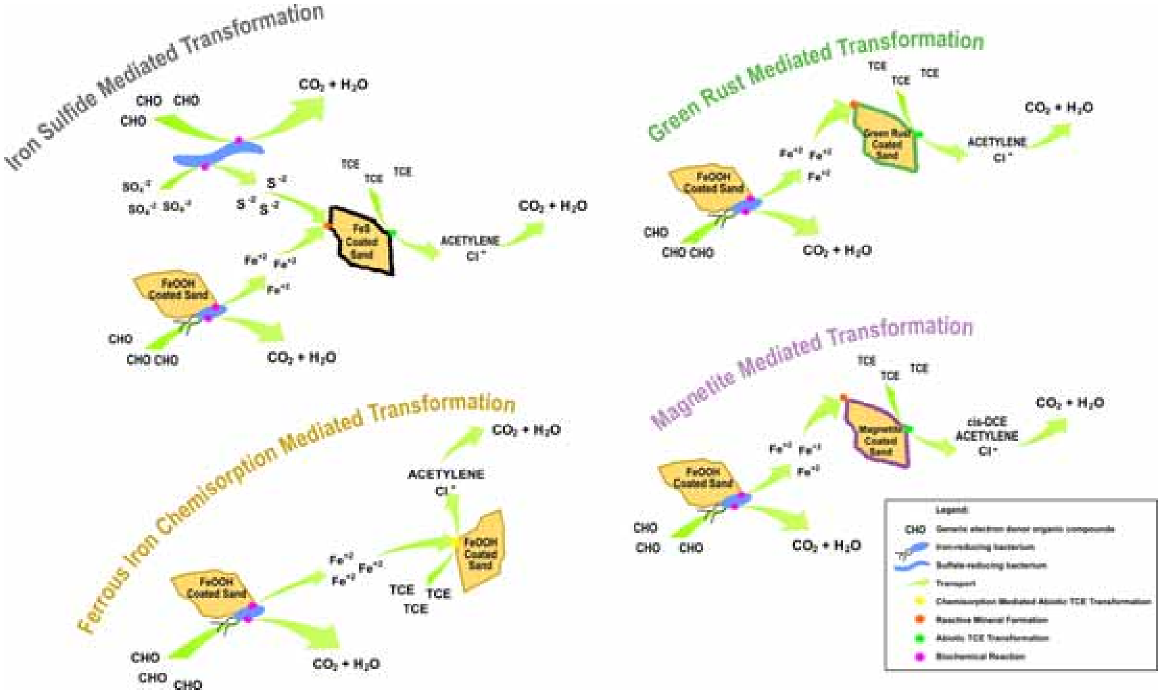
Workshop on *In Situ* Biogeochemical Transformation of Chlorinated Solvents

February 2008



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Workshop on *In Situ* Biogeochemical Transformation of Chlorinated Solvents

February 2008

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Contents

Appendices

Acronyms

AFCEE	Air Force Center for Engineering and the Environment
AVS	acid volatile sulfide
BiRD	biogeochemical reductive dechlorination
cis-DCE	*cis*-1,2-dichloroethene
CRS	chromium reducible sulfide
CSM	Conceptual site model
CVOCs	chlorinated volatile organic compounds
DCE	dichloroethene
DNAPL	dense non-aqueous phase liquid
DNT	dinitrotoluene
DoD	Department of Defense
EAB	enhanced anaerobic bioremediation
EDS	energy dispersive spectrometers
EISB	enhanced *in situ* bioremediation
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security & Technology Certification Program
FISH	fluorescent *in situ* hybridization
IRZ	*in situ* reactive zone
ISB	*in situ* bioremediation
ITRC	Interstate Technology Regulatory Council
MNA	monitored natural attenuation
O&M	operations and maintenance
PCE	tetrachloroethene
PLFA	phospholipids fatty acid
qPCR	Quantitative polymerase chain reaction
SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethene
T-RFLP	terminal restriction length polymorphism
WDS	wavelength dispersive spectrometers
XANES	X-ray absorption near edge structure
ZVI	zero valent iron

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Executive Summary

A workshop was held in San Antonio, Texas, from April 24 through 26, 2007 to promote an active discussion of ongoing research focused on the role of *in situ* biogeochemical transformation of chlorinated solvents, defined here as processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface. This workshop was convened to discuss the current understanding of these processes and identify research and demonstration needs among researchers, practitioners, site owners, and regulatory agencies. Prior to the workshop, participants were provided background material on the purpose and goals of the workshop, including a list of charge questions for their consideration and to stimulate discussion. A combination of whole group meetings and breakout sessions were used at the workshop in order to maximize participation and information exchange.

The participants identified key issues in each of the following topic areas:

- Fundamental understanding of *in situ* biogeochemical transformation
- Characterization of *in situ* biogeochemical transformation
- Implementation of remediation systems based on *in situ* biogeochemical transformation
- Regulatory acceptance of remediation using *in situ* biogeochemical transformation

Based on the key issues, research and demonstration needs were identified for remediation of chlorinated solvents using *in situ* biogeochemical transformation. In total, seven research and two demonstration needs were identified, with most of them focused on improving the fundamental understanding of mechanisms and processes that contribute to chlorinated solvent degradation. These research and demonstration need topics include:

- Biogeochemical mechanisms of chlorinated solvent degradation
- Geochemical and microbiological requirements for formation of active mineral phases
- Sampling and analysis requirements and protocols for characterization and monitoring of *in situ* biogeochemical transformation
- Geochemical modeling for predicting the development, effectiveness, and sustainability of *in situ* biogeochemical transformation
- Data mining, sampling, analysis, and geochemical modeling of existing sites to facilitate understanding of *in situ* biogeochemical transformation in the field
- Methods for selection of *in situ* amendments to promote formation of biogeochemically active mineral phases
- Applicability of *in situ* biogeochemical transformation to other contaminants

- Demonstration of a sampling and analysis protocol for characterization and monitoring of *in situ* biogeochemical transformation in the field

- Pilot-scale demonstrations with selected amendments that promote development of *in situ* biogeochemical transformation

Overall, the workshop participants have a positive view of using *in situ* biogeochemical transformation for remediation of chlorinated solvents. It is an emerging remediation approach that has promise for wide application at solvent-contaminated sites, but needs a fairly significant amount of research in order to improve the basic understanding of mechanisms involved.

Workshop participants agreed that additional bench- and pilot-scale testing of remediation based on *in situ* biogeochemical transformation should be performed, and data should be mined from the relatively small number of existing sites where this approach has been applied. Ultimately, sampling procedures and analytical methods, design guidance, and operation and maintenance (O&M) protocols need to be developed in order to maximize application and regulatory acceptance of technologies based on *in situ* biogeochemical transformation.

In situ biogeochemical transformation is a promising remediation technology that operates at the interface of physical, chemical, and biological phenomena. The interdisciplinary nature of environmental science and engineering has fostered cognizance of the power of this interface and will be a critical component in further development and application of this innovative technology. Future application of *in situ* biogeochemical transformation will result in more cost-effective ways of mitigating the risks associated with inorganic and organic contamination of soil, groundwater, and sediment.

Section 1
Introduction

Chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE) are found at approximately 80 percent of all Superfund sites with groundwater contamination, and more than 3,000 Department of Defense (DoD) sites in the United States [Strategic Environmental Research and Development Program (SERDP), 2006]. The life-cycle costs to remediate these sites are uncertain, but are likely to exceed several billions of dollars nationally. DoD alone could spend more than $100 million annually for hydraulic containment at these sites using pump-and-treat technologies, and estimates of life-cycle costs exceed $2 billion (SERDP, 2006). Chlorinated solvents are also among the most difficult contaminants to clean up, particularly when their dense non-aqueous phase liquid (DNAPL) sources remain in the subsurface.

Because of this, the DoD and the U.S. Environmental Protection Agency (EPA) have a keen interest in technology development in the area of chlorinated solvent remediation. For example, SERDP and the Environmental Security Technology Certification Program (ESTCP) have funded a number of basic and applied research projects through their DNAPL Source Zone Initiative and Chemical Oxidation Initiative, as well as many other projects related to dissolved phase solvent remediation. The Air Force Center for Engineering and the Environment (AFCEE) and analogous departments of the Army and Navy have funded many projects in the areas of bioremediation and natural attenuation of chlorinated solvent-contaminated groundwater. EPA performs management, oversight, and remediation at thousands of sites across the country, and also has its own internal research programs.

In situ bioremediation has become a widely-used technology for remediating chlorinated solvent sites, as a result of several recent technological advances. Some of the first applications, in the late 1980s and early 1990s, were based on stimulating aerobic cometabolism, particularly for TCE contamination. However, the vast majority of bioremediation applications for chlorinated solvents have involved stimulating anaerobic reductive dechlorination, a process known as enhanced anaerobic bioremediation (EAB). This technology, also known as enhanced *in situ* bioremediation (EISB), *in situ* reactive zone (IRZ), and *in situ* bioremediation (ISB), has been applied at hundreds of sites across the country. As bioaugmentation, an enhancement of EAB that involves addition of microorganisms, has become more common, advancements have been made in the ability to characterize microbial communities, individual bacterial species, and even enzymes and metabolic functions of interest.

A related area of research and development that has been receiving increased attention recently is the role of abiotic processes in chlorinated solvent degradation. Understanding and exploiting these processes has the potential to improve the performance and cost-effectiveness of EAB, or increase the use of monitored natural attenuation (MNA) at sites where it may be appropriate.

Iron-mediated abiotic reactions are of particular significance. It has long been known that iron can donate electrons and degrade chlorinated solvents abiotically, as this approach has been used in zero valent iron (ZVI) permeable reactive barriers. However, recent studies have shown that reactive iron minerals formed under anaerobic conditions during EAB can also abiotically degrade chlorinated solvents.

1.1 Overview of Abiotic Transformation

A thorough review of developments in abiotic degradation of chlorinated solvents by ferrous-iron containing minerals is provided in Brown et al., 2006. A summary from that reference is provided here.

Early in the development of ZVI technology, the potential role of ferrous iron in reductive dechlorination was considered. Ferrous iron, formed by the corrosion (reaction) of ZVI, was thought also to react with chlorinated solvents (Matheson, 1994; Tratnyek, 2006). Additionally, parallel to the investigation of ferrous iron associated with ZVI technology, other researchers specifically investigated the reductive reactivity of reduced iron minerals such as pyrite. They demonstrated that a suspension of pyrite was able to dechlorinate carbon tetrachloride (Kriegman-King, 1994) and reduce dinitrotoluene (DNT) (Jiayang, 1996). Additional research has shown that chemically precipitated ferrous iron is also an active reductant for chlorinated volatile organic compounds (CVOCs) (Brown, 2005).

One of the key advances in the development of biogeochemical transformation has been the discovery that surface-bound ferrous iron can react directly with chlorinated solvents by mechanisms similar to those observed for ZVI. Chloroacetylenes were observed as products in the reaction of TCE with reduced iron-containing sediments (Szecsody et al., 2004). Subsequent work on reductive reactions with ferrous iron has shown that the reactions are surface catalyzed (Elsner, 2002). The reactivity of bound ferrous iron was found to be a function of the surface area and of the geochemical conditions. In general, iron sulfides and oxides were the most reactive reduced minerals.

Recent studies have suggested that soluble ferrous iron has a role in the activity of certain iron minerals. The reduction of *cis*-1,2-dichloroethene (*cis*-DCE) with magnetite was enhanced in the presence of soluble ferrous iron (Ferrey, 2004). The role of the soluble ferrous iron is unknown but may be related to the regeneration of active sites (Scherer, 2005). A comprehensive list of references related to abiotic transformation processes is provided in Section 9 of this document.

