

SUMMARY REPORT

SERDP and ESTCP Workshop on Research and Development Needs for Chlorinated Solvents in Groundwater

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List of Acronyms

| ASM | Adaptive Site Management |
|-------|---|
| BTEX | benzene, toluene, ethylbenzene and xylene |
| CE | continuing education |
| CSIA | compound specific stable isotope analysis |
| CSM | conceptual site model |
| CVOC | chlorinated volatile organic compound |
| DCA | dichloroethane |
| DCE | dichloroethene |
| DNAPL | dense nonaqueous phase liquid |
| DoD | Department of Defense |
| EMT | Enhanced Monitoring Tools |
| EPA | U.S. Environmental Protection Agency |
| ESTCP | Environmental Security Technology Certification Program |
| HRSC | high resolution site characterization |
| ISCO | in situ chemical oxidation |
| ITRC | Interstate Technology Regulatory Council |
| LSP | Licensed Site Professional |
| LSRP | Licensed Site Remediation Professional |
| MBT | molecular biological tools |
| MCL | maximum contaminant level |
| MNA | monitored natural attenuation |
| NSZD | natural source zone depletion |
| O&M | operation and maintenance |
| P&T | pump and treat |
| PCB | polychlorinated biphenyl |
| PCE | tetrachloroethene |
| PE | Professional Engineer |
| PFAS | per- and polyfluoroalkyl substance |
| PI | Principal Investigator |
| RC | Response Complete |
| RI/FS | Remedial Investigation and Feasibility Study |

| RIP RPM | Remedy in Place Remedial Project Manager |
|------------|--|
| SERDP | Strategic Environmental Research and Development Program |
| TCE | trichloroethene |
| VI | vapor intrusion |

1.0 INTRODUCTION

Chlorinated solvents (chlorinated ethenes, ethanes and methanes) have been used extensively by the Department of Defense (DoD) as cleaners and degreasers, sometimes resulting in accidental releases. As DoD's environmental research programs, the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) have funded research and demonstrations for treatment of contaminated groundwater with chlorinated solvents since the early 1990s. In addition, the Programs have held several workshops over the years (2001, 2006, 2011, and 2014), allowing researchers and users to share perspectives and to assist the Programs in developing a strategic plan for funding research and validation projects.

During the last 20 years, the focus of SERDP and ESTCP has been on developing better characterization tools, decision management and support systems, and remedial technologies to aid DoD users. Principal Investigators (PIs) for the Programs have completed projects on dense nonaqueous phase liquid (DNAPL) source identification and delineation, impacts of treating sources, plume loading, challenges with fractured media, improved distribution of amendments, plume response, remediation treatment technologies' success and vapor phase intrusion. The collective understanding gained through this work has yielded important scientific knowledge that continues to help DoD manage its solvent-contaminated sites.

Nonetheless, the potential magnitude of the DoD's chlorinated solvents liabilities will require a sustained and continuous effort to characterize, treat, monitor, and manage these sites. Recent research efforts have focused on remedy optimization, fine scale delineation, post remediation performance, long-term attenuation, mixed contamination, and abiotic attenuation. These research areas reflect the fact that most of the less complex sites have been cleaned up to some extent, and the remaining sites are often highly challenging.

Given these investments, SERDP and ESTCP held a strategic workshop to review the current state of the science and identify the most pressing needs for future research, demonstrations, and technology transfer. A considerable amount of work has been completed; hence, based on user needs and technology challenges, the primary concern is what research remains to be addressed with respect to management of groundwater sites contaminated with chlorinated solvents.

The objectives of this workshop were to (1) review the current state of the science regarding chlorinated solvent contamination in groundwater; (2) evaluate whether currently available characterization, remediation, and monitoring technologies meet users' needs and requirements; and (3) identify and prioritize remaining research needs and opportunities.

The two-day workshop held July 18-19, 2018 in Seattle, WA consisted of formal presentations describing the state of the science and current management challenges as well as barriers and limitations to achieving cleanup goals. The presentations were followed by group breakout discussions intended to identify the optimal role for SERDP and ESTCP in improving management of DoD's current chlorinated solvent sites.

2.0 WORKSHOP APPROACH

The workshop was attended by approximately 60 invited personnel, representing DoD and EPA remedial project managers (RPMs), federal and state regulatory scientists and engineers, university researchers, industry representatives, and environmental consultants. The agenda for the workshop is provided in Appendix A, and the attendee list is provided in Appendix B.

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 presentations intended to establish the current status of management of chlorinated solvent contaminated groundwater, both from the perspective of the private sector and the DoD.

Two breakout sessions, each with five working groups, facilitated discussions of the current state of the science of management of contaminated groundwater sites, reviewed where DoD facilities are in their management of these sites, and determined what specific tools, demonstration, or information transfer needs existed that would facilitate cost effective site management.

On Day 1, each working group addressed the same charge comprised of a list of key questions formulated by the Program Office. These questions, which were provided in advance to the participants, are as follows:

- 1. Future Directions
 - Are there issues associated with contaminated groundwater that have not yet been addressed adequately? Do we need to revisit issues we thought to be complete (e.g., petroleum hydrocarbons, etc.)?
- 2. Defining the new conceptual site model (CSM) for remaining sites in the DoD inventory
 - Do we have source zones that still need to be addressed?
 - How should we address back-diffusion?
 - How does the presence of contaminants such as per- and polyfluoroalkyl substances (PFASs), halogenated ethanes, 1,4-dioxane, and other emerging and recalcitrant compounds impact the CSM?
- 3. Site characterization and fine scale delineation
 - Do we have the tools we need?
 - What major challenges and opportunities in characterizing and managing chlorinated solvent sites remain?
- 4. Long term performance of remediation technologies
 - What are the most promising technologies?
 - What are the opportunities to reduce monitoring and operation and maintenance (O&M) costs?
- 5. Technology transfer issues
 - Where is technology transfer most critically absent?
 - What methodologies could be used to improve technology transfer to key communities?

The second breakout session built on the first by developing prioritized research, demonstration, and technology transfer needs. Needs were prioritized as either critical or high priority, largely based on the sequence of events required to impact DoD site management within 3 to 5 years of research and demonstration initiation (Table 1).

The entire group then participated in a final discussion to select the critical and high priority research, demonstration, and technology transfer needs. Following the meeting, several of the participants contributed to sections of this report describing specific issues and needs, and/or edited the draft versions.

| | Critical | High | |
|------------------------|---|--|--|
| Research | Research that potentially could have a significant impact on cost-effective management of DoD's chlorinated solvents contaminated groundwater in the near term. | not be able to be initiated until critical research needs are addressed or may be | |
| Demonstration | Field demonstrations or assessments that can improve on cost-effective management of DoD's chlorinated solvents contaminated groundwater. | tive are of high priority but may not be able to ated be implemented until critical | |
| Technology Transfer | Specific actions that could be undertaken immediately to promote technology transfer of key concepts or technologies. | undertaken to promote technology | |

 Table 1. Criteria for Prioritizing Needs

3.0 OVERARCHING ISSUES

A number of issues were identified during the workshop that did not necessarily fit into a research need but are considered important for the Programs to consider. A summary of these issues is provided in the following sections.

3.1 Fostering New Breakthroughs

Rather than assuming existing technologies can address all issues associated with contaminated groundwater, it is important to recognize that new breakthroughs are likely and need to be fostered. Funding agencies need to ensure continued support for potential breakthrough discoveries and innovative technologies so that these ideas are not lost. Characterization technologies as well as remediation technologies need some level of continued investment. There is an associated management challenge, in that the episodic nature of new breakthroughs will likely require variable levels of funding year to year.

3.2 Establishing Testing and Evaluation Sites

Many ESTCP projects invest heavily in initial site characterization activities that aim to define the sources and extent of contamination, the transport characteristics of site-specific contaminants and the pathways of contaminant migration. This information is often used to refine existing CSMs, creating a potentially valuable resource in the resulting well-characterized sites or areas within sites. One approach that could improve the cost effectiveness and speed of ESTCP-sponsored field studies would be to use some of these areas as permanent, well-instrumented test sites. These sites would ideally have different contaminant profiles and hydrogeological settings and would be operated to enable the testing of novel site characterization and remedial processes.

An important benefit of this approach, beyond the financial savings associated with initial site characterization efforts, would include the abilities to develop quantitative CSMs and directly compare the effectiveness of different remediation approaches at the same site. These sites would likely be managed differently than prior ESTCP test sites. For example, these may be long-term DoD sites with agreements in place that foster ongoing research and development, rather than ESTCP-managed sites. Continued work at a few sites would result in ever-growing, multi-dimensional databases of critical characterization, monitoring and modeling information that could provide invaluable support to new projects exploring both basic science and innovative technologies.

