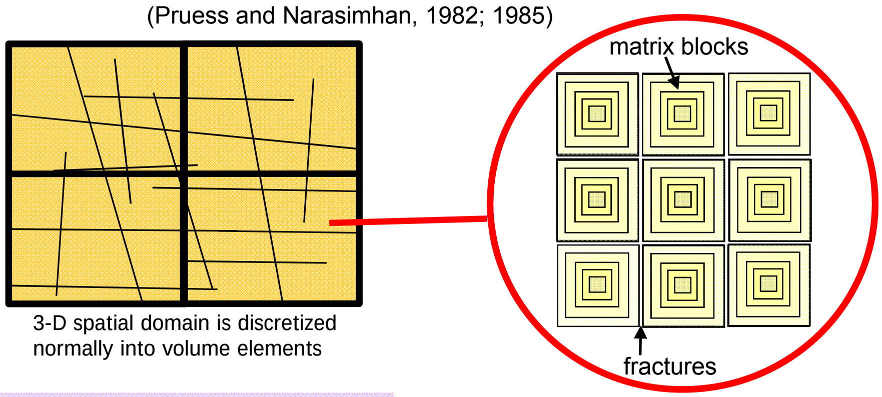
$$mass\ \ flow = \beta(C_m - C_{im})$$



$$mass\ \ flow = \frac{A_{im}}{V}\phi\tau D_w \frac{(C_m - C_{im})}{d}$$

Multiple Interacting Continua (MINC) may be a better approach

(Pruess and Narasimhan, 1982; 1985)



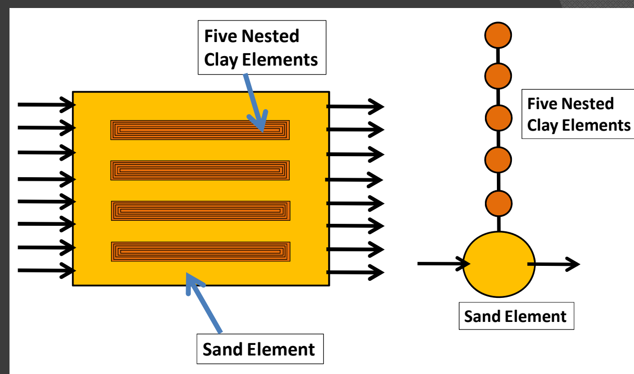
3-D spatial domain is discretized normally into volume elements

The fracture elements are globally connected in 3-D. This is similar to a dual porosity formulation, but gradients in the matrix are resolved much more accurately

Each gridblock is subdivided into a fracture element, and multiple nested matrix elements. The fracture and matrix elements are locally connected to each other in 1-D

Example: simulation of Doner-Sale matrix diffusion experiment

Experiment



MINC conceptual model

mathematical model

Simulation of matrix diffusion experiment

- 22 day loading period followed by >100 days of flushing
- 6 element MINC model simulation takes 0.05 seconds
- MINC model is easily applied to field scale 3D problems

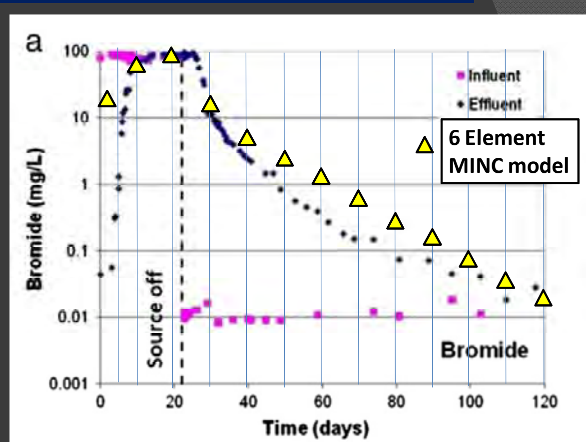


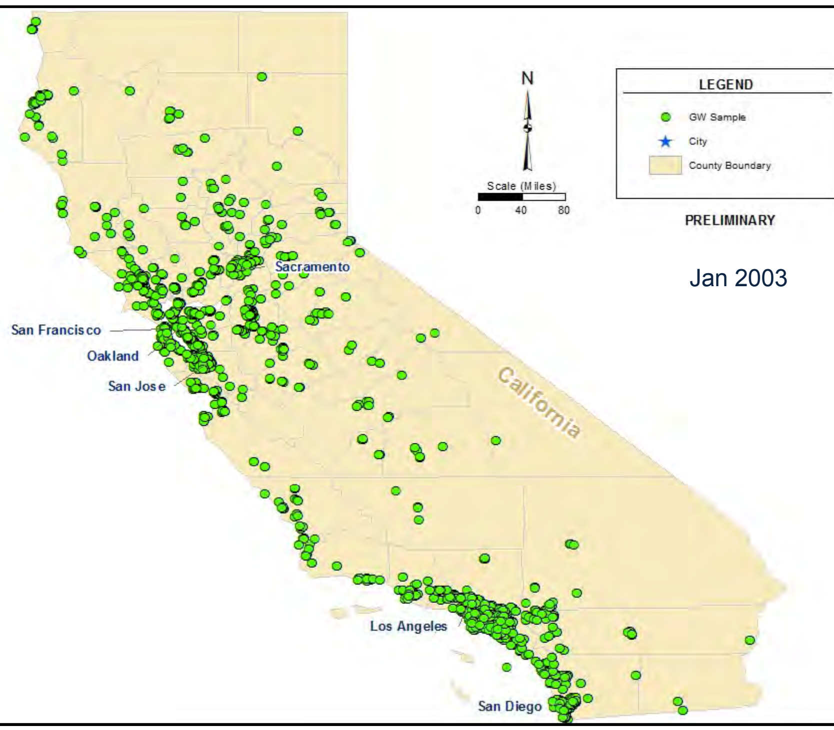
Figure modified from Chapman et al., 2012

Possible research needs – plume modeling

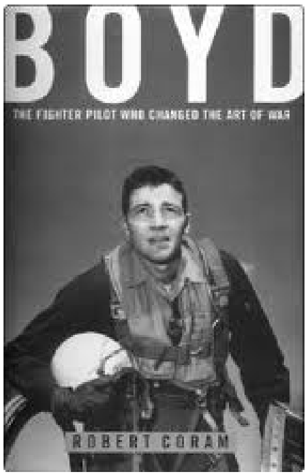
- Efficient methods for incorporating matrix diffusion at subgridblock scale (MINC; semi-analytical approaches)
- Better understanding of contaminant degradation processes in the low K zones
- Better methods for characterizing matrix diffusion properties (area to volume ratios, volume fractions, characteristic thickness, etc)
- Incorporation of matrix diffusion in screening-level models

How **Monitoring** Fits Into Long Term Management Of Contaminated Groundwater Sites

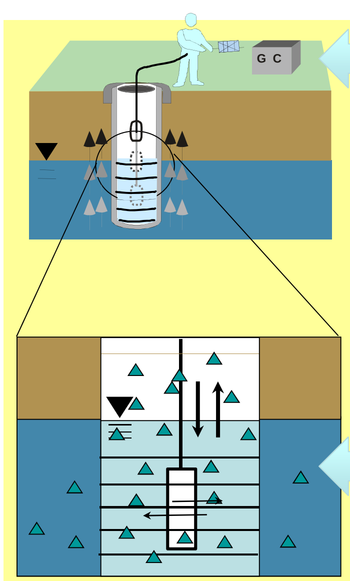
Charles Newell

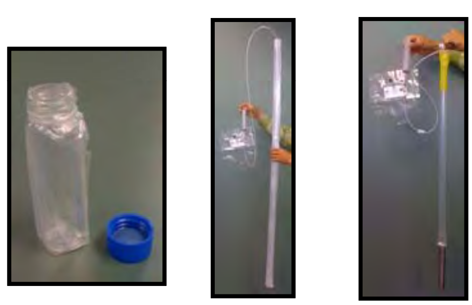


Idea 1: Faster is Better



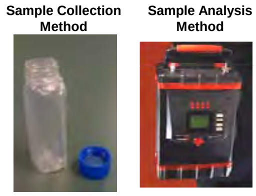
Passive Gas Diffusion Samplers

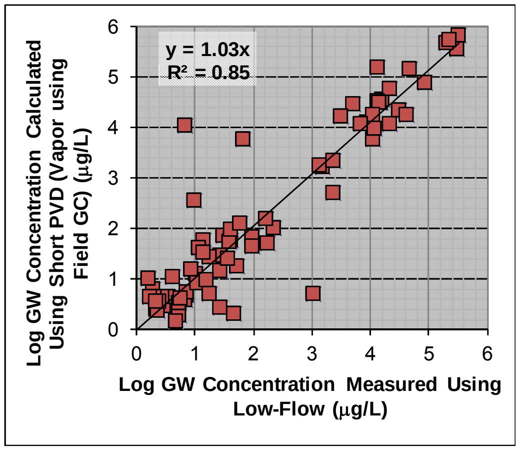




Task 4 – Expanded Field Testing: RESULTS

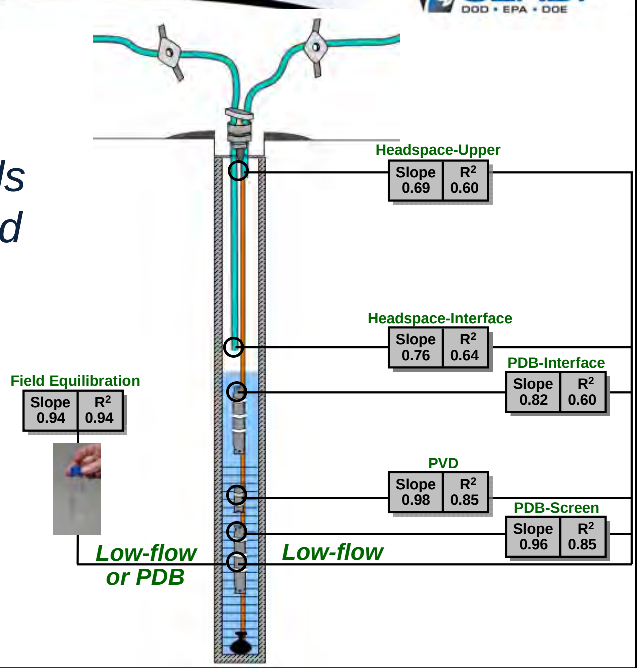
Short PVD Sampler (USGS Design)





Notes: Good correlation. No bias.

Idea 2: Monitoring Wells are Complicated



Thermal Stratification: Texas Study

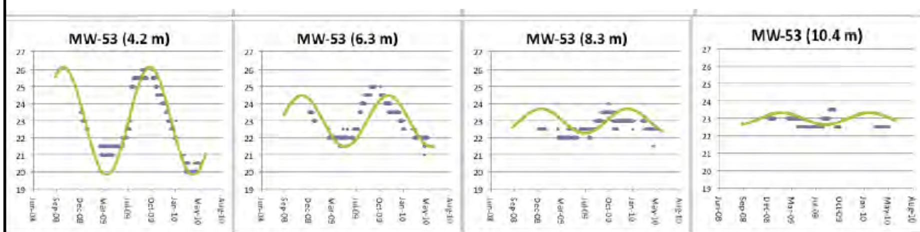
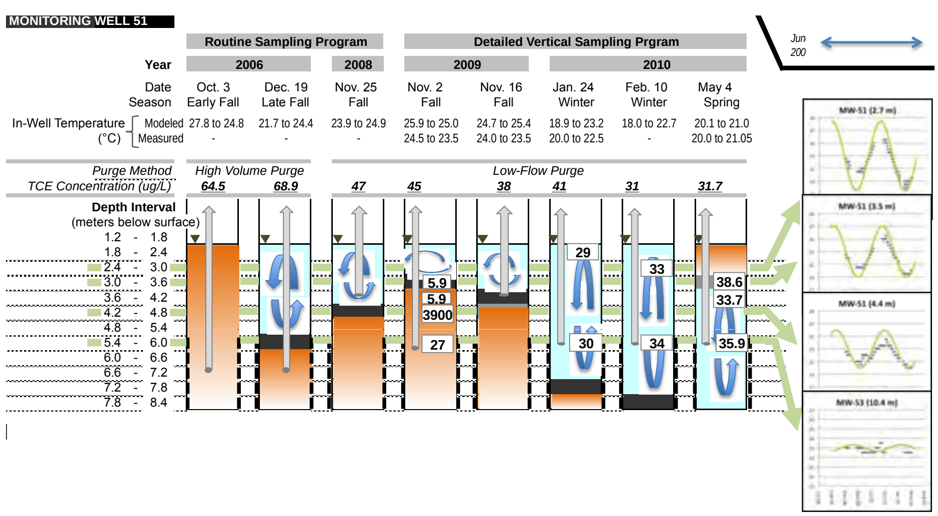
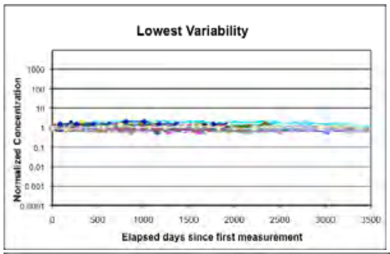
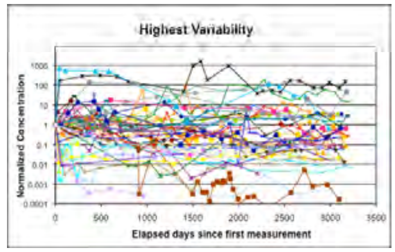


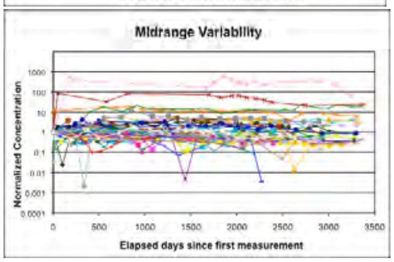
Figure 3: Measured and predicted groundwater temperatures. Blue diamonds show measured groundwater temperatures and green lines show predicted temperatures using model by Hillel, 1982. Model input values shown in this text.



MONITORING WELL VARIABILITY (Hill AFB)







Key Point:

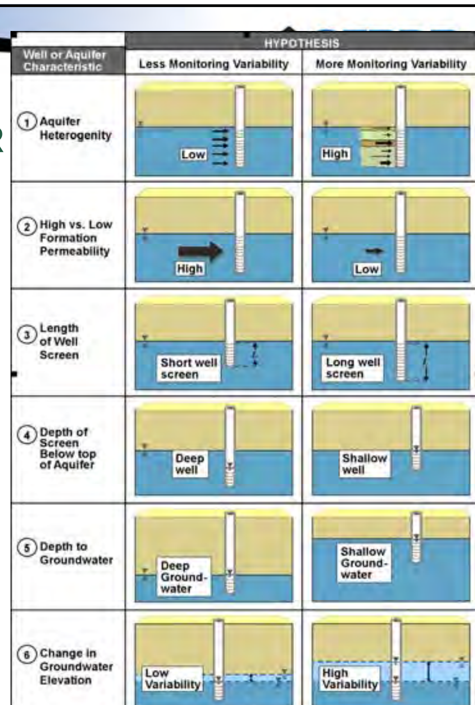
Large differences in monitoring variability between different monitoring wells at Hill AFB.

RESULTS: WELL AND AQUIFER CHARACTERISTICS

Hypothesis:

Monitoring variability is correlated with specific well and aquifer characteristics.*

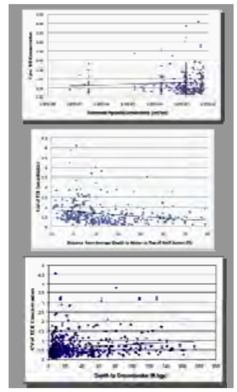
***Specific predications based on idea that stratification in VOC concentration in well or aquifer would correlate with higher variability.**



SERDP
DOD • EPA • DOE

RESULTS: AQUIFER AND WELL CHARACTERISTICS

Hydraulic Conductivity	$p = 0.04$	$R^2 = 0.01$
Water Above Well Screen	$p < 0.001$	$R^2 = 0.05$
Depth to Groundwater	$p = 0.002$	$R^2 = 0.02$



Key Point: Identified aquifer and well characteristics account for < 10% of monitoring variability in dataset

SERDP
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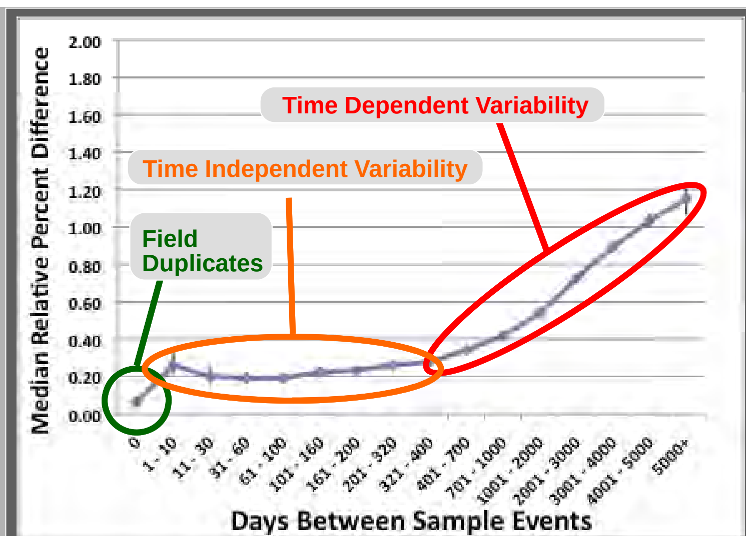
How Long for Real Trends To Emerge?



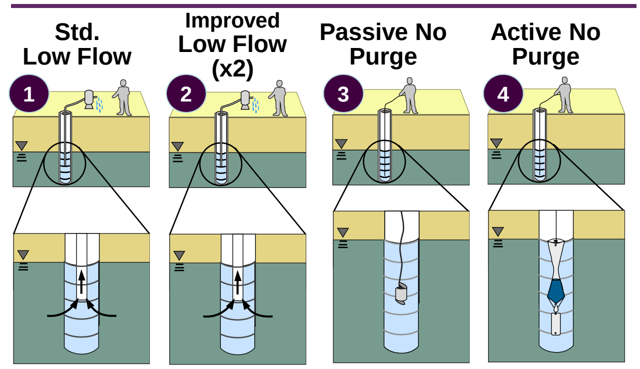
Technical Approach

Task 1: Field Demonstration of Improved Sampling Method GSI and ProHydro

Objective

Demonstrate that improved (highly repeatable) sampling method will reduce monitoring variability.

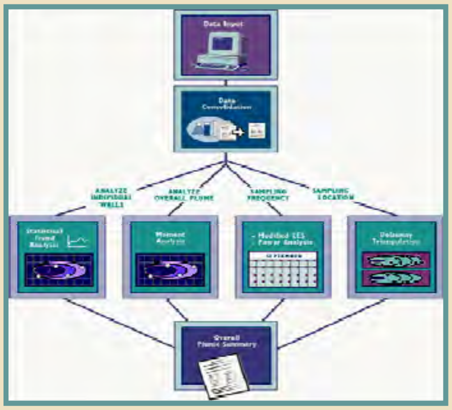
Approach: Compare Five Sampling Methods



Long Term Groundwater Monitoring Developments in Three Places...

MAROS 3 SOFTWARE

New version of MAROS freeware tool – Access Platform
Mann-Kendall, Regression. Many new features.

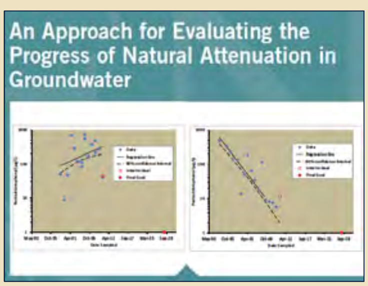


Typical applications:

- **"Ask the Mann": Which one of 6 trend categories?**
- **Lump the wells: Is my plume stable?**
- **"Optimization:" Add, subtract wells?**

Data Processing / Stats
Center for Long Term Monitoring Data

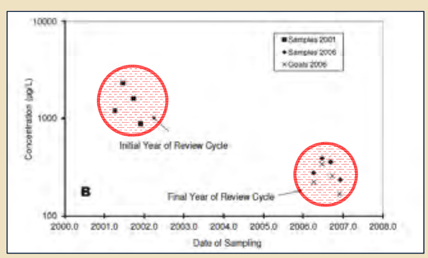
US EPA MONITORING FOR MNA



Guidance Designed for either:

- *During site characterization*
- *During long term monitoring*

Key Idea: 5 Year Review Cycle

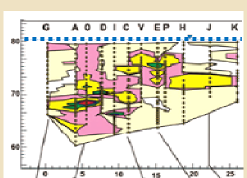


Key Idea: Likely be "problem wells" (increasing, variability):

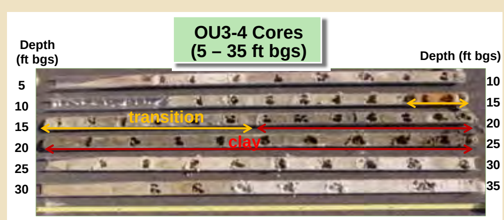
If the final concentration in a problematic well < the most contaminated well, it does not mean "not attaining"

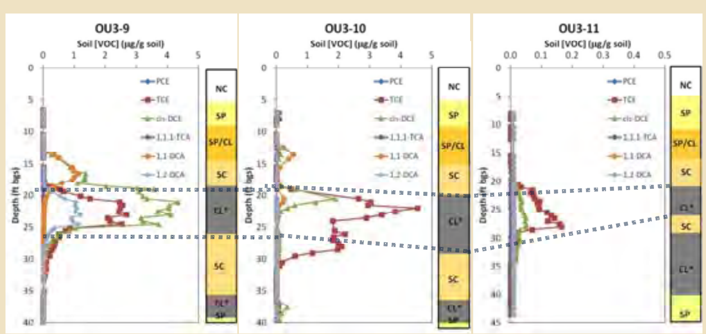
Long Term Groundwater Monitoring Developments in Three Places…

Where Do We Apply Standards?



Guilbeault et al., 2005





Adamson et al., 2013

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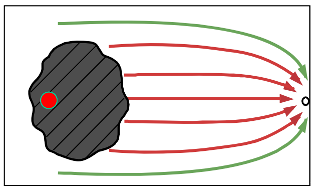
Idea 1: Mass Flux/Mass Discharge

Site A:

Very wide source

Very fast groundwater

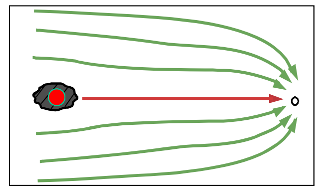


But same maximum groundwater Concentration…

Site B:

Tiny source

Almost stagnant groundwater



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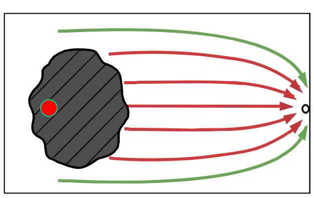
Idea 1: Mass Flux/Mass Discharge

Site A:

Very wide source

Very fast groundwater



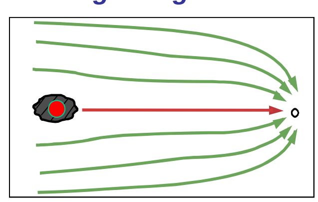
"Mega Site"

But same maximum groundwater Concentration…

Site B:

Tiny source

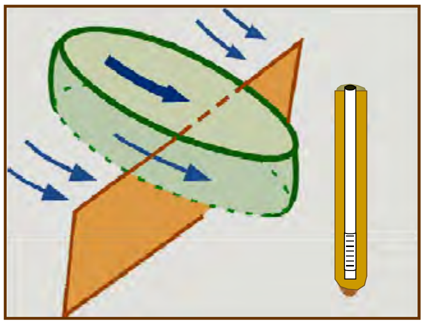
Almost stagnant groundwater



"Piss-Ant Site"

21

Idea 1: Mass Flux/Mass Discharge



Milligrams per liter: Bad

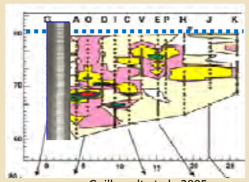
Grams per day: Good

Plume Magnitude Classification System

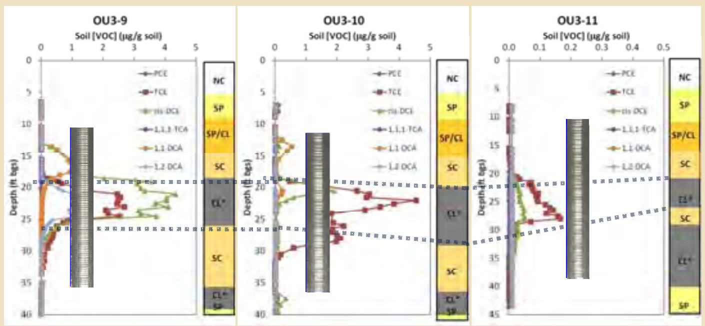
Mass Discharge (grams/day)	Plume Category
< 0.0001 to 0.001	"Mag 1 Plume"
0.001 to 0.01	"Mag 2 Plume"
0.01 to 0.1	"Mag 3 Plume"
0.1 to 1	"Mag 4 Plume"
1 to 10	"Mag 5 Plume"
10 to 100	"Mag 6 Plume"
100 to 1,000	"Mag 7 Plume"
1,000 to 10,000	"Mag 8 Plume"
10,000 to 100,000	"Mag 9 Plume"
>100,000	"Mag 10 Plume"

Newell et al., 2011

Idea 2: Long Well Screens ("Low Resolution Sampling")



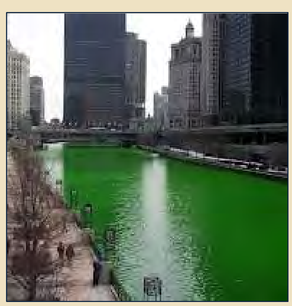
Guilbeault et al., 2005



Adamson et al., 2013

Idea 3: Air vs. Surface Water vs. Groundwater Sampling Frequency

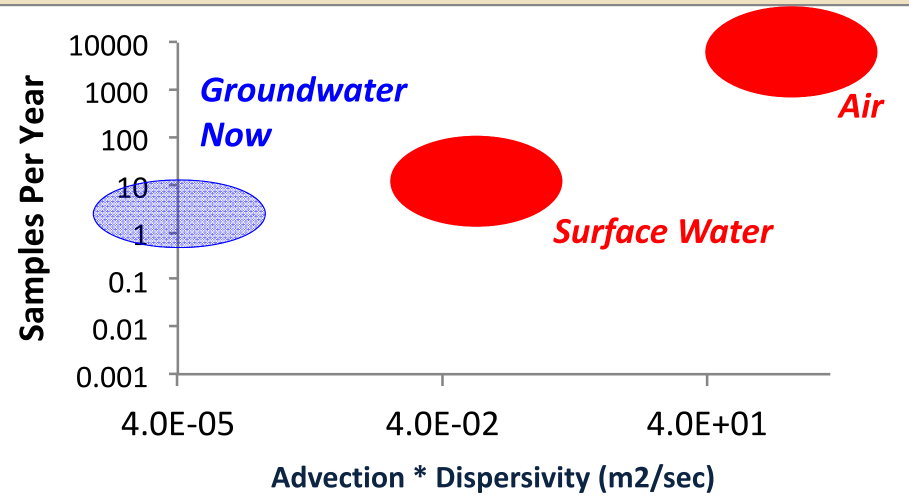
Once per Hour?