1.2 *In Situ* Biogeochemical Transformation

The interface between biological and abiotic processes is just beginning to be tapped for potential application to treatment of chlorinated solvents and other contaminants. Because of the overlapping and synergistic effects of biological, abiotic, and geochemical processes involved, the term "*in situ* biogeochemical transformation" is used in this document. As defined here, *in situ* biogeochemical transformation refers to processes where contaminants are degraded by abiotic reactions with minerals formed that are either naturally occurring or are biogenically produced in the subsurface. These reactive minerals are thought to include reduced sulfide minerals such as iron monosulfide (e.g., Butler and Hayes, 1999 and 2000), green rusts which are layered structures composed of mixed divalent and trivalent iron oxides interspersed with water and anions including sulfate, chloride, and carbonate (Christianson and Stipp, 2003, Lee and Batchelor, 2002), or magnetite which is a ferromagnetic mineral composed of mixed divalent and trivalent iron with the formula Fe_3O_4 (e.g., Ferrey et al., 2004). In many cases these minerals are formed by, at least in part or indirectly, from anaerobic biological processes. For example, chlorinated solvents such as PCE and TCE may be reduced in an abiotic reaction with iron monosulfide that is formed in the subsurface under iron- and sulfate-reducing conditions. Alternatively, *cis*-DCE may be oxidized by reaction with magnetite, which could be a product of anaerobic biological ferric iron reduction. An advantage of these transformation reactions is that, in general, regulated intermediate dechlorination products are not produced.

Figure 1 is a conceptual model of some of the myriad biogeochemical processes and reactions that play potential roles during *in situ* biogeochemical transformation. Iron sulfide mediated transformation (Butler and Hayes, 1999 and 2000), ferrous iron chemisorption mediated transformation (Williams and Scherer, 2004), green rust mediated transformation (Lee and Batchelor, 2002), and magnetite mediated transformation (Ferrey et al., 2004) are shown here and demonstrate how both biochemical and geochemical reactions can be linked to result in the generation of reactive surfaces. The interplay of these reactions and their implications for remediation of contaminated environments is just beginning to become understood.

1.3 Workshop Objectives

A workshop of more than 20 experts was convened in April of 2007 in San Antonio, Texas, to discuss the current understanding of biogeochemical transformation processes affecting chlorinated solvents and to identify research and demonstration needs among researchers, practitioners, site owners, and regulatory agencies. This workshop was hosted by the Air Force Center for Engineering and the Environment (AFCEE), the Naval Facilities Engineering Service Center (NFESC), the Environmental Security Technology Certification Program (ESTCP), and the United States Environmental Protection Agency (EPA). Specifically, the objectives of the workshop were to accomplish the following:

- Promote an active discussion of ongoing research focused on the interface between biotic and abiotic mechanisms (i.e., biogeochemical) of chlorinated solvent transformation
- Document the current understanding of these processes
- Identify data gaps and possible discrepancies in current research
- Identify future research needs to resolve these discrepancies with a focus on practical application of technologies based on *in situ* biogeochemical transformation

This document summarizes the methods, conclusions, and recommendations that resulted from this workshop.

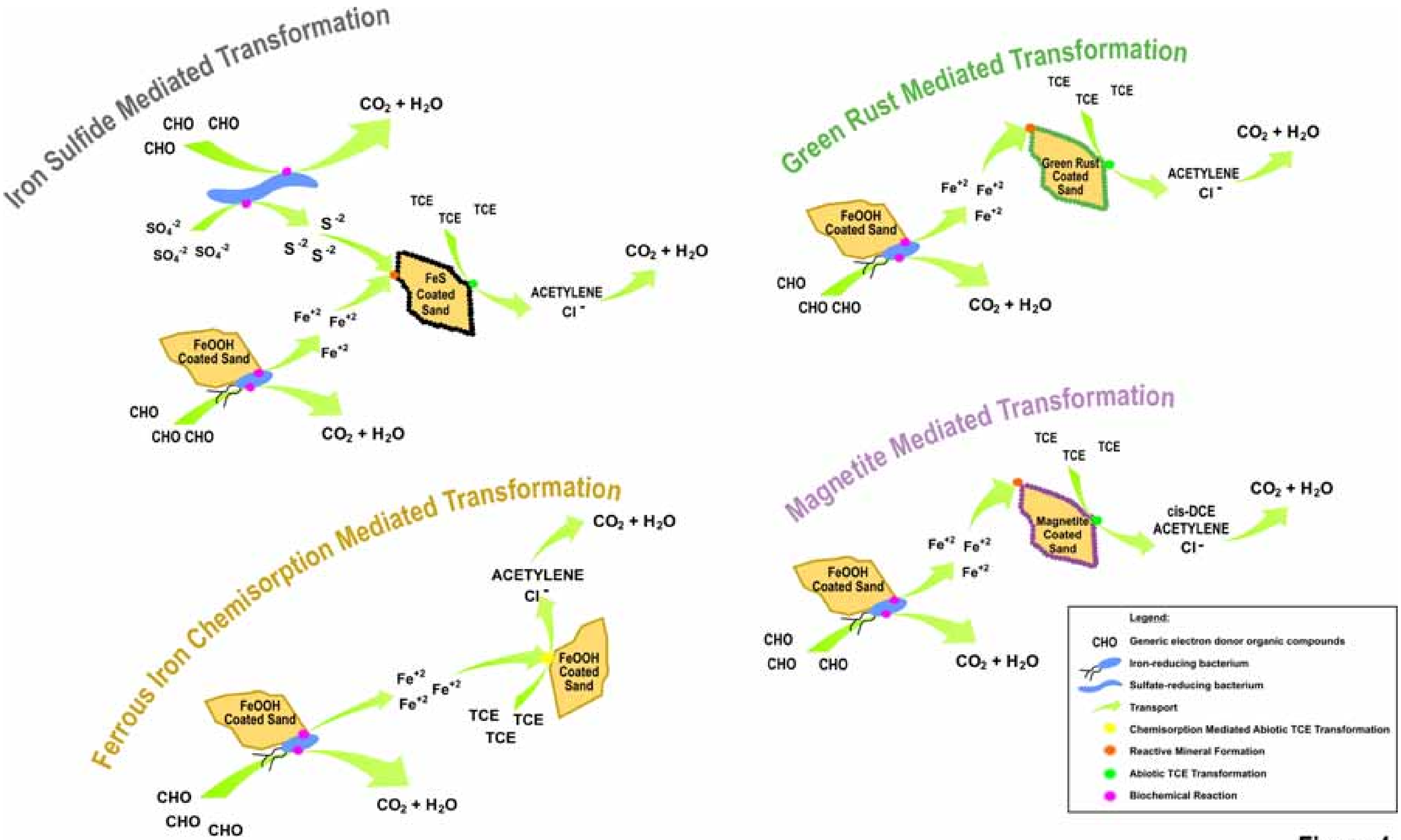

Figure 1.
Potential In Situ Biogeochemical Transformation Mechanisms

Section 2
Method

A workshop on the use of *in situ* biogeochemical transformation for degradation of chlorinated solvents was held in April 2007 at AFCEE Headquarters (see Appendix A for a list of the attendees). More than 30 participants were invited with the goal of including knowledgeable experts in the fields of microbiology, biochemistry, geochemistry, analytical chemistry, and remediation engineering and science. This mix represented a broad range of perspectives, including academic researchers, regulators, remedial project managers, consultants, and government agency representatives.

Prior to the workshop, participants were provided background material on the purpose and goals of the workshop, including a list of charge questions for their consideration. The agenda (see Appendix B) was designed to identify the most pressing needs in a focused manner, while ensuring that all participants could express their views. Meetings of the entire group of experts and smaller breakout groups were used to maximize participation and information exchange.

The workshop opened with several presentations intended to provide background information on *in situ* biogeochemical transformation and its current applications, as well as to highlight key issues. These presentations are included in Appendix C. Participants were then divided into three smaller working groups to address the specific charge questions. These breakout groups were facilitated by discussion leaders, and extensive notes were taken in each session.

The first breakout session was convened for 5 hours spread over 2 days. During this first breakout session, participants in each group were asked to identify key issues in each of the following topic areas:

- Fundamental understanding of *in situ* biogeochemical transformation
- Characterization of *in situ* biogeochemical transformation
- Implementation of remediation systems based on *in situ* biogeochemical transformation
- Regulatory acceptance of remediation using *in situ* biogeochemical transformation

Following the first breakout session, the discussion leaders presented the discussions held in each session to the entire group. After these presentations, a second 3-hour breakout session was held in which participants identified research and development needs related to the topic areas listed above. Each discussion leader again summarized their sessions in presentations to the entire group. The entire group then participated in the final discussions and the selection of the key issues and the research and demonstration needs.

The remainder of this document presents the results of the breakout sessions and whole group meetings. Section 3 presents the charge questions and issues identified related to the fundamental understanding of the mechanisms involved in biogeochemical transformation; Section 4 discusses issues related to characterizing the relevant processes; Section 5 presents issues related to design and implementation of remediation based on *in situ* biogeochemical transformation; and Section 6 discusses relevant regulatory issues. In each of these sections, the charge questions given to the group are presented followed by the key issues identified by the participants. The charge questions were intended to stimulate thinking and discussion rather than to elicit specific answers. Therefore, the identified key issues comprise many of the topics addressed by the charge questions but each key issue is not tied to any specific charge question. Section 7 presents the research and development needs identified by participants. These research and development needs are designed to address the key issues identified in Sections 3 through 7. Conclusions are presented in Section 8; and Section 9 provides references, those cited in this document, as well as additional references.

Section 3
Fundamental Understanding of *In Situ* Biogeochemical Transformation

The first topic for discussion in the breakout groups was the fundamental understanding of *in situ* biogeochemical transformation. Section 3.1 presents the charge questions that were posed to the participants, and Section 3.2 describes the key issues identified at the workshop related to the charge questions.

3.1 Charge Questions

The charge questions posed to the participants pertained to the current scientific understanding of biological, abiotic, and biogeochemical reactions; the connection and potential synergies between biological and abiotic reactions; and their importance/role in both MNA and engineered approaches. Specifically, participants were asked to review and/or identify the following:

- Enhancing bioremediation of chlorinated solvents – the role/importance of novel reactions
- Biotic and abiotic mechanisms playing a role in the remediation of chlorinated solvents – what is known?
- Identify data gaps related to the enhancement of the role of biogeochemical reactions in the remediation of chlorinated solvents
- Identify data gaps for potential future work in the laboratory and in the field where *in situ* biogeochemical transformation could be manipulated and/or enhanced.

3.2 Key Issues

Several key issues were identified at the workshop related to these charge questions. These issues are discussed in detail below.

In situ biogeochemical transformation refers to processes where contaminants are degraded by abiotic reactions with minerals formed in the subsurface. These reactive minerals are thought to include reduced sulfide minerals such as iron monosulfide, carbonate and sulfate green rusts (layered multivalent iron minerals), and magnetite. In many cases these minerals are formed, at least in part or indirectly, by anaerobic biological processes.

3.2.1 Defining *In situ* Biogeochemical Transformation Relevant to Chlorinated Solvent Degradation

Participants agreed that the individual processes relevant to chlorinated solvent degradation are not sufficiently understood, and better definition of these processes is needed. Evidence to date suggests that abiotic mechanisms can play an important role in chlorinated solvent remediation. However, several different but related processes can occur, and each may be important to the desired activity. For example, magnetite has been shown to be capable of degrading *cis*-DCE at rates comparable to biological reductive dechlorination (Ferrey and Wilson, 2002). The magnetite can be biogenically-formed, produced during ferric iron reduction by iron-reducing bacteria. This combination of biological iron reduction, magnetite formation, and subsequent abiotic degradation is one example of biogeochemical transformation, and it may occur naturally or as a result of EAB.