3.3 Developing Interim Remedial Goals

Many aquifer remediation decisions are driven by Safe Drinking Water Act requirements to meet maximum contaminant levels (MCLs) that reflect potential risks to human health derived from long-term exposure to contaminated drinking water. Meeting aquifer restoration requirements can sometimes require decades of phased remedial action. However, in many instances, MCLs are used to drive the design and judge the effectiveness of remediation processes for sites where contamination does not impact sources of drinking water. More efficient and relevant remediation decisions should be developed for sites that do not pose an actual drinking water risk. Accordingly,

developing interim goals for source control and decisions based on reduction in contaminant flux over time will allow recognition for progress made towards reaching longer-term objective. Greater efforts should also be placed on developing a holistic understanding of the overall environmental significance of discharges of partially remediated groundwater on surface waters. Interim goals can also be used when aquifer restoration requirements are based upon contaminated groundwater discharge to surface water limits driven by the Clean Water Act.

3.4 Launching Conceptual Site Model Initiative

The CSM is an iterative "living" representation of a contaminated site that provides a concise summary of contamination sources and distribution, release mechanisms, exposure pathways, migration routes, and human and ecological receptors (USEPA, 2011). The CSM should identify and quantify the physical, chemical and biological processes that control contaminant fate and transport. Although there is regulatory guidance on CSMs (ASTM, 2014, USEPA, 2011), participants agreed that there is little industry-wide consistency in CSM development and application for contaminated site management. Remediation decisions could be improved by developing more standardized and more quantitative CSMs. A sufficiently accurate and comprehensive CSM is critical for enabling effective treatment technology screening and conceptual design of remediation approaches. It also supports monitoring and process control during remedy implementation, verifying performance and achievement of remediation objectives and goals, and enabling decisions regarding no further action and future land uses. An industry-wide standard approach for CSMs could be facilitated by launching a CSM initiative focused on developing a rigorous objective-based CSM framework and associated training tools.

3.5 Developing Quantitative Decision Tools

Over the years, SERDP and ESTCP have funded an enormous amount of research and demonstrations of emerging technologies in support of groundwater remediation and site restoration. The value of that research has not been fully realized, in part because there has been relatively little integration of the information from different projects. It should be possible at this point to synthesize existing information with the objective of developing useful quantitative decision support tools. Meta-analysis of existing information could lead to more effective site characterization, reasonable expectations for the efficacy and limitations of treatment approaches, better understanding of fate and transport processes, and quantitative assessments of the site characteristics that govern treatment effectiveness.

3.6 Reframing Research Objectives

Many projects and calls for proposals have understandably focused on the characterization and treatment of specific contaminants. However, there can be considerable value in focusing instead on specific *processes* – processes that affect chlorinated ethenes but that also can be important for other contaminants. Biological and abiotic processes affecting chlorinated volatile organic compounds (CVOCs) represent one example, but hydrodynamic processes and the processes affecting amendment distribution and contaminant distribution within the subsurface also have broad applications. There is considerable value in funding work that addresses key processes that are relevant to both CVOCs and other classes of contaminants. These projects will be formulated

primarily in terms of high-level processes that are highly cross-cutting with respect to contaminants, but that are studied and calibrated for CVOCs. This issue is discussed further in Section 4.2.4.

3.7 Improving Technology Transfer, Training and Continuing Education

SERDP and ESTCP funding has been an important resource for training both current and future remedial managers. However, workshop panelists agreed that inexperienced practitioners may need help, both in terms of formal education and on the job training. The demand for continuing education will only increase while funding is decreasing. Additionally, learning approaches have changed rapidly, and SERDP and ESTCP have already invested in some innovative technology transfer efforts. Needs include efficient tools to train relatively inexperienced scientists and engineers, short videos to inform practitioners of new developments in research and demonstration projects, and critical assessments of past technology transfer efforts to guide future initiatives. Modifying the existing technology transfer practices may also be warranted. It is worth noting that these problems are not unique to environmental restoration research.

4.0 RESEARCH NEEDS

The research needs identified during the workshop are described in this section; demonstration and technology transfer needs are described in Sections 5.0 and 6.0, respectively. The needs are categorized as either critical priority needs (most urgent), followed by high priority needs. The order in which the needs are listed does not imply any prioritization.

4.1 Critical Priority Research Needs

4.1.1 Improve Understanding and Quantification of Natural Attenuation Mechanisms in Plumes

Natural attenuation (NA) will continue to be a critical component of long-term site management for large and/or complex groundwater sites, and can even be a primary remedy at some sites. In either case, the efficacy of NA has a major impact on remediation timeframe and long-term costs. Questions about NA's efficacy result in both risks and opportunities for DoD RPMs. The risks include (but are not limited to):

- Lack of acceptance of less understood degradation mechanisms (e.g., biogeochemical reduction and cometabolic oxidation) by regulatory agencies can limit use of NA in cases where it represents a viable, cost-effective remedy component.
- "Lumping" of degradation mechanisms with hydrologic effects that reduce contaminant concentrations over time can overestimate long-term degradation rates and underestimate long-term financial liability (e.g., Sorenson et al., 2000).
- Lack of performance monitoring tools and quantitative interim performance goals can create dissension, whether internal or with regulatory agencies, regarding the timing of transition from active treatment to NA, or regarding the long-term performance of NA.

Improving our understanding of the efficacy of NA will also lead to opportunities for DoD RPMs, including:

- Further validation and guidance regarding "novel" NA mechanisms, including realistic degradation rates, conditions under which NA occurs, and methods to document performance will facilitate acceptance of NA as a cost-effective component of remedies when appropriate.
- Methods to distinguish degradation from dispersion (including diffusion) and dilution <u>quantitatively</u> will provide more realistic estimates of NA performance, leading to more reliable estimates of remediation timeframes and long-term financial liability.
- Higher confidence in long-term degradation rate estimates, including the sustainability of those rates, will facilitate: (a) acceptance of established quantitative points for transition from active treatment to NA and (b) establishment of reasonable interim performance goals for NA.
- Degradation mechanisms that are either not yet identified or that are known low rate processes, such as natural radiation, may become increasingly important for site management. Although such low rate degradation mechanisms may be difficult to identify and study, over tens of years they could be significant.

In light of these risks and opportunities, potential research focus areas include the following:

- *Reduction of CVOCs by iron-containing minerals:* While several studies have demonstrated that such minerals have the potential to reduce CVOCs biogeochemically, there is not yet a simple, reliable method to predict, let alone quantify, this mechanism. More data are needed that provide confidence regarding when, where, and for how long these mechanisms can be expected. Methods for assessing the occurrence and rate of these mechanisms are also needed for reliable field application.
- *Complete microbial reduction of CVOCs:* Enhanced anaerobic bioremediation of CVOCs has been successfully implemented at many sites; however, common degradation products from chloroethene dechlorination such as DCE and vinyl chloride (VC) can persist over long periods at some sites, which is often referred to as a DCE or VC "stall". The reasons for stalls are not resolved and understanding the causes of stalling could substantially reduce remediation time and cost.
- Oxidation of chlorinated CVOCs under various conditions: Previous studies have shown that oxidative degradation of TCE and DCE occurs under aerobic conditions in some aquifers, and that enzymes capable of oxidizing these compounds are present in those aquifers. More data to understand when these or other oxidative degradation processes occur, the rates at which they occur, and the conditions under which they occur are needed to facilitate regulatory performance and to predict long-term performance. Understanding these processes sufficiently to quantify them with some degree of confidence is especially important in dilute plumes where active treatment is either inefficient or prohibitively expensive.
- *Estimating plume cleanup timeframes:* Currently available modeling tools are adequate to predict remediation timeframes when microbial, hydrologic, and geochemical processes are well characterized; however, more methods to determine realistic, site-specific degradation rates are needed to facilitate transition from active treatment to NA and to set interim and long-term performance monitoring goals.

4.1.2 Develop Quantitative Understanding of the Effect of Co-contaminants on CVOCs

Most contaminated DoD sites involve multiple contaminants. CVOCs frequently occur with a variety of different co-contaminants in groundwater, including but certainly not limited to per- and polyfluoroalkyl substances (PFAS), 1,4-dioxane, and heavy metals. Other chemicals such as polychlorinated biphenyls (PCBs); munitions constituents; benzene, toluene, ethylbenzene and xylenes (BTEX); gasoline oxygenates; and chlorinated phenols also are present with CVOCs at select sites. There is a need for a deeper understanding of how co-contaminants impact remediation of chlorinated ethenes. For example, there is limited information on the extent to which PFAS affect the rate and extent of microbial reductive dechlorination of chlorinated ethenes. At some sites where significant numbers of unidentified contaminants are present, their potential impact on chlorinated ethene remediation needs to be ascertained. This includes impacts on enhanced remediation and monitored NA (MNA).

Although limited research has been conducted in this area (e.g., impacts of PFAS on dechlorinating microbial communities [Weathers et al., 2016; Harding-Marjanovic et al., 2016]), the overall

impacts of co-contaminants on the physical, chemical and biological processes that affect the fate and treatment of CVOCs are poorly understood. Some relevant questions include the following:

- Which co-contaminants are most commonly detected at CVOC sites, and which combinations are most prevalent and relevant (e.g., 1,1,-dichloethane (DCA) and 1,4-dioxane)?
- Which of these co-contaminants are likely to affect the fate and/or treatment of CVOCs and at what concentrations do impacts occur?
- How does the presence of co-contaminants impact remediation approaches and are joint treatment technologies effective?
- How do co-contaminants influence the aerobic or anaerobic biodegradation of CVOCs?