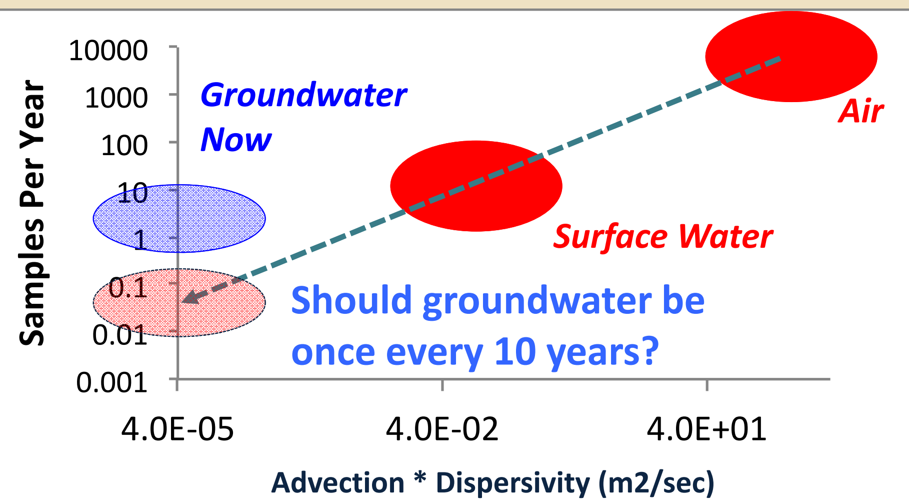
Once per Month?

How Often?

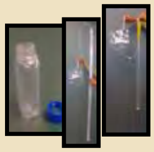
Extrapolatory Sampling Frequency Based on Other Environmental Media

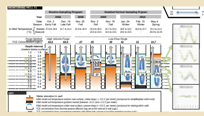


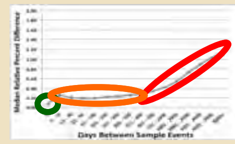
Extrapolatory Sampling Frequency Based on Other Environmental Media

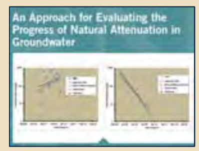


It Fits in These Three Places…

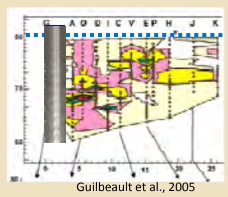




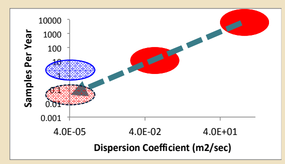




5 Years



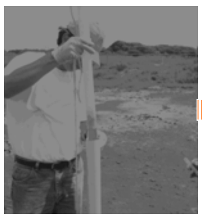
Guilbeault et al., 2005

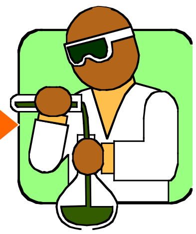


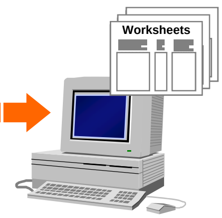
EXTRA SLIDES

Lots of Hand-offs and Waiting….

Sample Collection — *Handling & Shipping* — *Lab Analysis* — *Data Evaluation*







3 Different Groups

3 Separate Transfers of Physical Specimen

2 Handoffs of Sampling Information

GOAL: **Reduce the number of steps to increase efficiency!**

Site Prioritization Using Mass Discharge

Site	COC	Pre-Treatment Mass Discharge (g/day)
Unidentified Site	Total COC	56,000
Thermal Treatment Site 5	Total COC	1,874
Ft. Lewis Before Treatment	TCE	596
St. Joseph, MI	Total Ethenes	425
Midwestern US	TCE	389
Dover AFB, DE	CVOC	280
Long Island	MTBE	250
Thermal Treatment Site 2	Total COC	164
Unidentified Site	Unknown	160
Port Hueneme, CA	MTBE	150
Thermal Treatment Site 1	Total COC	141
Thermal Treatment Site 3	Total COC	134
Florida	TCE	102
Borden Site	TCE	93
Thermal Treatment Site 4	Total COC	87
Strasbourg	CH	86
Hill AFB Before Treatment	TCE	77
Neckar Valley, Germany	PCE	77
Ontario	PCE	56.2

56,000 Grams Per day ↕ **0.00078 Grams Per day**

Site	COC	Pre-Treatment Mass Discharge (g/day)
Site 1, Alameda Naval Air Station	cis-1,2-DCE	31
Testfeld Site, Germany	PAH	30
Thermal Treatment Site	Total COC	26
Thermal Treatment Site 13	Total COC	25
Thermal Treatment Site 6	Total COC	13
Elizabeth City, NJ	MTBE	7.6
Thermal Treatment Site 8	Total COC	7
Unnamed	MTBE	4
Thermal Treatment Site 14	Total COC	3.6
Thermal Treatment Site 12	Total COC	3.4
Australia	TCE	3
Landfill Site, Heidelberg, Germany	TCE	2.5
Thermal Treatment Site 9	Total COC	1.1
Borden Site Chemox Treatment	PCE	0.88
Sampson County, NC	MTBE	0.77
Unidentified Dry Cleaner Site	PCE	0.4
Thermal Treatment Site 11	Total COC	0.3
Unidentified Site	RDX	0.3
Vandenberg AFB, CA	MTBE	0.029
Thermal Treatment Site 10 – Shallow Plume Only	Total COC	7.80E-04

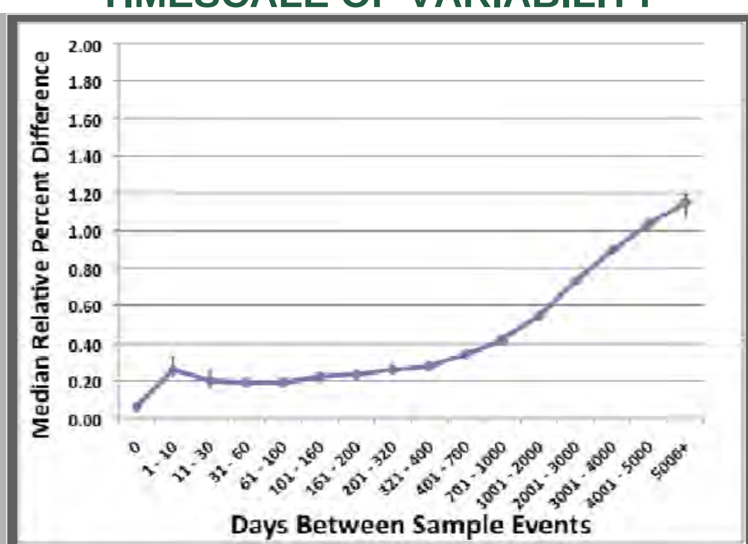
Task 4 – Three Passive Gas Diffusion Samplers

Short PVD Sampler

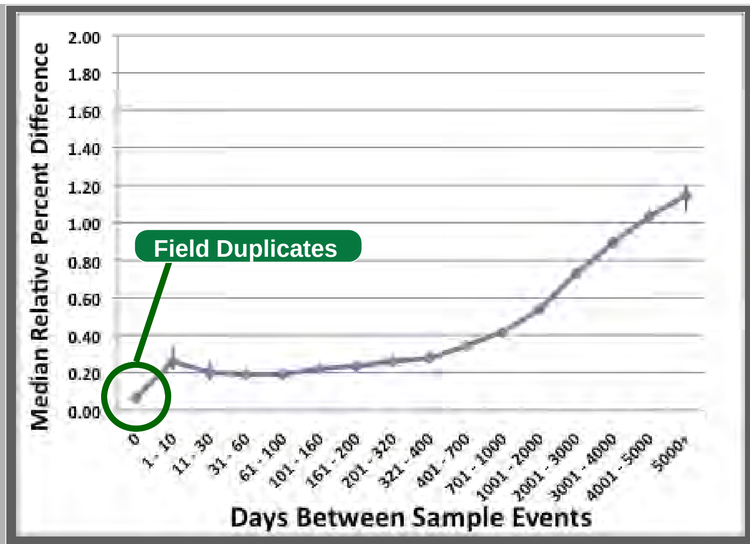
GSI Extended-Length Sampler

Haas Balloon Sampler

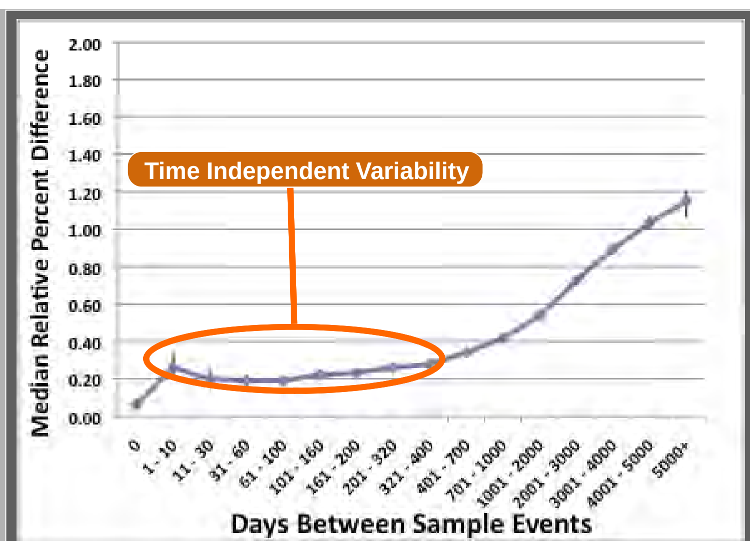
RESULTS: TIMESCALE OF VARIABILITY



RESULTS: TIMESCALE

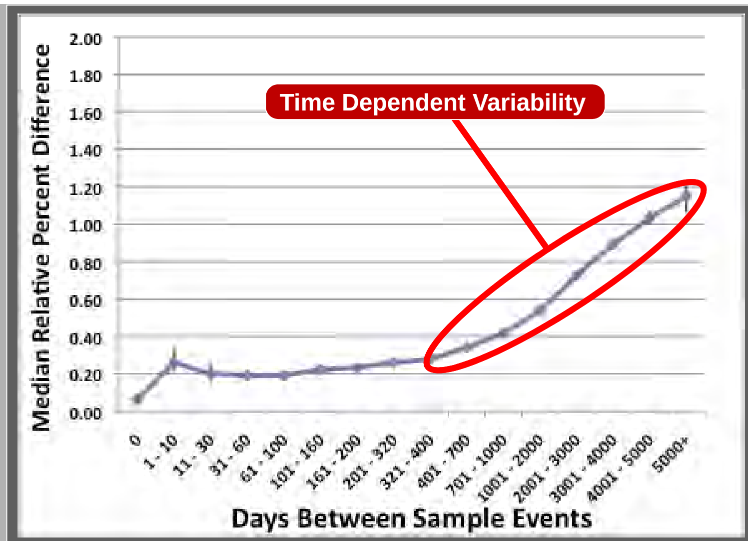


RESULTS: TIMESCALE



SERDP DOD • EPA • DOE

RESULTS: TIMESCALE



SERDP DOD • EPA • DOE

Lets Compare: Low Flow Std vs. Improved

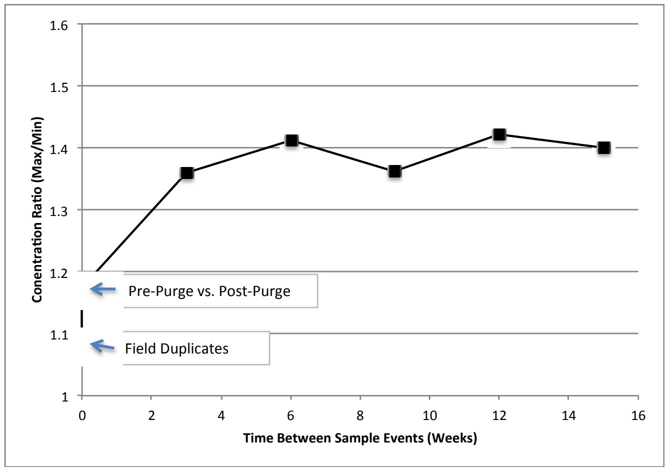
GSI and ProHydro

	Standard	Improved
Equipment	Install day of sampling	Install in advance
Intake Depth	Approximately constant	Constant sample depth
Well Purge	Parameter stability	Fixed volume
Flow rate	Varies between purge and sample	Constant during purge and sample
Vial fill	Side pour	Bottom fill
Vial bubbles	Remove >1mm bubbles	> 2 mL (5%) headspace >> replace vial

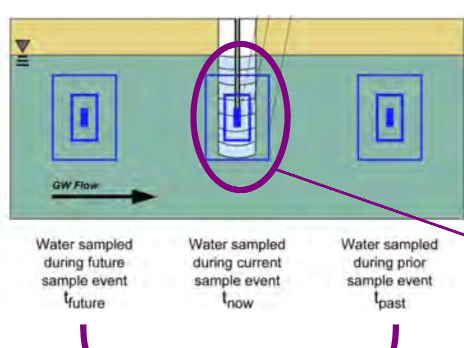
Temporal Variability: Texas Site

Key Point:

Median concentration change of 40% in only three weeks.



Monitoring Variability: Summary



1) Field duplicate variability: NOT significant

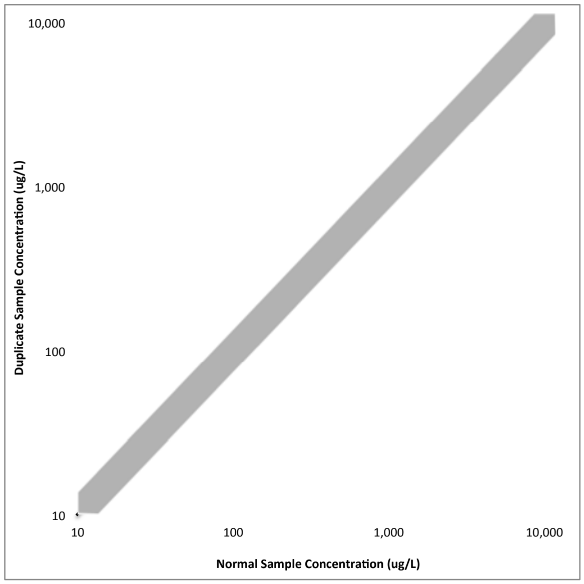
2) Purge variability: Significant

3) Short-term variability: More significant

Duplicate Variability

<u>Key Point</u>:

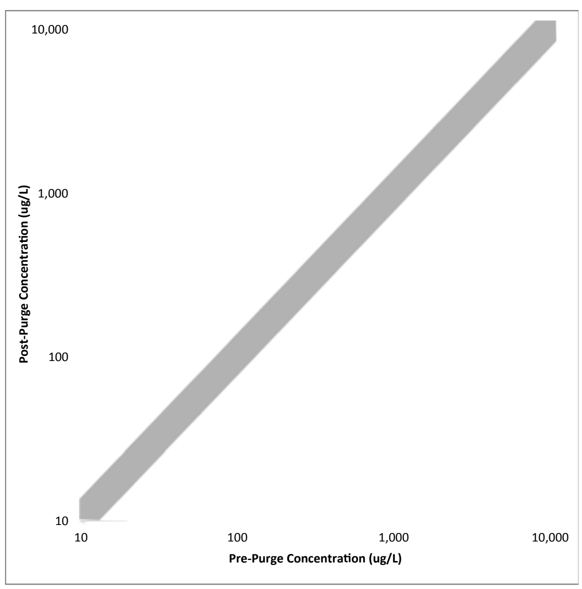
Field duplicates typically show excellent agreement



Purge Variability: Texas Site

<u>Key Point</u>:

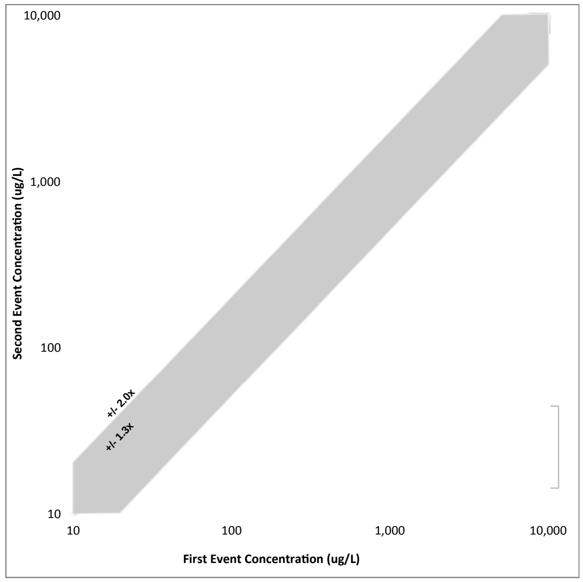
Purge variability is much higher than dup variability.

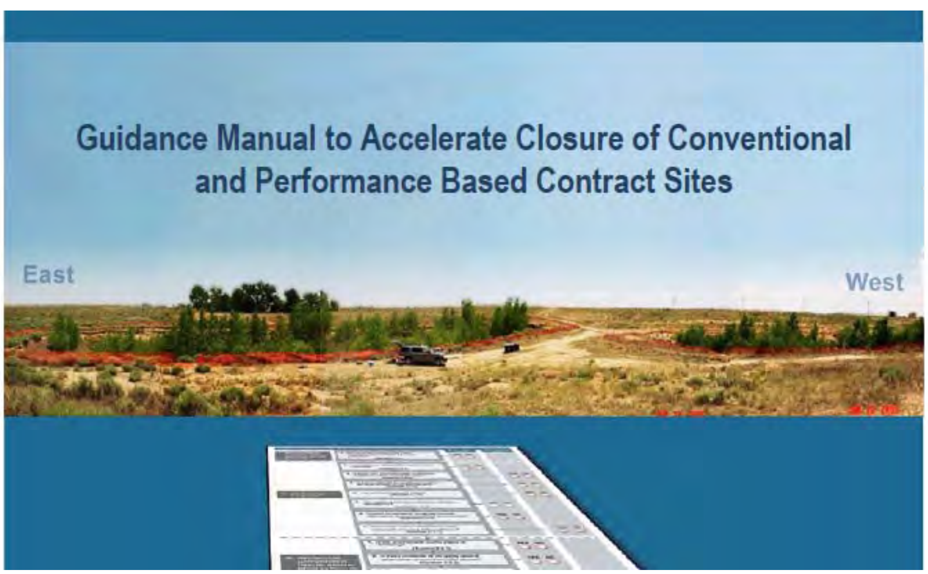


Temporal Variability: Texas Site

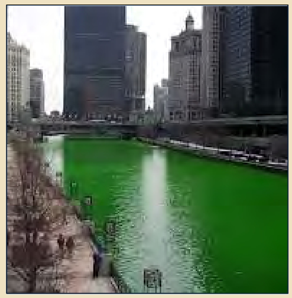
Key Point:

Short-term variability is much higher than purge variability.





Idea 3: A Speculative Analysis of Sampling of Three Environmental Media



A Speculative Analysis of Sampling of Three Environmental Media

Media	Typical Velocity (meters per day)	Typical Dispersion Coefficient (meters^2 per sec)
Air	350,000	400
Surface Water	50,000	0.1
Groundwater	0.3	0.00004

INDIVIDUAL WELL ANALYSIS

Summary Statistics – *NEW!*

- *Detection Frequencies*
- *Kaplan-Meier – Ave., Median, SD.*
- *Outliers by Dixon's*
- *Shapiro-Wilk Normality*

Well Scoring – *NEW!*

- *Individual Well Summary*
- *Well Score – prioritization*

PLUME-LEVEL ANALYSIS

1,1-DICHLOROETHENE | TETRACHLOROETHYLENE(PCE) | TRICHLOROETHYLENE (TCE) | VINYL CHLORIDE

Aggregate Trends

Area	Number Of Wells	Aggregate Trend	Aggregate Mass %
Source	5	PD	96%
Tail	8	PD	4%
Custom Group 1	3	D	10%
Custom Group 2	7	PD	90%

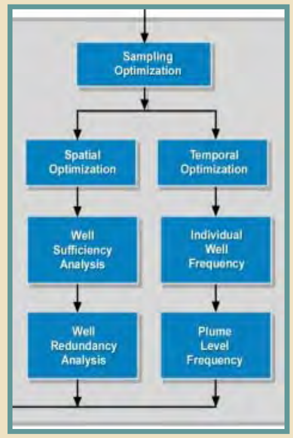
MAROS Analysis – Aggregate Trends

- *Source and Tail*
- *Two custom groups – NEW!*
- *Aggregate MK Trend*
- *% Mass for the well group – NEW!*

OPTIMIZATION

Network Optimization

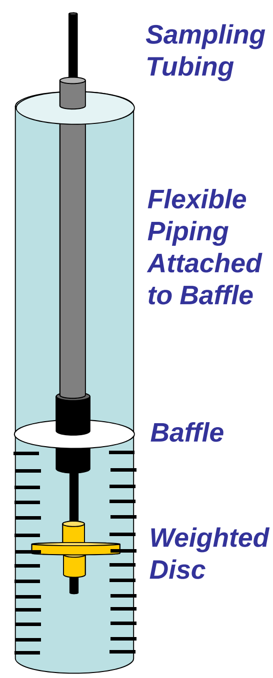
- *Spatial*
  - *Slope Factor/Delaunay*
  - *Decision Logic – **NEW!***
- *Frequency*
  - *Individual Well*
  - *Network Level – **NEW!***



Mixing Device: Construction

Key Components of Device

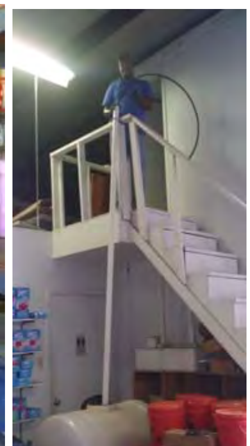
- **Firm piping with baffle:** situated at the top of the screen
- **Sampling tubing:** feeds through both the piping and baffle
- **Weights:** attached to the end of the sampling tubing beneath the baffle
- **Disc:** placed between weights to facilitate physical mixing in the well screen as the sampling tubing is moved up and down



Mixing Device: Construction

Details

- **Materials:**
  Constructed using supplies from Home Depot and a 2” well developer tool
- **Construction Time:**
  Less than 20 minutes
- **Cost:**
  Less than $100 per device



Mixing Device: Field Test

SERDP Ground Water Variability Project

- **Previous Work:**
  Identified Sources of Groundwater Variability (Sampling Method, Temporal Variation, Vertical Stratification)
- **New Work:**
  Test methods to reduce observed variability in samples over 1 year

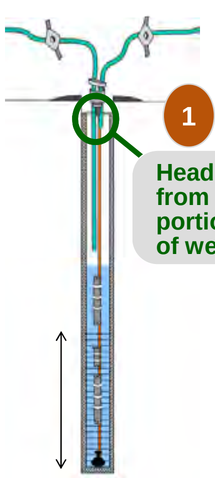
Mixing Device: Field Test

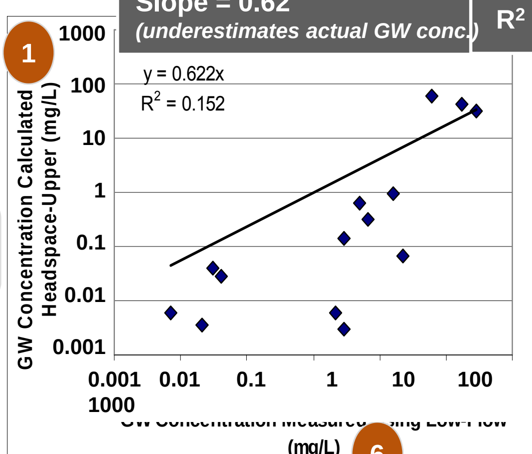
Objective	Test mixing device in 8 water wells during 3 sampling events over the course of a year.

Upper Headspace Sample

Slope = 0.62
(underestimates actual GW conc.)