Another approach to using biogeochemical degradation is the deliberate addition of iron minerals to electron donor formulations in order to stimulate biological and abiotic degradation simultaneously. AFCEE has used this approach during installation of several biowalls, by amending mulch or compost with iron minerals, to attempt to increase the reactivity and longevity of the biowalls (Parsons, 2007b). Yet another approach that has been proposed is the addition of iron chlorides to precipitate sulfides and relieve inhibition of dechlorinating bacteria. Finally, some investigators have proposed the injection of electron shuttle compounds to increase the rates of chlorinated solvent degradation.

One of the most significant challenges related to detection of abiotic degradation is that, currently, the predominant evidence for its occurrence is a lack of accumulation and disappearance of daughter products as observed in biological reductive dechlorination. The basis for this is that reduction of chlorinated solvents by iron minerals may be mechanistically similar in some ways to reduction by zero valent iron, which can produce a wide range of products in addition to ethene and ethane, but generally results in very low percentages of reductive daughter products (Brown et al., 2006). However, it is important to keep in mind that the lack of daughter products is suggestive of, but not conclusive evidence of abiotic degradation.

Nevertheless, it is often assumed that abiotic degradation is occurring simply because known biological processes are not sufficient to explain contaminant disappearance. However, other processes (e.g., anaerobic oxidation, aerobic cometabolism, or electron shuttle-mediated transformation) may also cause contaminant degradation without daughter product accumulation (Wymore et al., 2007). Therefore, detection or proof of abiotic or *in situ* biogeochemical transformation using standard characterization methods can be challenging, and represents a significant data gap.

While all chlorinated solvents are amenable to degradation by *in situ* biogeochemical transformation, the mechanisms can vary greatly depending on the specific compound. For example, chemical elimination, a purely abiotic reaction, is important in the transformation of chlorinated ethanes but not for the ethenes. Biogeochemical reactions, such as those promoted by biogenically produced green rust, may be important in the transformation of chlorinated ethenes. Also, *in situ* biogeochemical transformation likely has an important role in the transformation of other contaminants such as nitrate and N-nitrosodimethylamine, which are known to be chemically reducible.

3.2.2 Current Understanding of Mechanisms Contributing to Chlorinated Solvent Degradation

It is known that reduced iron minerals are responsible for abiotic degradation of chlorinated solvents. These minerals can be naturally present in the aquifer matrix, or they can be microbially generated (either naturally or artificially induced) *in situ* under anaerobic conditions (Butler and Hayes, 1999; Elsner et al., 2004a and 2004b; Ferrey et al., 2004; Kriegman-King and

Reinhard, 1994; Lee and Batchelor, 2003; Lee and Batchelor, 2004; Macalady et al., 1986; Scherer, 2005). While it appears that microbially generated iron minerals are the most effective at contaminant degradation, the biogeochemical mechanisms of *in situ* mineral formation are not well understood. For example, microbes can form different minerals under different geochemical conditions (Drzyzga et al., 2002; Elsner et al., 2004a; Elsner et al., 2004b; Erbs et al., 1999; Lovley, 1991), but it is not known how to manipulate redox conditions prescriptively for optimal mineral formation while maintaining biological degradation capabilities. Also, it is not known which minerals are optimal for chlorinated solvent degradation.

Significant uncertainty exists regarding the interplay between biological and abiotic mechanisms as they contribute to *in situ* biogeochemical transformation. Quantitatively allocating degradation to specific biological and abiotic mechanisms is difficult to impossible using standard characterization approaches and parameters. Yet, despite these difficulties, it is important to determine what the rate limiting step or mechanism is within the overall biogeochemical process. Remediation systems based on *in situ* biogeochemical transformation can then be designed or optimized to overcome the rate limitation.

Workshop attendees agreed that the mechanisms that contribute to *in situ* biogeochemical transformation are not fully understood. As discussed in the previous section, degradation is attributed to abiotic mechanisms when it is apparent that biological mechanisms cannot explain all of the disappearance. However, other novel degradation mechanisms/factors need to be considered, such as anaerobic oxidation, the role of electron shuttles, and aerobic cometabolism. Developing a better understanding of these mechanisms, their effects on chlorinated solvents, and how they collectively contribute to what occurring at a given site is essential in order to determine the contribution of each.

3.2.3 Types of Active Iron Mineral Phases Involved in *In Situ* Biogeochemical Transformation

Workshop attendees concurred that several forms of iron minerals can be involved in *in situ* biogeochemical transformation that are relevant for chlorinated solvents. Some examples of iron minerals that can play a role in *in situ* biogeochemical transformation are iron sulfides, pyrite, magnetite, and green rust, among others. The reactivity of these minerals toward chlorinated solvents is different for the various iron minerals, and even depends on the interaction between these minerals and the surrounding environment. For example, chemisorption of soluble ferrous iron onto mineral surfaces appears to promote electron transfer and generate a reactive complex more powerful than the mineral surface in the absence of chemisorbed ferrous iron (Amonette et al., 2000; Elsner, 2002; Elsner et al., 2004a, Elsner et al., 2004b; Williams and Scherer, 2004). Also, biologically derived iron sulfides may be more reactive than naturally occurring iron minerals, possibly because of increased surface area.

In addition to the inherent variability of the reactivities of the different iron minerals, the reactivity of a given mineral may decrease over time as iron is oxidized, or iron monosulfide is transformed to iron disulfide. The mechanisms causing loss of reactivity and the overall sustainability of the reactivity are not well understood, nor is the ability to predict when the reaction rates will decrease.

Identification and characterization of active mineral species is just beginning to occur. While species including iron sulfides, magnetite, and green rust have been identified as prime candidates, further research into the specific forms of these minerals that promote *in situ* biogeochemical transformation is needed. In addition, other mineral species that have not been identified may also exist. Finally, the relationship between groundwater chemistry and the mineral phases insofar as it affects reactivity is in need of further research.

3.2.4 Microbiological and Geochemical Conditions for Active Mineral Formation

It is well established that in order to stimulate biological reductive dechlorination, anaerobic conditions need to be established. Anaerobic conditions are also needed to form the reactive iron minerals that abiotically degrade chlorinated solvents. Redox conditions need to be at least iron reducing in order to form soluble ferrous iron, which can then react with other species to form reactive minerals. Minerals can also be formed under sulfate reducing conditions, when sulfide is produced.

However, workshop attendees agreed that these processes are complex, and not easily predictable. For example, the mechanisms for mineral formation may be different under iron-reducing conditions than under sulfate-reducing conditions. Also, different electron donors may stimulate mineral formation at different rates, even under the same redox conditions at the same site. Finally, the significance of the mechanisms for mineral formation in redox transitions zones (i.e., transitions between aerobic and anaerobic) is not well understood.

3.2.5 Representativeness of Laboratory Studies to the Field

The final key issue related to the fundamental understanding of *in situ* biogeochemical transformation discussed at the workshop is the representativeness of laboratory studies to field conditions. As is the case for most *in situ* technologies, it is difficult to extrapolate the quantitative laboratory results to the field, especially degradation rates. One approach that may be of use is to develop a common method for rate calculations that can be applied to multiple laboratory studies of *in situ* biogeochemical transformation. Possible options include a rate per unit mass of minerals or per unit active mineral surface area. Issues with these approaches may include: lack of understanding which minerals are significant; unavailability of standard analytical methods for their measurement; and a requirement to measure surface areas of specific minerals which is difficult if not impossible in a complex matrix such as soil.

Another issue that complicates extrapolation to the field is that the biogeochemical degradation rates observed in lab studies have varied widely. While these variations are dependent on the specific conditions tested, some general observations can be made. First, it appears that microcosm studies designed specifically to investigate abiotic degradation have yielded slow rates, but have generally provided reasonably good mass balances of reactants and products (Butler and Hayes, 2000). In contrast, abiotic column studies appear to show faster degradation rates, possibly because they better simulate a dynamic system where ferrous iron is continuously produced, transported with groundwater, and then deposited on mineral surfaces to generate biogeochemically reactive species such as green rust, iron sulfides, or magnetite (Elsner et al., 2004b). However, the column studies also tend to yield worse mass balances compared to microcosms. Overall, long duration studies may be required in order to elucidate degradation mechanisms whether microcosm or columns are used because of the potential for slow degradation rates. One potential method for accelerating degradation rates observed in lab studies is to use minerals in a form with higher surface area. This theoretically has the potential to increase rates, but again, it needs to be determined how to extrapolate rates observed under these conditions to the field, where surface area of the minerals may not be the limiting factor, and where it may not be possible to generate a significant amount of high surface area minerals.

The final significant issue related to lab studies is the fact that biological and abiotic reactions are dependent on each other during *in situ* biogeochemical transformation. In fact, de-coupling abiotic and biological mechanisms is difficult to do in lab studies. For example, sterilizing samples from field sites in order to kill the microorganisms can actually alter the structure of the minerals that are being studied, which can bias the experiment. Of currently available methods for sterilization, irradiation appears to be the least intrusive, but it still is not benign toward the iron minerals. Because of these factors, it may not be appropriate to de-couple the mechanisms. De-coupling of biological and abiotic mechanisms is likely to eliminate beneficial synergisms and makes study of the overall process less representative of what is observed in the field. Overall, methodologies used in laboratory studies for *in situ* biogeochemical transformation have varied widely, as have the results, and this variation is possibly attributable to dissecting the individual processes rather than taking a holistic approach. More consistent approaches for conducting these studies and for interpreting results need to be developed.

Section 4
Characterization of *In Situ* Biogeochemical Transformation

The second topic for discussion in the breakout groups at the workshop was characterization of *in situ* biogeochemical transformation. Section 4.1 presents the charge questions that were posed to the participants, and Section 4.2 describes the key issues identified at the workshop.

4.1 Charge Questions

The charge questions posed to the participants related to what site parameters need to be evaluated in to order to perform a field assessment of biogeochemical transformation rates. Specifically, participants were asked the following:

- What biogeochemical parameters need to be measured? What would be the most effective and accurate methodologies to measure these parameters in the field? How would the results be interpreted? How can the results be used to estimate biogeochemical sustainability within the system?
- Identify fundamental questions on whether one could modify systems based on *in situ* biogeochemical transformation. Identify how one would recognize if a site is a candidate for remediation through manipulation/enhancement of biogeochemical transformation, either through field assessment or laboratory analysis.
- Discuss reactivity of metal sulfide materials depending upon different regimes (e.g., iron dominated and sulfate dominated), etc.
- Identify what would need to be monitored in the field to successfully enhance *in situ* biogeochemical transformation, either through an engineered system or MNA. Will credibility be tied to being able to predict biogeochemical potential? Discuss the disparity between current published biogeochemical rate constants and experienced rate constants in the field.
- Identify needs for instruction on identification of sampling locations (e.g., discreet sampling versus homogenization, tools for identifying sampling locations, etc.), proper field sampling techniques, sample shipment and preparation, analytical procedures, etc., all aimed at providing true readings of reactivity of a site, to more accurately predict the biogeochemical potential of a site.

Characterization of *in situ* biogeochemical transformation requires an interdisciplinary approach. For example, geochemical analyses of groundwater facilitate understanding of the microbiological potential for various electron accepting reactions and the electrochemical potential for production of certain active mineral phases. Geochemical analyses of sediments or other solid phases facilitate identification and quantification of specific active phases that promote the transformation reactions. Microbiological analyses facilitate identification of specific bacteria or enzymatic activities that are able to use certain geochemical species in energy producing reactions and are able to produce precursors of biogeochemically active phases.