More broadly, the roles of naturally occurring organics and/or those derived from remedial additives and processes on long-term abiotic and biotic transformations of chlorinated solvents and their byproducts also remain poorly understood. Research is needed to mechanistically understand and quantify the impacts of these organics on remedial site management for the entire lifecycle of the site. It is anticipated that this research would aid in defining DoD's problem and improve the understanding of the overall assimilative capacity of aquifers for chlorinated solvents. For example, when organic amendments are added to aquifers to generate H₂ for *Dehalococcoides* and other dehalogenating bacteria, a wide variety of other small metabolites also are generated as side-products, either from the microbial fermentation (e.g., alcohols, ketones, esters, organic acids, methane) or via dechlorination of the CVOCs themselves (e.g., ethane, ethene). The production and fate of these metabolites during in situ remediation have received relatively little study; however, they are expected to be readily biodegradable under aerobic conditions and are likely to stimulate a variety of oxygenase enzymes that may contribute to the cometabolic attenuation of residual contaminants moving downgradient from a CVOC source area.

Another area relevant for contaminant attenuation with currently limited scientific understanding is the principle of biologically mediated abiotic degradation. Abiotic processes can play relevant roles for contaminant attenuation, particularly in large dilute plumes with co-mingled contaminants. A key realization is that the reactive mineral phases (e.g., magnetite, green rust, manganese dioxide) are generated as a result of dynamic mechanisms, including biogeochemical processes and hydrogeologic fluctuations. Integrated research efforts are needed to better understand biotic-abiotic interactions so that reactive mineral phase formation can be predicted and controlled. This would improve remedial design and allow RPMs to fully capitalize on coupled biotic-abiotic degradation processes to achieve contaminant degradation.

4.1.3 Integrate Information from Fine-Scale Delineation Tools for Improved Decision Making at Complex Sites

A wide range of high-resolution site characterization (HRSC) tools have been developed over the past 10 to 15 years to advance the fine-scale characterization of complex sites needed to improve understanding of contaminant fate and transport in highly heterogeneous environments. These tools span from sensors that can provide point scale assessment of solid, aqueous and vapor phase contaminants from direct push technologies or boreholes to geophysical tools that can image aquifer heterogeneity controlling contaminant transport between boreholes or from the Earth's surface. Over this same period, many advances have been made in the development of both

screening-level and statistical modeling tools that can be employed to support complex site characterization, management, and quantification of prediction uncertainty in heterogeneous environments. Mathematical models have been developed for a range of applications, from field characterization of permeability, to mass flux quantification, to sampling network optimization. To date, however, most of the modeling tools have been developed and evaluated using limited synthetic (numerically generated) data sets, with very few applications to real contaminated sites and diverse data types. Thus, in general, these new HRSC and modeling tools remain under-utilized; datasets acquired using new HRSC tools remain poorly integrated into site management models, decision tools, and data mining and interpretation frameworks. Technologies and models that can advance the integration of information from fine-scale delineation tools for improved decision making at complex sites are therefore needed to bridge this gap between advances in HRSC and effective site management.

Based upon the above, there is a critical need for the development of quantitative models/technical tools and interpretation frameworks that effectively integrate HRSC data to improve CSMs and remedial decisions. These quantitative tools should be able to learn from historical datasets acquired over a wide range of geological settings, to incorporate diverse types of site data/information, and be implementable in real-time with the acquisition of new fine-scale data at complex sites. Then, using real sites also as research sites, these modeling tools could be used to optimize the application of HRSC tools to inform short- and long-term remediation strategy design and demonstrate the potential to reduce uncertainty in decision making associated with site management.

These new tools also could be employed to optimize the collection and use of HRSC data to improve understanding of the physical, chemical and microbiological processes that contribute to long-term contaminant persistence at sites where contaminant concentrations remain persistently above clean up targets. These new tools could inform time-resolution of data across different complex sites for optimized information content, identifying critical stages in the characterization and remediation when additional value can be obtained with marginal investment. Development and application of these integrative modeling tools also could advance the use and enhancement of geophysical tools to assess fine scale structures beyond boreholes, methodologies for quantifying diffusion rates controlling mass storage in low permeability media (back diffusion), and novel techniques for assessing contaminant sorption, desorption, and bioavailability. These tools will maximize the information content obtained from boreholes by highlighting in-hole technologies (e.g., geophysical logging methods) that have the potential to dramatically enhance fine-scale delineation of aquifer properties controlling contaminant fate and transport.

4.1.4 Develop Comprehensive Decision Framework for Remedy Selection

As discussed in Section 3.5, many and diverse informational tools have been developed and are currently available that provide qualitative and/or quantitative guidance related to various elements of the restoration process (e.g., BioPIC, RemChlor, Matrix Diffusion Toolkit). However, these tools typically pertain to relatively focused topics, specific hydrogeologic settings, and/or technologies such as enhanced bioremediation or site characterization. A holistic decision framework that integrates state of the art knowledge is needed to facilitate improved remedy selection as well as DoD's on-going remedy optimization efforts. This effort would greatly benefit from (and could be informed by) an objective machine learning approach to synthesize as much existing data as can be practicably compiled.

4.1.5 Improve CSMs for Understanding the Factors Sustaining and Controlling Persistent Chlorinated Solvent Plume Behavior

Existing CSMs often fail to account for the range of possible mechanisms and processes that sustain and control the persistence of dilute chlorinated solvent plumes. This failure is typically due to several factors, including the inability to verify that all suspected degradation processes are occurring, the inability to sufficiently quantify the significance of the process, and/or the lack of appropriate modeling tools to incorporate the process into fate and transport models. Examples of mechanisms and processes that are often neglected or poorly characterized and quantified in CSMs include (but are not limited to):

- *Persistent low-intensity source areas*. Often, source areas persist even after the bulk of the contaminant mass has been removed, and after the contaminant flux has been substantially reduced. Improved tools and techniques to identify trace and discrete contaminant sources are needed for such persistent source areas so that they can be effectively captured within CSMs.
- *Naturally occurring long-term biotic and abiotic transformation processes*. Even very slow dechlorination processes can have a substantial impact on plume attenuation when considering timescales of decades. However, it is difficult to incorporate these processes in CSMs because of a lack of reliable kinetic data and an inadequate understanding of when these mechanisms and their relative degradation rates are and are not likely to be appropriate for inclusion in a CSM. There is a need for tools, methods, and approaches to extract useful rate constants for these interactions. These tools should provide some estimate of the uncertainty in the estimated rate constants, to allow for a sensitivity analysis of their contribution in the overall CSM.
- Interactions with low permeability materials. Quantifying the processes that occur within low permeability zones (LPZs), and characterizing the interactions between LPZs and hydraulically conductive zones, remains difficult. Proper descriptions of contaminant release and uptake into such zones can require more characterization data than is usually available, and in fact it is often impractical to collect sufficient data with current tools. Development of tools and techniques to quantify the processes governing the slow release of contaminants from LPZs is needed so that they can be appropriately accounted for in CSMs.

Overall, there is an absence of tools and techniques to validate the contribution of these processes on plume persistence. Fundamental and applied research is needed that will facilitate improved CSMs to enable the DoD to limit costs associated with site management and to develop long-term strategies that result in closure or minimal site maintenance.

4.1.6 Improve Fundamental Understanding of Processes Influencing the Effectiveness and Fate of Particulate Amendments

A number of technology vendors are now promoting in situ particulate/colloidal amendments (e.g., powdered activated carbon) designed to adsorb contaminants in groundwater, subsequently reducing their dissolved phase concentration. Biodegradable contaminants, such as CVOCs, are reported to initially concentrate on the sorptive matrix and subsequently be biodegraded by naturally occurring or augmented bacteria. The primary concern with this approach is that the

technology has not yet received the scientific scrutiny needed to understand issues such as those listed below:

- The distribution of particulate amendments in heterogeneous aquifers, and the efficacy of methods to improve distribution. Specific needs include improved understanding of the extent and impacts of preferential flow paths, the impacts of enhancements such as fracturing, and the potential for plugging in situ.
- The long-term adsorptive capacity of the amendments and the factors that may influence this capacity (e.g., co-contaminants, fermentable substrates).
- The extent to which the adsorbed contaminants are biodegraded and the influence of contaminant, geochemical and microbiological factors on biodegradation kinetics and extent.
- The properties and long-term adsorption capacity and potential for re-release of CVOCs or co-contaminants such as PFASs over time.
- The potential detrimental effects, such as transport of injected amendments into local monitoring wells or reduction in aquifer permeability.
- The extent to which these amendments influence CVOC back-diffusion.

There is a clear need to provide objective data to address the above questions before these amendments become more widely applied at contaminated sites. Laboratory- and field-scale pilot studies that provide a fundamental understanding of the fate of these particulate amendments as well as their contaminant sorption properties and capabilities, and influence on contaminant biodegradation are of interest. Small-scale field evaluations of adsorbent transport and potential effects on both contaminant distribution and aquifer properties are also relevant.