$R^2 = 0.15$





- Statistically-significant difference vs. low-flow GW

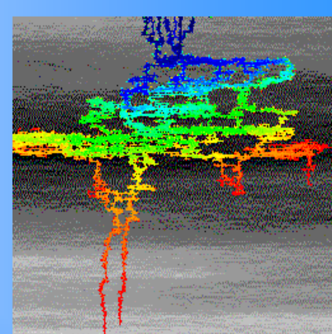
Enhanced Attenuation

Robert C. Borden

Solutions-IES
Industrial & Environmental Services

Complex Sites (NRC, 2013)

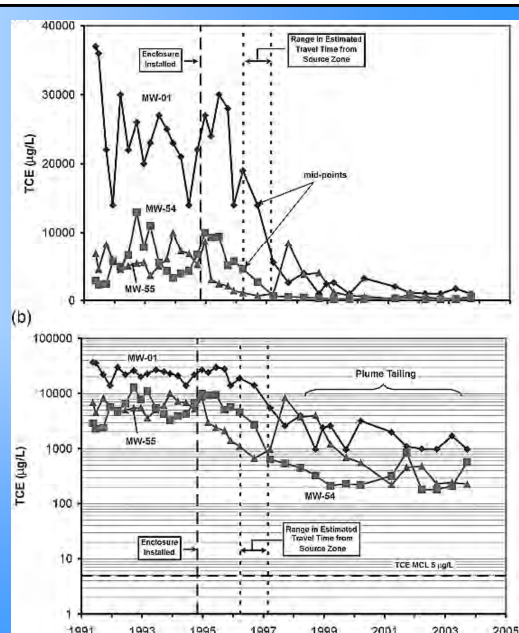
- Characteristics
  - Large sites
  - DNAPL
  - Heterogeneous geology
  - Recalcitrant contaminants
  - ‘Unrestricted Use’ Cleanup > 50 years
- Management alternatives
  - Long-term active management (e.g., P&T, other active remedies)
  - Long-term passive management (e.g., MNA, PRBs, etc)



DNAPL Migration
Ewing and Berkowitz, 1998

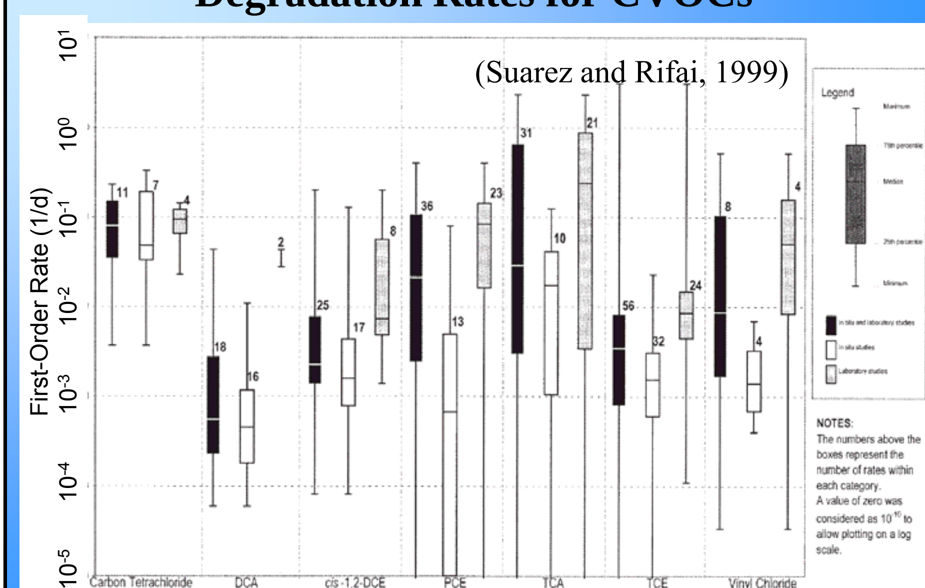
A ‘Simple’ Site

- **High K Sand Aquifer**
  - **Low organic carbon**
  - **No silty or clayey lenses.**
  - **Overlies thick silt/clay aquitard**
- **TCE DNAPL ‘completely’ enclosed by sheet pile in 1994**
- **TCE > MCL for centuries**



(Chapman and Parker, 2005)

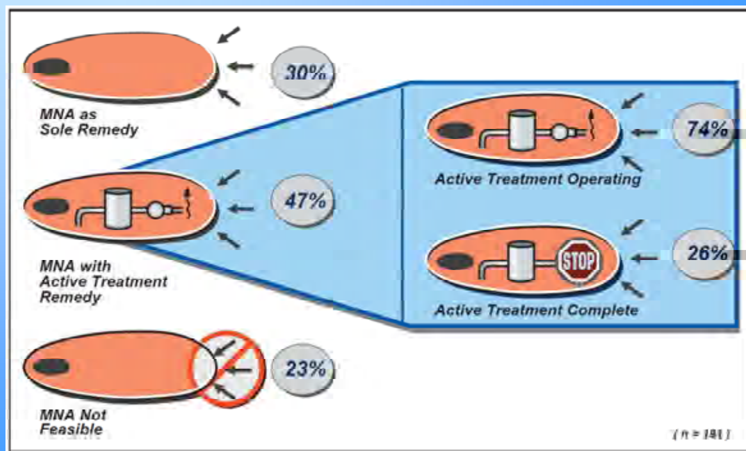
Degradation Rates for CVOCs



(Suarez and Rifai, 1999)

MNA Challenges

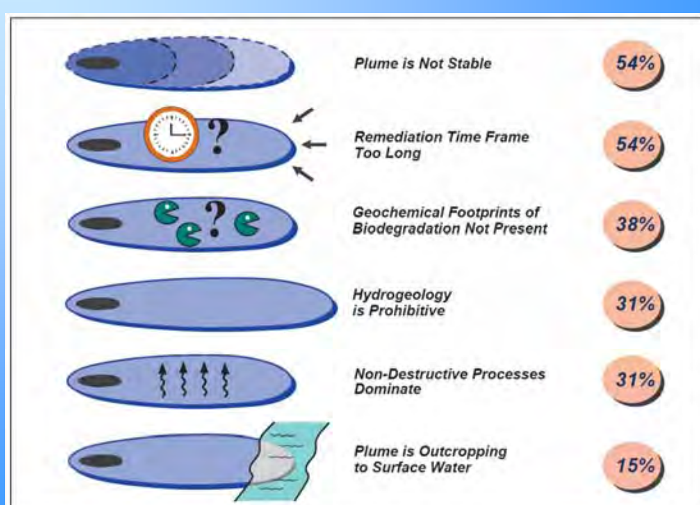
- Not appropriate for many CVOC sites



(McGuire et al., Historical and Retrospective Survey of MNA... WSRC-TR-2003-00333)

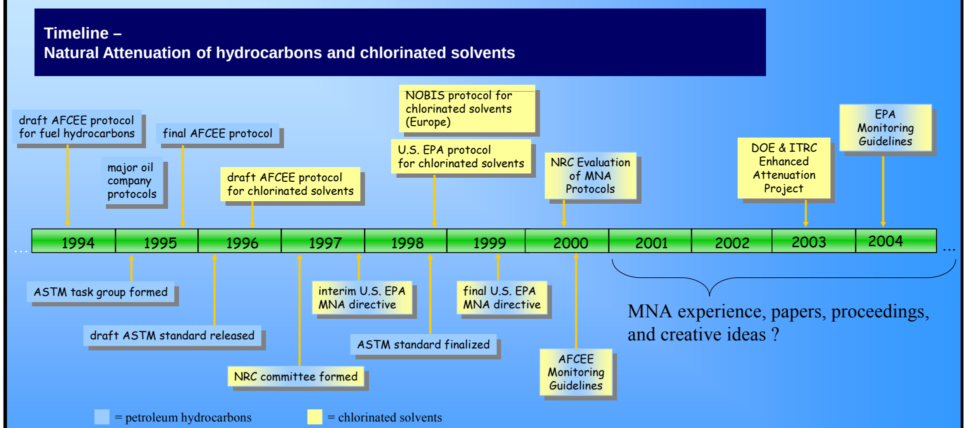
MNA Challenges

- Factors prohibiting use of MNA as a remedy at CVOC sites



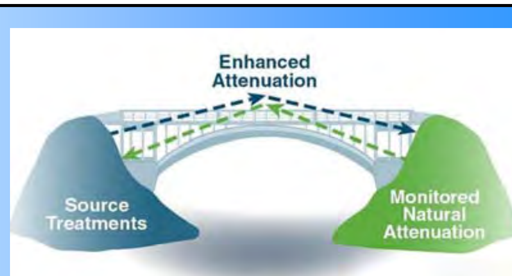
(McGuire et al., Historical and Retrospective Survey of MNA... WSRC-TR-2003-00333)

Historical Perspective – Natural Attenuation



(modified from Wiedemeier and Barden, 2002 and ITRC, 2008)

Enhanced Attenuation

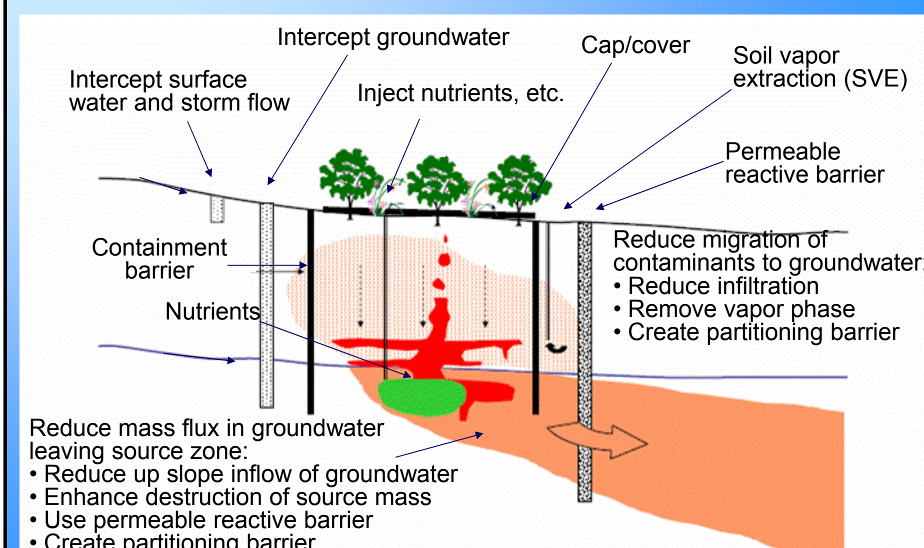


- Bridge between active treatment and MNA
- Sustainable
  - Little / no human intervention after implementation
  - Attenuation continues until remedial objectives are met
- Mass balance approach
  - Contaminant loading < attenuation capacity
- Allows human intervention to ‘permanently’
  - Reduce loading
  - Increase attenuation capacity

Enhanced Attenuation

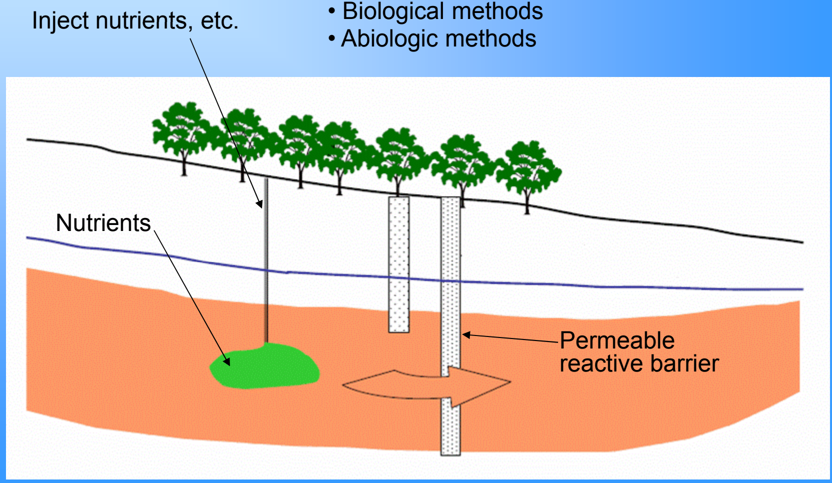
- **Enhancements - technologies that:**
  - **Reduce source loading**
    - **Hydraulic Manipulation**
      - **Surface runoff/stormflow water interception and diversion**
      - **Covers/cap**
      - **Diffusion barriers (e.g. edible oils)**
    - **Passive Residual Source Reduction**
      - **Passive vapor extraction from vadose zone (e.g. baroballs)**
  - **Increase attenuation capacity**
    - **Biological Processes**
      - **Biostimulation**
      - **Bioaugmentation**
      - **Plant-based methods**
    - **Abiotic**
      - **Abiotic reactions with reduced iron and sulfur phases**
      - **Sorption**
      - **Reactive Barriers**

Enhancement – Source Zone



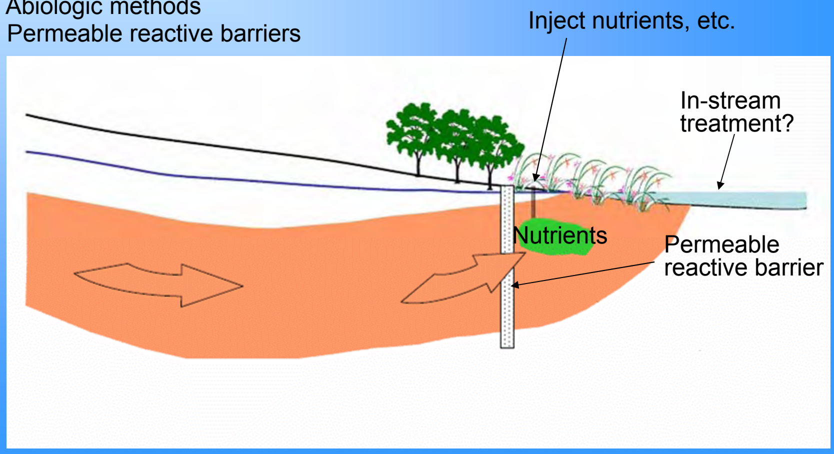
Enhancement – Primary Plume

Reduce mass flux of contaminants in plume:
- Phytoextraction
- Plant-based hydraulic control
- Biological methods
- Abiologic methods



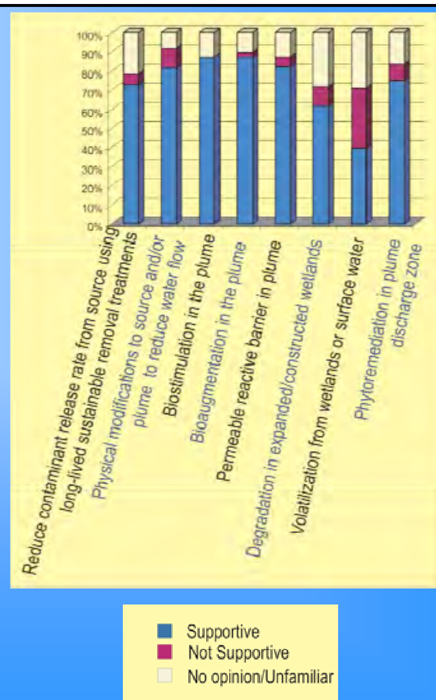
Enhancement – Near Discharge

Reduce mass flux of contaminants at groundwater / surface water interface:
- Plant-based methods
- Biological methods
- Abiologic methods
- Permeable reactive barriers



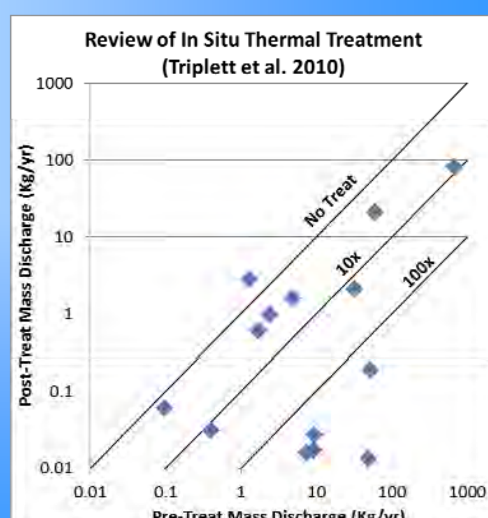
ITRC
Enhanced Attenuation of Chlorinated Organics

- Regulator Survey
  - High Support
    - Source control
    - Plume enhancements
  - Medium Support
    - Plume Discharge enhancements (e.g., wetlands, phyto., etc.)
  - Least support
    - Volatilization following discharge



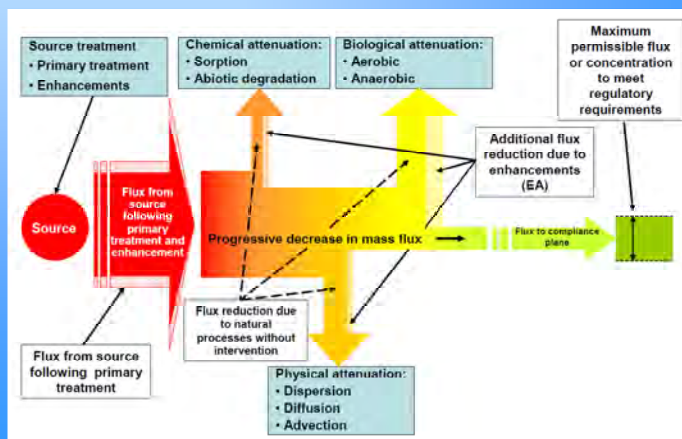
EA Opportunity

- Source Control
  - 1 to 2 Oom reduction in mass loading
  - 1 to 3 Oom reduction needed to meet MCLs
- EA provides mechanism to 'take credit' for mass reduction



EA Paradigm

- EA based on mass balance approach
  - Source loading – attenuation capacity = contaminant discharge
- Good tools available to estimate mass discharge
- How do you estimate attenuation capacity?



How To Estimate Attenuation Capacity?

- If plume is stable
  - Attenuation capacity > Source Loading
  - Can probably get MNA approved without EA
- If plume is NOT stable
  - Fit 1st order decay model to plume
    - High uncertainty if plume is not stable or controlled by pumping
    - What happens if geochemical conditions change?
  - Mechanistic Models (SEAM3D, RT3D)
    - Multiple, poorly defined parameters
  - Need independent indicators of attenuation rates

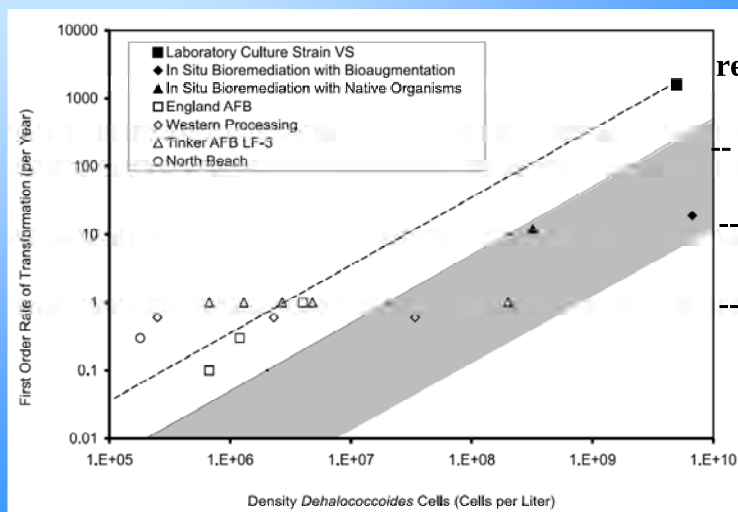
Biotic Attenuation

Time for 100x removal

-- 0.05 yr

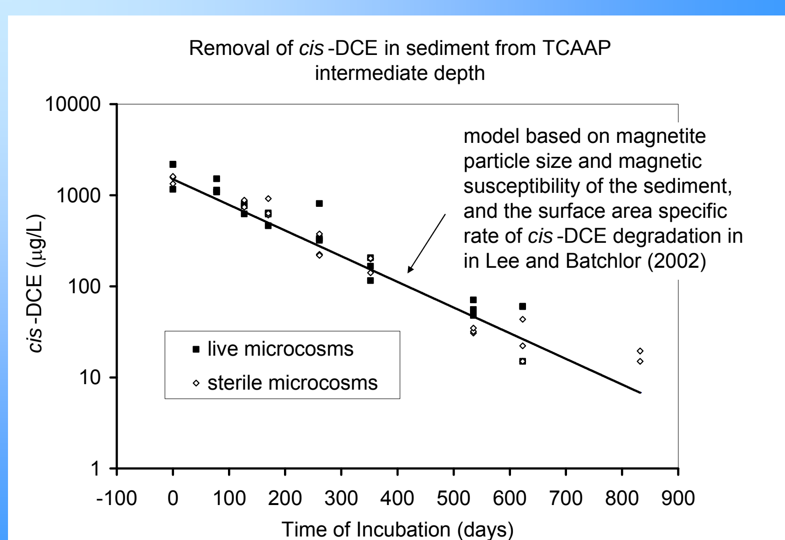
-- 0.5 yr

-- 5.0 yr



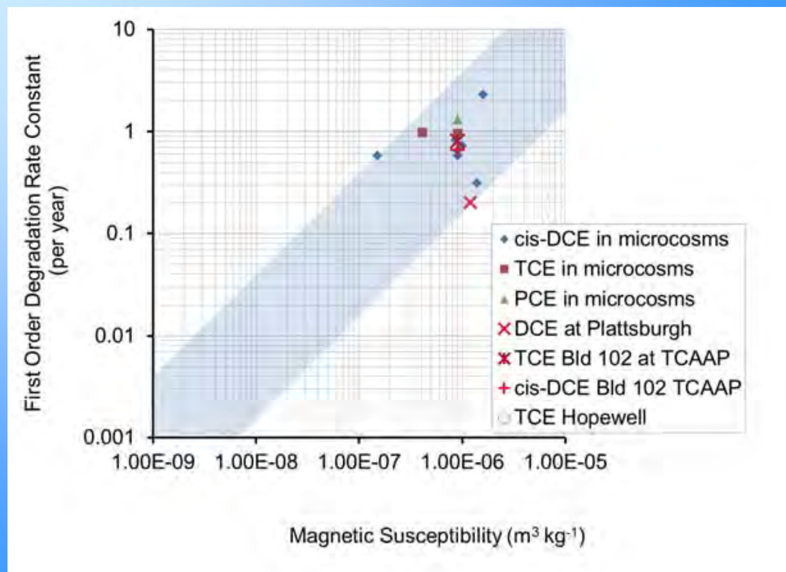
(Lu, Wilson and Kampbell, Water Research, 40:16, 3131-3140, 2006)

Abiotic Attenuation



He et al. 2009. Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water

Abiotic Attenuation

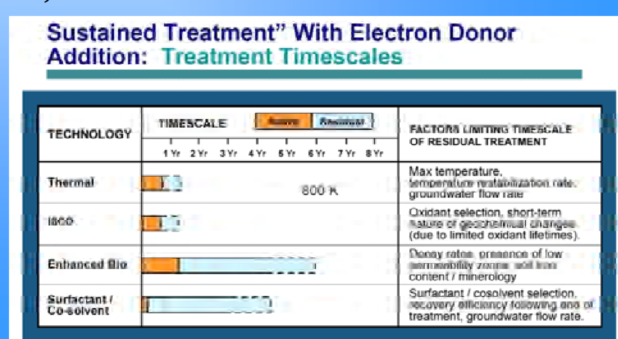


(Courtesy John Wilson)

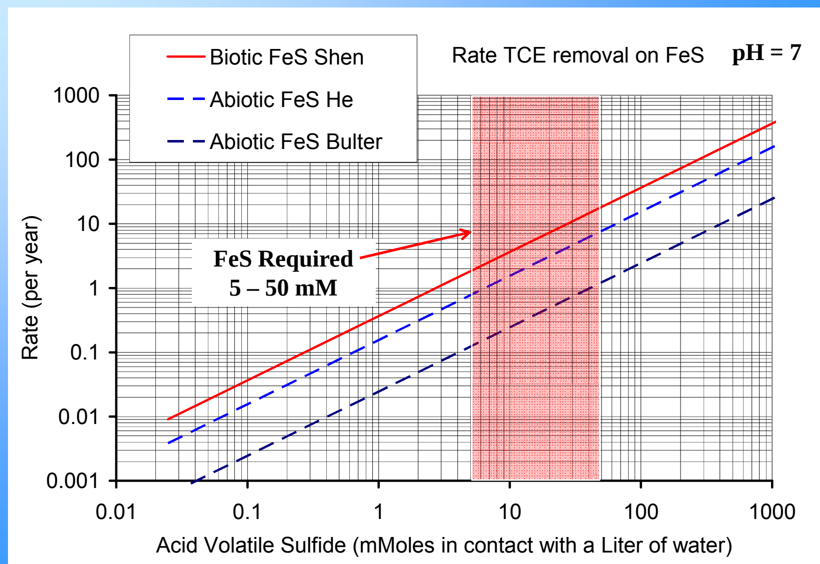
EA Opportunities

- **Remediation Technologies**
  - **Major focus on source area remediation**
  - **Limited attenuation to plume treatment**
- **Is faster always better?**
  - **Thermal - rapid removal, high cost and carbon footprint**
  - **ISCO – rapid removal, potential for rebound**
  - **ERD – slower removal, less rebound**

Implications for Treatment Timescales Associated with Source Depletion Technologies (Adamson et al., 2011, Remediation).



Enhancing Abiotic Dechlorination

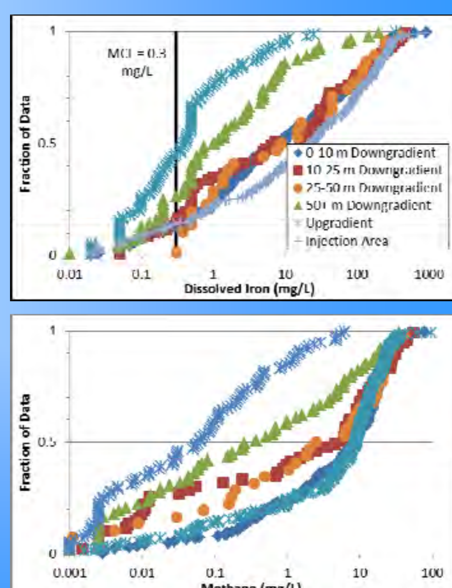


EA Challenge

- **Abiotic dechlorination -- How do you form a large Fe(II) enriched zone?**
- **Monitoring data at ERD sites show**
  - **Increased Fe(II) > 50 m**
  - **Increased CH_4 > 50 m**

Sediment Analyses

Site	Substrate	Fe(II) mM	FeS mM
Bemidji	Crude Oil	5-120	NS
Altus	EVO	15-120	0.3-30
Dugway	EVO	50-168	5-41



Max. Fe(II) and CH_4 downgradient of ERD systems

EA Challenge
Effect of pH on Anaerobic VC Biodegradation

- VC → ethene
- pH= 8.5
  - Complete inhibition
- pH= 7
  - Optimum
- pH= 6.5
  - Some inhibition
- pH= 6.0
  - Strong inhibition
- pH= 5.5
  - Complete inhibition

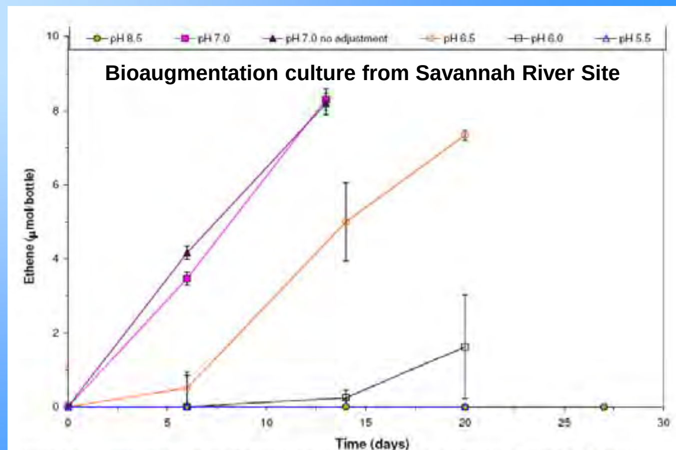
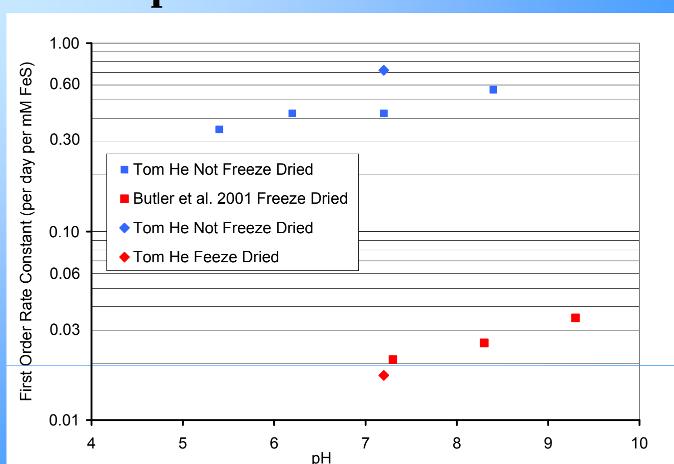


Figure 4.172 Comparison of pH effect on ethene production based on the first PCE and TCE addition at all pH levels (averages of triplicates). Error bars represent ± one standard deviation.

Ashley Eaddy, 2008. *Scale-Up and Characterization of an Enrichment Culture for Bioaugmentation of the P-Area Chlorinated Ethene Plume at the Savannah River Site*. M.S. Thesis, Clemson University, under the direction of David Freedman.

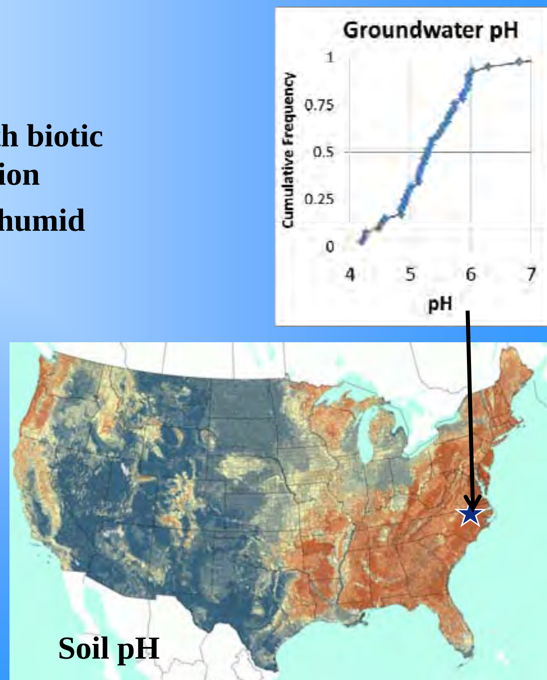
EA Challenge
Effect of pH on Abiotic Dechlorination



He et al., Impact of iron sulfide transformation on trichloroethylene degradation, Geochimica et Cosmochimica Acta 74 (2010) 2025–2039

EA Challenge

- Low pH can inhibit both biotic and abiotic dechlorination
- Groundwater in many humid areas has low pH
- Many aquifers are strongly buffered
  - Lots of base required to raise pH
  - Once pH increases, will stay high for years/decades



Questions

EA Session Charge

- What is the likely role of enhanced attenuation in long term site management?
- What are the most promising methods available to provide such enhancements?
- How can current and/or emerging diagnostic tools help define the need for enhanced attenuation or evaluate its performance?
- What are the highest priority research and development needs that will lead to effective enhanced attenuation technologies?
- What are the highest priorities for demonstration and technology transfer efforts to implement enhanced attenuation technologies?