4.2 Key Issues

Several key issues were identified at the workshop related to these charge questions. These issues are discussed in detail below.

4.2.1 Types of Data Needed

There is a wealth of parameters that can be monitored to assess/characterize active *in situ* biogeochemical transformation, many of which are similar to those that are sampled for an EAB site. However, it is not known which parameters are the most critical and valuable to understanding *in situ* biogeochemical transformation. A better understanding of these parameters and more specific guidelines for the specialty analytical methods are needed. Table 1 is a comprehensive but not necessarily exhaustive list of analyses that could be included in a sampling program whose goal is to characterize *in situ* biogeochemical transformation. This list is not intended to be a presentation of recommended analytes, nor is it presented in order of importance; rather, it is a list of parameters to consider. Also, interpretation of data generated from these analyses is not discussed here. Finally, these parameters vary in commercial availability, cost, ease of use, and the number of applications.

Table 1 Monitoring Parameters

Data Type	Examples of Specific Parameters	General Purpose/Data Interpretation
Standard Groundwater Parameters (widely available among commercial labs)		
Redox-Sensitive Parameters	Dissolved oxygen (DO), oxidation-reduction potential (ORP), ferrous iron, sulfate, nitrate, and dissolved methane	General indication of dominant terminal electron accepting process and important factors affecting geochemistry
Contaminants and Degradation Products	Chlorinated ethenes, chlorinated methanes, chlorinated ethanes, ethene, ethane, acetylene, chloride	Indication of biodegradation pathway and extent of degradation
Electron Donor Parameters	volatile fatty acids (e.g., butyrate, propionate, acetate), total or dissolved organic carbon, and chemical oxygen demand	Indication of carbon source; potential for sustained biological reduction
Water Quality Parameters	Specific conductance, temperature, total dissolved solids, pH, alkalinity	Important factors affecting geochemistry and biological activity
Dissolved Gases	Dissolved hydrogen, hydrogen sulfide	Indicator of dominant terminal electron accepting process in natural environments; product of sulfidogenesis and precursor to production of iron sulfides; sometimes observed byproduct of abiotic chlorinated solvent degradation
Other Groundwater Parameters – generally available commercially, but less common		
Trace metals/complete anion-cation analysis	Sodium, calcium, potassium, aluminum, copper, magnesium, *etc.*	Important geochemistry parameters
Compound specific stable carbon isotopes	Isotope analysis for chlorinated ethenes, methanes, and ethanes	Specialty analysis that may indicate dominant degradation mechanisms

Table 1 Monitoring Parameters

Data Type	Examples of Specific Parameters	General Purpose/Data Interpretation
Microbial analyses – becoming more commonly used for EAB sites		
Bacterial cell membrane characterization	Phospholipid fatty acid (PLFA) analysis	General bacterial analysis that is very dependent on environmental conditions
Community level profiling	Terminal restriction length polymorphism (T-RFLP)	Analysis that characterizes the diversity and relative abundance of bacteria present; can be used in conjunction with clone libraries to identify members of the community
Metabolic assessment	Fluorescent *in situ* hybridization (FISH)]	Analysis of active enzymes in bacterial community
DNA Analysis	Quantitative polymerase chain reaction (qPCR) for targeted species or enzymes	Detection and quantification of key organisms and genes
Soil/biowalls matrix parameters – Varying commercial availability		
Iron species analyses	Bioavailable iron and manganese; weak acid/strong acid extraction of iron	Presence of precursors that can be biologically reduced and subsequently converted to active mineral species; quantification of various forms of iron with differing bioavailability
Total metals	Metals associated with sediment matrix	Important parameters for geochemistry analysis
Electron donors	Total organic carbon	Source of carbon for biological reduction
Electron shuttles	Humic acids (no commercially available method) –	Potential accelerators of biogeochemical processes.
Sulfide minerals	Acid volatile sulfide (AVS), chromium reducible sulfide (CRS)	Potential indicators of active mineral species
Iron minerals/speciation	Mossbauer or Raman spectroscopy; X-Ray absorption near edge structure (XANES) spectroscopy speciation of iron	Measurement of iron valence and mineral type
Mineral composition	Electron microprobe using wavelength dispersive and energy dispersive spectrometers (WDS and EDS); specific surface area	Measurement of mineral composition, morphology, size, and surface area.

4.2.2 Sample Collection, Handling, and Preservation Requirements

From the list of parameters above, sampling is required from both groundwater and soil/sediment matrices. Protocols for groundwater sample handling are generally well-developed, although samples that consist of anaerobic water, as well as samples for microbial testing, require care not to disturb or aerate the sample unnecessarily during transport or analysis.

Because the minerals that appear to be involved in *in situ* biogeochemical transformation are labile, workshop attendees agreed that soil and groundwater sample collection, handling, and preservation are very important. Sampling and preservation procedures for groundwater are well established. This is not the case for soil containing reactive minerals produced under anaerobic conditions. Oxidation of the solid phases readily occurs and must be prevented to the extent possible. This is important both for collection of samples to be used in laboratory studies, and for collection of samples for specific analyses. Along these lines, the analytical procedures to be performed on the samples must also take the labile nature of these species into account. There is a need to develop procedures for collection, preservation, and handling of solid matrix samples. One approach is to freeze core samples in liquid nitrogen, except for those samples to be used in microcosms. A protocol outlining this approach has been developed by EPA (EPA, 2006).

4.2.3 Field Data Quality, Interpretation, and Use

Workshop attendees noted that another issue related to characterization of *in situ* biogeochemical transformation is that of data quality and interpretation for samples collected from field sites. Standard groundwater parameters analyzed using EPA methods have well established procedures and data quality requirements that are widely accepted throughout the U.S. (EPA, 2008). Conversely, data generated from innovative mineralogical (e.g., XANES, AVS, and CRS) and microbial analyses (e.g., FISH, PLFA, and qPCR) do not have established data quality procedures. While it may not be appropriate to institute quality measures of the same rigor as exists for groundwater samples, workshop attendees agreed that some form of guidelines and requirements needs to be established.

Regarding the collection and use of data from field sites, another issue identified at the workshop is data interpretation. This can be similar to an EAB project for many of the parameters collected (e.g., redox parameters, bioactivity indicators, water quality samples, etc.) where simultaneous evaluation of multiple data types must be conducted to develop a complete understanding of the *in situ* processes. Similarly, biogeochemical process evaluation will likely require simultaneous evaluation of multiple data types and multiple lines of evidence including soil or biowall geochemical parameters to develop a comprehensive understanding. A challenge associated with analysis of soil or biowall geochemical parameters is that the exact roles, degradation mechanisms, and kinetic parameters of active mineralogical species (e.g., iron sulfides, green rust, magnetite, etc.) are not yet understood. These challenges complicate interpretation of analytical data and illustrate the need for development of practical methods of sample analysis and data interpretation.

Another aspect of data interpretation is the expected trends in contaminant and daughter product concentrations. As discussed in Section 3.2.1, abiotic degradation generally does not produce significant concentrations of reductive daughter products. Because of this, accumulation and disappearance of chlorinated daughter products at sites where both biological and abiotic mechanisms are active may not occur. However, both degradation mechanisms can result in production of ethene, ethane, or methane, depending on the type of chlorinated solvent present. Still, these final end products may not accumulate to expected levels for other reasons (e.g., volatilization). Because of these factors, less common mineralogical analyses and/or compound specific stable carbon isotope analysis may be useful for documenting active degradation mechanisms.

4.2.4 Need to Leverage Existing Sites for Data

Workshop attendees agreed that the number of field sites where *in situ* biogeochemical transformation have been tested or implemented is relatively small, especially compared to other *in situ* technologies. These sites include but are not limited to AFCEE biowall sites (e.g., see Table 2), biogeochemical reductive dechlorination (BiRD) sites, and possibly some monitored natural attenuation (MNA) sites. Several electron donor substrates have been used on these sites, including vegetable oil, emulsified vegetable oil, and mulch, among others. Some of these sites involved addition of iron minerals in the form of iron oxide-coated sands. Other sites including those where EAB has been implemented may prove to involve *in situ* biogeochemical transformation reactions even though their stimulation was not the original intent. In many cases, these projects were initially undertaken with the intent of stimulating biological degradation only. The abiotic reactions were not purposely stimulated, except at some of the AFCEE sites (Table 2).

Despite this, these sites can be invaluable for furthering technology based on *in situ* biogeochemical transformation through additional characterization and investigation. There is a need to mine the existing data from these sites in order to begin to develop correlations between certain conditions/parameters and performance. In some cases, it may be appropriate to collect samples for additional laboratory studies from these sites. Also, because the degradation pathways may be similar at zero valent iron sites and *in situ* biogeochemical transformation sites, it may be appropriate to examine some zero valent iron sites and sites that use combinations of electron donors and zero valent iron as a source of biogeochemical process data.

Table 2 Summary of DoD Permeable Mulch Biowall Applications

Site	Location	Installation Date	Dimensions	Backfill Material	Contaminants (µg/L)[a/]	Background Geochemistry[b/]	References
OU-1	Altus AFB, Oklahoma	July 2002 (pilot)	455 feet long by 24 feet deep by 1.5 feet wide.	Tree mulch, cotton gin compost, river sand	TCE: 8,000	DO: 0 to 2 mg/L	Appendix D.2 of AFCEE Protocol; Parsons, 2007a; Kennedy and Everett, 2003
					DCE: 1,800	ORP: 0 to +150 mV	
					VC: Non-detect prior to installation	Sulfate: 1,500 to 2,000 mg/L	
SS-17	Altus AFB, Oklahoma	March-May 2005 (full-scale)	5,400 feet wide by 35 feet deep by 2 feet wide.	Tree mulch, cotton gin trash, river sand	TCE: 31,800	DO: 0 to 2 mg/L	Parsons, 2007b
					DCE: 6,400	ORP: 0 to +150 mV	
					VC: 11,600	Sulfate: 1,500 to 2,000 mg/L	
WP-14	Dover AFB, Delaware	December 2004 (pilot)	Dual Wall 250 feet long by 25 feet deep by 2 feet wide.	Tree mulch, silty river sand, and limestone. Gypsum added to half of each biowall section.	PCE: 3,400	DO: 1 to 5 mg/L	Parsons, 2007c; Kennedy *et al*,. 2006.
					TCE: 930	ORP: +200 to +400 mV	
					DCE: 2,000	Sulfate: <25 mg/L	
					VC: 63		
Ash Landfill	Seneca Army Depot, New York	August 2005 (pilot)	Dual Biowall 200 feet long by 32 feet deep by 2.0 feet wide.	Mulch and Sand. Upgradient biowall mulch coated with vegetable oil.	TCE: 860	DO: 2 to 4 mg/L	Appendix D.1 of AFCEE Protocol; Parsons, 2006
					DCE: 980	ORP: 0 to +100 mV	
					VC: 86	Sulfate: 400 to 800 mg/L	
Ash Landfill	Seneca Army Depot, New York	October 2006 (full-scale)	Single Double-Wide and Dual Biowall System. 1,500 linear feet, 10 to 15 feet deep by 3.0 to 6.0 feet wide.	Mulch and Sand. Upgradient biowall's mulch coated with vegetable oil.	TCE: 2,000	DO: 2 to 4 mg/L	Unpublished data.
					DCE: 960	ORP: 0 to 100 mV	
					VC: 95	Sulfate: 500 to 900 mg/L	
					DCE: <1.0	ORP: <0 mV	
					VC: Non-Detect	Sulfate: 10,470	

[a/] Contaminants are maximum concentrations prior to treatment or upgradient of treatment zone in micrograms per liter (µg/L).
[b/] Background geochemistry is an average or range.