4.1.7 Improve Analysis of Performance Data from Pump-and-Treat Systems to Predict Decline in Mass Discharge over Time

Sites where pump-and-treat (P&T) remedies have been applied typically have many years of data on concentrations of contaminants in the extracted water over time and the volume of water pumped over time. These data sets constitute an important source of information about the magnitude and temporal changes in mass discharge emanating from chlorinated solvent source zones. There is a need for approaches, methods, and models that analyze the performance data from a P&T system at a particular site to predict the decline in the mass discharge of contaminants over time as the P&T remedy proceeds into the future, and after the active pumping has ceased.

The performance of a P&T remedy is controlled in part by the rate at which the contaminants at the site are transferred from a sequestered phase to flowing groundwater. Transfer processes can include dissolution from residual nonaqueous phase liquid, desorption from aquifer solids, or diffusion from regions in the aquifer with immobile pore water (matrix diffusion). As a P&T system matures, the mass captured by the remedial system is limited by the rate of mass transfer of the contaminant from all sequestered phases in aquifer material that is included in the zone of capture of the P&T system. It should be possible to evaluate mass captured over time in the active remedy to estimate the mass discharge of contaminants from the source material to flowing groundwater. In this way, P&T systems can serve as important monitoring networks to assess historic and future temporal changes in source mass discharge rates due to source depletion or

active remediation. This role is in addition to their primary role of ensuring that dissolved contaminants are physically captured and cannot migrate downgradient to impact a receptor.

Robust analysis and projections of the decline in the mass discharge of contaminants over time can be used to predict the future performance of the P&T system and may identify a time when the value of the mass discharge is low enough to terminate a P&T remedy and allow a transition to MNA.

4.1.8 Develop Methodologies to Determine Ability to Transition from Active Measures

At certain concentrations, contaminants in groundwater are attenuated by the natural assimilative capacity of the aquifer matrix and are unlikely to impact downgradient receptors such as a pumped water supply well, a sentinel monitoring well, or a body of surface water.

There is a need for approaches, methods, and models that will identify the maximum concentration of a contaminant that can be allowed in groundwater leaving a source of contamination such that the concentration of the contaminant will not exceed acceptable concentrations at a receptor of concern. Such approaches, methods and models should be appropriate for in situ remedial technologies that are evaluated using traditional monitoring wells.

These approaches, methods, and models could be used to determine when it is appropriate to stop pumping groundwater or to transition from active treatment of a source or plume to a more passive treatment strategy. The methods would need to evaluate uncertainty associated with temporal and spatial variations in groundwater flow direction, velocity, and variation in contaminant concentrations.

To support these approaches, methods, and models, it is necessary to develop protocols and procedures to determine rate constants for degradation processes. To develop interim measures of success, it is also necessary to develop procedures to determine the contributions of dilution and dispersion to the attenuation of concentrations prior to reaching surface water receptors, selected monitoring wells, or interim goals.

4.2 High Priority Research Needs

4.2.1 Develop Tools to Select Between Specific Vendor Products

There is a diverse and rapidly evolving range of amendments and other products that are available from vendors of remediation products and services. In addition, there are many amendments that have proven to be effective individually that increasingly are being used in combinations, but the effectiveness of these combinations has often not been well evaluated. Examples include: 1) activated carbon + zerovalent iron, 2) nanoscale zerovalent iron + emulsified vegetable oil, and 3) zerovalent iron + complex carbon solids.

The abundance of competing products of some types (e.g., electron donors for bioremediation and iron metals for chemical reduction) reflects a healthy market. However, it also makes it challenging to select among options when planning remedies for specific sites, and it appears that these selections are often influenced by incidental factors (such as prior experience with particular technologies or vendors). To overcome this - and improve the efficiency of market interactions and remedial outcomes - —there is a need for a new class of decision support tools designed to

help evaluate and compare different amendments and/or technologies for specific applications. In some cases, these tools might require new fundamental knowledge of the properties and processes that control the performance of specific amendments, but they also will require data for representative types of products. The research needed to develop these tools might address specific issues (e.g., predicting the effects of combining amendments), and it could help standardize the protocol for treatability studies for amendments. Furthermore, all amendments will influence the resident aquifer microbiome, but the effects and consequences on the microbiology and overall environmental health are not clear.

4.2.2 Develop New Assessment Techniques to Identify and Prioritize Structures for Further Investigation of Vapor Intrusion

Considerable uncertainty remains in accurately and comprehensively assessing potential exposures from vapor intrusion (VI) pathways at contaminated sites. Specifically, preferential pathways such as those associated with utility corridors and sewer tunnels can result in significant deviations in vapor transport relative to predictions from conventional models that assume diffusive flux. New assessment techniques and/or tools are needed to identify and prioritize candidate homes/buildings for further VI investigation.

4.2.3 Assess and Predict Long Term Performance and Impacts of Chlorinated Solvent Treatment Technologies

As discussed in Section 3.6, many projects and calls for proposals have focused on specific contaminants, but there can be considerable value in focusing instead on specific *processes* that affect chlorinated ethenes but may be important for other contaminants as well. Examples where this approach might be desirable include: the relationship between enhanced biodegradation performance and the dose of donor amendments, methods to improve delivery of amendments, the effect of contaminant sorption on biotic and abiotic degradation, and the impact of forward diffusion on remedial outcomes. Specific research areas of interest include:

- Improved understanding of coupled biotic-abiotic processes that lead to more effective contaminant detoxification
- Knowledge and predictive understanding of why CVOC degradation stalls (notably PCE/TCE at DCE or VC), and productive approaches that can overcome bottlenecks at 'stuck sites', so that cleanup targets can be achieved.
- Advanced omics tools that generate predictive understanding of contaminant fate and longevity and are applicable to various DoD sites

4.2.4 Conduct Critical Assessment of Past Project Results

SERDP and ESTCP chlorinated solvents projects have produced an immense quantity of data, results, and overall learning opportunities. Final project reports tend to be large, detail-oriented, and difficult to rapidly assimilate into effective practice. Research and projects funded under SERDP and ESTCP have resulted in both optimal and less than optimal results in the past, but these "failure-based" learning opportunities are not well "advertised" despite their importance to practitioners as a way of reducing cost at sites through understanding past difficulties at similar sites or with similar technologies.

There is a need to critically assess groups of related projects to develop and publicize general conclusions and lessons learned. To perform such critical assessments, it probably will be

necessary to develop a centralized access point to allow researchers to obtain, cross-reference, and compare data produced during SERDP and ESTCP funded projects. These assessments may be relatively simple statistical analyses, or more complex process-based assessments designed to understand what is behind the data. Further, in-person meetings to candidly discuss "failures" and "lessons learned" are needed. This will facilitate the timely exchange of important information and insights to develop suggested solutions.

4.2.5 Exploit Untapped Feedback Loops and Synergisms to Enhance Degradation Processes

Following the site Remedial Investigation and Feasibility Study (RI/FS), a remedial action is typically selected which then is designed and implemented to achieve site-specific cleanup goals. In the past, the focus was often on single, stand-alone technologies even though other degradation processes may contribute to contaminant attenuation. This realization has spurred the idea of combined remedy or treatment train approaches, where the implementation of an initial remedial technology is followed by a second technology (or an individual technology has an initial and a secondary effect) to achieve more complete contaminant removal.

Independent of the primary remedial action selected, the treatment will affect the aquifer microbiome and geochemistry, and can decrease (negative feedback) or increase (positive feedback) biotic and/or abiotic degradation processes. For example, aggressive source zone treatment by surfactant flushing can be used to remove the bulk of the DNAPL at a site, and residual contamination can then be subsequently treated via bioremediation. Surfactant remaining in the aquifer can undergo fermentation and increase the flux of hydrogen and support microbial reductive dechlorination by indigenous dechlorinators, which can be a crucial process for removing residual contaminants (Ramsburg et al., 2004; Amos et al., 2007). Along the same lines, thermal treatment is often applied to achieve contaminant removal and destruction in defined source zone areas. Heating causes the release of soluble organic compounds and hydrogen from the aquifer matrix, which serve as electron donors for organohalide-respiring bacteria (Marcet et al., 2018a). Further, elevated groundwater temperatures as a consequence of thermal treatment accelerate the rates of microbial reductive dechlorination (Marcet et al., 2018b). Thus, thermal treatment generates conditions that favor microbial reductive dechlorination following thermal treatment in downgradient zones.

Positive feedback loops and synergistic effects can have substantial contributions to cleanup efforts but are generally not recognized and therefore not included in the feasibility study used to develop remedial alternatives. Information acquired to develop the RI/FS level CSM needs to include sufficient data to allow the development of remedial alternatives that include an understanding of how engineered remedial approaches can be expected to interact with naturally occurring biotic and abiotic attenuation processes.