Emerging Contaminants

SERDP/ESTCP Workshop:

Long Term Management of Contaminated Groundwater Sites

August 13, 2013

Charles Schaefer, Ph.D.
CB&I

Defining Emerging Contaminants

AFCEC (www.afcec.af.mil/resources/emergingissues)

- "chemicals or materials characterized by a perceived or real threat to human health or the environment, for which the scientific basis of the standard is evolving or being re-evaluated"

- Contaminants with new pathways or detection limits

USEPA (EPA 505-F-11-009)

- "a chemical or material that is characterized by a perceived, potential, or real threat to human health or the environment or by a lack of public health standards"

- A contaminant with a new source, pathway, detection method, or treatment technology

Emerging Contaminant List

- Nanomaterials
- NDMA
- PFOS/PFOA
- Pharmaceuticals & Personal Care Products
- **Hexavalent Chromium**
- Decabromodiphenyl ether (flame retardant)
- Phthalate esters (plasticizer)
- **Naphthalene**
- Be
- **Pb**
- RDX
- 1,4-dioxane
- Ethylene dibromide (EDB)
- **Trichlorethene**

Who is Interested in Emerging Contaminants?

-USEPA	- NSF
- DoD	- USDA
- USGS	- NASA
- NIEHS	- NOAA
- DoE	- State and City governments

Recent DoD Focus

PFOS/PFOA

1,4-Dioxane

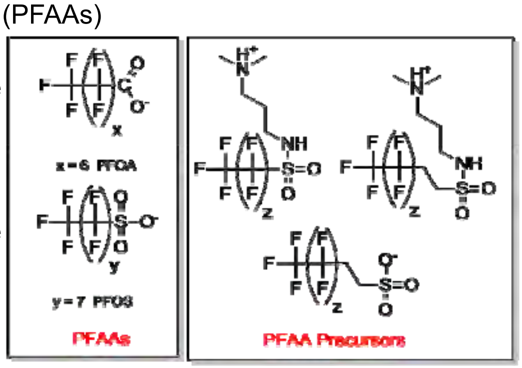
- Potentially widespread
- Not readily biodegradable
- Mobile
- Effectiveness of conventional treatment technology limited

PFOA/PFOS

Perfluoroalkyl acids (PFAAs)

Carboxylate

Sulfonate



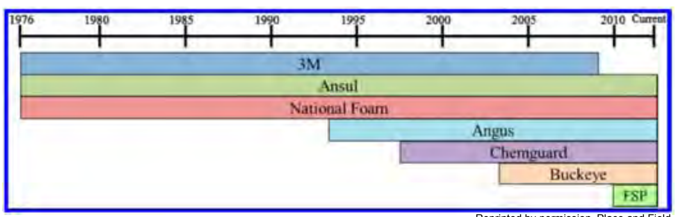
Compound	Solubility (mg/L)	Henry's Law (dimensionless)	Vapor Pres. (mm Hg)	Log K_{oc}	Provisional Health Advisory Level (µg/L)
PFOA	9500	NM	0.017	2.1	**0.4**
PFOS	570	0.045	0.11	3.3	**0.2**

Sources: Zhang et al., 2012; Rayne and Forest, 2009; USEPA, 2012

PFOA/PFOS Sources

- AFFF (applied at FTAs)
- non-stick surfaces
- food-contact paper
- stain repellant

AFFF Sources



Reprinted by permission, Place and Field, 2012. Environ. Sci. Technol., 46, 7120-7127, ACS

	Ansul 2005 mg/L	Chemguard 2010 mg/L	Angus 2002 mg/L	National Foam 2003 mg/L	Buckeye Fire Equipment 2009 mg/L	Fire Service Plus NR[a] mg/L
4:2 FtTAoS[c]	26	ND	25	ND	ND	ND
6:2 FtTAoS	6,100	11,000	4,900	ND	ND	ND
8:2 FtTAoS[c]	1,100	24	170	ND	ND	ND
4:2 FtS	ND	ND	ND	ND	ND	ND
6:2 FtS	ND	ND	ND	42	ND	53
8:2 FtS	ND	ND	ND	19	ND	56
6:2 FtTHN[c]	ND	ND	2,200	ND	ND	ND
6:2 FtSaB	ND	ND	ND	4,600	ND	4,800
8:2 FtSaB[d]	ND	ND	ND	540	ND	1,800
10:2 FtSaB[d]	ND	ND	ND	450	ND	830
12:2 FtSaB[d]	ND	ND	ND	210	ND	430
6:2 FtSaAm	ND	ND	ND	2,100	ND	3,400
8:2 FtSaAm[e]	ND	ND	ND	450	ND	720
5:1:2 FtB	ND	ND	ND	ND	2,000	ND
7:1:2 FtB	ND	ND	ND	ND	4,700	ND
9:1:2 FtB	ND	ND	ND	ND	1,900	ND
5:3 FtB	ND	ND	ND	ND	530	ND
7:3 FtB	ND	ND	ND	ND	610	ND
9:3 FtB	ND	ND	ND	ND	430	ND

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Importance of Precursors

ENVIRONMENTAL Science & Technology

Article

pubs.acs.org/est

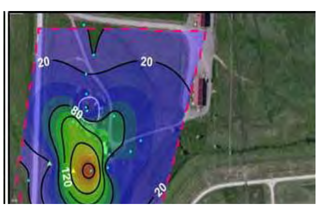
Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

Erika F. Houtz,[†] Christopher P. Higgins,[‡] Jennifer A. Field,[§] and David L. Sedlak[†,*]

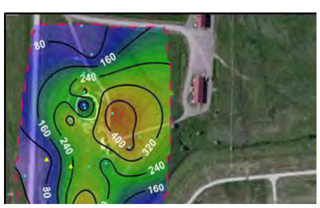
[†]Department of Civil and Environmental Engineering, University of California at Berkeley, Berkeley, California, 94720, United States
[‡]Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, Colorado 80401, United States
[§]Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States

- Greater fraction of perfluorinated carboxylates and sulfonates in groundwater than in AFFF
- Suggests conversion of precursors to PFAAs

PFOA/PFOS Groundwater Plume
Ellsworth AFB

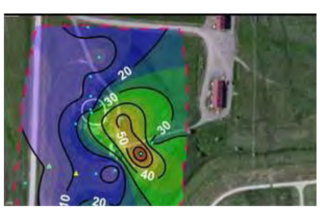


PFOA



PFOS

Aerobic bioremediation for treatment of BTEX likely facilitated transformation of carboxylate precursors to PFOA



Carboxylate Precursors

AFCEC BAA #689

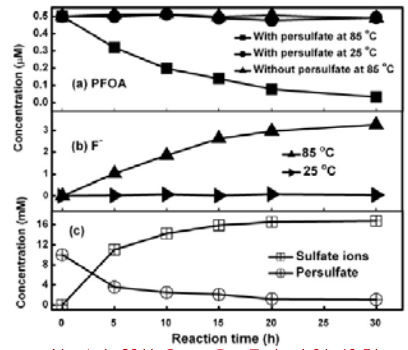
Treatment Approaches

Validated *in situ* field scale approaches are lacking

Processes being evaluated:

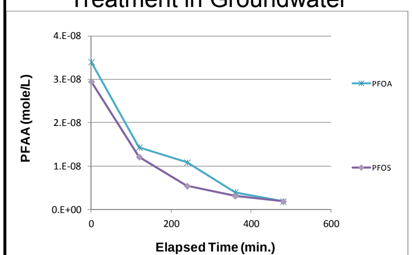
- Chemical oxidation
- Electrochemical treatment
- Catalytic
- Bioremediation

(AFCEC BAA 712 – Deeb & Mahendra)



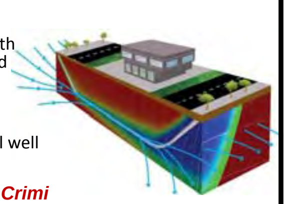
Liu et al., 2011. *Separ. Pur. Technol.* 91, 46-51.

PFOS and PFOA Electrochemical Treatment in Groundwater



<u>*In Situ* Treatment Train</u>

1. Horizontal well is packed with activated carbon to sorb and concentrate contaminants
2. Activated persulfate is introduced to the horizontal well to regenerate the carbon



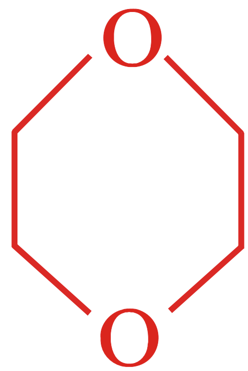
Courtesy of Professor M. Crimi

Challenges for *In Situ* Treatment of Perfluorinated Compounds

- Interactions with NAPL
- Analytical
- Precursors and complex chemistry
- Low target levels
- Identifying daughter products

1,4-Dioxane

- Chem/Phys/Tox
  - Cyclic Ether
  - High Miscibility in Water
  - VP = 38 mm Hg
  - Low Henry's Law Coefficient -- 4.9 x 10^{-6}atm-m^3/mol
  - Low Partitioning Coefficient – log K_{oc}= 0.09
  - Probable Human Carcinogen



- Low action levels in several states:
  - California (3 ppb)
  - Florida (5ppb)
  - Maine (70 ppb)
  - Massachusetts (50 ppb)
  - Michigan (1ppb)
  - North Carolina (7ppb)

1,4-Dioxane Uses

- Stabilizer in 1,1,1-TCA
  -up to 5%
- Stabilizer in TCE
  -<1%
- Paints, cosmetics, fumigants, shampoo aircraft deicing fluids, antifreeze

Santa Clara Valley Water District

1,4-Dioxane

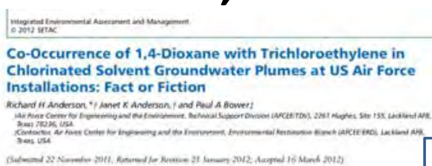
and other

SOLVENT STABILIZERS

WHITE PAPER

Santa Clara Valley Water District

1,4-Dioxane Occurrence


Integrated Environmental Assessment and Management
© 2012 SETAC

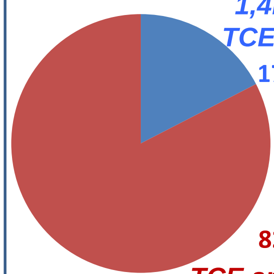
Co-Occurrence of 1,4-Dioxane with Trichloroethylene in Chlorinated Solvent Groundwater Plumes at US Air Force Installations: Fact or Fiction

Richard H Anderson,*† Janet K Anderson,‡ and Paul A Bower‡

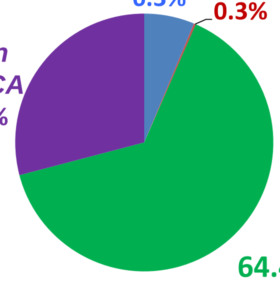
†Air Force Center for Engineering and the Environment, Technical Support Division (AFCEE/TDV), 2261 Hughes, Ste 155, Lackland AFB, Texas 78236, USA

‡Contractor, Air Force Center for Engineering and the Environment, Environmental Restoration Branch (AFCEE/ERD), Lackland AFB, Texas, USA

(Submitted 22 November 2011; Returned for Revision 23 January 2012; Accepted 16 March 2012)



If TCE or TCA is present, how likely is it that 1,4D is present?

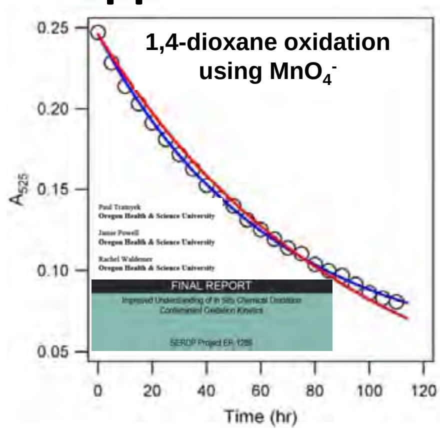


How often does 1,4D occur with TCE and/or TCA?

In-Situ Remedial Approaches

<u>Chemical Oxidation</u>

- activated persulfate
- H_2O_2/O_3
- permanganate
- unactivated persulfate

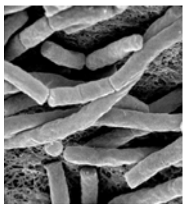


ER-201324 (Dr. Pat Evans, CDM Smith)
Sustained In Situ Chemical Oxidation (ISCO) of 1,4-Dioxane Using Slow Release Chemical Oxidant Candles

Christensen et al., Chemosphere 89:6, 680-887, 2012

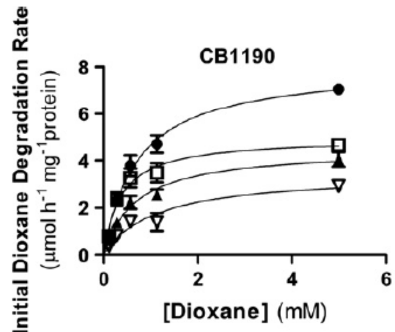
In-Situ Remedial Approaches

Aerobic Bioremediation
- metabolic



Pseudonocardia Dioxanivorans (CB1190)

Courtesy of AECOM



Chemosphere

Technical Note

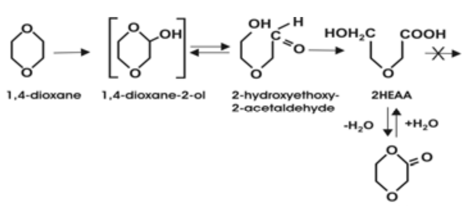
The impact of chlorinated solvent co-contaminants on the biodegradation kinetics of 1,4-dioxane

Shaily Mahendra, Ariel Grostern, Lisa Alvarez-Cohen

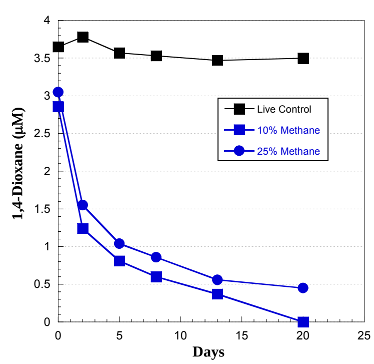
Upcoming Field Demonstration: Bioaugmentation to Enhance 1,4-Dioxane Biodegradation (AFCEC BAA – R. Mora, S. Mahendra)

In-Situ Remedial Approaches

Aerobic Bioremediation
- cometabolic
  - -THF, methane, propane butane, ethene, toluene

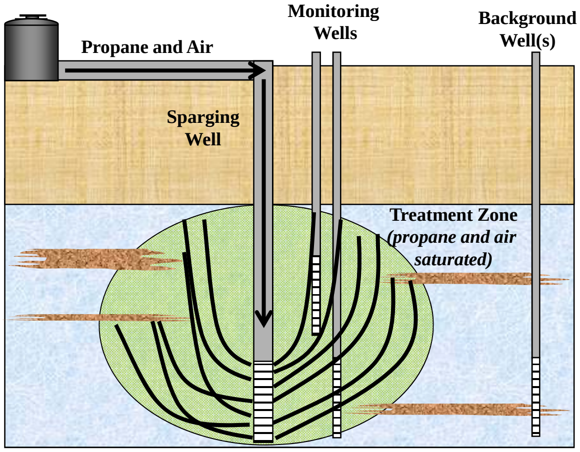


From: Vainberg et al., 2006. Appl. Environ. Microbiol. 72:5218-5224



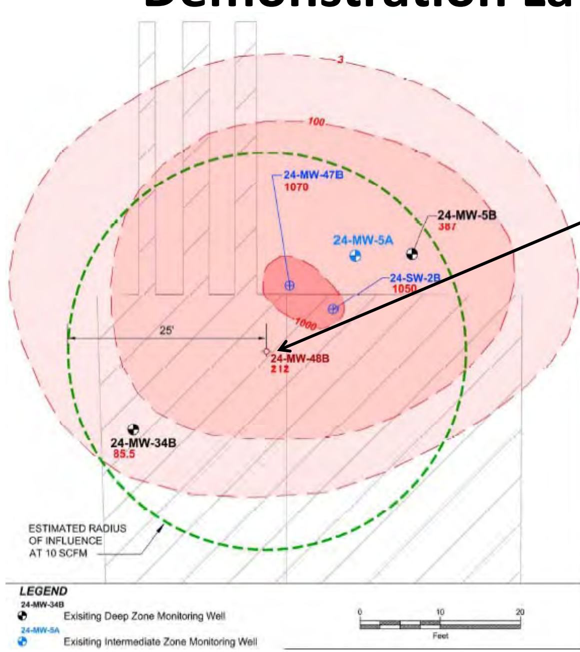
In-Situ Remedial Approaches

Aerobic Bioremediation – Field Demonstration
(AFCEC BAA 518, PI – R. Steffan)



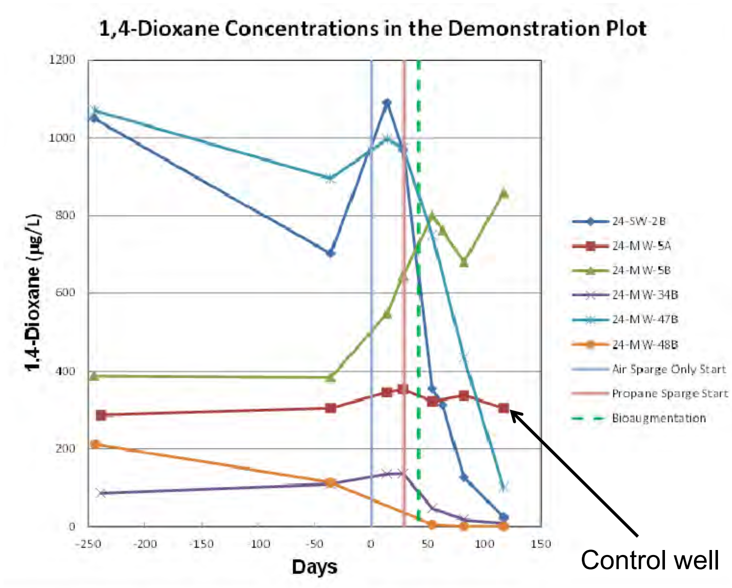
Biosparging for in situ treatment of 1,4-dioxane

Demonstration Layout



Biosparge well

- ***Bioaugmented with ENV425***



Preliminary Results

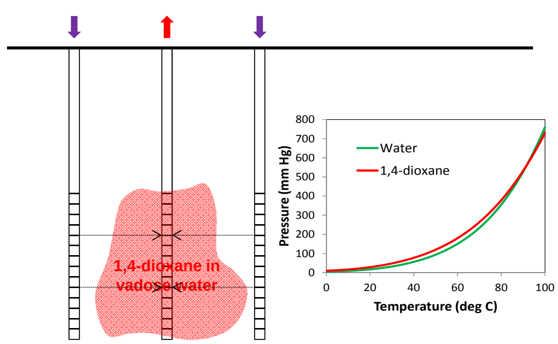
XSVE

Removal of 1,4-Dioxane from the Vadose Zone

XSVE Focus:

Removal of both vadose water & 1,4-dioxane.

ESTCP Project ER-201326



XSVE Enhancements:

Focused extraction, drier and/or heated air injection, reduced infiltration

Vadose 1,4-dioxane cleanup time on same order as SVE for solvents.

Courtesy of Dr. Rob Hinchee, IST

Challenges for Treatment and Evaluation of 1,4-Dioxane Plumes

- Presence of chlorinated solvents

- Daughter products

- Verification of degradation (bio-markers/CSIA)
  AECOM/UCLA (R. Mora, D. Chiang, S. Mahendra)
  Rice University (P. Alvarez)

- Low target levels

- Need to bioaugment?

- Distribution and growth of bioaugmented cultures

Acknowledgements

Rebecca Mora (AECOM)

Dr. Rob Hinchee (IST)

Dr. Michelle Crimi (Clarkson University)

Dr. Chris Higgins (Colorado School of Mines)

Dr. Rob Steffan (CB&I)

Dr. Paul Hatzinger (CB&I)

David Lippincott, P.G. (CB&I)

SERDP/ESTCP

AFCEC

Source Control

Manage the contaminants or manage the aquifer?

John Wilson

Senior Research Microbiologist

R.S. Kerr Research Center

Ada, Oklahoma

National Risk Management Research Laboratory

Office of Research and Development, U.S. EPA

U.S. EPA Risk
Management Paradigm.

Destroy the Hazard

or

Prevent Exposure

Things we don't do well:

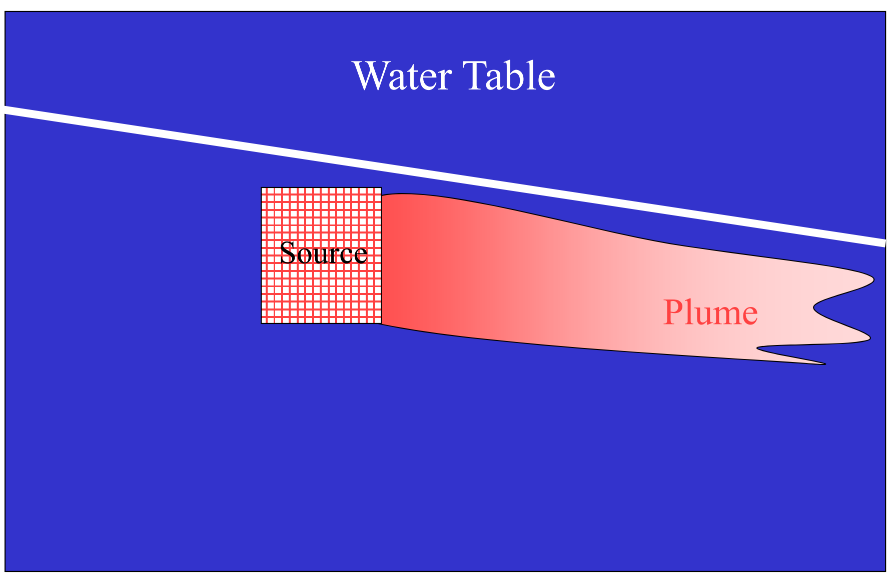
1) Find NAPL source areas

2) Circulate fluids through NAPL source areas

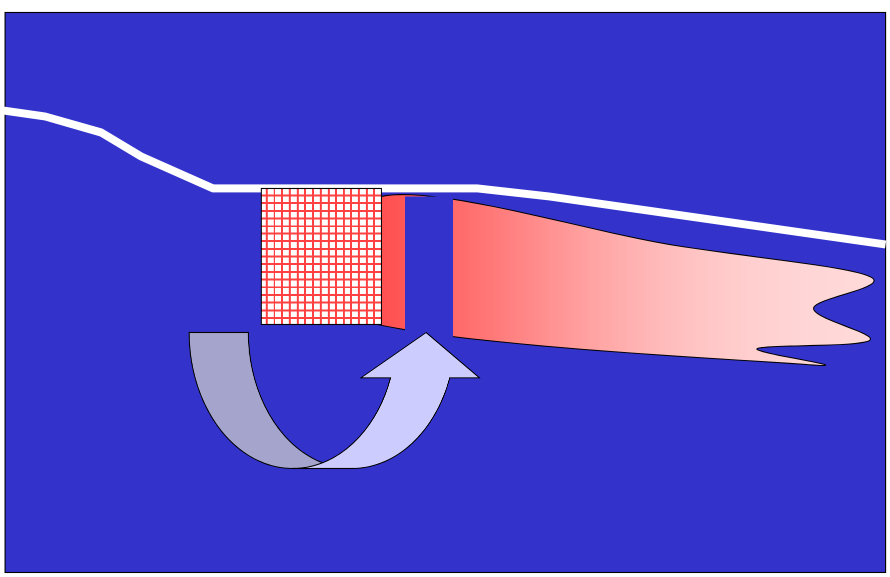
3) Achieve substantial mass removals of NAPL below the water table

Things we can do well:

1) Measure the piezometric heads of ground water
2) Predict the direction of ground water flow
3) Pump ground water from wells

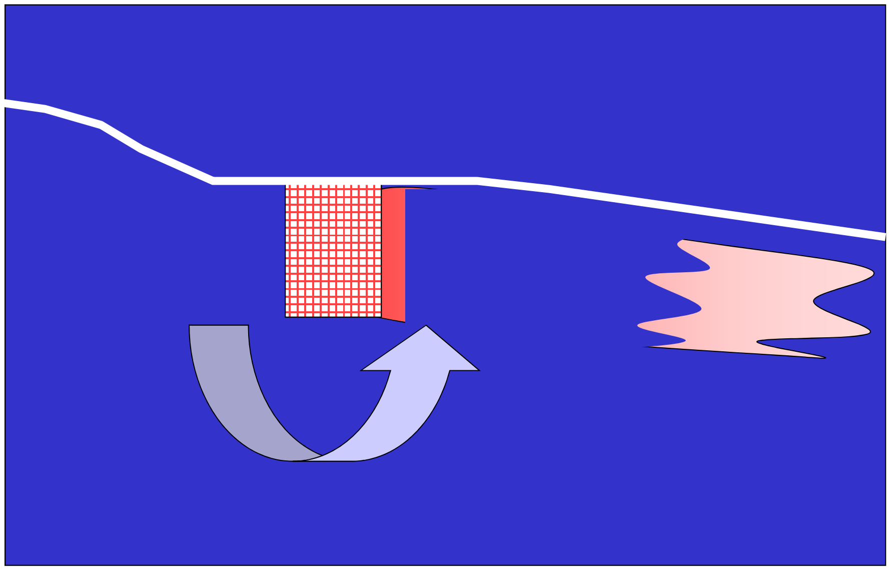


Manage the plume by diverting the flow of ground water around the source area

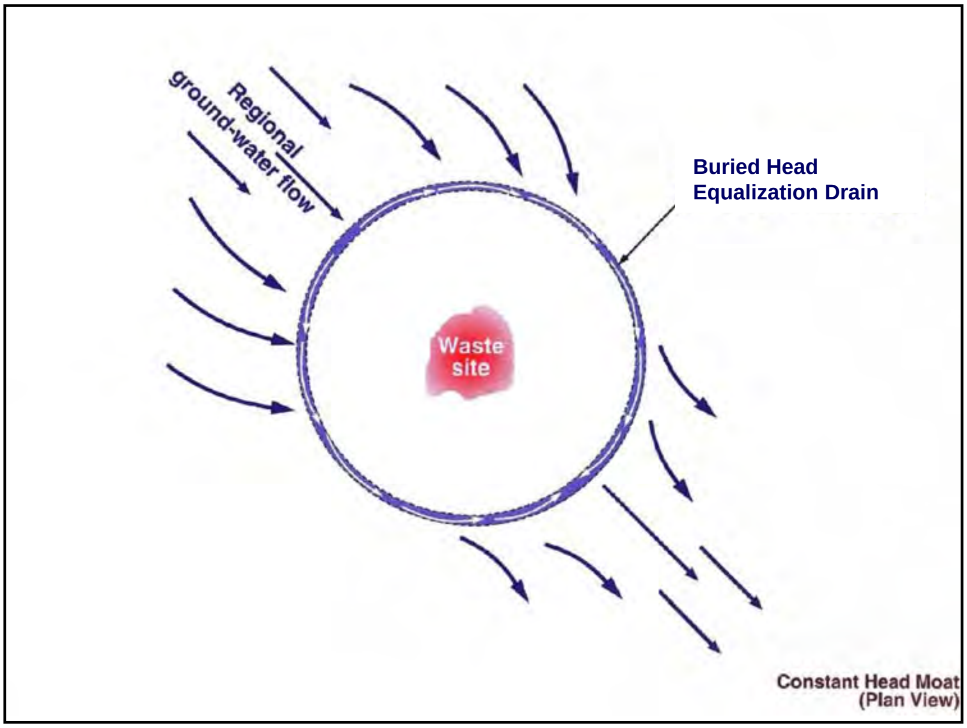


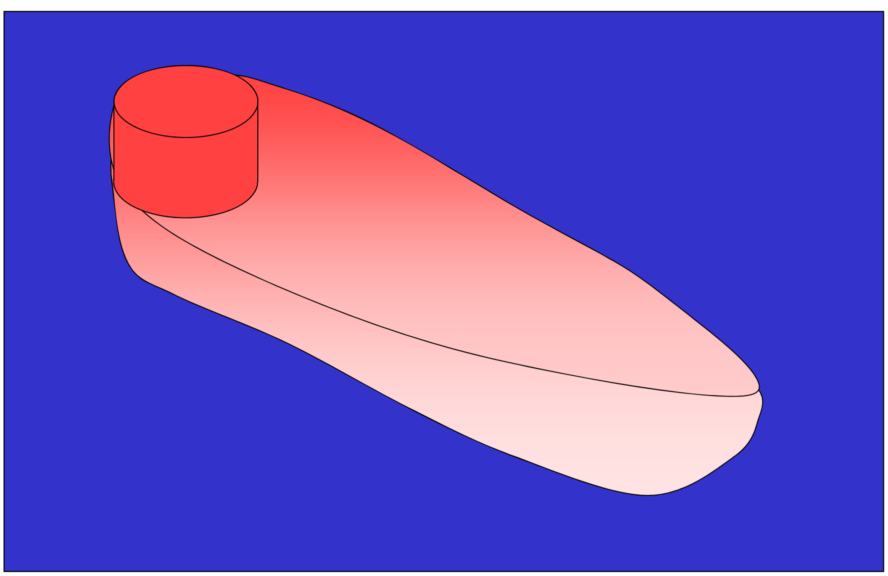
Once the source area is isolated, the plume will flush out or attenuate through natural biodegradation.