Section 5
Implementation of Remediation Systems Based on *In Situ* Biogeochemical Transformation

The third topic for discussion in the workshop breakout groups was implementation of remediation systems based on *in situ* biogeochemical transformation. Section 5.1 presents the charge questions that were posed to the participants, and Section 5.2 describes the key issues identified at the workshop.

5.1 Charge Questions

The charge questions posed to the participants were related to progress in the field: e.g., pilot- and full-scale engineered systems based on biogeochemical transformations. Specifically, participants were asked the following:

- Provide an understanding of progress to date and identify / review case studies where biogeochemical transformations have been observed and manipulated. Cite examples of engineered biogeochemical systems. Has anyone really attempted to "engineer" the process at full-scale?
- What materials have been used? What results have been observed? What are the potential reasons for what was observed?
- What sites are available for further investigation, either via lab experiments or in the field?
- Identify hurdles to implementation of conceptual engineered systems where *in situ* biogeochemical transformation are maximized and relied upon for site remediation.
- Identify future needs for understanding biogeochemical mechanisms in MNA and engineered systems where biogeochemical transformations are heavily relied upon. For example, what is the longevity of such a system, what are the cheapest and easiest ways to create it, how does it change over time, etc.

Implementation of a remediation system based on *in situ* biogeochemical transformation requires several steps including determination of whether the site is suitable, development of engineering design criteria, identification of operation and maintenance approaches for the system, and establishment of reasonable performance criteria. Considering the relatively young state of the science for *in situ* biogeochemical transformation, it is premature to develop each of these steps fully. Nevertheless, initial progress can be made by identifying the specific site characteristics or the niche where *in situ* biogeochemical transformation has been observed to date, understanding rate limiting steps in the transformation process that will drive system design, applying lessons learned from potentially analogous treatment systems including biowalls, and development of reasonable performance expectations for the technology.

5.2 Key Issues

Several key issues were identified at the workshop related to these charge questions. These issues are discussed in detail below.

5.2.1 Determination of Site Conditions that Support *In situ* Biogeochemical Transformation

Workshop attendees agreed that the field experience with remediation using *in situ* biogeochemical transformation is limited at this time. Because of this, such remediation has not been tested under a wide range of field conditions. Based on current field experience, a "niche" definition needs to be created for such remediation. In other words, the workshop attendees agreed that the site conditions and characteristics that are supportive of *in situ* biogeochemical transformation must be identified.

This niche may include sites where reactive iron minerals are most likely to be formed or sites where significant accumulation of daughter products is not observed. The niche may also include sites where EAB has been used for an extended time, and significant contaminant removal rates are still being observed even though the biodegradation rates have decreased. In any case, workshop attendees agreed that parameters that would indicate good potential for *in situ* biogeochemical transformation at a site (including longevity and sustainability) need to be determined.

5.2.2 Design of Remediation Systems Based on Biogeochemical Requirements

While some field applications of remediation using *in situ* biogeochemical transformation have been successful including some of the sites listed in Table 2, workshop attendees agreed that the remediation community is far from having standard design protocols for such approaches. The lack of basic understanding of the biological and abiotic components of these systems makes design and engineering difficult at this time. For example, designs can be much more successful if the rate limiting step or mechanism is known. The key geochemical parameters that indicate amenability still need to be defined (see section 5.2.1). In addition, it is unknown what materials are best included in a biowall or biobarrier that is intended to promote contaminant degradation using *in situ* biogeochemical transformation under various conditions. Materials that have been used include mulch, sand, iron-coated sands, emulsified vegetable oil, and gypsum. While these materials have been used, there is no clear understanding of whether these are the best materials, what other materials should be considered, and what material mixtures should be used under various specific site conditions. For example, groundwater containing high sulfate concentrations may warrant use of a different material mixture compared to groundwater containing low sulfate concentrations.

Workshop participants also identified the need to evaluate and develop a better understanding of the hydraulics of permeable reactive barriers in general. This has been done to some extent for ZVI barriers, but it also needs to be applied to biowalls and biobarriers. Also, the microbiological aspects of *in situ* biogeochemical transformation need to be better defined, especially as they relate to mineral formation (see section 3.2.2). This needs to be done at a molecular level and at the community level. Ultimately, the need exists for engineering design standards or guidelines for implementation of *in situ* biogeochemical transformation, but the technology is likely still too young to develop such a resource. Once basic design criteria are known, a remediation system based on *in situ* biogeochemical transformation can be designed to optimize conditions, overcome limitations, and maximize degradation rates.

5.2.3 Operation and Maintenance of Remediation Systems Based on Biogeochemical Requirements

As with design of remediation systems using *in situ* biogeochemical transformation, workshop attendees agreed that operation and maintenance (O&M) requirements are not well defined. Still, some observations can be made based on the existing projects (see Section 4.2.4). For barriers, experience has shown that they potentially need to be designed with the capability for "recharging" the barrier either with carbon or potentially with iron minerals in order to sustain the processes. The frequency of recharge events is dependent on contaminant loading and flux of competing electron acceptors through the walls. Also, the hydraulics of barriers can change unfavorably over time and may need to be modified (ITRC, 2005a).

For projects where amendments are delivered throughout the treatment area (e.g., using rows of injection wells rather than a barrier configuration), similar considerations for recharging carbon sources and possibly iron minerals exist. While carbon addition for EAB is relatively well known, requirements for such systems performing injections to stimulate *in situ* biogeochemical transformation will likely be different in terms of injection frequency, concentration, and volume. Overall, O&M standards and guidance need to be developed for remediation system based on *in situ* biogeochemical transformation.

5.2.4 Expected Performance of Remediation Systems Based on Biogeochemical Requirements

Workshop attendees agreed that experience with remediation based on *in situ* biogeochemical transformation needs to be significantly more developed in order to be able to predict performance. At this point, performance is not predictable or reproducible even at the current sites where such systems are being implemented (see Section 4.2.4). For example, single biowalls appear to have variable performance at different sections of the wall. Data from more sites is needed in order to begin building an ability to predict performance reliably (refer to Section 3.2.5).

Section 6
Technology Transfer for Remediation Systems Based on *In Situ* Biogeochemical Transformation

The fourth topic for discussion in the workshop breakout groups was regulatory acceptance of remediation systems based on *in situ* biogeochemical transformation. Section 6.1 presents the charge questions that were posed to the participants, and Section 6.2 describes the key issues identified at the workshop.

6.1 Charge Questions

The charge questions posed to workshop participants were related to discussions of the potential impact to existing protocols (i.e., MNA, biowall, EAB, etc.) by both the current and expected future developments related to *in situ* biogeochemical transformation. Attendees were also asked about the need for new protocols, and the assessment of overall regulatory views regarding remediation using *in situ* biogeochemical transformation. Specifically, participants were asked to consider the following:

- Need for a stand-alone biogeochemical protocol. What would it include?
- Need for a sampling protocol
- Identify ways to help site owners be comfortable in amending engineered systems to biogeochemical reactions or to design new systems based on biogeochemical transformation

In situ biogeochemical transformation as a remediation technology is just beginning to be understood, documented, and applied. Understandably, few practitioners, remedial project managers, and regulators are familiar with the technology. Therefore a key step towards technology acceptance and implementation must include education and technology transfer. While the technology is not sufficiently developed to allow technology implementation protocols to be written and implemented, concepts associated with the technology can be introduced to regulatory agencies in the context of conceptual site models. Protocols for sampling and analysis can and have been written that can foster regulatory acceptance of the data used to develop these conceptual site models.

6.2 Key Issues

Several key issues were identified at the workshop related to these charge questions. These issues are discussed in detail below.

6.2.1 Site Assessments Should Include Evaluation of *In Situ* Biogeochemical Transformation

As discussed throughout this document, remediation using *in situ* biogeochemical transformation is an emerging technology that needs a fairly significant amount of research, development, and testing. Still, workshop attendees agreed that the current evidence for the prevalence and effectiveness is sufficient such that it should be discussed with regulatory agencies as another possible degradation mechanism that may be occurring at sites. In some cases, it may be worth considering as an enhancement of other technologies. In addition, monitoring for biogeochemical transformation should be considered using some of the parameters described in Section 4.2.1, at least at sites where the data are otherwise confounding.

6.2.2 Remediation Technology is Not Ready for a Protocol

The primary thrust of this set of charge questions was related to an assessment of impacts to existing protocols, as well as whether a stand-alone protocol for remediation using *in situ* biogeochemical transformation is warranted at this time. The consensus of the participants at the workshop is that not enough is understood to begin developing a protocol for implementation at this time. In addition, the existing protocols should not be modified until more experience is gained with the technology. The results from the workshop and the recommendations of the participants are intended to identify activities that can fill the data gaps identified herein; once these data gaps have been addressed, it is likely that a new protocol, or perhaps updates to existing protocols, will be needed.

6.2.3 Dynamic/Evolving Protocol for Sampling and Analysis of *In Situ* Biogeochemical Transformation Parameters is Possible

Workshop attendees agreed that one area where protocols would be useful is in the area of soil and biowall matrix sampling and analysis. One sampling protocol already has been developed by EPA (EPA, 2006); however, alternative methods for preservation and transport should be examined and protocols developed as appropriate. Protocols for analysis including recommended analyses should also be developed as appropriate.

6.2.4 Technology Acceptance Requirements

An aspect of regulatory assessment of remediation using *in situ* biogeochemical transformation is overall recognition of this approach by regulatory entities as a viable remediation approach. One specific aspect is that some chemicals injected as a part of the process may be of regulatory concern [e.g., dithionite, sulfate (at high concentrations), pesticides, and agri-chemicals that are residues in mulch used in biowalls, as well as some electron shuttles]. Despite this, sites with significant abiotic contributions to degradation could gain regulatory acceptance as long as adequate data have been collected and are presented appropriately to regulators, in the context of a sound conceptual site model (CSM). In order to achieve this, practitioners need to be better educated about *in situ* biogeochemical transformation and the processes involved. Also, the long-term sustainability of the processes needs to be demonstrated in order to convince all parties involved that it can be relied upon as a long-term remedy. Finally, workshop attendees agreed that regulators need to be provided with the current understanding and experience written up in the form of sources that can be referenced (i.e., peer-reviewed publications, EPA reports and guidance documents, etc.).

Once the technologies based on *in situ* biogeochemical transformation are more proven and have an established niche, then they will likely be suitable for implementation at more types of sites. For example, there may be sites where EAB is discarded as a remedial alternative because sulfate is too high. In that case, remediation using *in situ* biogeochemical transformation may be appropriate. Another might be a site where degradation is occurring under intrinsic conditions at rates sufficient for natural attenuation, but the mechanism is not reductive dechlorination. An example is a site with a *cis*-DCE plume was shown to be degrading abiotically (Ferrey and Wilson, 2002).

Finally, significant advances toward widespread regulatory acceptance can be made through the Interstate Technology & Regulatory Council (ITRC, www.itrcweb.org). An appropriate ITRC team should be contacted regarding ongoing and upcoming field projects where remediation using *in situ* biogeochemical transformation is being implemented. Ideally, an ITRC team would include this technology to be within their purview, and would establish contact with regulators and individual principal investigators and project managers for those projects.

Section 7
Identification of Research and Development Needs

The final topic for discussion in the workshop breakout groups was identification of research and development needs for remediation using *in situ* biogeochemical transformation. Section 7.1 presents the charge questions that were posed to the participants. Section 7.2 describes the research needs identified at the workshop, and Section 7.3 describes the demonstration needs.