4.2.6 Develop Enhanced Monitoring Tools in Support of Adaptive Site Management (ASM) Enhanced monitoring tools (EMT), particularly molecular biological tools (MBTs) and compound-specific stable isotope analysis (CSIA) can provide crucial information during site assessment, and assist RPMs in deciding on the most promising remedial action. In addition, EMTs provide key information about the process during and following implementation of a remedy, and inform the progress of the cleanup effort. SERDP and ESTCP have invested in the development and validation of EMTs, and some of these tools have reached high maturity levels. However, the instrumentation and technology continue to advance at a fast pace and new, improved methodologies and tools can provide additional insights that will lead to better-informed site management decisions. EMTs generate prognostic and diagnostic information and will play a crucial role for ASM of complex chlorinated solvent sites at DoD installations. Not all available tools have been applied to support remedial actions, even though the information gleaned from these tools can provide relevant information about contaminant degradation and will support decision-making.

It is important to realize that the informational content generated by different EMTs differs, and it can be confusing for non-experts to select the most beneficial suite of EMTs to make informed site management decisions. Further, the interpretation of EMT data can be challenging for non-experts, and training and guidance are key components to ensure that the information these powerful tools generate does translate into improved decision-making. Since costs are associated with EMT analysis, only a single or a subset of tools is generally applied during monitoring regimes, a practice that can complicate data interpretation. Additional research is needed to test and validate new tools, demonstrate the value of different EMTs for ASM decision-making, and clearly explain how integrated tool application generates multiple lines-of-evidence that biotic and/or abiotic processes are occurring and contribute to contaminant attenuation. Efforts also should evaluate what combinations of tools provide the most robust and meaningful information to guide decision-making at a specific site. With a refined toolbox, validated approaches, and guidelines for data interpretation available, EMTs are expected to generate information that reliably predicts a plume's trajectory and transition more sites from active to passive (i.e., MNA) remediation status.

5.0 DEMONSTRATION NEEDS

This section presents the demonstration needs that were identified during the workshop. These relate primarily to treatment and to measurement and prediction – techniques that can be used to improve the CSM, evaluate potential remedial strategies, and effectively predict and monitor remedy performance. Demonstration needs that were determined to be critical priority (most urgent) are presented first, followed by high priority needs. The order in which the needs are listed does not imply any further prioritization.

5.1 Critical Priority Demonstration Needs

5.1.1 Improve Understanding and Quantification of Natural Attenuation Mechanisms in Plumes

As described in Section 4.1.1, NA efficacy can have a major impact on long-term site management timeframes and costs. As more intrinsic degradation mechanisms for CVOCs have been postulated and demonstrated, the potential for use of NA as a protective and cost-effective remedy component seems to be increasing; however, few sites exist where a broad suite of tools has been applied. The result is significant uncertainty in many cases regarding what NA mechanisms might operate at a site, what degradation rates can be expected and how degradation can be differentiated from dispersion/dilution, whether those mechanisms are likely to occur indefinitely (i.e., what are the constraints and can they be identified and quantified), and how to set interim and long-term performance goals. Better documentation of degradation mechanisms and rates at field scale, including guidance for applying a broad suite of diagnostic tools will facilitate regulatory acceptance of MNA as a remedy component where appropriate, as well as helping establish reasonable performance metrics for MNA.

Some specific examples of demonstration needs include the following:

- Applications of broad suites of new and existing NA assessment tools at full-scale field sites to illustrate the pros and cons of these techniques, and to illustrate which mechanisms are likely to occur under various conditions, and at what rates. These sites should have historical contaminant concentration trends to aid in rate quantification, and to help in differentiating between degradation and dispersion/dilution.
- Fully instrumented sites that can be monitored for long periods of time could be useful for validating MNA performance predictions, as well as for testing new tools/techniques developed over time.
- New tools to validate and quantify known and novel NA mechanisms reliably and costeffectively under in situ conditions are still needed.
- Guidance regarding the use of the full suite of currently available MNA assessment tools, and how to apply them to determine transition points from active treatment to MNA, and to establish interim and long-term performance goals is needed.

5.1.2 Evaluate Techniques for Optimized Delivery and Distribution of Amendments in Heterogeneous Environments

A critical challenge preventing many chlorinated solvent sites from reaching groundwater cleanup goals is the long-term release of residual contaminants from low permeability (low-k) zones (e.g.,

clays, silts). For example, sites dominated by matrix diffusion processes are very difficult to remediate and have the effect of significantly prolonging restoration timeframes and drastically increasing site management and remediation costs. Innovative technologies are needed that can enhance amendment delivery in heterogeneous environments and treat residual contaminants trapped in low-k zones. Since technology performance is often intricately linked to whether amendment distribution was effectively achieved, high-resolution pilot-scale evaluations are needed to assess the extent of amendment delivery in various environments and identify factors that limit adequate delivery. Further, methods for real-time tracking of amendments after introduction into the subsurface are critical for accurate remedy evaluation and process optimization.

5.1.3 Improve Remedy Performance Monitoring and Process Control

To reduce operation and maintenance and long-term management costs, smarter methods/tools for data collection are needed that facilitate real-time and continuous reevaluation of selected remedies and monitoring optimization. The introduction of real-time/automated tools (e.g., rapid field-based assays, sensor networks) could significantly reduce costs and facilitate timely process improvements. Although advancements in sensor technology have been made, site management decision-making still relies primarily on analytical results from periodic site monitoring events, which require considerable time for data collection, validation, and analysis. Cost-effective, real-time tools that provide accurate information on remedy performance and process control are critical for adaptive site management approaches.

5.1.4 Develop Best Management Practices for Back Diffusion and Plume Management Strategies

It is likely that matrix diffusion (forward and backward) of CVOCs is not adequately accounted for in estimates of remediation timeframes and total long-term environmental liability for a large fraction of DoD's contaminated groundwater sites. This means that site closures will continue to be pushed out into the future, and cost estimates to complete remediation at these sites will not decrease as expected. Quantification of diffusive fluxes is not the issue; diffusion coefficients for CVOCs are well documented, as are techniques for determining diffusion distances in aquifers. Current analytical and numerical models represent the mathematics of diffusion sufficiently. Rather, a means to adequately incorporate these values into remediation timeframe estimates is needed.

In addition, long-term strategies are needed to reduce the diffusive flux of CVOCs from low permeability matrices back into higher permeability flow zones, thus potentially reducing their long-term downgradient migration. Biotic or abiotic processes operating at the interfaces between lower and higher permeability zones may reduce any such diffusive flux, but there is a lack of long-term data on mass fluxes into or out of LPZs to evaluate the impacts of these processes. For example, modeling studies have suggested that measurable rebound might occur as much as several years after active bioremediation has ceased, but there are few studies to evaluate this possibility. Similarly, carbon-based amendments ranging from oils to activated carbon might provide a decrease in diffusive flux into high permeability flow zones for some period of time, but the long-term effects are not clear, either in terms of degradation or sequestration. Finally, the long-term effects of aggressive delivery techniques (e.g., "permeability enhancement technology" or "grout bombers") on diffusive mass flux have not been documented. Demonstrations that address these data gaps will provide strategies for long-term plume management that provide

higher confidence in long-term environmental liability projections as well as predictions of site closure timeframes.

5.1.5 Integrate Information from Fine-Scale Delineation Tools for Improved Decision Making at Complex Sites

As noted in Section 4.1.3, there have been significant advances in HRSC tools and screening level/statistical model development related to contaminated site characterization and monitoring. However, relatively little work has been conducted to demonstrate the integration of these tools or to assess their ability to improve decision making at real sites. In addition, many RPMs involved in decision making may lack the technical expertise required to identify potential HRSC tools that are available, and/or understand their key capabilities and limitations. Thus, there is a critical need for the demonstration and assessment of the integrated performance of both established and newly developed technologies at a range of sites and the development of guidance to promote and support their implementation. This work will require collaborative investigations should facilitate the real-world assessment of what tools/techniques have worked where and why. Similarly, these studies should provide insight into those cases where specific HRSC tools have failed to deliver, thus identifying technological gaps, shortfalls and limitations in current approaches. The outcomes should facilitate an assessment of the information content of specific tools for a given site/performance objective, along with an evaluation of any data redundancy.

5.1.6 Develop Adaptive Site Management Tools

There is a need to develop a suite of tools to aid in implementing ASM of complex chlorinated solvent sites at DoD installations. Based on recent recommendations from the Interstate Technology & Regulatory Council (ITRC) Complex Site Management Team, ASM is a preferred approach to managing complex sites. In addition, The U.S. Environmental Protection Agency (EPA) recently issued OLEM Memorandum 9200.3-120 (July 2018) that provides a working definition of ASM and an implementation plan to expand the use of ASM at Superfund sites. Tools and guidance are needed to assist DoD RPMs and other site managers to continuously re-evaluate CSMs and prioritize site management activities based on new information and changing site conditions. The use of ASM will allow DoD to focus limited resources on making better-informed decisions throughout the cleanup process. Proposed tools and guidance may include but are not limited to the following:

- Dynamic remediation goal development tools based on a comparative analysis of source zone mass flux analysis and downgradient plume natural assimilative capacity
- Transition assessment tools to aid RPMs in determining when to transition sites from active remediation to long-term passive management (e.g., MNA)
- Case study analysis and lessons learned of example sites where ASM has been successfully applied to manage complex chlorinated solvent sites

ASM is a new name for a long-standing strategy that enables RPMs to take a planned, iterative approach to remediation with clear goals for each step and use of feedback from changing site conditions and new information to adjust, as needed. Implementation of an ASM approach will require decisions during each step to determine adjustments needed, identify when it is appropriate to transition to the next step, and verify the remedy configuration of the subsequent step. These decisions will need an appropriate technical basis, in particular when transitioning from active to

passive remediation approaches. Currently, guidance is available for the planning aspects of ASM (e.g., ITRC Remediation of Complex Sites [https://rmcs-1.itrcweb.org/]; anticipated efforts through EPA Superfund Task Force, Recommendation 3 – Broaden Adaptive Site Management [https://www.epa.gov/superfund/superfund-task-force]), but specific tools and methodologies to support plume assessments and stability analyses and transitioning between remedy steps are needed.