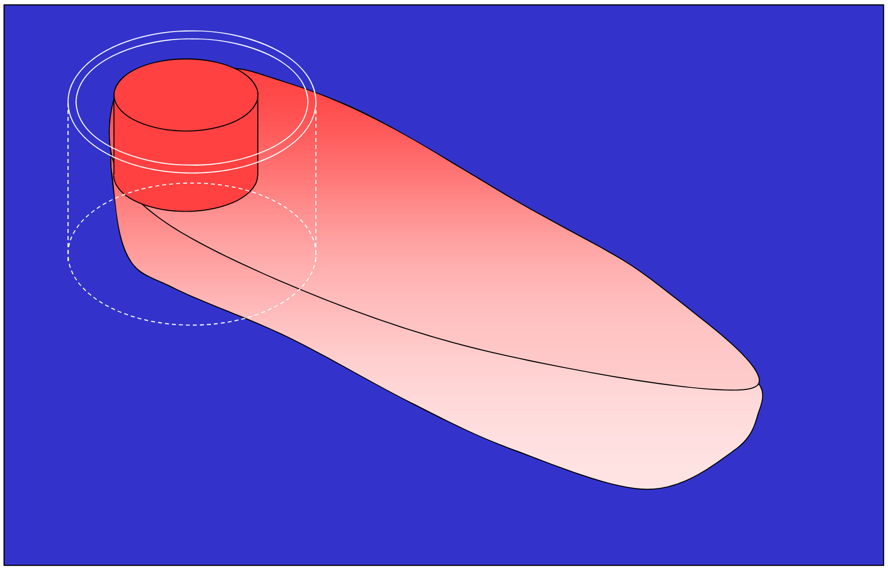
Ground water does not move through the source because the hydraulic gradient is zero.

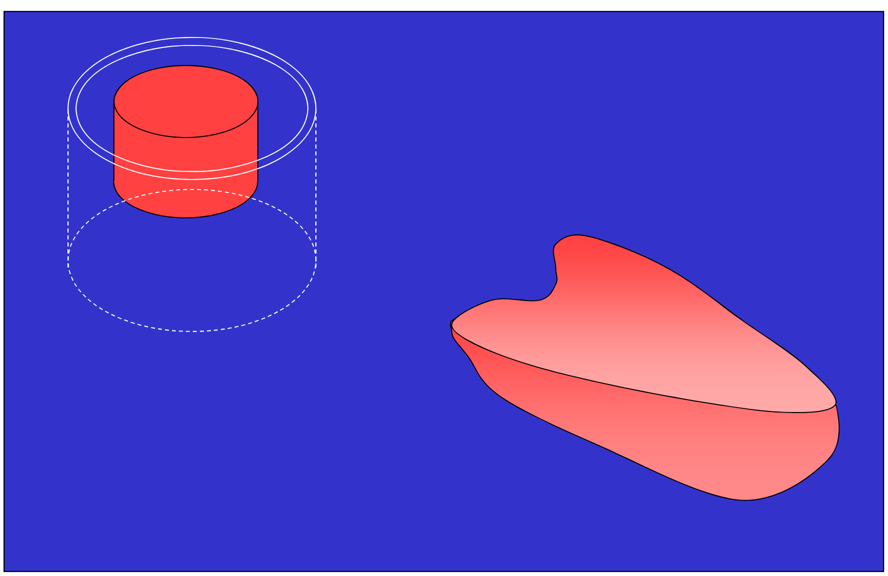


Source Control by Hydrological Isolation: Application of the Ankeny Moat


Regional
ground-water flow
Buried Head
Equalization Drain
Waste
site
Constant Head Moat
(Plan View)

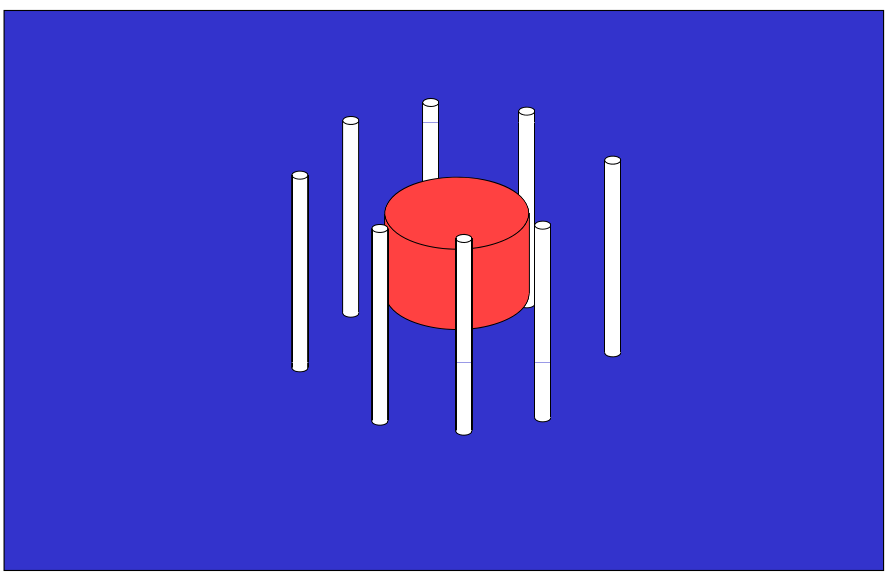


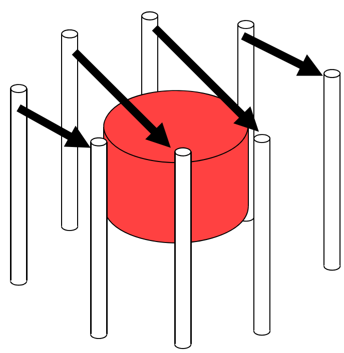


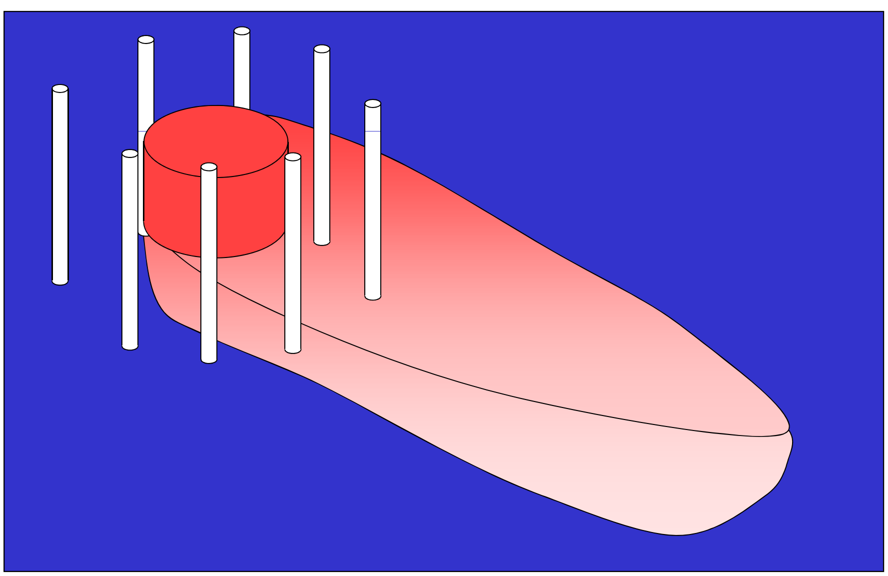


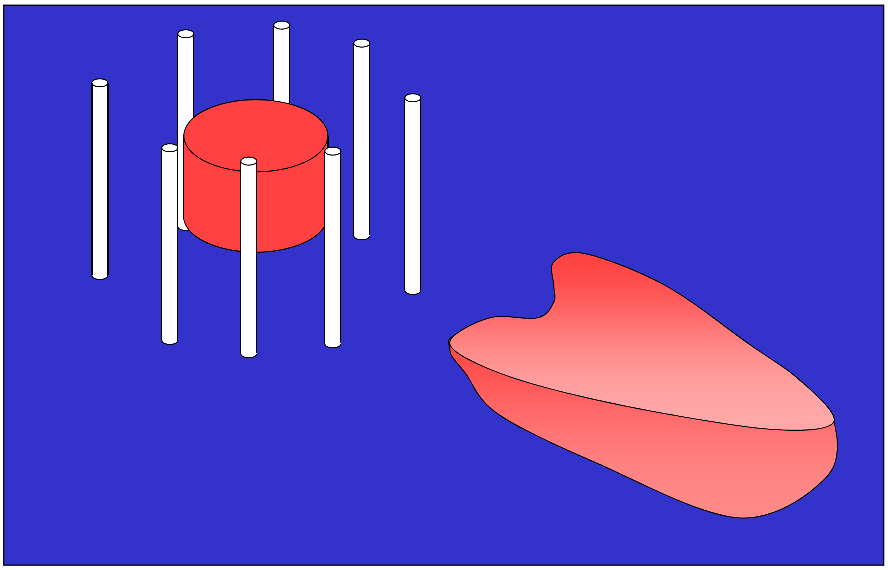
Source Control by Hydrological Isolation:

Facsimile of the Ankeny Moat using extraction wells and injection wells







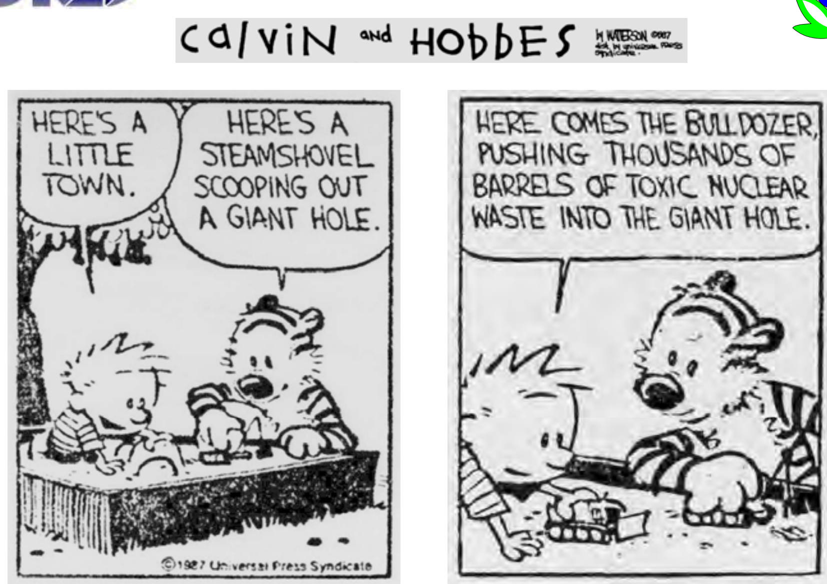


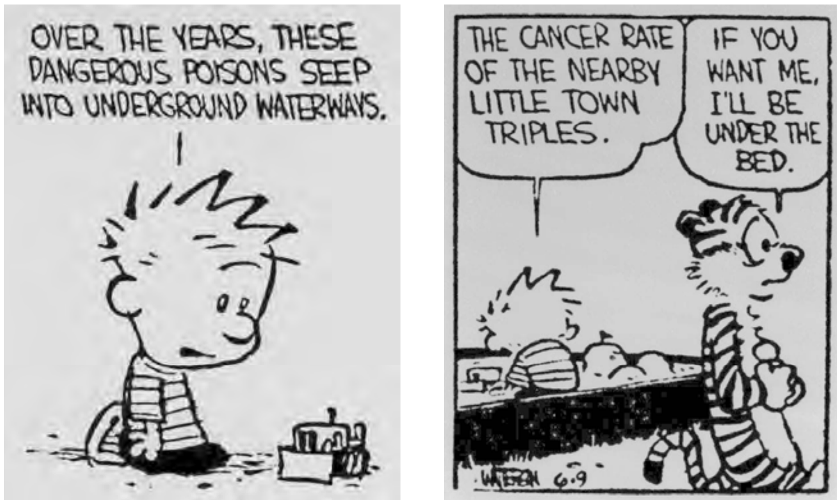
Advantages:

1) Immediately stops new ground water contamination.
2) Relatively indifferent to heterogeneous in subsurface material.
3) Easy to monitor
4) Not disruptive to base activities
5) Will allow MNA to clean up the down gradient plume

Disadvantages:

1) Water rights and water discharge issues.
2) Will have to monitor contaminants in the ground water that is discharged or relocated.
3) O&M may go on forever.
4) The approach has not been proven to work.
5) Sediment and fines may plug the relocation wells.





Recommendations:

1) Don’t hide under the bed.

Recommendations:

1) Calculate the discharge of your plumes.

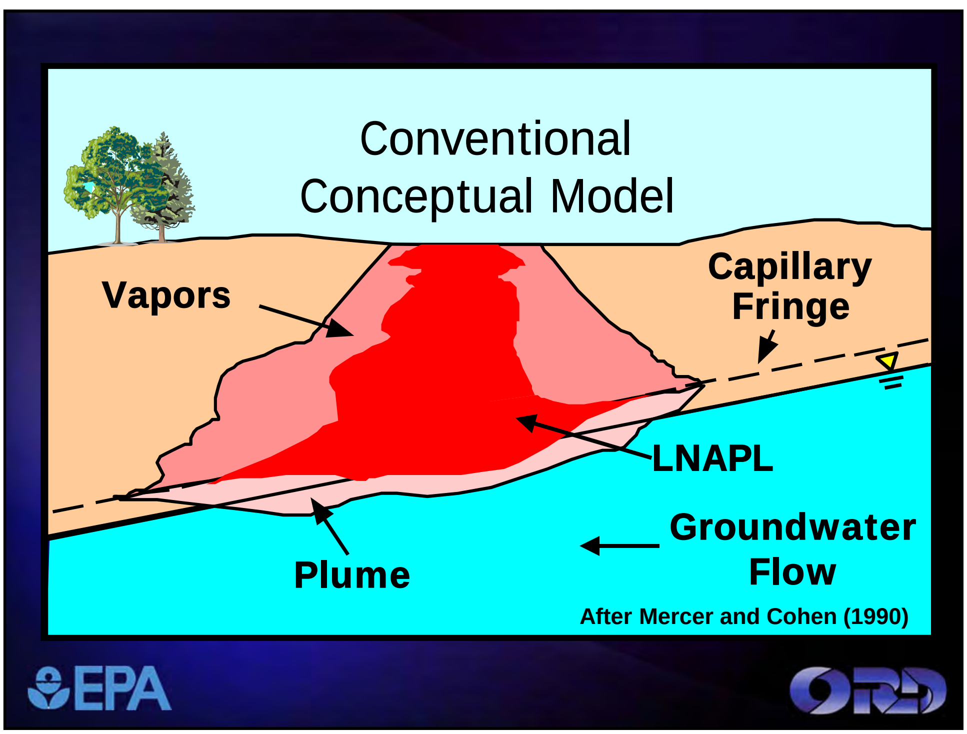
2) Determine the flow of ground that would be diverted to stop continued formation of the plume.

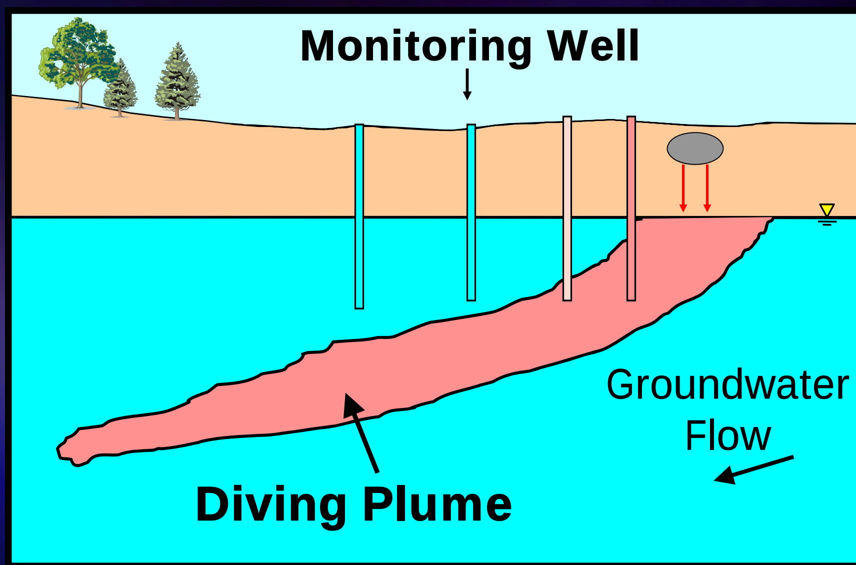
3) Conduct a engineering cost estimate to divert the clean ground water from the source area of the plume.

Influence of Stratigraphy on a Diving MTBE Plume and Its Characterization

A Case Study

USEPA / ORD / NRMRL / GWERD





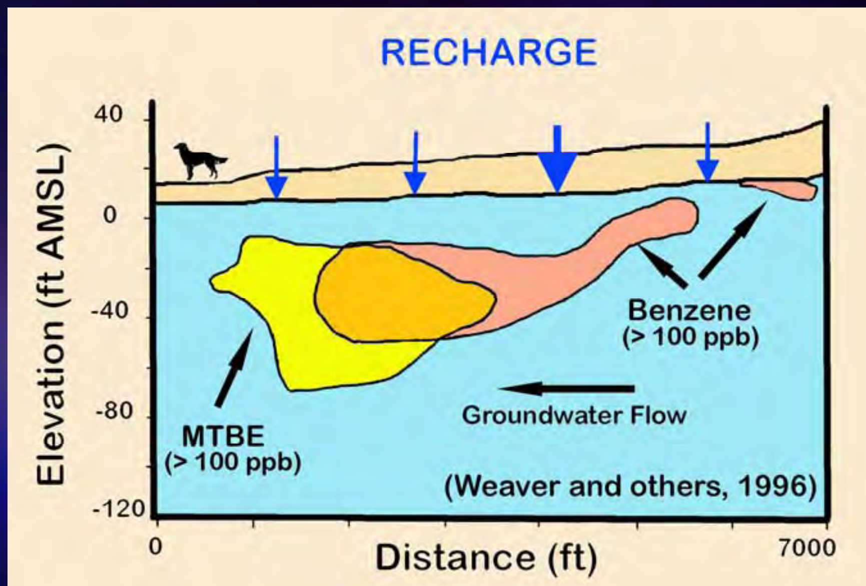
EPA ORD

RARE Project (Region 5)

Identifying and Predicting Diving Plume Behavior at Sites Contaminated with MTBE

- Characterization of Diving Plumes (3 sites in Region 5)
- Issue Paper
- Upgrade On-Line Calculator www.epa.gov/athens/onsite/index.html

EPA ORD

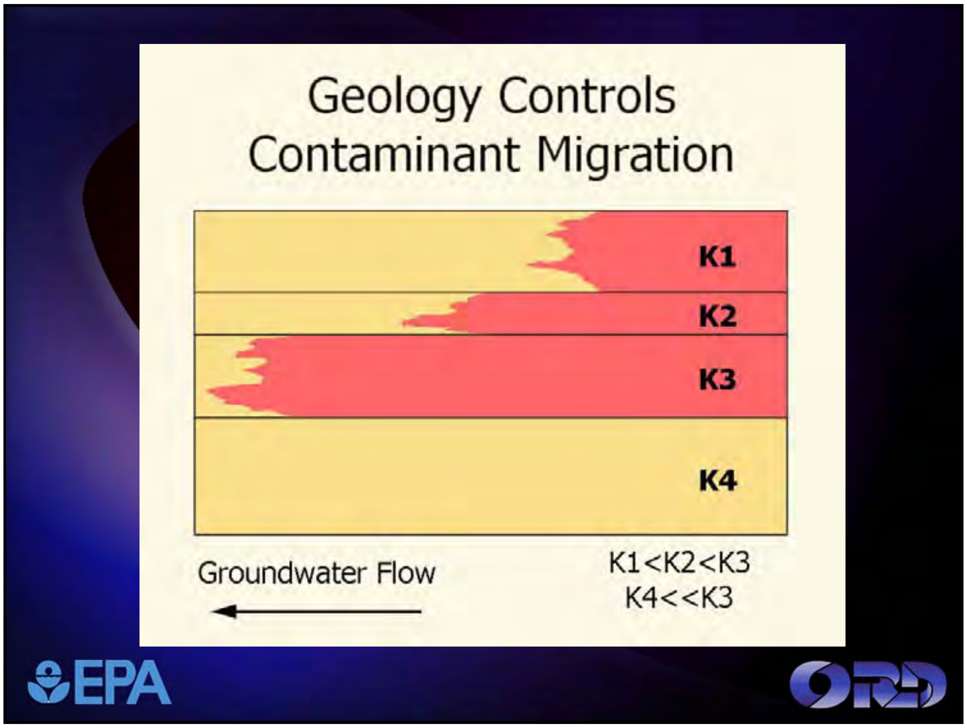


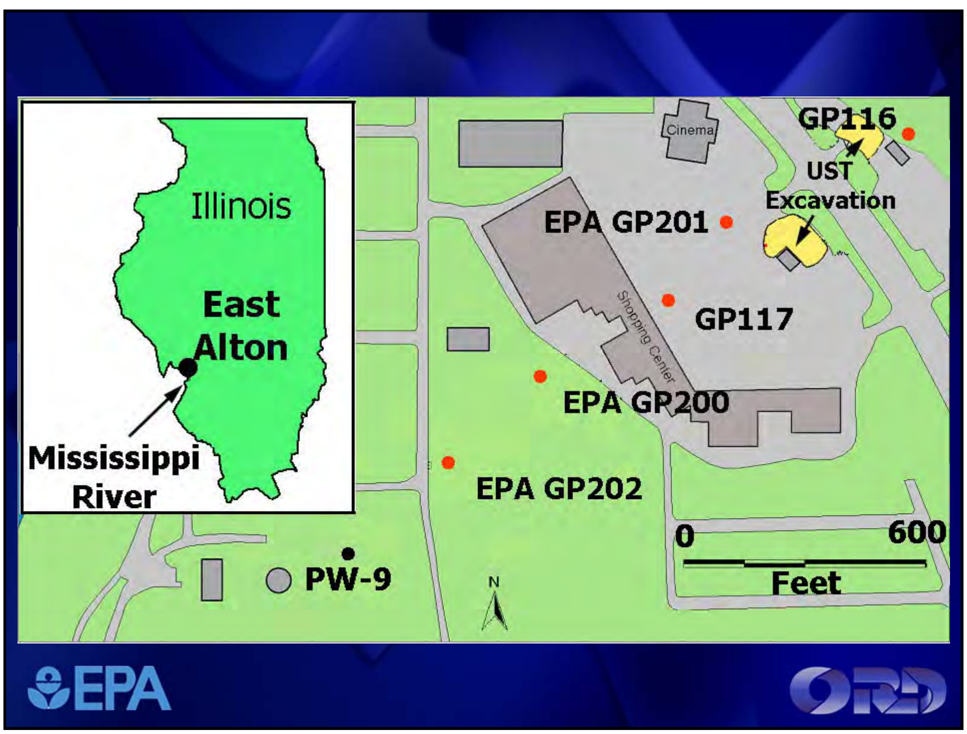
EPA ORD

PLUME DIVING SITUATIONS

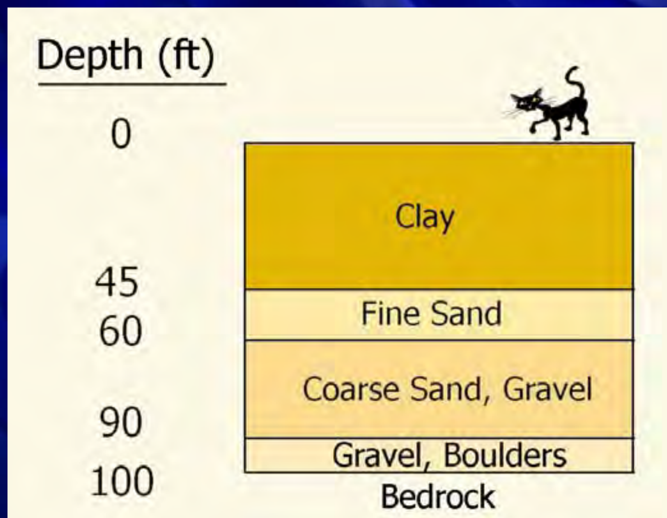
- Recharge at water table
- Pumping wells
- Preferential migration pathways
- Differences in biotransformation with depth

EPA ORD


Geology Controls
Contaminant Migration
K1
K2
K3
K4
Groundwater Flow
K1<K2<K3
K4<<K3
EPA