7.1 Charge Questions

The charge questions posed to the workshop participants were related the future outlook for biogeochemical transformation research and development and applied efforts over the next 5 years. Specifically, participants were asked the following questions:

- Can these identified needs be prioritized? Which are near-term? Which are long-term? Near-term referring to within 2 years and long-term within next 5 to 10 years. From what has been identified, what can be most easily transitioned to the field?
- Which organizations / efforts should be involved / tapped who are not represented at this workshop? To what audience should future efforts be targeted?
- This workshop concentrates on biogeochemical reduction of chlorinated solvents; should the effort be expanded to other contaminants? What contaminants could be addressed in the short-term? The long-term? Near-term referring to within 2 years and long-term within next 5 to 10 years.
- What, if anything, needs to be considered in regard to biogeochemical reactions in order to obtain regulatory approval, either for MNA based on biogeochemical reactions or engineered biogeochemical systems?
- Identify three to five specific opportunities that can be monopolized as a result of this workshop with immediate implementation. Discuss the benefits. How can these best be realized?

7.2 Research Needs

Several basic research needs were identified at the workshop based on the key issues described in Sections 3 through 6. These are described in detail below.

7.2.1 Biogeochemical Mechanisms of Chlorinated Solvent Degradation

Much is unknown regarding the mechanisms of biogeochemical chlorinated solvent degradation and the supporting processes that are important. Investigation is needed into degradation mechanisms and pathways for *in situ* biogeochemical transformation, as well as the variations of those processes under different redox conditions and at sites with different geochemical compositions. This broad research need is intended to encompass basic laboratory work whose goal is the elucidation of both biological and abiotic mechanisms, the interface between these two mechanisms, and associated processes related to chlorinated solvent degradation. This research also needs to compare biogeochemical process rates relative to rates of purely biological or abiotic processes and identify rate-limiting steps. Finally, this research should identify and characterize the active mineral species responsible for solvent degradation using *in situ* biogeochemical transformation (refer to Sections 3.2.1., 3.2.2, and 3.2.5).

7.2.2 Geochemical and Microbiological Requirements for Formation of Active Mineral Phases

The current understanding of *in situ* biogeochemical transformation suggests that active mineral phases are formed under certain geochemical and microbiological conditions (e.g., iron-reducing or sulfate-reducing conditions, within certain pH range, etc.). However, the optimal geochemistry conducive to production of the most reactive mineral species is unknown. The microbial community structure and activity that is most favorable for active mineral formation also is not well understood. This research need includes investigation of microbial ecology and metabolism and geochemical conditions that are conducive to formation of active minerals (refer to Sections 3.2.3 and 3.2.4).

7.2.3 Sampling and Analysis Requirements and Protocols for Characterization and Monitoring of *In Situ* Biogeochemical Transformation

Many parameters can be measured to assess the geochemical and contaminant profiles in groundwater. However, it is not known which parameters are key indicators of active *in situ* biogeochemical transformation. The utility of innovative analyses for other sample matrices (e.g., soil, sediment, biowall material) has not been fully explored. Also, the procedures for collection and handling of samples derived from matrices other than groundwater are not well established or demonstrated. This research need encompasses investigations related to elucidation of key parameters that can be used to characterize and assess the performance of *in situ* biogeochemical transformation. It also includes establishment and verification of sample collection and handling techniques (refer to Sections 4.2.1 and 4.2.2).

7.2.4 Geochemical Modeling for Predicting the Development, Effectiveness, and Sustainability of *In Situ* Biogeochemical Transformation

Geochemical models have been developed that can predict the formation of various mineral phases based on groundwater and solid-phase chemistry. These models are typically equilibrium based models and do not take biological processes into account. Nevertheless, geochemical models based on kinetics are being developed.

Collection and analysis of solid samples for active biogeochemical phases is difficult and not always practical or inexpensive. Because of the difficulty in measuring and monitoring active biogeochemical phases, development of geochemical models that can predict the formation and fate of all active biogeochemical phases including green rusts in addition to iron sulfides and magnetite is needed. This research need would involve development of models that ideally would integrate aspects of equilibrium and kinetic geochemical models, microbiological processes, and both groundwater and solid-phase chemistry (refer to Sections 3.2.2, 3.2.3, 3.2.4, 5.2.2, and 5.2.3).

7.2.5 Data Mining, Sampling, Analysis, and Geochemical Modeling of Existing Sites to Facilitate Understanding of *In Situ* Biogeochemical Transformation in the Field

Several sites exist where *in situ* biogeochemical transformation has been stimulated using biowalls, biobarriers, or other configurations (Table 2). These sites should be thoroughly investigated to begin to develop correlations between certain conditions/ parameters and performance. This research need includes data mining, additional sampling and analysis, creation of geochemical models to simulate site conditions, and comparison of model results to observed field results (refer to Section 4.2.4).

7.2.6 Methods for Selection of *In Situ* Amendments to Promote Formation of Biogeochemically Active Mineral Phases

Much has been learned about amendment selection to promote biological reduction of chlorinated solvents at a variety of sites, including how to select amendments with the most favorable characteristics for a given application (ITRC, 2005b). A similar body of knowledge, including methods for selecting among amendments, is needed for *in situ* biogeochemical transformation. This research need involves evaluation and testing of amendments and *in situ* mineral formation to optimize biogeochemical degradation processes (refer to Section 5.2.2).

7.2.7 Applicability of *In Situ* Biogeochemical Transformation to other Contaminants

Applications of *in situ* biogeochemical transformation to date have been for remediation of chlorinated solvents. However, *in situ* biogeochemical transformation may be applicable to other contaminants, particularly those that are chemically reducible. This research need involves bench-scale testing of *in situ* biogeochemical transformation for degradation of other contaminants (refer to Section 3.2.1).

7.3 Demonstration Needs

Two demonstration needs were identified at the workshop related to the key issues described in Sections 3 through 6. These are described in detail below.

7.3.1 Demonstrate a Sampling and Analysis Protocol for Characterization and Monitoring of *In Situ* Biogeochemical Transformation in the Field

Once protocols are developed for sample collection, handling, and analysis of media for biogeochemical process evaluation (see Sections 4.2.3 and 6.2.3), field demonstration of the protocols is required. In addition, once the key parameters that are indicators of success for *in situ* biogeochemical transformation are determined (see Sections 5.2.1 and 5.2.4), the associated analytes need to be measured at field sites to verify whether they are indicative of success at real sites. This demonstration need includes activities related to validation of any protocols that are developed related to collection, handling, and analysis of samples from field sites. It also includes the application of key parameters that are intended to assess performance of *in situ* biogeochemical transformation, in order to verify whether the parameters provide the information needed to assess and predict performance.

7.3.2 Perform Pilot-Scale Demonstrations with Selected Amendments that Promote Development of *In Situ* Biogeochemical Transformation

Finally, well-controlled pilot-scale demonstrations are needed in order to verify design and O&M requirements for remedies that rely on *in situ* biogeochemical transformation. This demonstration need encompasses any aspect of pilot testing for engineered remedies relying on *in situ* biogeochemical transformation. This includes amendment testing and comparison, iron mineral addition, assessing performance under different redox regimes, etc. Results from these pilot studies, combined with bench-scale findings documenting degradation mechanisms and other important processes, will ultimately establish remediation using *in situ* biogeochemical transformation as a treatment technology that is available to clean and close sites.

Section 8
Conclusions

Overall, the workshop participants expressed a positive view of the potential for using *in situ* biogeochemical transformation for remediating chlorinated solvents. It is an emerging technology, but it has considerable potential both to increase the performance and cost-efficiency of enhanced *in situ* bioremediation, as well as to provide a technical basis for monitored natural attenuation at some sites. However, there is still a limited basic understanding of the processes involved, and a significant amount of research and development is needed.

Specifically, the hypothesized degradation mechanisms or pathways need to be confirmed, mechanisms of active mineral formation need to be defined, and the interplay between abiotic and biological degradation processes requires more investigation. This interplay is especially important, as the production and continuous regeneration of high surface area mineral phases with high activity is dependent on biological activity (thus the use of the term "*in situ* biogeochemical transformation" as opposed to abiotic processes).

Workshop attendees agreed that guidance is needed for field sample collection, analysis, and data interpretation, including a determination of which parameters are indicators of success at field sites. Guidance is also needed with respect to identification of materials and amendments that can be used to promote *in situ* biogeochemical transformation for chlorinated solvent degradation for the purposes of developing and designing a remediation system for the field.

In order to fill these data gaps, additional bench- and pilot-scale testing should be performed to elucidate mechanisms and confirm performance, and data should be mined from the relatively small number of existing sites where the technology has been applied. Ultimately, sampling procedures, design guidance, and O&M protocols need to be developed in order to maximize application and regulatory acceptance of the technology.

In situ biogeochemical transformation is a promising remediation technology that operates at the interface of physical, chemical, and biological phenomena. The interdisciplinary nature of environmental science and engineering has fostered cognizance of the power of this interface and will be a critical component in further development and application of this innovative technology. Future application of *in situ* biogeochemical transformation will result in more cost-effective ways of mitigating the risks associated with inorganic and organic contamination of soil, groundwater, and sediment.

Section 9
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Kennedy, L.G. 2006. “Biogeochemical Reductive Dechlorination, A New Perspective on Remediation and Natural Attenuation of Chlorinated Solvents and Other Contaminants.” Workgroup Presentation. Ada, OK.

Kennedy, L.G. 2003. “Evaluation of Abiotic TCE Remediation Potential by Iron Sulfide Oxidation at Altus Air Force Base, Altus, Oklahoma.” *In situ* and On-Site Bioremediation Conference. Presentation. Orlando, FL.

Kennedy, L.G., J.W. Everett, and J. Gonzales. 2003. “Aqueous and Mineral Intrinsic Bioremediation Assessment: Results from Three Sites.” Presentation.

Kennedy, L.G., J.W. Everett, and J. Gonzales. 2003. “Biogeochemical Treatment of Chlorinated Ethenes.” Presentation.

Kennedy, L.G., J.W. Everett, and E. Becvar. 2004. “Biogeochemical Reductive Dechlorination of TCE: Theory and Field Demonstration.”

Kennedy, L.G., A. Whallon, and J.W. Everett. 2006. “Biogeochemical Reductive Dechlorination in Organic Mulch Permeable Reactive Barriers Under Natural and Engineered Conditions. “ Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA. Poster.

Lee, M.D., M.T. Lieberman, R.C. Borden, J. Everett, L. Kennedy, and J.R. Gonzales. 2003. “Pilots to Enhance Trichloroethene Reductive Dechlorination and Ferrous Sulfide Abiotic Transformation.” *In situ* and On-Site Bioremediation Conference. Orlando, FL.

Lim, H., J. Park, and T. Lee. 2003. “Perchloroethylene Degradation using Reduced iron produced by Dissimilatory Iron Reducing Bacteria Mixture.” Proceedings of the Seventh International Symposium of *In situ* and On-Site Bioremediation. Orlando, FL. June 2003. Paper K-12. Battelle Press. Columbus, Ohio.

“Performance of Flow-through Column Study to Predict Behavior of the SS-17 Biowall.” 2005. Altus AFB Biowall Briefing, R.S. Kerr Center. Ada, OK.

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Sivavec, T.M. and D.P. Horney. 1997. “Reduction of Chlorinated Solvents by Fe(II) Minerals.” Proceedings of the 213th American Chemical Society National Meeting. 115-117.

Whallon, A., E. Becvar, J. Gonzales, B. Henry, and P. Haas. 2006. “Biowall Performance Evaluation at Multiple U. S. Air Force Installations.” Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA.

Wilson, J.T. 2003. “Abiotic Reactions May Be An Important Mechanism In Natural Attenuation of Chlorinated Solvents.” Partners in Environmental Technology Technical Symposium & Workshop Presentation. Washington DC.