ASM may be particularly applicable for sites where one or more active treatments are needed to reduce contaminant concentrations before transitioning to passive remediation approaches and long-term management. Thus, a robust methodology and supporting tools for calculating aquifer attenuation capacity and quantifying plume conditions (e.g., mass discharge rates, plume stability) are important to document passive CVOC attenuation for applying ASM. Performance assessment approaches for active remedies that provide feedback to support remedy adjustments, such as when remediation systems reach points of diminishing returns in terms of performance and cost-effectiveness, and when to transition to subsequent steps are also important to implementation of ASM. Decision tools to facilitate data evaluation and to determine the most appropriate configuration for each step of an ASM approach may be of particular use at more complex sites where there are multiple options with costs and benefits to consider when configuring the remedy steps. Focused guidance for the decision process and implementing the technical methodologies that support the stepwise application of ASM would also complement existing guidance on the overall ASM approach.

5.1.7 Develop Comprehensive Decision Framework for Remedy Selection

Section 4.1.4 described the need to develop a holistic decision framework that integrates state of the art knowledge, to improve remedy selection at CVOC sites, as well as the ongoing remedy optimization efforts. This decision framework would greatly benefit from (and could be informed by) an objective machine learning approach to synthesize as much existing data as can be practicably compiled. Development and transitioning of this framework will require field-scale demonstration and evaluation.

5.1.8 Improve CSMs for Understanding the Factors Sustaining and Controlling Persistent Chlorinated Solvent Plume Behavior

The need for research into the mechanisms and processes that sustain and control persistent chlorinated solvent plume behavior was discussed in Section 4.1.5. While fundamental research is still required for fully elucidating several of these processes, the extent and rate to which some of the recognized processes are occurring and confirmation and quantification of their occurrence in situ often is lacking. In addition, accepted tools and approaches for characterizing these processes have not been widely demonstrated, thereby limiting their practical applications. Demonstration of tools and techniques for assessing persistent low-intensity source areas, slow abiotic or biotic dechlorination processes, and processes occurring in low permeability zones is a critical need for full incorporation into CSMs. Specific demonstration needs include, but are not limited to:

- In situ tools and techniques for verifying and quantifying identified mechanisms that sustain persistent plumes
- Quantification of in situ rates of contaminant transformation or depletion
- Demonstration of the impacts of these processes/mechanisms on long-term plume behavior by incorporation into available or refined models

5.1.9 Evaluate Mass Discharge Data to Assess Closure

Mass discharge data can provide considerable insight into the benefits of remediation efforts, the strength of residual sources, and the risks to downgradient receptors of concern. The results can be valuable in prioritizing residual sources for further treatment, evaluating whether to transition to MNA, or whether site closure is warranted. There is a need to develop and demonstrate methods and approaches to characterize the mass discharge of contaminants from residual sources and use that information to make a robust evaluation of the risk posed by the residual source to groundwater quality near source areas and to downgradient receptors.

Historical mass discharge data are often available from existing P&T systems, although other methods to measure discharge also should be evaluated. The performance data from existing P&T systems should be evaluated to determine the historic and current mass discharge of contaminants, and the impacts of natural and enhanced attenuation. Mass discharge estimates should be performed to assess impacts to groundwater quality close to the source areas as well as upgradient of receptors such as water supply wells or surface water bodies. Mass discharge evaluations at several field sites should lead to useful guidance on evaluating and using mass discharge data for decisions such as transitioning to passive management, further remediation of source areas, or prioritizing site risks.

5.2 High Priority Demonstration Needs

5.2.1 Conduct Adaptive Site Management Pilot Studies

As discussed in Section 5.1.6, ASM is a newly emphasized approach that will enable sites to take a planned, iterative approach to remediation with clear goals for each step and use of feedback from changing site conditions and new information to adjust, as needed. Implementation of an ASM approach will require decisions during each step to determine adjustments needed, identify when it is appropriate to transition to the next step, and to verify the remedy configuration of the subsequent step. These decisions will need an appropriate technical basis, in particular when transitioning from active to passive remediation approaches. Currently, guidance is available for the planning aspects of ASM (e.g., ITRC Remediation of Complex Sites [https://rmcs-1.itrcweb.org/]; EPA Superfund Task Force, Recommendation 3 – Broaden Adaptive Site Management [https://www.epa.gov/superfund/superfund-task-force]), but specific tools and methodologies to support plume assessments and stability analyses and transitioning between remedies (e.g., active versus MNA) are needed.

The U.S. EPA's Superfund Task Force is developing an Adaptive Management Pilot Program. The purpose of the Adaptive Management Pilot Program initiative is to evaluate the effectiveness of adaptive management at Superfund sites across the country and to develop appropriate policy and guidance. Development of appropriate pilot efforts within DoD to leverage the policy, guidance, and tool application efforts of this EPA program would facilitate translation of findings to DoD-specific environmental sites. As such, pilot studies/case studies on ASM conducted jointly or in parallel with the EPA program would be of value with outcomes that provide specific implementation guidance relevant to the DoD.

Pilot studies are needed to demonstrate planning approaches, development of effective interim objectives that facilitate remedy management and transition decisions, implementation of

remediation with the feedback mechanisms needed for adaptive management, and decision tools for progressing through the remedy implementation toward more passive elements and/or closure. In addition to a full pilot study, testing of specific adaptive management tools (e.g., decision support, data analysis for performance and transition assessments) using DoD site data would facilitate determining tool effectiveness for DoD site applications and provide appropriate implementation guidance.

5.2.2 Conduct Rigorous Statistical Analyses to Communicate Dynamic CSMs

CSMs are the foundation for most critical decisions along the path to site closure. Accurate CSMs allow for proper decision making, should be viewed as dynamic objects, and should clearly encompass and communicate uncertainty. Existing guidance on CSMs was, for the most part, developed prior to the introduction of "big data" to the environmental world with the advent and general acceptance of real-time, cm-scale data acquisition tools and approaches (ITRC, 2011, EPA, 1998, EPA, 2000,). A significant body of work exists on the use of statistical approaches for sampling design and understanding the expectation of the reduction of uncertainty through additional data. However, statistical tools for decision making based on the extensive data underlying CSMs at many sites are poorly understood and therefore limited in general application. Statistical analysis of "static" data sets is common; however, statistical interpretation of dynamics within CSMs, and the use of the statistical findings in the communication of dynamic CSMs is less well developed and has clear benefits to the remaining DoD sites that have not achieved Response Complete (RC) or Remedy in Place (RIP) status.

SERDP and ESTCP funded projects on chlorinated solvents have produced an immense quantity of data, results, and overall learning opportunities that for the most part have only been utilized in a discrete and limited way. A summative program that provides integration of the other analyses and general findings into a "lessons learned" deliverable, that is developed and produced to be accessible to all practitioners in a variety of formats would be extremely beneficial and significantly increase the value of previous investments to current DoD needs in addressing liabilities.

6.0 TECHNOLOGY TRANSFER NEEDS

SERDP and ESTCP have an established technology transfer program that includes, but is not limited to, a webinar series, on-demand videos, environmental remediation wiki articles, conferences and workshops, software, protocols, user manuals, guidance documents, and technical fact sheets and summary reports. SERDP and ESTCP also have published monographs on several technical topics and have worked in collaboration with environmental experts, Federal agencies and the ITRC to disseminate practical and trustworthy information. Technology transfer needs identified in this section are expected to dovetail with or expand upon existing approaches and partnerships.

6.1 Critical Priority Technology Transfer Needs

6.1.1 Refine Existing Technology Transfer Communication Strategies to Improve Outreach to Site Managers

Workshop participants, especially DoD site managers, argued that the information generated from the Programs' research and validation projects must be presented in a concise yet informative manner and preferably not just in relationship to a specific highlighted technology but more so, with respect to how that technology/approach may be of use to site managers. SERDP and ESTCP are responsible for a great amount of the scientific progress in chlorinated solvent site assessment and remediation over the last 30 years. However, this information has often been passed down to users as it relates to specific projects. Users want to see the information as it relates to their needs. Further, users argued that, as a scientific community, we already have the tools needed to employ ASM, but users need to better understand how to employ these tools.