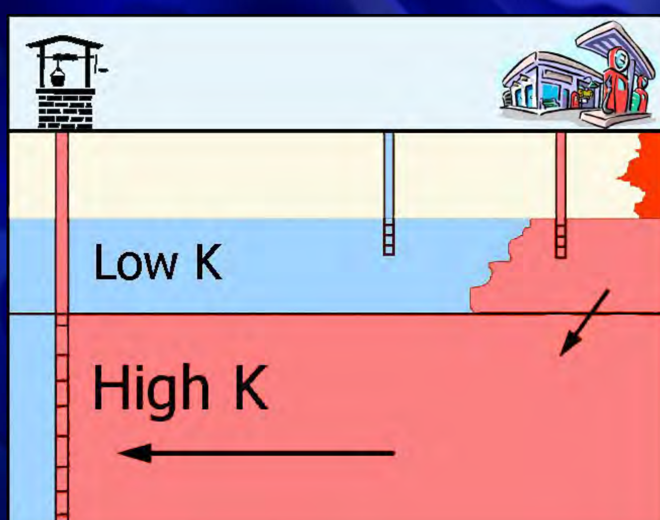

Illinois
East
Alton
Mississippi
River
Cinema
GP116
UST
Excavation
EPA GP201
Shopping Center
GP117
EPA GP200
EPA GP202
0
600
Feet
PW-9
N
EPA

GENERALIZED STRATIGRAPHY



EPA ORD

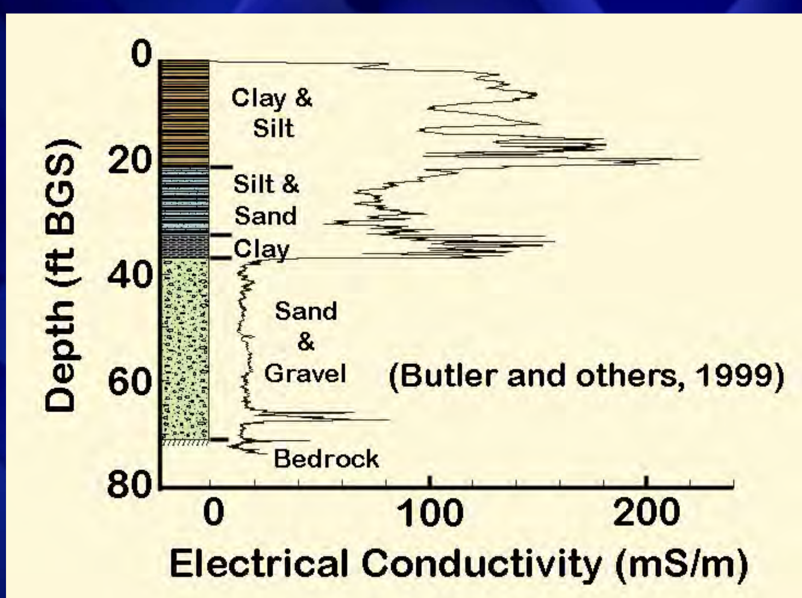
INITIAL CONCEPTUAL MODEL

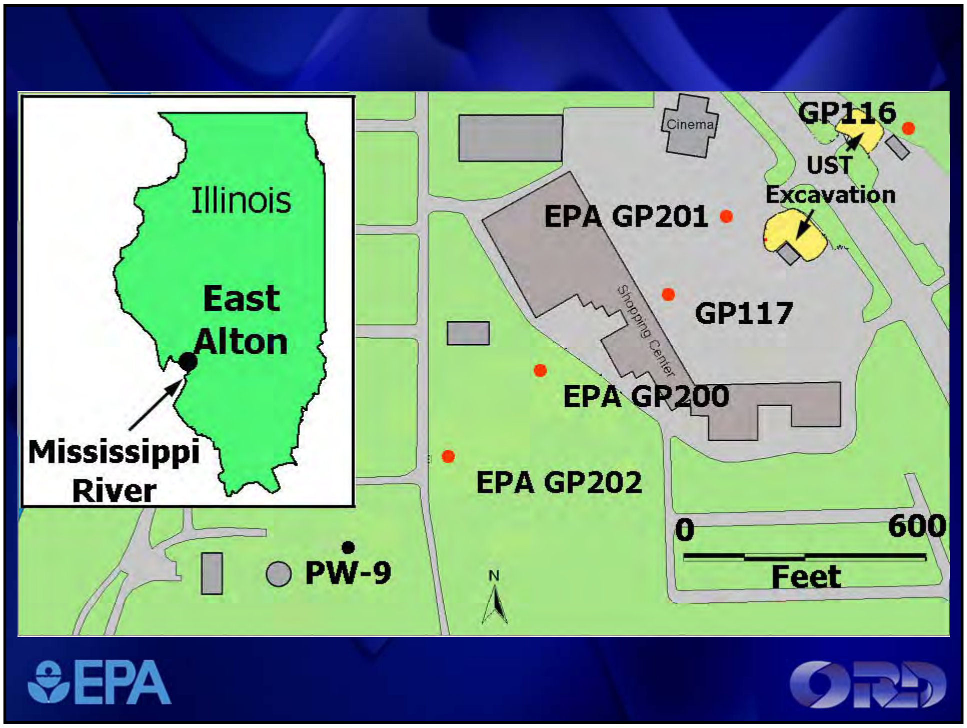


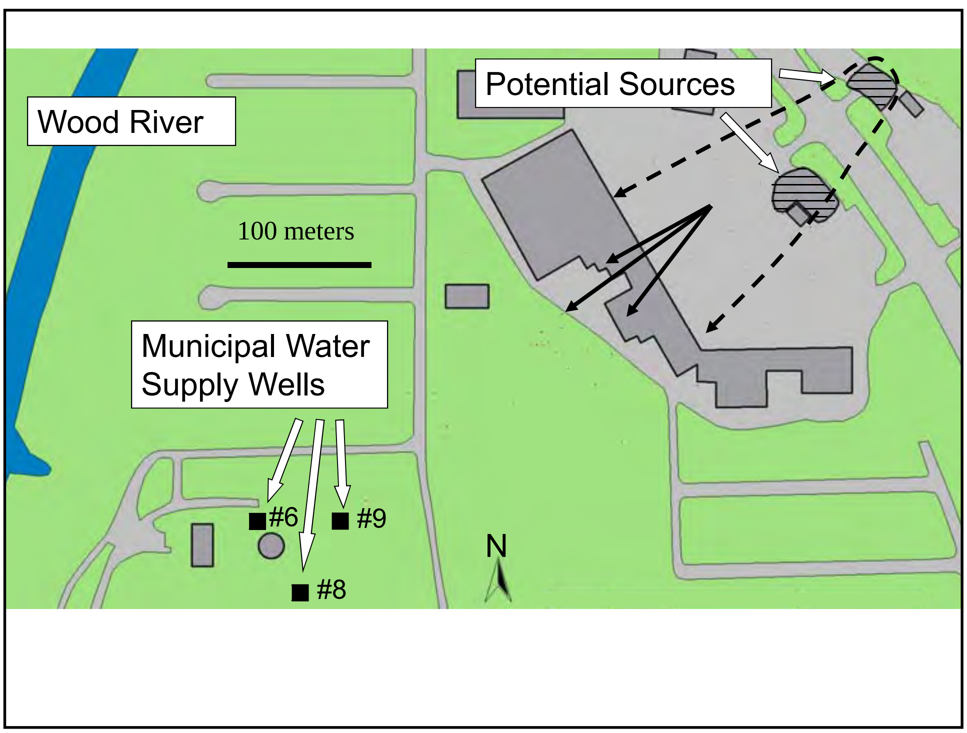
EPA ORD

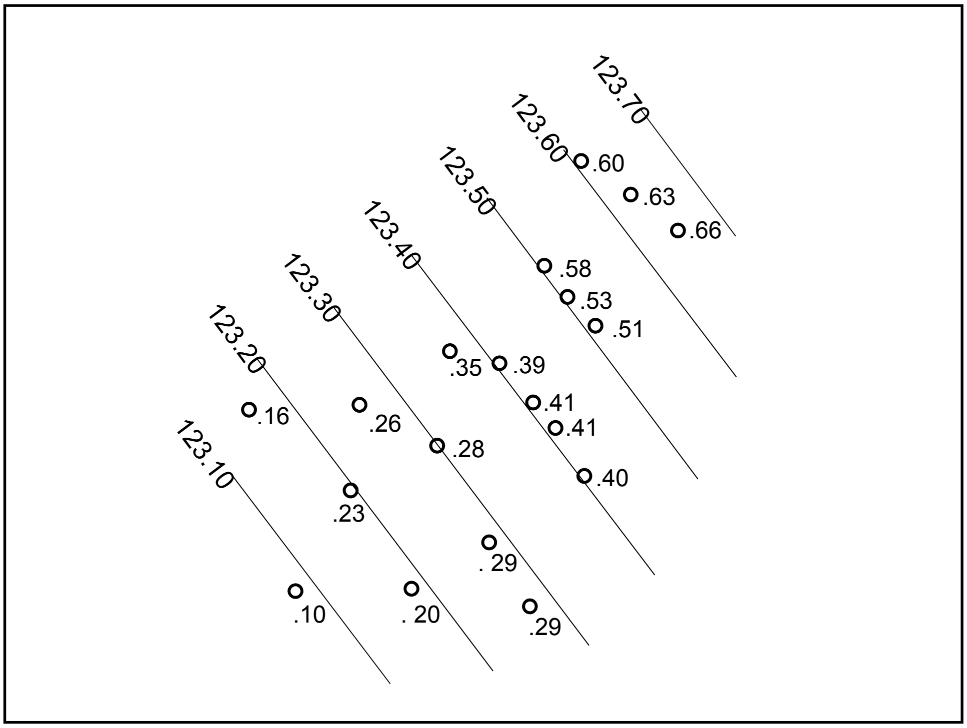
HYDROGEOLOGIC CHARACTERIZATION

- Soil electrical conductivity probe (Direct Push)
- Electromagnetic borehole flowmeter (EPA/600/R-98/058)




Illinois
East Alton
Mississippi River
Cinema
GP116
UST Excavation
EPA GP201
Shopping Center
GP117
EPA GP200
EPA GP202
0
600
Feet
PW-9
N
EPA
ORD


Wood River
Potential Sources
100 meters
Municipal Water Supply Wells
#6
#9
#8
N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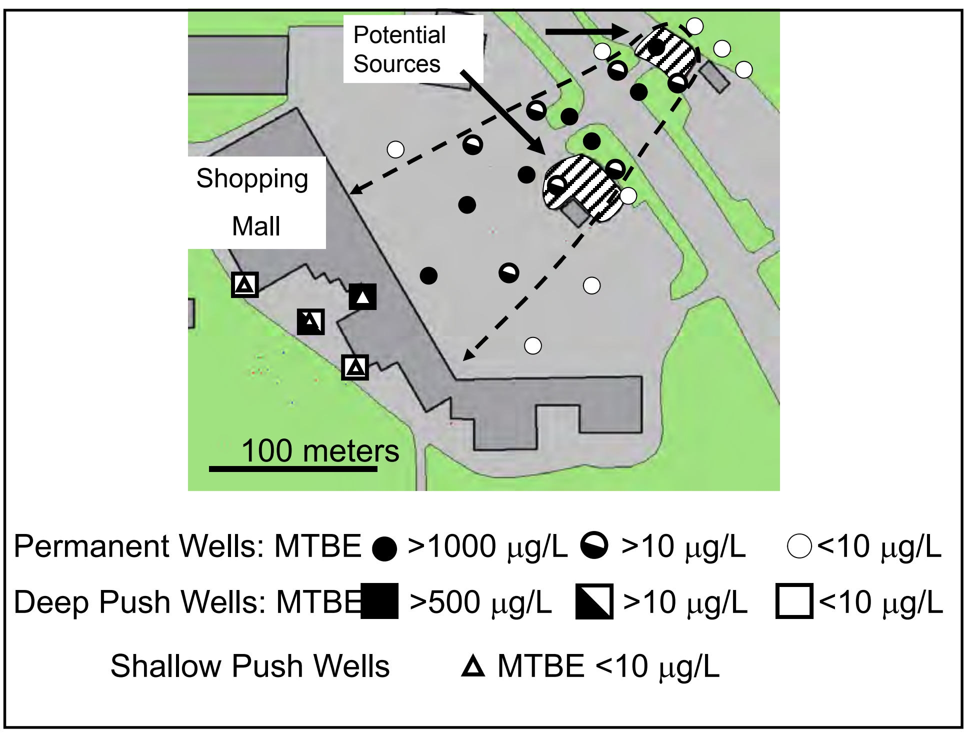
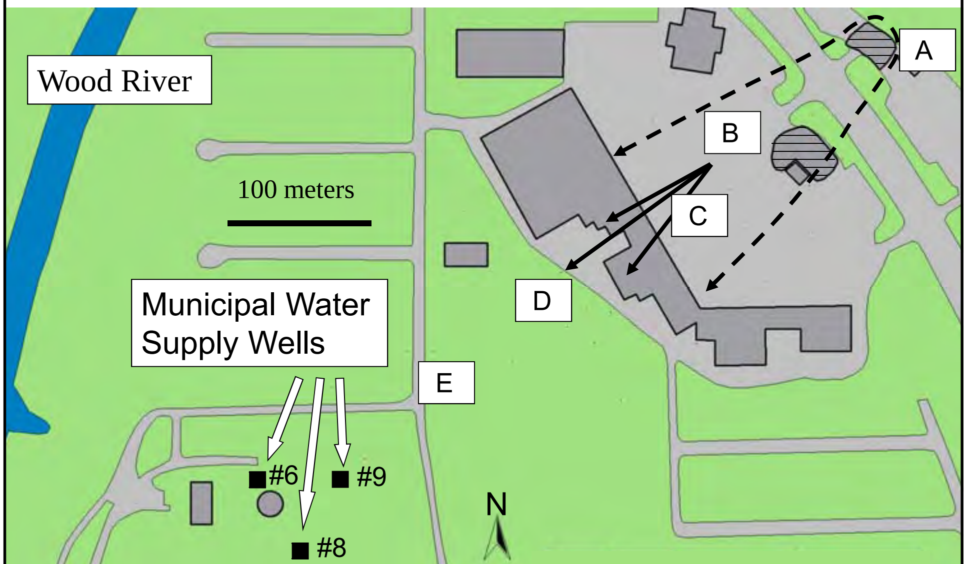
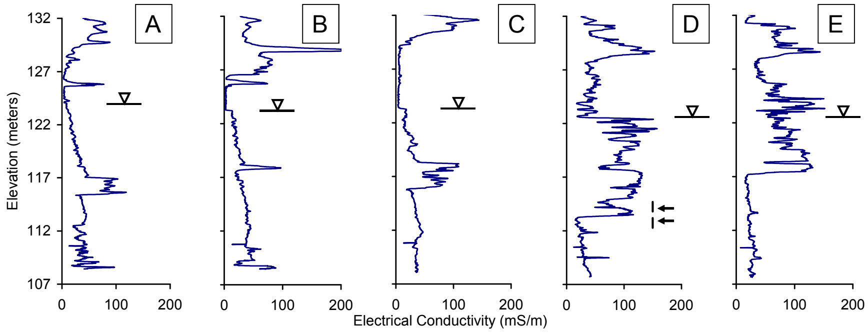
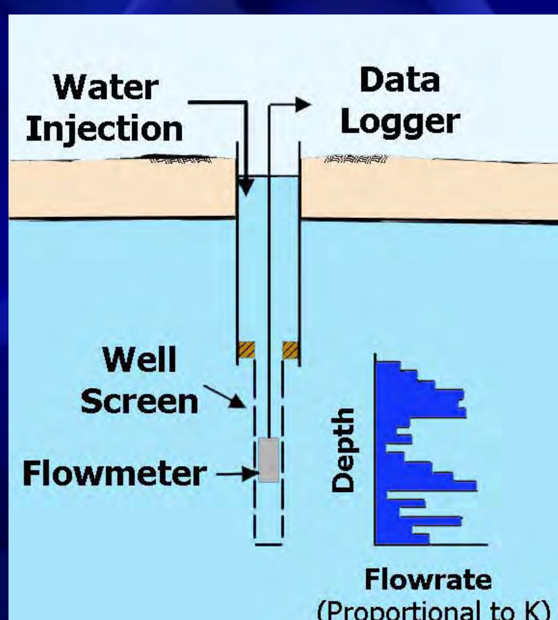

Potential Sources
Shopping Mall
100 meters
Permanent Wells: MTBE >1000 µg/L >10 µg/L <10 µg/L
Deep Push Wells: MTBE >500 µg/L >10 µg/L <10 µg/L
Shallow Push Wells MTBE <10 µg/L

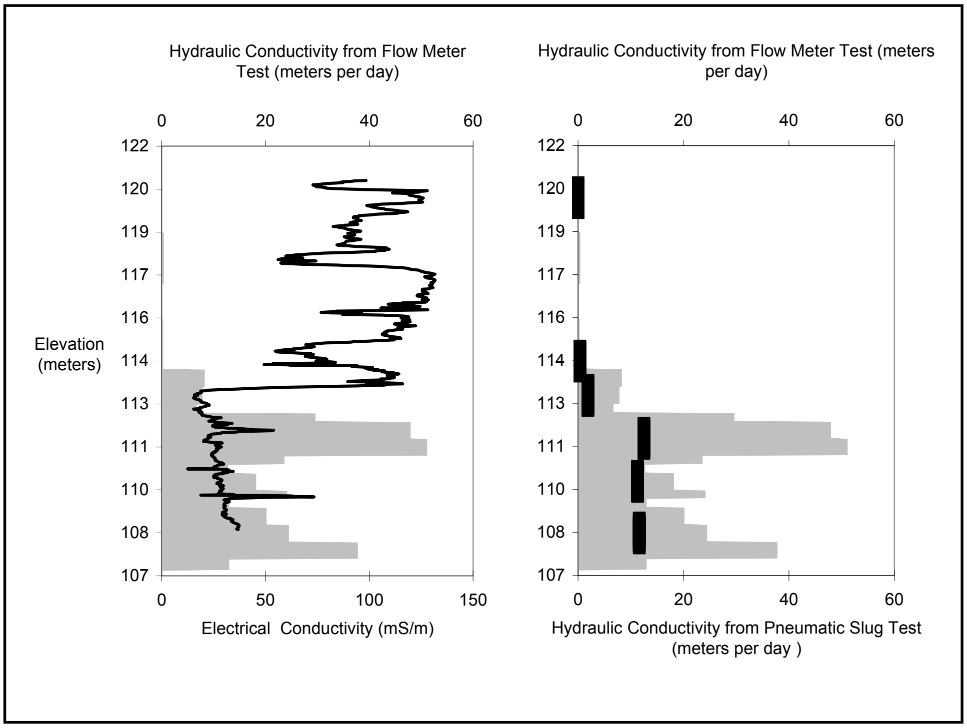

Wood River
100 meters
Municipal Water Supply Wells
A
B
C
D
E
#6
#9
#8
N


A
B
C
D
E
Elevation (meters)
132
127
122
117
112
107
0
100
200
Electrical Conductivity (mS/m)

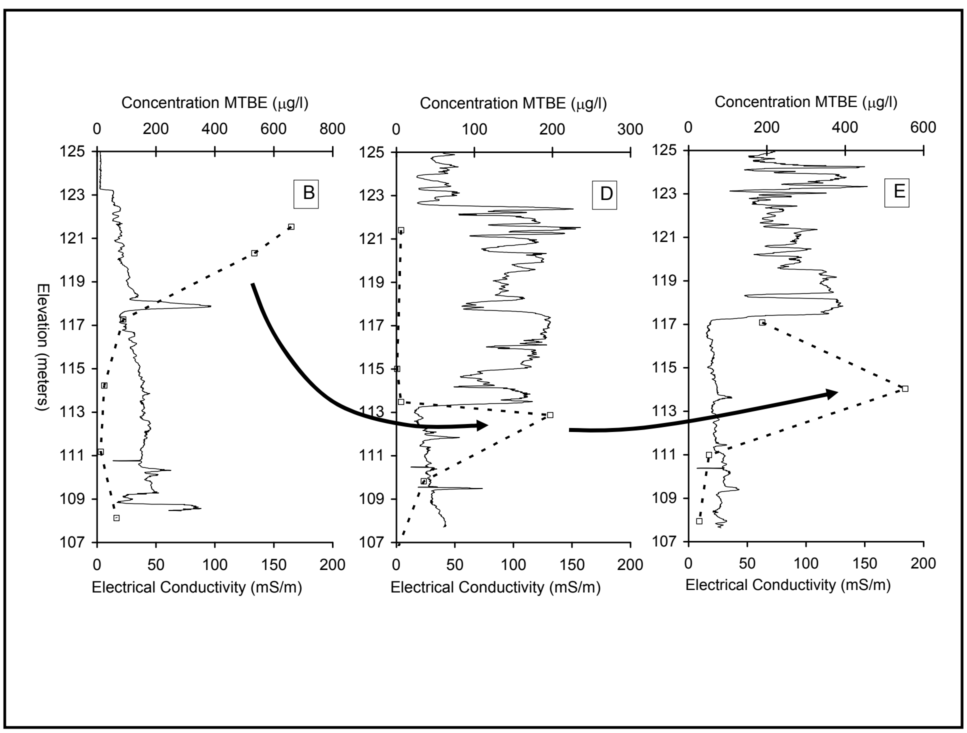
113.7 meters amsl,
location D

112.8 meters amsl,
location D





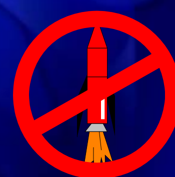
Hydraulic Conductivity from Flow Meter Test (meters per day)
Hydraulic Conductivity from Flow Meter Test (meters per day)
Elevation (meters)
Electrical Conductivity (mS/m)
Hydraulic Conductivity from Pneumatic Slug Test (meters per day)



Concentration MTBE (μg/l)
Concentration MTBE (μg/l)
Concentration MTBE (μg/l)
B
D
E
Elevation (meters)
Electrical Conductivity (mS/m)
Electrical Conductivity (mS/m)
Electrical Conductivity (mS/m)

CONCLUSIONS

- Geology is a primary control on contaminant migration
- Soil electrical conductivity
  - Representative of geologic/hydraulic properties
  - Rapidly obtained & inexpensive data



APPENDIX D

Relevant SERDP Statements of Need and ESTCP Projects

SUMMARY REPORT

SERDP and ESTCP Environmental Restoration Program Overview

August 2013

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- -

1. INTRODUCTION

SERDP and ESTCP have funded research and demonstrations for treatment of contaminated groundwater for over a decade. Since 2001, the Program Office has periodically held Expert Panel workshops to help guide investments in this area. In 2001, an Expert Panel was convened to discuss the current knowledge concerning remediation of chlorinated solvents (both in the dissolved phase and in the source zone). A second workshop was held in 2006 which focused on reducing uncertainty in DNAPL source zone management and remediation. In 2011, SERDP and ESTCP hosted a workshop to evaluate existing and potential future issues associated with site closure, and identify research and demonstration strategies that could improve remediation approaches, reduce risk, and ultimately reduce the cost to complete site closure. Results from these workshops impacted the SONs released in subsequent years, as well as selection of technology demonstrations under ESTCP.

This document serves to provide background information on the projects funded in the Environmental Restoration program area within SERDP and ESTCP over the past few years. SERDP projects are selected based on responses to relatively specific Statements of Need. Figure 1 provides an overview of SONs released since FY00 that addressed issues associated with contaminated groundwater. Sections 2 through 15 provide the objectives of each of these Statements of Need, followed by a listing and link to the fact sheet for the projects selected within that SON.

ESTCP projects are selected based on response to specific Topic Areas; however, Topic Areas are quite broad (i.e. remediation of groundwater). Therefore, in Section 17, ESTCP projects focused on contaminated groundwater are simply listed and grouped by either ongoing or completed projects.

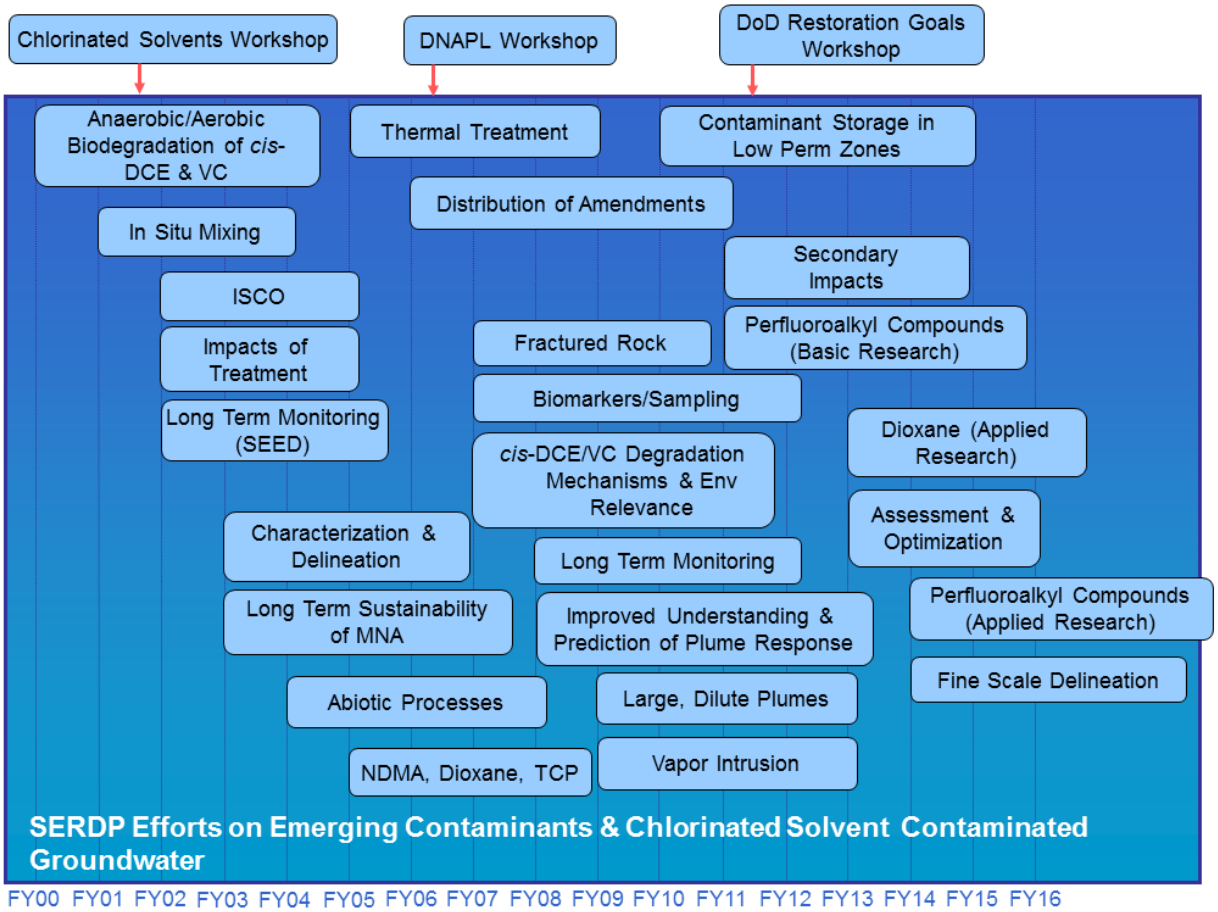

Figure 1 SERDP Efforts on Emerging Contaminants and Chlorinated Solvent Contaminated Groundwater

2. FY14 SERDP SONs

2.1 Improved Remediation Operation through Fine Scale Delineation of Contaminated Subsurface Environments

SON Objectives

The objective of this Statement of Need (SON) is to improve the operation of remedial technologies through fine-scale delineation of contaminated subsurface environments. Work may include more detailed and cost-effective techniques and data analyses and interpretation to delineate processes within either the unsaturated or saturated zones, and within either consolidated or unconsolidated media. Clear linkage between the proposed techniques and resulting data interpretation, and contaminated site management decisions should be demonstrated with the recognition that many sites are likely to have already completed initial characterization efforts, but site challenges necessitate additional investigation.