Wilson, J.T. 2005. "Expected Abiotic Transformations, John Wilson Altus AFB Biowall Briefing." Workgroup Presentation. Ada, OK.

Appendix A
Attendees

Name	Organization
Becvar, Erica	AFCEE
Borden, Bob	Solutions-IES / NC State Univ.
Brown, Dick	ERM
Butler, Elizabeth	University of Oklahoma
Cwiertny, David	University of Iowa
Evans, Patrick	CDM
Ferrey, Mark	Minnesota Pollution Control Agency
Finneran, Kevin	University of Illinois
Freedman, David	Clemson University
Gonzales, Jim	AFCEE
Hayes, Kim	University of Mich
He, Yongtian (Tom)	US EPA
Henry, Bruce	Parsons
Joo, Sung Hee	Solutions-IES
Lebron, Carmen	NFESC
Lee, Hope	North Wind, Inc.
Leeson, Andrea	SERDP / ESTCP
Loeffler, Frank	Georgia Institute of Technology
Lollar, Barbara Sherwood	University of Toronto
Miller, Ross	Parsons
Olsen, Roger	CDM
Rider, Deanne	HydroGeoLogic, Inc.
Socash, Joann	BAH
Spormann, Alfred	Stanford University
Stroo, Hans	HydroGeoLogic, Inc.
Tratnyek, Paul G.	Oregon Health & Science University
Wice, Rick	Shaw Environmental, Inc.
Wilson, John	EPA
Wymore, Ryan	CDM

Appendix B
Agenda

Summit on Biogeochemical Processes in the Degradation of Chlorinated Solvents

Air Force Center for Environmental Excellence (AFCEE)
Strategic Environmental Research and Development Program (SERDP)
Environmental Security Technology Certification Program (ESTCP)
Naval Facilities Engineering Service Center (NFESC)
National Risk Management Research Laboratory, US Environmental Protection Agency (EPA)

Bldg 532, 3300 Sidney Brooks, Brooks City-Base, San Antonio, Texas
25 – 26 April 2007

WEDNESDAY, APRIL 25, 2007		
Introduction (Conference Room 154)		
1300	*Welcome, Introduction, and Objectives*	Erica Becvar, AFCEE/TDE
1310	*Summary of SERDP/ESTCP Enhanced In Situ Bioremediation (EISB) and Biogeochemical Efforts and Objectives*	Andrea Leeson, SERDP/ESTCP
1325	*Summary of AFCEE EISB Initiative*	Jim Gonzales, AFCEE/TDE
1340	*Biogeochemical Reduction – Thoughts for Consideration*	John Wilson, US EPA
Specific Topics of Discussion		
1400	**Breakout Session I Discussions:** • Current scientific understanding of biotic, abiotic and biogeochemical reactions • Progress in the field – pilot- and full-scale engineered systems based on biogeochemical transformations • Evaluating and estimating transformation of chlorinated solvents by different biogeochemical processes **Breakout Groups (all groups have same charge):** • Breakout Group 1 –Conference Room 117 • Breakout Group 2 – Conference Room 149 • Breakout Group 3 – Conference Room 154	Breakout Groups
1530	**Break** (Conference Room 154)	
1545	**Breakout Session I Continues** • Breakout Group 1 –Conference Room 117 • Breakout Group 2 – Conference Room 149 • Breakout Group 3 – Conference Room 154	Breakout Groups
1700	**Adjourn for the day**	

THURSDAY, APRIL 26, 2007		
0730	**Coffee and Mingling** (Conference Room 154)	
0800	**Breakout Session I Continues:** • Breakout Group 1 – Conference Room 117 • Breakout Group 2 – Conference Room 143 • Breakout Group 3 – Conference Room 154	Breakout Groups
1000	**Break** (Conference Room 154)	
1030	**Reports from Breakout Session I** (Conference Room 154)	Group Leaders
1115	**Lunch** (On your own)	
Identification of RDT&E Needs		
1215	**Breakout Session II Discussions:** • Identification and prioritization of RDT&E Needs • Future outlook for biogeochemical transformation research and development and applied efforts • Available opportunities **Breakout Groups (all groups have same charge):** • Breakout Group 1 – Conference Room 117 • Breakout Group 2 – Conference Room 143 • Breakout Group 3 – Conference Room 154	Breakout Groups
1500	**Break** (Conference Room 154)	
1530	**Reports from Breakout Session II**	Group Leaders
1615	**Summary and Concluding Remarks**	Large Group
1700	**Summit Concludes**	

Appendix C
Introductory Presentations

HEADQUARTERS U.S. AIR FORCE

Summit on Biogeochemical Processes in the Degradation of Chlorinated Solvents

Environmental Restoration Division,
AFCEE/TDE

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Summit Partners

- Air Force Center for Environmental Excellence (AFCEE)
- Strategic Environmental Research and Development Program (SERDP)
- Environmental Security Technology Certification Program (ESTCP)
- Naval Facilities Engineering Service Center (NFESC)
- National Risk Management Research Laboratory, US Environmental Protection Agency (EPA)

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Summit Goal

- Develop future directions and protocols needed to be able to:
  - Evaluate and predict degradation of chlorinated solvents by biogeochemical processes
  - Evaluate, estimate, and enhance biogeochemical processes playing a role in the transformation of chlorinated solvents
  - Identify solutions that could lead to engineered systems based on biogeochemical processes
- Outcomes:
  - Identified solutions
  - Identified needs will help guide future research, demonstration, test, and evaluation (RDT&E) efforts
  - Publish summit findings and make available to all participants

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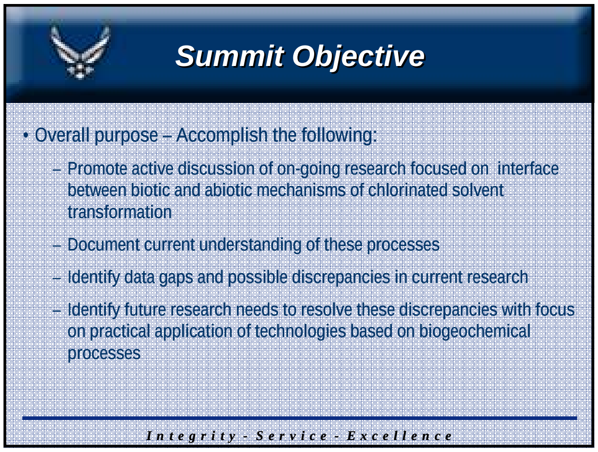

Summit Objective

- Overall purpose – Accomplish the following:
  - Promote active discussion of on-going research focused on interface between biotic and abiotic mechanisms of chlorinated solvent transformation
  - Document current understanding of these processes
  - Identify data gaps and possible discrepancies in current research
  - Identify future research needs to resolve these discrepancies with focus on practical application of technologies based on biogeochemical processes

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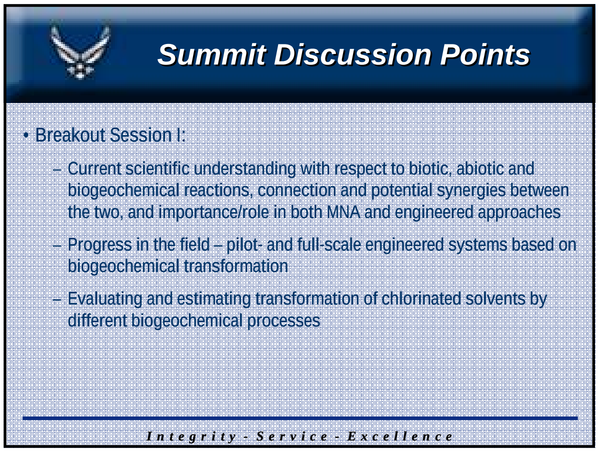

Summit Discussion Points

- Breakout Session I:
  - Current scientific understanding with respect to biotic, abiotic and biogeochemical reactions, connection and potential synergies between the two, and importance/role in both MNA and engineered approaches
  - Progress in the field – pilot- and full-scale engineered systems based on biogeochemical transformation
  - Evaluating and estimating transformation of chlorinated solvents by different biogeochemical processes

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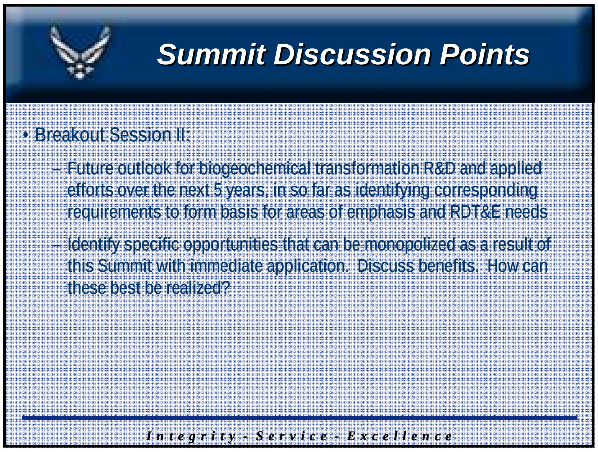

Summit Discussion Points

- Breakout Session II:
  - Future outlook for biogeochemical transformation R&D and applied efforts over the next 5 years, in so far as identifying corresponding requirements to form basis for areas of emphasis and RDT&E needs
  - Identify specific opportunities that can be monopolized as a result of this Summit with immediate application. Discuss benefits. How can these best be realized?

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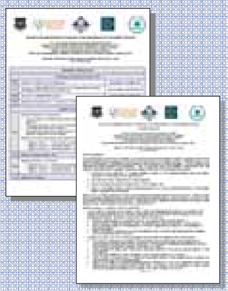
Summit Overview

- Wednesday, 25 April 2007
  - Introductory presentations
  - Thoughts for consideration
  - Breakout Session I Discussions
- Thursday, 26 April 2007
  - Breakout Session I Discussions, Continued
  - Reports from Breakout Session I
  - Breakout Session II Discussions
  - Reports from Breakout Session II
  - Summary and Concluding Remarks



SERDP & ESTCP Environmental Restoration Program Overview: Summary of EISB & Biogeochemical Efforts

Environmental Restoration Program Manager

25 April 2007

Environmental Drivers:

Sustainability of Ranges and Range Operations

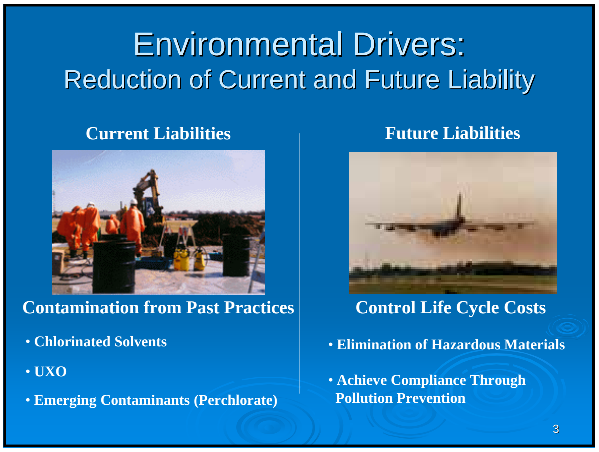
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

Unexploded Ordnance

Urban Growth & Encroachment

Noise NOX and PM



Environmental Drivers:

Reduction of Current and Future Liability

Current Liabilities	Future Liabilities
Contamination from Past Practices	**Control Life Cycle Costs**
• Chlorinated Solvents • UXO • Emerging Contaminants (Perchlorate)	• Elimination of Hazardous Materials • Achieve Compliance Through Pollution Prevention