Further, workshop participants discussed the option of modifying the Programs' required final report formatting to include concise information that answers questions of most concern to site managers such as (not an inclusive list):

- What do I need to know about my site to see if this technology is appropriate?
- How well can this technology be expected to work at my site? (expressed as range of expected end points)
- How can I estimate a reasonable cost to implement the technology at my site?
- How does the information help to advance the CSM?

Similarly, information concerning biogeochemical and other critical conditions that preclude the use of the technology is important. Several options were suggested with respect to reaching out in an effective manner, among them:

- Survey successful remedial strategies and develop holistic guidance for each strategy that describes where it worked and where it failed, and the controlling factors that most influenced these outcomes.
- The Programs are in a position to establish benchmarks of success for the regulatory bodies. It would be beneficial to group all similar sites and establish benchmarks with respect to performance metrics that are achievable. This could be communicated via

webinars, case study classes, or cutting edge remedial and characterization courses developed by the Program.

• Seminars which include exercises and guidance were noted to be particularly useful for providing training in decision-making.

6.1.2 Increase Access to Technical Expertise on Project Specific Technology Implementation Issues

DoD site project teams often do not have access to the technical expertise necessary to determine, on a site-specific basis, what technologies are available and how they are appropriately applied. This issue could be significantly alleviated if a mechanism were in place to support direct interaction between principal investigators, experts in the field, and RPMs.

Contracting constraints frequently prevent direct research/site manager interactions. Access to expertise through an ESTCP and SERDP-managed technical support "people network" could provide significant value for focused technology transfer of specific technologies at specific sites. The proposed network could be built on interactions of individual researchers and site personnel, or small teams of researchers could be assembled around different technology themes. The latter could facilitate real-time project review. A wide variety of support configurations are possible.

6.1.3 Improve Adaptive Site Management Tools

As discussed in Sections 5.1.6 and 5.2.1, there is a need for improved ASM tools in a variety of areas. Specific technology transfer tools and guidance that may be helpful include, but are not limited to, the following:

- Dynamic remediation goal development tools based on a comparative analysis of source zone mass flux analysis and downgradient plume natural assimilative capacity
- Transition assessment tools to aid RPMs in determining when to transition sites from active remediation to long-term passive management (e.g., MNA)
- Case study analysis and lessons learned from example sites where ASM has been successfully applied to manage complex chlorinated solvent sites

6.1.4 Develop Technology "Myth-busting" to Avoid Preventable Mistakes

There is an opportunity to leverage the very large DoD remedy performance database to clearly identify failure modes and conditions of likely suboptimal performance for specific technologies. This work could include both process-based and empirical analyses and would result in a rules-based framework or decision logic that would identify remedies that will not work or may need special consideration to mitigate against poor performance, narrowing choices down to the remedies with the highest likelihood of success. This tool would enhance transparency to decision making, strengthen collaboration and consensus among stakeholders, and minimize preventable mistakes and associated unnecessary costs

6.1.5 Produce Experience Based Rational Design and Guided Optimization for In Situ Treatment of Chlorinated Solvents

There are a number of in situ technologies that have been frequently applied for the treatment of chlorinated solvents. Much useful guidance has been published and is readily available to practitioners and RPMs. This guidance provides a sound technical basis for understanding the underlying principles of the in situ treatment technologies, but often lacks a substantial experience

base. Many lessons are learned by practitioners as technologies are applied; much can be gained by sharing both successes and failures. Unfortunately, much of the peer-reviewed literature tends to emphasize success stories, whereas failures go largely unreported. There is a lack of guidance regarding the practical selection and implementation considerations for these technologies. Experience-based guidance is needed, specifically including:

- Detailed independent review of sites where the various major technologies (thermal, biological, chemical, and P&T) have been applied. These reviews should evaluate success, lessons learned, cost, and ultimate performance. The objective is to show what is working, what is not, and why. Some of these sites should show examples of how modeling can be effectively incorporated into design and optimization.
- Experience-based lessons learned document(s) for use by RPMs, specifically:
 - Rules of thumb that practitioners rely on for decision making.
 - Calculations commonly used to design remedies for a particular site (well/injection point spacing, amendment masses, etc.).
 - Experience-based applicability of technologies with respect to site conditions and remedial goals.
 - Characterization needs as well as the sensitivity of remedial performance to the level of characterization and uncertainty in characterization.
 - Value of monitoring tools for implementing ASM.
 - Data interpretation to evaluate the performance of technologies relative to natural source zone depletion processes and remedy transition.

Much of this information is already known to experienced practitioners, but not well documented. An understanding will facilitate technology selection, design, and optimization as well as inform reasonable expectation of costs, particularly with respect to the degree of treatment expected.

6.1.6 Improve CSMs for Understanding the Factors Sustaining and Controlling Persistent Chlorinated Solvent Plume Behavior

Research and demonstration needs related to improved CSMs that incorporate the processes and mechanisms controlling persistent chlorinated solvent plume behavior were discussed in Sections 4.1.5 and 5.1.8, respectively. While current research and demonstration needs in these areas clearly exist, several previous SERDP- and ESTCP-funded research efforts have yielded very important and beneficial results for improving CSMs with respect to these processes. Examples include, but are not limited to, application of mass flux methods, reductive dechlorination by organohalide-respiring bacteria, co-metabolic biodegradation, naturally occurring abiotic dechlorination, and high-resolution characterization methods. Despite successful research and demonstration, the applications of these tools and techniques remain limited. It is suspected that technology transfer barriers are, in large part, impeding the use of these tools. Thus, technology transfer approaches that will facilitate their acceptance into widespread practice, incorporation into industry-accepted models, and acceptance by both regulators and RPMs are needed.

6.1.7 Develop Effective, Immersive Training Tools

A significant opportunity exists to leverage existing and historical SERDP and ESTCP projects to increase the capabilities of RPMs as well as site consultants, contractors and the next generation of practitioners about to enter the workforce. Technologies used to investigate and remediate chlorinated solvent sites continue to evolve and staying abreast of current research and practice

remains difficult. Guidance documents, summary reports, and webinars are all useful approaches to memorialize change and evolution; however, they are one-way vehicles that should not be considered the only means of effective training. Proper training requires effective, authentic, and immersive processes and tools that are widely accessible and adaptable to different learning styles. Training tools need to focus on both the early- and later-career professionals, who tend to use technology differently. The one-way technology transfer vehicles of the past may not be as effective for younger professionals, although more conventional approaches also are needed, since most decision-makers are late-career professionals who still require understanding of change and technology evolution.

There are a number of places where the body of knowledge of chlorinated solvents developed over the 20 years of SERDP and ESTCP funding could be leveraged into training tools that are accessible to a wide variety of learning approaches. These elements include conceptual site model development, remedial options assessment, remedy design, transition assessment, optimization of remediation and monitoring, and risk assessment and management. Targeted training programs/classes associated that cover the full spectrum of the remediation process would provide context for these elements of the remediation process and with respect to technology and remediation decisions. These programs should complement the existing and emerging immersive training tools and the available and emerging remediation guidance (e.g., ESTCP, ITRC, EPA documents).

6.2 High Priority Technology Transfer Needs

6.2.1 Produce Brief Fact Sheets

Workshop participants discussed the need to update projects' timely findings through informal ways such as Tech Data Sheets. Such sheets can be placed as a handout in the SERDP and ESTCP Conference Booth. Specifically, of particular interest are Tech Data Sheets summarizing the results of several projects under the same topic area.

6.2.2 Provide Continuing Education Credits to Certify Professional Engineers/Geologists

One potential approach to increase participation in SERDP and ESTCP Technology Transfer activities, such as on-line and on-site seminars, is to provide credits to professionals who are required to annually participate in continuing education (CE). Such professionals include those holding a Professional Engineer (PE) certification as well as Licensed Site Professionals (LSP) in Massachusetts and Licensed Site Remediation Professionals (LRP) in New Jersey, each of which are certified to render decisions concerning appropriate site cleanup activities and procedures in their respective states. Procedures are available through the organizations governing each of these certifications to officially approve CE training.

6.2.3 Compile and Disseminate Data on Unintended Consequences of Remediation

Many remedies result in unintended consequences at sites that, in turn, may require additional treatment/mitigation to allow the selected remedy to work or to fully remediate a site. These unintended consequences encompass biological, chemical and physical impacts at sites. Compilation and dissemination of existing data that can be used to identify the site conditions that result in these adverse effects and how best to overcome the effects without causing additional unintended consequences are needed. To date, no systematic process for anticipating such problems has been developed. In essence, unintended consequences of remedial efforts illustrate

that systems understanding has not been achieved. This is partly due to remaining science gaps but also because the lessons learned from prior projects are not adequately being captured, so that RPMs can use these lessons learned to inform and improve decision-making. Examples of unintended consequences include:

- Metals mobilization,
- Excessive pH changes,
- Loss of aquifer permeability,
- Excessive production of sulfides and methane,
- Persistent products of organic amendments (e.g., alcohols and ketones), and
- Unintended effects on microbial communities and/or influences on natural abiotic processes

6.2.4 Assess and Predict Long Term Performance and Impacts of Chlorinated Solvent Treatment Technologies

A better general understanding of the long-term performance and impacts of treatment technologies based on site conditions is needed. Further, RPMs amongst workshop participants expressed the need to be able to anticipate and predict not just technology performance, but impacts of particular applications with respect to unfavorable site conditions. Although SERDP and ESTCP have been successful at identifying secondary groundwater quality impacts for bioremediation (ER-2131, ER-2129) and thermal (ER-200314) approaches, environmental managers argue that what is needed is a concise matrix (i.e., screening tool as opposed to lengthy reports) combining the knowledge gained through SERDP and ESTCP projects that can further help RPMs develop more successful implementation strategies.