Proposed research should focus on developing technologies that address the following issues:

- Improved delineation of contaminant distribution after initial characterization activities have been conducted and while the remedial action-operation phase is in progress;
- Improved measurements of key biogeochemical processes at relevant scales; and
- Improved resolution of key hydrogeological features.

Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort. Technologies and approaches should be applicable to a variety of hydrogeologic settings. Proposals that propose a new tool without clearly demonstrating how the collected data will improve site management decision making will not be considered.

2.2 In Situ Remediation of Perfluoroalkyl Contaminated Groundwater

SON Objectives

The objective of this Statement of Need (SON) is to seek applied research to develop cost effective in situ remedial alternatives for perfluoroalkyl contaminated groundwater. Proposed efforts should focus on the following objectives:

- Develop cost effective, in situ remedial approaches for treating perfluoroalkyl contaminated groundwater.
- Assess the impact of common co-contaminants on the remedial process given that these compounds were commonly utilized at sites contaminated with petroleum hydrocarbons and possibly chlorinated solvents (e.g., historical fire training sites).
- Determine the necessity for treatment train approaches to facilitate treatment of co-contaminants.

Contaminants of interest include perfluoroalkyl sulfonates and perfluoroalkyl carboxylates, such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), contained in historical aqueous film forming foam (AFFF) formulations. Research and development activities at laboratory-, bench-, and field-scale will be considered, although work does not necessarily have to culminate in a field-scale effort. Technologies and approaches should be applicable to a variety of hydrogeologic settings. Ex situ technologies will not be considered. Proposers should be cognizant of previous SERDP-funded research that focused on developing a better understanding of fate and transport properties of perfluoralkyl contaminants in groundwater, and of the mechanisms involved in contaminant destruction (projects ER-2126, ER-2127, ER-2128).

3. FY13 SERDP SONs

3.1 In Situ Remediation of 1,4-Dioxane Contaminated Groundwater

SON Objectives

The objective of this Statement of Need (SON) is to seek innovative research to develop cost effective in situ remedial alternatives for 1,4-dioxane-contaminated groundwater. Consideration also must be given to common co-contaminants and how these co-contaminants impact the proposed treatment technology. Proposed research should focus on developing technologies that address the following issues:

- Develop cost effective, in situ remedial alternative to current approaches;
- Elucidate the impact of co-contaminants on the remedial process; and
- Evaluate whether remedial processes for 1,4-dioxane contamination can operate in parallel or in series with traditional treatment processes for co-contaminants.

Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort. Technologies and approaches should be applicable to a variety of hydrogeologic settings. Ex situ technologies will not be considered.

Projects Selected

ER-2300	In Situ Biodegradation of 1,4-Dioxane: Effects of Metals and Chlorinated Solvent Co-Contaminants	Shaily Mahendra (UCLA)
ER-2301	Developing and Field-Testing Genetic Catabolic Probes for MNA of 1,4-Dioxane with a One-Year Timeframe	Pedro Alvarez (Rice University)
ER-2302	Facilitated Transport Enabled In Situ Chemical Oxidation of 1,4-Dioxane-Contaminated Groundwater	Kenneth Carroll (PNNL)
ER-2303	Evaluation of Branched Hydrocarbons as Stimulants for In Situ Cometabolic Biodegradation of 1,4-dioxane and Its Associated Co-Contaminants	Michael Hyman (North Carolina State University)
ER-2304	Development of a Passive Flux Meter Approach to Quantifying 1,4-Dioxane Mass Flux	Michael Annable (University of Florida)
ER-2305	Proof-of-Concept Study: Novel Microbially-Driven Fenton Reaction for In Situ Remediation of Groundwater Contaminated With 1,4-Dioxane, PCE & TCE	Thomas DiChristina (Georgia Tech)
ER-2306	In Situ Bioremediation of 1,4-Dioxane by Methane Oxidizing Bacteria In Coupled Anaerobic-Aerobic Zones	Charles Schaefer (CB&I)
ER-2307	In Situ Treatment and Management Strategies for 1,4-Dioxane-Contaminated Groundwater	David Adamson (GSI Environmental)

3.2 Improved Assessment and Optimization of Remediation Technologies for Treatment of Chlorinated Solvent-Contaminated Groundwater

SON Objectives

The objective of this Statement of Need (SON) is to solicit proposals for applied research to improve our understanding of how to assess and optimize treatment of complex contaminated groundwater plumes and to determine cost effectively the performance limitations of a remedial approach. Specific objectives include:

- Determination of which parameters or processes may be measured to quickly determine the feasibility of a treatment approach.
- Development of field measurements or methodologies that provide predictive capability of performance to reduce the uncertainty associated with long-term performance so that decisions can be made early in the remedial process to avoid years of suboptimal operation.
- Development of field measurements or methodologies that provide data to optimize treatment if current operations are not expected to meet performance objectives.
- Development of assessment procedures and methodologies that aid in the decision to discontinue operation of a technology and implement an alternative technology.

Assessment procedures and methodologies are likely to be technology-specific; therefore, proposals should focus on standard remedial technologies, such as bioremediation, thermal treatment, monitored natural attenuation (MNA), and chemical addition. Procedures and methodologies for the more challenging sites are the focus of this call (i.e., dense nonaqueous phase liquid [DNAPL] source zones; fractured matrices; or large, dilute plumes). Assessment procedures and methodologies should be applicable to a variety of hydrogeologic settings as well as to evaluation of technologies at various stages of the remedial process, including pilot-scale testing, active operation, and post-monitoring.

Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort. Proposals focused solely on modeling efforts will not be considered; proposed efforts must be tied into field measurements and assessments, but may incorporate modeling aspects. Proposals focused on developing new treatment technologies also will not be considered.

In June 2011, SERDP and the Environmental Security Technology Certification Program (ESTCP) co-sponsored a Workshop on *Investment Strategies to Optimize Research and Demonstration Impacts in Support of DoD Restoration Goals.* This workshop identified high priority research topics involving improved assessment and optimization of remediation technologies for treatment of chlorinated solvent-contaminated groundwater. A more detailed description of these issues can be found in the report from the workshop (www.serdp-estcp.org/content/download/12020/145838/version/2/file/Investment+Strategies+Workshop+Report_October+2011.pdf). Proposers are strongly encouraged to review the workshop report for additional detail.

Projects Selected

ER-2308	Practical Assessment and Optimization of Redox-Based Groundwater Remediation Technologies	Paul Tratnyek (Oregon Health & Science University)
ER-2309	Development of Field Methodology to Rapidly Detect Dehalococcoides and Dehalobacter Spp. Genes On-Site	Alison Cupples (Michigan State University)
ER-2310	A Practical Approach for Remediation Performance Assessment and Optimization at DNAPL Sites for Early Identification and Correction of Problems Considering Uncertainty	Jack Parker (University of Tennessee)
ER-2311	Development of an Integrated Field Test/Modeling Protocol for Efficient In Situ Bioremediation Design and Performance Uncertainty Assessment	Linda Abriola (Tufts University)
ER-2312	Advanced Environmental Molecular Diagnostics to Assess, Monitor, & Predict Microbial Activities at Complicated Chlorinated Solvent Sites	Frank Löffler (University of Tennessee)
ER-2313	Forecasting Effective Site Characterization and Early Remediation Performance	Michael Kavanaugh (Geosyntec)

4. FY11 SERDP SONs

4.1 In Situ Remediation of Perfluoroalkyl Contaminated Groundwater

SON Objectives

The objective of this Statement of Need (SON) is to seek fundamental or applied research to develop cost effective in situ treatment technologies for perfluoroalkyl-contaminated groundwater. Research is needed to better understand fate and transport properties of perfluoralkyl contaminants in groundwater, as well as to gain a basic understanding of the mechanisms involved in contaminant destruction, either via chemical, physical, or microbial means, in order to develop cost-effective remedial technologies. Consideration must also be given to common co-contaminants and how these co-contaminants impact degradation, and fate and transport. Proposed research should focus on one or more of the following specific objectives:

- Improve the fundamental understanding of the mechanisms involved in fate and transport processes in groundwater under varying natural and engineered conditions.
- Determine the impact of co-contaminants on fate and transport processes.
- Improve the understanding of the behavior of perfluoroalkyl contaminants under typical remedial technologies for co-contaminants. For example, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) may be present at sites contaminated with petroleum hydrocarbons and possibly chlorinated solvents (e.g., historical fire training sites); therefore, understanding the fate of PFOS and PFOA during monitored natural attenuation or enhanced anaerobic dechlorination is critical.
- Develop remedial strategies for perfluororalkyl contaminants, including consideration of the necessity for treatment train approaches to facilitate treatment of co-contaminants.

Contaminants of interest include perfluoroalkyl sulfonates and perfluoroalkyl carboxylates, such as PFOS and PFOA, contained in historical aqueous film forming foam (AFFF) formulations. Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort. Technologies and approaches should be applicable to a variety of hydrogeologic settings.

Projects Selected

2126-11	Behavior of Perfluoroalkyl Chemicals in Contaminated Groundwater	Christopher Higgins (Colorado School of Mines)
2127-11	Remediation of Perfluoroalkyl Contaminated Aquifer Using an In Situ Two-Layer Barrier: Laboratory Batch and Column Study	Qingguo «Jack» Huang (University of Georgia)
2128-11	Characterization of the Fate & Biotransformation of Fluorochemicals in AFFF-Contaminated Groundwater at Fire/Crash Testing Military Sites	Jennifer Field (Oregon State University)

4.2 Improved Understanding of Impacts to Groundwater Quality Post-Remediation

SON Objectives

The objective of this Statement of Need (SON) is to develop an improved understanding of the near- and long-term impacts to groundwater quality after implementation of common in situ remediation approaches. In addition, development of methods to predict and/or monitor such impacts and adjust remediation strategies to minimize negative effects while achieving remedial goals is of interest. Common treatment approaches result in removal of chemical contamination of concern, but may produce an aquifer that is degraded in terms of other important groundwater quality parameters. Proposals may address one or more of the following objectives:

- Improve our understanding of the impacts to groundwater quality due to implementation of common remediation approaches such as enhanced anaerobic remediation, thermal treatment, or in situ chemical oxidation.
- Develop methods and/or tools that will predict the near-term impacts of remediation efforts on groundwater quality and allow for the assessment of strategies to minimize negative effects while achieving remedial goals.
- Develop methods and/or tools to predict the long-term impacts to groundwater quality from remediation efforts and the potential for aquifer recovery.

Groundwater quality parameters of importance include dissolved metals, organic carbon amounts and quality, methane and otherwise hazardous gas generation, and geochemical parameters affecting natural attenuation processes. Research and development at the laboratory, bench, and field scales will be considered.

Projects Selected

2129-11	Secondary Impacts of In Situ Remediation on Groundwater Quality and Post-Treatment Management Strategies	Kurt Pennell (Tufts University)
2130-11	Assessing the Potential Consequences of Subsurface Bioremediation: Fe-oxide Bioreductive Processes and the Propensity for Contaminant-Colloid Co-Transport and Media Structural Breakdown	Phil Jardine (University of Tennessee)
2131-11	Numerical Modeling of Post-Remediation Impacts of Anaerobic Bioremediation on Groundwater Quality	Bob Borden (North Carolina State University)
2132-11	Impacts on Groundwater Quality following the Application of ISCO: Understanding the Cause of and Designing Mitigation for Metals Mobilization	Kevin Gardner (University of New Hampshire)

5. FY10 SERDP SONs

5.1 The Impact of Contaminant Storage in Low-Permeability Zones on Chlorinated Solvent Groundwater Plumes

SON Objectives

The objective of this Statement of Need (SON) is to solicit proposals for fundamental and applied research to improve our understanding of the impact that contaminants stored in low permeability zones in unconsolidated materials may have on the behavior of contaminated groundwater plumes. Contaminant storage in low-permeability zones may occur through diffusion or sorption of dissolved-phase contaminants over time and may serve as long-term sources of contaminants, thus limiting our ability to reach groundwater cleanup goals. Proposals should focus on the following objectives to fill gaps in the current knowledge base:

1. Improve our understanding of how low-permeability zone storage of contaminants occurs, the hydrogeochemical conditions that contribute to this process, and how the contaminants within these zones respond to standard treatment approaches.
2. Develop improved methods for assessing and predicting whether storage of contaminants in low-permeability zones has occurred and is contributing to sustaining the dissolved phase plume.
3. Develop approaches to improve our ability to measure and predict the performance of standard treatment approaches for dissolved-phase plumes that are sustained through storage of contaminants in low-permeability zones.

Proposals that focus on only Objectives 2 or 3 will not be considered, because the basic process of contaminant storage in low-permeability zones must be understood before assessment or management methods can be developed. In addition, proposals that focus on fractured geologic media or the development of new treatment approaches will not be considered.

Research proposals can involve laboratory-, bench-, and field-scale studies, as well as computer modeling to support such efforts. Key contaminants of interest are the chlorinated ethene solvents (tetrachloroethene [PCE], trichloroethene [TCE], and their daughter products).

Projects Selected

1737-10	Impact of Clay-DNAPL Interactions on Transport and Storage of Chlorinated Solvents in Low Permeability Zones	Avery Demond (University of Michigan)
1738-10	The Importance of Sorption in Low-Permeability Zone on Chlorinated Solvent Plume Longevity in Sedimentary Aquifers	Richelle Allen-King (SUNY – University at Buffalo)
1739-10	The Behaviour of Compound Specific Stable Isotopes During the Storage of Chlorinated Solvents in Low-Permeability Zones through Diffusion and Sorption	Orfan Shouakar-Stash (University of Waterloo)
1740-10	Basic Research Addressing Contaminants in Low Permeability Zones	Tom Sale (Colorado State University)

6. FY09 SERDP SONs

6.1 Reduced Uncertainty and Costs for Managing Large Dilute Contaminant Groundwater Plumes

SON Objectives

The objective of this Statement of Need (SON) is to solicit fundamental and applied research designed to improve our ability to manage large, dilute groundwater plumes of key contaminants of concern to the Department of Defense. Results of this research are expected to reduce the uncertainty and costs associated with managing these plumes and allow for more informed decision-making.

The research should focus on one or more of the following objectives:

- Develop more cost-effective techniques to remediate large, dilute groundwater plumes, including techniques to enhance natural attenuation processes. The focus is on deep plumes where traditional reactive barriers are ineffective.
- Improve the ability to evaluate, demonstrate, and measure relatively slow attenuation processes that may contribute to chlorinated solvent plume stabililization.
- Develop a better understanding and improved methods to evaluate and measure processes responsible for sustaining chlorinated solvent plumes following reduction of the contaminant influx. Such processes may include matrix storage of contaminants in low permeability zones and associated diffusion from these zones.

Research and development at the laboratory, bench, and field scales will be considered. Proposals may address any or all of the above topics. Key contaminants of interest for Objective 1 above include chlorinated solvents (tetrachloroethene [PCE], trichloroethene [TCE], and their daughter products), perchlorate, and 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX). Objectives 2 and 3 however, are relevant only to chlorinated solvent plumes. Please note, proposals that focus on development of cost-effective techniques for remediation of only shallow groundwater plumes are not encouraged.

Projects Selected

1683-09	Quantifying the Presence and Activity of Aerobic, Vinyl Chloride-Degrading Microorganisms in Dilute Groundwater Plumes by Using Real-Time PCR	Timothy Mattes (The University of Iowa)
1684-09	Semi-Passive Oxidation-Based Approaches for Control of Large, Dilute Groundwater Plumes of Chlorinated Ethylenes	Frank Schwartz (The Ohio State University)
1685-09	Coupled Diffusion & Reaction Processes in Rock Matrices: Impact on Dilute Groundwater Plumes	Charles Schaefer (CB&I Federal Services)

6.2 Improved Understanding of the Vapor Intrusion Pathway from Chlorinated Solvent-Contaminated Groundwater Plumes

SON Objectives

The objective of this Statement of Need (SON) is to solicit fundamental and applied research that leads to better pathway assessment for vapor intrusion from chlorinated solvent-contaminated groundwater. Specific objectives include:

- Gain a better understanding of natural spatial and temporal variations in vapor intrusion measurements and how to account for such variability in pathway assessment.
- Improve our ability to obtain accurate and cost-effective characterization of key site parameters that impact the vapor intrusion pathway.
- Improve our ability to predict vapor behavior under various physical, climatic, and/or geochemical conditions.
- Improve our understanding of vapor attenuation mechanisms.

Research proposals can involve laboratory-, bench-, and field-scale studies, as well as computer modeling to support such efforts; however, it is critical that modeling or laboratory efforts be integrated with field-observable data. The contaminants of interest are those chlorinated solvents that typically compose chlorinated solvent-contaminated groundwater plumes at DoD sites (tetrachloroethene [PCE], trichloroethene [TCE], and their daughter products.

Projects Selected

1686-09	Integrated Field-Scale, Lab-Scale, & Modeling Studies for Improving Ability to Assess Groundwater to Indoor Air Pathway at Chlorinated Solvent-Impacted Groundwater Sites	Paul Johnson (Arizona State University)
1687-09	Vapor Intrusion From Entrapped NAPL Sources and Groundwater Plumes: Process Understanding and Improved Modeling Tools for Pathway Assessment	Tissa Illangasekare (Colorado School of Mines)

7. FY08 SERDP SONs

7.1 Improved Methods and Practices for Long-Term Monitoring of Contaminated Groundwater

SON Objectives

The objective of this SON is to seek applied research leading to reductions in the costs of long-term monitoring (LTM) at sites with contaminated groundwater. The research should include one or more of the following:

- More cost-effective methods for efficient analysis of key contaminants of concern.
- Improved and more cost-effective tools (e.g., passive sensor systems) for data collection.
- Improved practices or guidance leading to more cost-efficient monitoring programs.

Research must be applied and must be able to demonstrate methods or tools that are cost effective through robustness and ease-of-use. Proposals which do not include an assessment of cost-effectiveness will not be considered. Contaminants of concern include chlorinated hydrocarbons (PCE, TCE, and daughter products), perchlorate, energetics (RDX, HMX, and TNT), and heavy metals. Other hydrogeochemical factors also may be considered, such as those needed for monitored natural attenuation assessments. The research must be focused on reducing the overall costs for LTM of contaminated sites.

Projects Selected

1601-08	New Cost Effective Method for Long Term Groundwater Monitoring Programs	Charles Newell (Groundwater Services, Inc.)
1602-08	A Portable Fiberoptic Surface Enhanced Raman Sensor for Real-Time Detection and Monitoring of Perchlorate and Energetics	Baohua Gu (ORNL)
1603-08	Micro ion mobility sensor (MIMS) for in situ monitoring of contaminated groundwater	Jun Xu (ORNL)
1604-08	Periodic Mesoporous Organosilicas (PMOs) as Pre-Concentration Elements for Improved LTM of Key Contaminants in Groundwater	Brandy White (Naval Research Laboratory)
1605-08	Novel Sensor for Real-Time Characterization and Monitoring of Chlorinated Hydrocarbons in Groundwater	Bill Major (NFESC)

7.2 Improved Understanding and Prediction of Plume Response to DNAPL Source Zone Architecture and Depletion

SON Objectives

The objective of this SON is to improve our understanding and ability to predict the response of the chlorinated solvent dissolved phase plume to the architecture and possible depletion of the DNAPL source zone. This SON has two primary objectives: (1) to integrate and assess the current understanding of DNAPL source zones with field-observed phenomenon, and (2) to develop techniques by which cost-effective measurements may be made of key parameters defining the DNAPL source zone that will enable the prediction of the source zone's impact on the resulting plume. Research should focus on one or more of the following specific objectives:

- Improve our understanding and assess the role and impact at field sites of the sorption and diffusion of DNAPLs into low-permeability matrices.
- Improve our understanding of the relation of the ganglia-to-pool ratio to DNAPL source zone dissolution and its significance under field conditions.
- Improve our understanding of the impact of DNAPLs located in low-permeability matrices on contaminant concentrations in more permeable media.
- Improve our understanding of how the depletion of DNAPLs in flow-limited and/or flow-accessible zones impacts plume response in terms of plume size, strength, and longevity.
- Develop and/or improve predictive models of the impacts of the DNAPL source zone on plume response in terms of plume size, strength, and longevity that are relevant to assist in cleanup decision making.
- Develop cost-effective methods for evaluating source function and other key parameters, such as the ganglia-to-pool ratio.
- Develop cost-effective methods for assessing the DNAPL source zone architecture.
- Develop guidelines for determining the level and type of characterization required at a given site.

The SERDP co-sponsored an Expert Panel Workshop on Reducing the Uncertainty of DNAPL Source Zone Remediation (March 2006) that identified high priority research topics in this area. Results from the Expert Panel Workshop emphasized the need for an understanding of plume response to DNAPL source zone architecture and depletion. A more detailed description of these issues can be found in the report from the Expert Panel Workshop (http://docs.serdp-estcp.org/viewfile.cfm?Doc=DNAPLWorkshopReport%2Epdf).

Research proposals can involve laboratory-, bench-, and field-scale studies, as well as computer modeling to support such efforts. However, it is critical that modeling or laboratory efforts be integrated with field-observable data and be relevant to cleanup decisions that must be made in light of significant uncertainties. The contaminants of interest are those chlorinated solvents that typically compose DNAPL source zones at DoD sites (PCE and TCE). Technologies and approaches may be applicable to a variety of hydrogeologic scenarios.

Given the broad scope of research required to address this SON, SERDP expects to confer multiple awards.

Projects Selected

1610-08	Computational and experimental investigation of contaminant plume response to DNAPL source zone architecture and depletion in porous and fractured media	Ed Sudicky (University of Waterloo)
1611-08	Practical Cost-Optimization of Characterization and Remediation Decisions at DNAPL Sites with Consideration of Prediction Uncertainty	Jack Parker (University of Tennessee)
1612-08	Metric Identification and Protocol Development for Characterizing DNAPL Source Zone Architecture and Associated Plume Response	Linda Abriola (Tufts University)
1613-08	Predicting DNAPL Source Zone and Plume Response Using Site-Measured Characteristics	Michael Annable (University of Florida)
1614-08	The Impact of DNAPL Source-Zone Architecture on Contaminant Mass Flux and Plume Evolution in Heterogeneous Porous Media	Mark Brusseau (University of Arizona)

8. FY07 SERDP SONs

8.1 Improved Understanding of Remediation Performance in Fractured Geological Settings

SON Objectives

This SON seeks to develop an improved understanding of how the complexities associated with fractured geology impact the performance and monitoring of contaminated groundwater remediation technologies. Research should focus on how best to deploy, modify, and/or assess existing remediation, characterization and monitoring technologies to improve success in the removal of groundwater contamination in fractured geological settings. Results from these efforts should lead to: (1) improved understanding of the impact of varying subsurface conditions on overall removal and destruction efficiency during remedial treatment; (2) identification of the limitations associated with remediation in fractured geological settings; and (3) development of improved application and monitoring methodologies.

Contaminants of greatest interest are chlorinated solvents, perchlorate, and munitions constituents (e.g., RDX, TNT). Proposals should focus on developing a better understanding of how the fractured bedrock matrix impacts remediation performance and assessment as opposed to proposing new technologies to remediate contaminants of concern. Research and development activities at the laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1553-07	Contaminant Mass Transfer During Boiling in Fractured Geologic Media	Ron Falta (Clemson University)
1554-07	DNAPL Dissolution in Bedrock Fractures and Fracture Networks	Charles Schaefer (CB&I Federal Services)
1555-07	A Comparison of Pump-and-Treat, Natural Attenuation, and Enhanced Biodegradation to Remediate Chlorinated Ethene-Contaminated Fractured Rock Aquifers	Allen Shapiro (USGS)

8.2 Identification of Biomarkers to Assess Groundwater Contaminant Degradative Potential of A Microbial Population

SON Objectives

The objective of this SON is to identify relevant biomarkers that will ultimately enhance our ability to effectively manage bioremediation of contaminated groundwater. Biomarkers are needed that expand our ability to assess the degradative potential of a microbial population. Proposals should focus on biomarkers for microbial processes involved in the degradation of contaminants that are common in DoD contaminated groundwater, such as chloroethanes, chloroethenes, energetic compounds, or perchlorate. Proposals should address one or more of the following specific objectives:

- Identify and develop biomarkers for organisms and their associated microbial communities that are involved in degrading chloroethenes or other relevant groundwater contaminants of concern to DoD.
- Identify and develop biomarkers to evaluate community structure and to assess the total degradative potential of a microbial population.
- Develop the relationship between existing or proposed biomarker measurements and functional activity or *in situ* contaminant degradation rates.
- Develop improved methods (i.e. culturing, metagenomic, proteomic etc.) in order to support identification and development of key biomarkers and their relationship to functional activity.

The SERDP co-sponsored an Expert Panel Workshop on Research and Development Needs for the Environmental Remediation Application of Molecular Biological Tools (August 2005), which has identified high priority research topics in this area. Results from the Expert Panel Workshop emphasized the need for identification of additional, critical biomarkers. A more detailed description of the issues described above can be found in the report from the Expert Panel Workshop (http://docs.serdp-estcp.org/viewfile.cfm?Doc=MBT%20Workshop%20Report%2Epdf). Proposers are encouraged to review this report for additional details. Research and development activities at laboratory-, bench-, and field-scales will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1563-06	Prokaryotic cDNA Subtraction: A Method to Rapidly Identify Functional Gene Biomarkers	Mary Jo Kirisits (University of Texas Austin)
1586-06	BioReD: Biomarkers and Tools for Reductive Dechlorination Site Assessment, Monitoring, and Management	Frank Löffler (University of Tennessee)
1587-06	Application of microarrays and qPCR to identify phylogenetic and functional biomarkers diagnostic of microbial communities that biodegrade chlorinated solvents to ethene	Lisa Alvarez-Cohen (UC Berkeley)
1588-06	Molecular Biomarkers for Detecting, Monitoring, and Quantifying Reductive Microbial Processes	Alfred Spormann (Stanford University)

8.3 Investigation of *cis*-Dichloroethene and Vinyl Chloride Degradation Mechanisms and Environmental Relevance

SON Objectives

The objective of this SON is to further define the mechanisms responsible for the destruction of *cis*-DCE and VC in groundwater environments. This SON seeks to reduce the uncertainties regarding the environmental fate of *cis*-DCE and VC at many sites and improve our ability to select and design appropriate remediation strategies. Proposed research should focus on one or more of the following objectives:

- Determine abiotic or biotic mechanisms of *cis*-DCE and/or VC degradation under either aerobic or anaerobic conditions.
- Develop a better understanding of the various degradation pathways and reaction kinetics for *cis*-DCE and/or VC, such that obtaining a mass balance is possible.
- Determine the relative significance of the various degradation mechanisms for *cis*-DCE and/or VC under field conditions.
-

Proposed research should be relatively narrow in scope and level of effort. Research and development activities at laboratory-, bench-, and field-scale will be considered, but should directly relate to understanding the fate of *cis*-DCE and VC in the field.

Projects Selected

1556-07	Characterization of Microbes Capable of Using Vinyl Chloride as a Sole Carbon and Energy Source by Anaerobic Oxidation	David Freedman (Clemson University)
1557-07	Elucidation of the Mechanisms & Environmental Relevance of cis-DCE and VC Biodegradation	Evan Cox (GeoSyntec)
1558-07	Microbial DCE and VC Oxidation and the Fate of Ethene and Ethane Under Anoxic Conditions	Paul Bradley (USGS)

8.4 Improved Sampling Techniques for Efficient Use of Molecular Biological Tools To Assess Groundwater Remediation

SON Objectives

The objective of this SON is to develop a better understanding of the effects of the sampling process on the accuracy and efficacy of molecular biological tools (MBTs) and to develop improved sampling techniques for the efficient use of MBTs in groundwater and associated saturated soils environments. Proposers should focus on those tools and techniques for relevant biomarkers that are currently available to measure nucleic acids, proteins or lipids. Proposals should address one or more of the following specific objectives:

- Develop a better understanding of the effects on the efficacy of MBTs of all steps in the sampling process, including sample collection, transport, storage/preservation, and processing.

- Develop improved sampling and processing techniques for groundwater and associated saturated soil samples that would support the use of biomarkers for environmental remediation.
- Develop a better understanding of the relationship between the density of gene copies or other relevant biomarkers in a groundwater or associated saturated soil sample and the true density of microorganisms in the aquifer, and the impacts that sampling procedures may have on establishing such a relationship.

The SERDP co-sponsored an Expert Panel Workshop on Research and Development Needs for the Environmental Remediation Application of Molecular Biological Tools (August 2005), which has identified high priority research topics in this area. Results from the Expert Panel Workshop emphasized the need for an understanding of the impacts of sampling on the efficacy of MBTs. A more detailed description of these issues can be found in the report from the Expert Panel Workshop (http://docs.serdp-estcp.org/viewfile.cfm?Doc=MBT%20Workshop%20Report%2Epdf). Proposers are encouraged to review this report for additional details. Research and development activities at laboratory-, bench-, and field-scales will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1559-07	Cryogenic Collection of Complete Subsurface Samples for Molecular Biological Analysis	Rick Johnson (Oregon Health & Science University)
1560-07	Impacts of Sampling and Handling Procedures on DNA- and RNA-based Microbial Characterization and Quantification	Francis de los Reyes (North Carolina State University)
1561-07	Standardized Procedures for Use of Nucleic Acid-Based Tools	Carmen Lebron (NFESC)

9. FY06 SERDP SONs

9.1 Improved Understanding of The Distribution and Impacts of Subsurface Remedial Amendments In Groundwater

SON Objectives

The objective of this SON is to seek fundamental or applied studies to develop an understanding of the migration and mixing of amendments injected to enhance the remediation of contaminated groundwater. The research should focus on one or more of the following specific objectives:

- Improved fundamental understanding of amendment distribution during and after emplacement.
- Validation of the distribution and effects of amendments through improved monitoring techniques, novel sensing methods, and/or three-dimensional visualization techniques after initial emplacement.
- Improved understanding of the extent to which amendments affect the flow-regime in and around the zone of emplacement.
- Improved understanding of novel and current delivery methods that can be used to increase the probability of achieving contact between amendment and contaminant.
- Improved understanding of the effects of injection pressures on the survival of both indigenous and added microorganisms.
- Improved understanding of the control of amendment reactivity.

Amendments of interest include, but are not limited to emulsified oil, nanoscale iron, electron donors, chemical oxidants and reductants, and biological cultures. Contaminants of greatest interest are chlorinated solvents, perchlorate, and munitions constituents (e.g., RDX, TNT). Proposals preferably should focus on developing an understanding of injection techniques and amendments that are commonly employed in the field; however, enhancements of existing technologies will be considered if a significant benefit can be demonstrated. The research should lead to a better understanding of which site specific factors control delivery, mixing, and contact processes in the subsurface environment and how to effectively monitor these factors to aid in the design of site-specific remediation approaches. Research and development activities at the laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1484-06	Control of Manganese Dioxide Particles Resulting from In Situ Chemical Oxidation Using Permanganate	Michelle Crimi (Colorado School of Mines)
1485-06	Fundamental Study of the Delivery of Nanoiron to DNAPL Source Zones in Naturally Heterogenous Field Systems	Greg Lowry (Carnegie Mellon University)
1486-06	Multi-Scale Experiments to Evaluate Mobility Control Methods for Enhancing the Sweep Efficiency of Injected Subsurface Remediation Amendments	John McCray (Colorado School of Mines)
1487-06	Development and Optimization of Targeted Nanoscale Iron Delivery Methods for Treatment of NAPL Source Zones	Linda Abriola (Tufts University)
1489-06	Enhanced Reactant-Contaminant Contact through the Use of Persulfate In Situ Chemical Oxidation	Rick Watts (Washington State University)
1490-06	Improved Monitoring Methods for Performance Assessment during Remediation of DNAPL Source Zones	Bob Siegrist (Colorado School of Mines)

10. FY05 SERDP SONs

10.1 Remediation of Emergent Contaminants

SON Objectives

The objective of this SON is to seek fundamental or applied studies to develop remedial alternatives for several emergent contaminants. Basic understanding of the mechanisms involved in contaminant destruction, either via chemical or microbial means, is needed in order to develop adequate remedial technologies. Consideration must also be given to common co-contaminants and how these co-contaminants impact degradation. The research should focus on the following specific research objectives:

- Improved fundamental understanding of the mechanisms involved in degradation processes under varying natural and engineered conditions.
- Elucidation of the impact of co-contaminants on degradation processes.
- Improved understanding of the behavior of emergent contaminants under typical remedial technologies for co-contaminants. For example, 1,4-dioxane is a co-contaminant with chlorinated solvents; therefore, understanding the reaction pathway for 1,4-dioxane during monitored natural attenuation or enhanced anaerobic dechlorination would be critical.
- Development of remedial strategies for emergent chemicals, including consideration of the necessity for treatment train approaches to facilitate treatment of co-contaminants.

Specific emergent contaminants of interest include 1,4-dioxane, N-nitrosodimethylamine (NDMA), and 1,2,3-trichloropropane (TCP). Proposals addressing other emergent contaminants will be considered, but the proposer must clearly define the potential contamination problem, current understanding of degradation pathways, and likelihood of occurrence at DoD and/or DOE facilities. Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort. Technologies and approaches should be applicable to a variety of hydrogeologic settings.

Projects Selected

1417-05	Oxygenase-Catalyzed Biodegradation of Emerging Water Contaminants: 1,4-Dioxane and N-Nitrosodimethylamine	Lisa Alvarez-Cohen (UC Berkeley)
1421-05	Abiotic and Biotic Mechanisms Controlling In Situ Remediation of NDMA	James P. McKinley (PNNL)
1422-05	Biodegradation of 1,4-Dioxane	Rob Steffan (CB&I Federal Services)
1456-05	Bioremediation Approaches for Treating Low Concentrations of N-Nitrosodimethylamine in Groundwater	Paul Hatzinger (CB&I Federal Services)
1457-05	Prospects for Remediation of 1,2,3-Trichloropropane by Natural and Engineered Abiotic Degradation Reactions	Paul Tratnyek (Oregon Health & Science University)

10.2 Improved Understanding of In Situ Thermal Treatment

SON Objectives

The objective of this SON is to seek fundamental or applied studies 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. Results from these efforts should lead to: (1) an improved understanding of the potential of in situ thermal treatment for the removal and destruction of DNAPLs; (2) identification of the limitations associated with thermal treatment; and (3) development of improved application and monitoring methodologies.

Results of this research should directly support the DoD's goal to develop guidance for the use of thermal treatment. Guidance is needed on selecting thermal treatment technology for specific site conditions, selecting among the different technical approaches that are available, and incorporating thermal treatment into an overall site cleanup strategy. Modeling efforts will be considered only to the extent they build on experimental data developed during the research.

Projects Selected

1419-05	Investigation of Chemical Reactivity, Mass Recovery and Biological Activity during Thermal Treatment of DNAPL Source Zones	Kurt Pennell (Tufts University)
1423-05	Large-Scale Physical Models of Thermal Remediation of DNAPL Source Zones in Aquifers	Ralph Baker (TerraTherm)
1458-05	In Situ Thermal Remediation of DNAPL Source Zones	Rick Johnson (OHSU)

11. FY04 SERDP SONs

11.1 Investigation of Abiotic Attenuation Processes Impacting Dissolved Chlorinated Solvents

SON Objectives

The objective of this SON is to clarify the role of abiotic degradation processes in the attenuation of dissolved chlorinated solvents. Specific objectives include: (1) examining the significance of abiotic degradation processes under conditions not normally supportive of reductive dechlorination, (2) defining predominant mechanisms of abiotic degradation processes such as chemical degradation reactions, covalent binding, and/or irreversible sorption; (3) quantifying contaminant removal rates due solely to abiotic degradation processes; and (4) determining geochemical factors that are of primary importance in controlling rates and extent of abiotic degradation processes. Abiotic degradation processes other than dilution, dispersion, volatilization, advection, or reversible sorption are of interest.

Proposed research should be relatively narrow in scope and level of effort. Studies should focus on the contaminants of concern including PCE, TCE, and their breakdown products. Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1368-04	Abiotic Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene in Anaerobic Environments	Elizabeth Butler (University of Oklahoma)
1369-04	Sustainability of Long-Term Abiotic Attenuation of Chlorinated Ethenes	Michelle Scherer (University of Iowa)

12. FY03 SERDP SONs

12.1 DNAPL Source Zone Delineation and Characterization

SON Objectives

The objective of this SON is to develop technologies and approaches to delineate and characterize chlorinated solvent DNAPL source zones. Specific objectives include:

(1) develop better tools and procedures to delineate and characterize DNAPL source zones, and
(2) develop protocols and guidance for cost-effectively characterizing source zones using existing and/or new technologies to aid in selection and design of remediation options

Technologies and approaches should be applicable to a variety of hydrogeologic settings as well as to a variety of source zone configurations. Tools and procedures that aid in our assessment of the impact of source zones on surrounding groundwater as well as the design of treatment options are desired.

Research on improved site characterization techniques should lead to methods that provide the types of information needed for remediation system selection and design. Site characterization often constitutes a large portion of the overall budget and time of a remedial effort. A practical assessment of critical data needs to complete system design is essential when developing site characterization technologies. The contaminants of concern include PCE, TCE, and their breakdown products. Results from this research will aid in developing a better understanding of the nature and extent of DNAPL source zones and in creating a realistic approach to source zone characterization recognizing the inherent limitations. Research and development activities at laboratory-, bench-, and field-scale will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1347-03	Search Strategy for the Definition of A DNAPL Source	George Pinder (University of Vermont)
1365-03	Fusion of Tomography Tests for DNAPL Source Zone Characterization: Technology Development and Validation	Walter Illman (University of Iowa)

12.2 Assessment of Long-Term Sustainability of Monitored Natural Attenuation of Chlorinated Solvents

SON Objectives

The objective of this SON is to seek applied studies to develop a better understanding of the long-term sustainability of natural attenuation of chlorinated solvents such as PCE and TCE and their breakdown products (DCE and VC). Guidance on appropriate characterization methods and development of accurate predictive models are needed as well as effective evaluation and assessment of all natural attenuation processes that might occur, including reductive dehalogenation, aerobic biodegradation, dilution, dispersion, sorption, volatilization, and abiotic degradation. This work should lead to development of a guidance document and tools for assessing the potential for long-term sustainability of natural attenuation of chlorinated aliphatic hydrocarbons at a given site.

Research and development activities at bench-scale level and field studies will be considered. Proposers should demonstrate how their effort will complement, interact, or build upon previous and current research and development activities involving the biotransformation of chlorinated aliphatic compounds in the environment. Proposers should also demonstrate how the anticipated results would assist practitioners to better assess and possibly reduce human and environmental risk associated with chlorinated aliphatic soil and groundwater contamination and assist in designing cost effective remediation approaches.

Projects Selected

1348-03	Using Advanced Analysis Approaches to Complete Long-Term Evaluations of Natural Attenuation Processes on the Remediation of Dissolved Chlorinated Solvent Contamination	Steve Brauner (Parsons)
1349-03	Integrated Protocol for Assessment of Long-Term Sustainability of Monitored Natural Attenuation of Chlorinated Solvent Plumes	Mark Widdowson (Virginia Tech)

13. FY02 SERDP SONs

13.1 Improved Understanding of In Situ Chemical Oxidation

SON Objectives

This SON seeks fundamental or applied studies 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. Results from these efforts should lead to: (1) an improved understanding of the potential of in situ chemical oxidation for the destruction of DNAPLs; (2) identification of the limitations associated with ISCO and (3) development of improved application methodologies.

Results of this research should directly support the DoD's goal to develop guidance for the use of ISCO. Guidance is needed on selecting ISCO technology for specific site conditions, selecting among the different technical approaches that are available, and incorporating ISCO into an overall site cleanup strategy. Modeling efforts will be considered only to the extent they build on experimental data developed during the research.

Projects Selected

1288-02	Improved Understanding of Fenton-Like Reactions for the In Situ Remediation of Contaminated Groundwater Including Treatment of Sorbed Contaminants and Destruction of DNAPLs	Rick Watts (Washington State University)
1289-02	Improved Understanding of In Situ Chemical Oxidation	Eric Hood (GeoSyntec)
1290-02	Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs	Bob Siegrist (Colorado School of Mines)
1291-02	Optimization of In Situ Oxidation via the Elucidation of Key Mechanistic Processes Impacting Technology Maturation and Development of Effective Application Protocol	Denise Macmillan (Army-ERDC)

13.2 Impacts of Source Zone Treatment

SON Objectives

The purpose of this SON is to develop an increased understanding and characterization tools to better assess the need for and impacts of source zone treatment technologies. Specifically, this SON seeks fundamental or applied studies that will 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. This SON seeks an improved understanding of the costs and benefits of technologies designed to remove or destroy residual sources of chlorinated solvents in the subsurface.

The focus of this SON is 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. The research can involve laboratory-, bench- and field-scale studies, as well as computer modeling to support such efforts. The research need not culminate in field-scale efforts. However, the influence of subsurface heterogeneities is considered sufficiently important that research at a level incorporating such heterogeneities should be included.

Projects Selected

1292-02	Decision Support System to Evaluate Effectiveness and Cost of Source Zone Treatment	Chuck Newell (Groundwater Services)
1293-02	Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment	Linda Abriola (Tufts University)
1294-02	Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools	Tissa Illangasekare (Colorado School of Mines)
1295-02	Impacts of DNAPL Source Zone Treatment: Experimental and Modeling Assessment of the Benefits of Partial Source Removal	Lynn Wood (EPA-NRMRL)

13.3 Alternative Technologies for Long Term Monitoring (SEED)

SON Objectives

This SON seeks improved engineering hardware/systems for cost-effective monitoring of contaminants in groundwater and/or soil. The purpose of this SON is to solicit proposals to develop technologies that can be implemented to reduce the financial, personnel, and technical resources necessary for long term monitoring of sites undergoing restoration. Potential applications of the technology include: groundwater and soil assessments.

The proposed work should focus on proof-of-concept for developing innovative engineered hardware/systems for quantifying chemical contaminants in complex environmental settings. Groundwater is the primary environmental media of concern, however, hardware/systems for monitoring soil will also be considered. Primary contaminants of concern include DoD relevant explosive and propellant compounds, heavy metals, and chlorinated solvents. In situ/on-site measurements are the goal, but interim technologies that are demonstrably able to meet the objective of reduced resource commitment for long term monitoring may be considered. The ideal candidate technology would have the following attributes: 1) on-site, 2) in-situ, 3) low initial investment, 4) extended service life, 5) demonstrable potential to meet regulatory requirements and obtain regulatory approval. Successful proposals shall include a short description of how the technology would be deployed in a field setting and a short evaluation of the projected life cycle cost of the proposed technology.

Development of sampling strategies, statistical data analysis, system optimization, and modeling do not fall within this statement of need.

Projects Selected

1296-02	Development of a Surface Enhanced Raman Spectroscopy (SERS)-Based Sensor for the Long-Term Monitoring of Toxic Anions	Pamela Boss (SPAWAR)
1297-02	Integrated Automated Analyzer for Monitoring of Explosives in Groundwater	Yuehe Lin (PNNL)
1298-02	Long-Term Monitoring for Explosives-Contaminated Groundwater	Mark Fisher (Nomadics)

14. FY01 SERDP SONs

14.1 Remediation Strategies to Enhance In Situ Mixing of Contaminants and Chemical/Biological Additives

SON Objectives

The purpose of this SON is to solicit proposals to develop engineering strategies to enhance the in-situ remediation of subsurface groundwater contamination by facilitating in-situ mixing of contaminants and chemical and/or biological additives. This SON seeks improved delivery systems/methodologies for chemical and/or biological additives in the subsurface that will overcome the limited extent of mixing that is achieved with current methods.

The research should focus on developing practical and cost-effective engineering subsurface delivery systems or methodologies. The research should lead to a better understanding of what site specific factors control these mixing processes in the subsurface environment and how to cost effectively identify them as an aid to design site specific remediation approaches. Studies that are aimed at improved characterization of subsurface heterogeneities and/or analysis of dispersion phenomena in geologic media are appropriate only to the extent that they will demonstrably lead to improved and economical remediation methods. Research and development activities at laboratory-scale level, bench-scale level, and field studies will be considered, but work does not necessarily have to culminate in a field-scale effort.

Projects Selected

1203-01	Foam Delivery of Hydrogen for Enhanced Aquifer Contacting and Anaerobic Bioremediation of Chlorinated Solvents	George Hirasaki (Rice University)
1204-01	Innovative Electrochemical Injection and Mixing Strategies for Stimulation of In Situ Bioremediation	Steven Larson (ERDC)
1205-01	Development of Permeable Reactive Barriers (PRBs) Using Edible Oils	Bob Borden (North Carolina State University)
1206-01	Low-Volume Pulsed Biosparging of Hydrogen for Bioremediation of Chlorinated Solvent Plumes	Chuck Newell (Groundwater Services)

15. FY00 SERDP SONs

15.1 Establish Better Understanding of Aerobic and Anaerobic Transformation of *cis*-Dichlorethene and Vinyl Chloride

SON Objectives

This SON seeks innovative laboratory- and bench-scale research approaches that will yield a better fundamental understanding of potential aerobic and anaerobic transformation mechanisms for *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC). In addition, it should lead to a better understand of what site specific factors control these transformation processes in the subsurface environment and how to cost effectively identify them as an aid to design site specific remediation approaches. Research and development activities at laboratory-scale level, bench-scale level, and field studies will be considered, but work does not necessarily have to culminate in a field-scale effort. The proposed work should be completed within three years. Proposers should demonstrate how their effort will complement, interact, or build upon previous and current research and development activities involving the biotransformation of chlorinated aliphatic compounds in the environment. Proposers should also demonstrate how the anticipated results would assist practitioners to better assess and possibly reduce human and environmental risk associated with chlorinated aliphatic soil and groundwater contamination and assist in designing cost effective remediation approaches.

Projects Selected

1167-00	Aerobic and Anaerobic Transformation of *cis*-DCE and VC: Steps for Reliable Remediation	Jim Tiedje (Michigan State University)
1168-00	Characterization of the Aerobic Oxidation of *cis*-DCE and VC in Support of Bioremediation of Chloroethene-Contaminated Sites	Jim Gossett (Cornell University)
1169-00	Factors affecting *cis*-DCE and VC Biological Transformation Under Anaerobic Conditions	Alfred Spormann (Stanford University)

16. ESTCP TOPIC AREA: MANAGEMENT OF CONTAMINATED GROUNDWATER

A topic area on contaminated groundwater has bbeen released in the ESTCP solicitation for several years. While the topic area language has changed over the years to include specific contaminants or matrices of interest, in general, the topic area has remained relatively broad in comparison to SERDP SONs. The topic area on contaminated groundwater released in FY14 is provided below as an example.

Objective

Demonstration projects are sought for tools, methodologies, or technologies that can reduce the cost of managing the Department of Defense's (DoD) long term liability associated with contaminated groundwater. Groundwater contaminants of concern include chlorinated solvents, energetic compounds, metals, emerging contaminants of interest to DoD, or mixtures of these contaminants.

The primary focus of this topic area is innovative technologies and approaches for managing sites and the associated risks where contamination will persist for a significant period of time after an initial remedy is selected. The following areas are of interest:

- Cost-effective management tools or technologies to specifically address chlorinated solvent source zones in complex geological environments that cause persistent groundwater plumes.
- Detailed performance assessments of existing source zone treatment technologies such as in situ bioremediation. Thermal treatment and in situ chemical oxidation assessments will not be considered since recent assessments have been conducted.
- Assessment of how to better combine existing or new technologies to address complex contaminated sites and make informed decisions on transitions from active remediation to passive technologies.
- Risk characterization or remediation of vapors that emanate from contaminated groundwater.
- Optimization, assessment, and/or long-term monitoring tools related to remediation of contaminated groundwater.

Background

The DoD's Installation Restoration Program has set goals to achieve Response Complete (RC) at 95% of Installation Restoration Program (IRP) sites at active installations, and IRP sites at Formerly Used Defense Sites (FUDS) by the end of FY 2021. The Cost to Complete (CTC) at these sites was calculated at $12.8 billion in FY 2010. Of these sites, groundwater contaminated with chlorinated solvents is often the most intractable problem. Substantial progress has been made in the past 20 years in the development of technologies for remediation of contaminated groundwater; however, challenges remain. Remedial costs are particularly high at sites where (1) contamination is extensive, but concentrations are low, (2) DNAPL is present in the subsurface, (3) site hydrogeology is complex (e.g., fractured bedrock), or (4) site conditions require extensive long-term monitoring. The recently released National Research Council study, "Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites" reviews and highlights the technical challenges DoD faces in managing these sites.

Proposed technologies should have completed all required laboratory work, although site-specific treatability work prior to the field demonstration is acceptable. Technologies and methods are sought that have well-defined demonstration/validation questions to address.

ESTCP demonstrations should address technical and/or regulatory issues that inhibit the widespread use of the proposed approach across DoD. ESTCP supports demonstrations at a scale sufficient to determine the operational performance of the remediation technology and to estimate its expected full-scale costs. Full-scale cleanup of specific sites is not performed under ESTCP. Specific DoD demonstration site(s) may be suggested in the pre-proposal, but are not required.

In June 2011, the Strategic Environmental Research and Development Program (SERDP) and ESTCP co-sponsored a Workshop on Investment Strategies to Optimize Research and Demonstration Impacts in Support of DoD Restoration Goals. This workshop identified high priority research topics involving improved assessment and optimization of remediation technologies for treatment of chlorinated solvent-contaminated groundwater. A more detailed description of these issues can be found in the report from the workshop (www.serdp-estcp.org/content/download/12020/145838/version/2/file/Investment+Strategies+Workshop+Report_October+2011.pdf). Proposers are strongly encouraged to review the workshop report for additional detail.

ESTCP has supported the demonstration of a number of technologies designed for protection and remediation of contaminated groundwater. Proposers should be familiar with the ESTCP portfolio of technologies and tools in order to avoid duplication of previous efforts. ESTCP groundwater project descriptions are available on the ESTCP website (http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater).

17. RECENT ESTCP PROJECTS FOCUSED ON CONTAMINATED GROUNDWATER

Ongoing Projects

Natural Attenuation and Biostimulation for In Situ Treatment of 1,2-Dibromoethane (EDB) (ER-201331)

Rapid Assessment of Remedial Effectiveness and Rebound in Fractured Bedrock (ER-201330)

Contaminant Flux Reduction Barriers for Managing Difficult-to-Treat Source Zones in Unconsolidated Media (ER-201328)

1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE) (ER-201326)

Electrokinetic-Enhanced (EK-Enhanced) Amendment Delivery for Remediation of Low Permeability and Heterogeneous Materials (ER-201325)

Sustained In Situ Chemical Oxidation (ISCO) of 1,4-Dioxane Using Slow Release Chemical Oxidant Candles (ER-201324)

Cost-Effective and High-Resolution Subsurface Characterization Using Hydraulic Tomography (ER-201212)

Frequently Asked Questions about Monitored Natural Attenuation in the 21st Century (ER-201211)

Designing, Assessing, and Demonstrating Sustainable Bioaugmentation for Treatment of DNAPL Sources in Fractured Bedrock (ER-201210)

Methods for Minimization and Management of Variability in Long-Term Groundwater Monitoring Results (ER-201209)

Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches (Monitored Natural Attenuation [MNA], Biostimulation and/or Bioaugmentation) at Chlorinated Solvent Sites (ER-201129)

In Situ Biogeochemical Transformation of Chlorinated Solvents (ER-201124)

Direct Push Optical Screening Tool for High Resolution, Real Time Mapping of Chlorinated Solvent DNAPL Architecture (ER-201121)

Development of an Expanded, High-Reliability Cost and Performance Database for In-Situ Remediation Technologies (ER-201120)

Demonstration of a Fractured Rock Geophysical Toolbox (FRGT) for Characterization and Monitoring of DNAPL Biodegradation in Fractured Rock Aquifers (ER-201118)

Solar-Powered Remediation and pH Control (ER-201033)

Determining Source Attenuation History to Support Closure by Natural Attenuation (ER-201032)

Enhanced Amendment Delivery to Low Permeability Zones for Chlorinated Solvent Source Area Bioremediation (ER-200913)

Demonstration and Validation of a Fractured Rock Passive Flux Meter (ER-200831)

Treatment of N-Nitrosodimethylamine (NDMA) in Groundwater Using a Fluidized Bed Bioreactor (ER-200829)

Field Demonstration of Propane Biosparging for In Situ Remediation of N-Nitrosodimethylamine (NDMA) in Groundwater (ER-200828)

Optimized Enhanced Bioremediation Through Four-Dimensional Geophysical Monitoring and Autonomous Data Collection, Processing, and Analysis (ER-200717)

Use of Enzyme Probes for Estimation of Trichloroethene Degradation Rates and Acceptance of Monitored Natural Attenuation (ER-200708)

Assessment of the Natural Attenuation of NAPL Source Zones and Post-Treatment NAPL Source Zone Residuals (ER-200705)

Completed Projects

Decision Support System for Matrix Diffusion Modeling (ER-201126)

Parallel In Situ Screening of Remediation Strategies for Improved Decision Making, Remedial Design, and Cost Savings (ER-200914)

Cooperative Technology Demonstration: Polymer-Enhanced Subsurface Delivery and Distribution of Permanganate (ER-200912)

Verification of Methods for Assessing the Sustainability of Monitored Natural Attentuation (ER-200824)

Combining Low-Energy Electrical Resistance Heating with Biotic and Abiotic Reactions for Treatment of Chlorinated Solvent DNAPL Source Areas (ER-200719)

DNAPL Removal from Fractured Rock Using Thermal Conductive Heating (ER-200715)

Decision and Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty (ER-200704)

In Situ Chemical Oxidation for Groundwater Remediation: Technology Practices Manual (ER-200623)

Protocol for Selecting Remedies for Chlorinated Solvent Releases (ER-200530)

Application of Nucleic Acid-Based Tools for Monitoring MNA, Biostimulation and Bioaugmentation at Chlorinated Solvent Sites (ER-200518)

Develop a Mass Flux Toolkit to Quickly Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives (ER-200430)

Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (ER-200424)

Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent-Contaminated Sites (ER-200318)

Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment (ER-200314)