In particular, attendees believe that the information needed to develop such decision matrices for the following treatment technologies is warranted: thermal treatment, bioremediation, in situ chemical oxidation (ISCO), P&T and natural source zone depletion (NSZD).

Several thoughts evolved during the discussion, among them the following:

- Technology assessments should be made by a third-party evaluator (i.e., someone not involved in the original project). We have plenty of guidance provided by individual PIs. What is needed is a generic broad approach to site remediation based on site characteristics.
- At a minimum, the decision matrix should help users minimize dead end approaches (i.e., if it is understood that a specific technology is not amenable to certain site characteristics, the decision matrix should help avoid repeating this mistake).
- Ideally, the decision matrix will allow users to quickly screen technologies that are applicable at their site from those that are unlikely to be beneficial. Similarly, the tool should highlight "unintended consequences" of the technology; for example, metals mobilization.

6.2.5 Establish "Lessons Learned" through Critical Analysis of Data from Past and Current Projects

SERDP- and ESTCP-funded projects on chlorinated solvents have produced an immense quantity of diverse data, results, and overall learning opportunities that for the most part have only been tapped in a discrete and limited way. A summative program that provides integration of the other analyses and general findings into a "lessons learned" deliverable would be extremely beneficial and significantly increase the value of previous investments to current DoD needs in addressing liabilities. The end deliverable, to be truly beneficial, must be provided in such a way as to be accessible to early-, mid-, and late-career professionals. Effective technology and information transfer vehicles are changing rapidly, due to personnel and sociological shifts in the workplace and increasing productivity and accountability demands within both public and private organizations.

7.0 SUMMARY AND CONCLUSIONS

There has been considerable progress over the past 25 to 30 years, including development of several in situ treatment technologies, understanding and use of NA processes, development of characterization tools (including HRSC methods), techniques to enhance amendment distribution, and numerous models and guidance documents to assist practitioners. Nevertheless, technical challenges remain, and there is also an opportunity to leverage the investments in CVOC remediation to improve treatment of other contaminants.

A series of overarching issues were identified that were not necessarily specific needs but larger themes that the Programs should consider in future funding decisions. These included: 1) SERDP should be sufficiently flexible to allow funding work in this area when unanticipated breakthroughs occur; 2) the Programs should consider ways to establish testing and evaluation sites; 3) remediation decisions often require developing credible interim goals rather than meeting regulatory criteria site-wide, and managers still need help in developing such interim goals; 4) participants identified a need for a CSM initiative that could lead to industry-wide guidance on CSM development; 5) there is an opportunity to synthesize the large amount of prior research in this area to develop useful quantitative decision tools; 6) there is value in reframing research objectives to focus on specific processes that are important for many contaminants, rather than the past practice of largely focusing on specific contaminants of concern; and 7) the Programs need to continue innovative approaches to technology transfer as communications technologies and learning styles continue to evolve.

A major focus of the workshop was the need to improve the quality and increase the use of CSMs and ASM strategies. Specifically, there are needs for better rate estimates (especially for slower NA processes), for better methods to determine transition points during ASM, and for a holistic decision-making framework to aid remedy selection and operation. Another broad theme was that the programs have funded a very large body of work over the years and there is an opportunity and a need to critically assess this work and synthesize information from related projects to develop general lessons and rules of thumb to assist practitioners and RPMs. These broad themes provide the context for many of the research and demonstration needs identified during the workshop.

Critical research needs included: 1) quantifying the impacts of co-contaminants on CVOC degradation, 2) evaluating mass discharge data from pump-and-treat systems to improve predictions of source strength over time, 3) improved understanding of the factors that sustain and control persistent CVOC plumes, 4) a fundamental understanding of the efficacy and fate of particulate amendments, 5) integrating information from fine-scale delineation tools, and 6) advanced tools for implementing knowledge-based ASM decision making. High priority research needs included: 1) guidance to help RPMs select between different vendor products, 3) methods to prioritize structures for vapor intrusion investigations, 4) further assessments of long-term performance and impacts of treatment technologies, and 5) critical assessments of the results from past SERDP and ESTCP projects.

Critical demonstration needs included: 1) quantification of NA mechanisms in plumes, 2) optimized delivery and distribution of amendments, 3) improved remedy performance monitoring methods, 4) strategies for managing back diffusion, 5) methods to integrate fine-scale delineation

results into CSMs, and 6) integrated application of existing tools to improve ASM approaches. High priority needs included: 1) an ASM pilot project designed to provide guidance on developing interim remedial goals, and 2) demonstration of rigorous statistical analytical tools that can improve the use and understanding of dynamic CSMs.

Finally, technology transfer remains an important need. Critical needs included: 1) refining existing technology transfer strategies to target site managers and RPMs, 2) providing technical expertise for specific project needs, 3) communicating innovative ASM tools, 4) developing "myth-busting" products designed to help RPMs avoid preventable errors, 5) developing experience-based guidance for in situ treatment of CVOCs, 6) improving CSMs for persistent CVOC plumes, and 7) developing innovative "immersive" training tools. High priority needs included: 1) preparing brief fact sheets based on summaries of related projects, 2) providing continuing education credits for practitioners, 3) communicating the unintended consequences of remediation, 4) developing tools to assess and predict long-term remediation performance, and 5) establishing lessons learned based on critical assessments of past project results.

8.0 REFERENCES AND ADDITIONAL INFORMATION

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APPENDIX A

AGENDA

Workshop on Management of DoD's Chlorinated Solvents in Groundwater Sites

July 18-19, 2018

U.S. Army Corps of Engineers, Seattle District, 4735 E Marginal Way S. Seattle WA

| Wednesday, July 18, 2018 | | | |
|--------------------------|---|--|--|
| 0800 | Registration | | |
| 0830 | Welcome and Introduction: Workshop Objectives and Structure | Andrea Leeson SERDP and ESTCP | |
| 0845 | SERDP and ESTCP Contributions : What have the Programs Delivered in the Past 26 Years of Research and Development on Chlorinated solvents in Groundwater | Andrea Leeson SERDP and ESTCP Hans Stroo Stroo Consulting LLC | |
| 0910 | Opportunities for Practical Applications: Applying Knowledge In Making Day-To-Day Decisions | John Wilson Scissortail Environmental | |
| 0935 | State of the Practice: Do we have enough tools? Are the tools utilized / implemented widely? Are there barriers to achieving implementation goals? | Rob Hinchee IST | |
| 1000 | Break | | |
| 1015 | Navy Perspective on Research Needs vs. Tools available What remains to be addressed with respect to the Navy's requirements | Michael Singletary NAVFAC South | |
| 1040 | Air Force Perspective on Research Needs vs. Tools available | Hunter Anderson Air Force | |
| 1105 | Regulatory Perspective on Research Needs vs. Tools | Kira Lynch EPA Region 10 | |
| 1130 | Lunch | | |
| 1215 | Breakout Session I Discussions | Breakout Groups | |
| 1500 | Break | | |
| 1615 | Recap of Day/Overview for Next Day | Andrea Leeson SERDP and ESTCP | |
| 1630 | Meeting Adjourn | | |

| Thursday, July 19, 2018 | | | |
|-------------------------|---|----------------------------------|--|
| 0800 | Coffee/Tea Service | | |
| 0830 | Recap and Logistics | Andrea Leeson SERDP and ESTCP | |
| 0845 | Breakout Session II Discussions Data Gaps & Priority Ranking | | |
| 1030 | Break | | |
| 1045 | ⁴⁵ Breakout Session II Discussions Data Gaps & Priority Ranking (continuation) | | |
| 1200 | Lunch | | |
| 1245 | Breakout Session Reports | Breakout Group Chairs | |
| 1500 | Refreshment Break | | |
| 1515 | General Group Discussion | | |
| 1600 | Closing Summary and Remarks | Andrea Leeson SERDP and ESTCP | |
| 1615 | Workshop Adjourn | | |

APPENDIX B

ATTENDEE LIST

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Lisa Alvarez-Cohen University of California, Berkeley

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Gunarti Coghlan NAVFAC HQ

Chuck Coyle USACE

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Michelle Crimi Clarkson University

Anthony Danko NAVFAC EXWC

> Craig Divine ARCADIS

Elizabeth Edwards University of Toronto

> Murray Einarson Haley & Aldrich

Ron Falta Clemson University

David Freedman Clemson University

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> Robert George SPAWAR

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> Paul Hatzinger APTIM

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> Sarah Kearsley Noblis

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