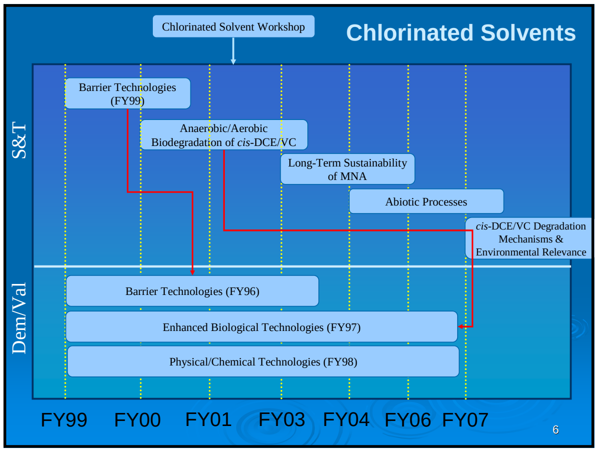
---

Environmental Restoration Program Characteristics

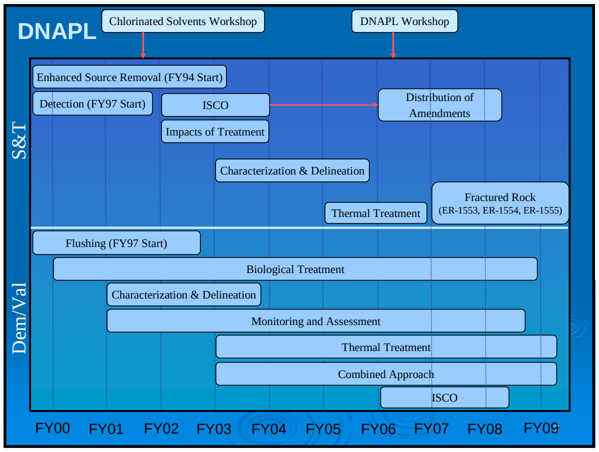
- >200 active projects
- Projects range from $100K to 1.0M/year, average size is $400K/year
- 95% of projects are partnered
- Project length runs 1 to 5 years
- Turn over roughly 25% of the program each year

Environmental Restoration Research Focus Areas

- Chlorinated Solvents
  - Dissolved Phase
  - DNAPL Source Zones
- Munitions Constituents
  - Perchlorate
  - Energetics
  - Heavy Metals
- Sediments
- Risk Assessment
- Site Characterization and Monitoring
- Performance Assessment & Optimization



Chlorinated Solvents



DNAPL

Chlorinated Solvents Workshop

DNAPL Workshop

S&T

Enhanced Source Removal (FY94 Start)

Detection (FY97 Start)

ISCO

Distribution of Amendments

Impacts of Treatment

Characterization & Delineation

Fractured Rock (ER-1553, ER-1554, ER-1555)

Thermal Treatment

Dem/Val

Flushing (FY97 Start)

Biological Treatment

Characterization & Delineation

Monitoring and Assessment

Thermal Treatment

Combined Approach

ISCO

FY00 FY01 FY02 FY03 FY04 FY05 FY06 FY07 FY08 FY09

Relevant Projects

- Web Pages
  - Project listings with fact sheets
  - ESTCP projects also have document links
  - http://www.serdp.org/Research/er-chlorinated-solvents.cfm
  - http://www.estcp.org/Technology/ER-Chlorinated-Solvents.cfm
- On-Line Library
  - http://docs.serdp-estcp.org/
  - Search by project number or key word

Sample Fact Sheet

Investigation of Chemical Reactivity, Mass Recovery and Biological Activity During Thermal Treatment of DNAPL Source Zones

Background

Objective

Process/Technology Description

Expected Benefits

Contact Information

Overview of SERDP & ESTCP Projects

- Categories
  - New Understanding of Microbial Processes
  - New Understanding of Abiotic Processes
  - MNA Evaluations
  - Development of Approaches to EISB
  - Not included: tools to assist with EISB (i.e., monitoring, design tools, etc)
- SERDP projects in orange, ESTCP in green

New Understanding of Microbial Processes: Completed Projects

- Aerobic and Anaerobic Transformation of cis-DCE and VC: Steps for Reliable Remediation (ER-1167, Frank Löffler: Georgia Tech)
- Characterization of the Aerobic Oxidation of cDCE and VC in Support of Bioremediation of Chloroethene-Contaminated Sites (ER-1168, Jim Gossett: Cornell University)
- Factors Affecting cis-DCE and VC Biological Transformation Under Anaerobic Conditions (ER-1169, Alfred Spormann: Stanford University)
- Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (ER-1294, Tissa Illangasekare: Colorado School of Mines)

New Understanding of Microbial Processes: Ongoing Projects

- Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment (ER-1293, Linda Abriola: Tufts University)
- Investigation of Chemical Reactivity, Mass Recovery and Biological Activity During Thermal Treatment of DNAPL Source Zones (ER-1419, Kurt Pennell: Georgia Tech)
- Characterization of Microbes Capable of Using Vinyl Chloride as a Sole Carbon and Energy Source by Anaerobic Oxidation (ER-1556, David Freedman: Clemson Univ)
- Elucidation of the Mechanisms and Environmental Relevance of cis-Dichloroethene and Vinyl Chloride Biodegradation (ER-1557, Evan Cox: GeoSyntec)
- Microbial Dichloroethene and Vinyl Chloride Oxidation and the Fate of Ethene and Ethane Under Anoxic Conditions (ER-1558, Paul Bradley: USGS)

New Understanding of Abiotic Processes

- Abiotic Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene in Anaerobic Environments (ER-1368, Liz Butler: Univ of Oklahoma) (ongoing)
- Sustainability of Long-Term Abiotic Attenuation of Chlorinated Ethenes (ER-1169, Michelle Scherer: Univ of Iowa) (complete)

MNA Evaluations

- Using Advanced Analysis Approaches to Complete Long-Term Evaluations of Natural Attenuation Processes on the Remediation of Dissolved Chlorinated Solvent Contamination (ER-1348, Mark Widdowson: Virginia Tech) (near completion)
- Integrated Protocol for Assessment of Long-Term Sustainability of Monitored Natural Attenuation of Chlorinated Solvent Plumes (ER-1349, Steve Brauner: Parsons) (near completion)
- Assessment of the Natural Attenuation of NAPL Source Zones and Post-Treatment NAPL Source Zone Residuals (ER-0705, Paul Johnson: Arizona State Univ) (new start in FY07)

Development of Approaches to EISB: Completed Projects

- Development of Permeable Reactive Barriers Using Edible Oils (ER-1205, Bob Borden: NCSU)
- Low-Volume Pulsed Biosparging of Hydrogen for Bioremediation of Chlorinated Solvent Plumes (ER-1206, Chuck Newell: GSI)
- Treatability Test for Reductive Anaerobic Biological In-Situ Treatment Technology (RABITT) (ER-9719, Bruce Alleman: Brown & Caldwell)
- Molasses-Induced Reactive Zones to Treat Chlorinated Hydrocarbons (ER-9920, Chris Lutes: ARCADIS)
- Biodegradation of DNAPLs through Bioaugmentation of Source Areas (ER-0008, NFESC)
- Evaluation of Performance and Costs Associated with Anaerobic Dechlorination (ER-0125, NFESC)

Development of Approaches to EISB: Ongoing Projects

- In Situ Bioremediation of Chlorinated Solvent Source Areas with Enhanced Mass Transfer (ER-0218, Kent Sorenson: CDM)
- Edible Oil Barriers for Treatment of Chlorinated Solvent and Perchlorate-Contaminated Groundwater (ER-0221, Bob Borden: Solutions IES)
- Enhanced Oxidative Bioremediation of Cis-Dichloroethene and Vinyl Chloride Using Electron Shuttles (ER-0316, NFESC)
- Reductions in DNAPL Longevity Through Biological Flux Enhancement (ER-0438, Herb Ward: Rice University)
- A Low-Cost, Passive Approach for Bacterial Growth and Distribution for Large-Scale Implementation of Bioaugmentation (ER-0513, NFESC)

Development of Approaches to EISB: Ongoing Projects (cont’d)

- Bioaugmentation for Groundwater Remediation (ER-0515, Rob Steffan: Shaw)
- Enhancing Natural Attenuation Through Bioaugmentation with Aerobic Bacteria that Degrade *cis*-1,2-Dichloroethene (ER-0516, Dave Major: GeoSyntec)
- Enhanced Monitored Natural Attenuation of Dichloroethene Through Manganese Addition (ER-0625, Bob Borden: NCSU)
- Improving Effectiveness of Bioremediation at DNAPL Source Zone Sites Applying Partitioning Electron Donors (ER-0716, NFESC)
- Combining Low-Energy Electrical Resistance Heating With Biotic and Abiotic Reactions for Treatment of Chlorinated Solvent DNAPL Source Areas (ER-0719, U.S. Army COE)

Questions?

HEADQUARTERS U.S. AIR FORCE

Summary of AFCEE Enhanced In Situ Bioremediation (EISB) Initiative

Chief, Environmental Restoration Div (TDE)
Technical Directorate
Air Force Center for
Environmental Excellence (AFCEE)

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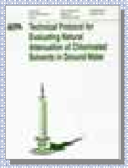
Where We Started



2.2.1.2.3 Type 3 Behavior
Type 3 behavior dominates in areas that are characterized by inadequate concentrations of native and/or anthropogenic carbon, and concentrations of dissolved oxygen that are greater than 1.0 mg/L. Under these aerobic conditions, reductive dechlorination will not occur.

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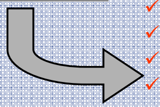
What We Did

2.2.1.2.3 Type 3 Behavior
Type 3 behavior dominates in areas that are characterized by inadequate concentrations of native and/or anthropogenic carbon, and concentrations of dissolved oxygen that are greater than 1.0 mg/L. Under these aerobic conditions, reductive dechlorination will not occur.



- ✓Edible Oil
- ✓Hydrogen
- ✓Molasses
- ✓In-situ Bioreactors
- ✓Biowalls
- ✓Biogeochemical Reductive Dechlorination

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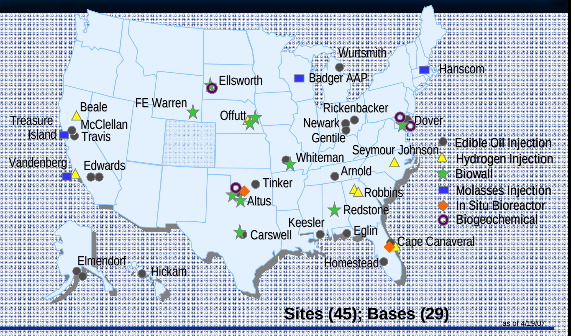
Where We Went



- ● Edible Oil Injection
- △ Hydrogen Injection
- ★ Biowall
- ■ Molasses Injection
- ◆ In Situ Bioreactor
- ○ Biogeochemical

Sites (45); Bases (29)

as of 4/19/07

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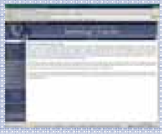
Resources Produced



AFCEE EISB Web Site
- www.afcee.brooks.af.mil/products/techtrans/bioremediation/defaut.asp

Online Resources
- AFCEE Enhanced In Situ Bioremediation Technology Roadmap
- AFCEE Technology Transfer Workshops

EISB Protocols
- Aqueous & Mineral Intrinsic Bioremediation Assessment (AMIBA) Protocol
- Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents
- Enhanced Anaerobic Bioremediation of Chlorinated Solvents Cost Estimating Tool
- Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls, May 07
- Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil, May 07

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Current Issues

- Long lag times
- DCE stall
- VC accumulation
- Need to bioaugment
- Mass balance limitations
- Preferential flow paths
- Insufficient residence time
- Inhibitory conditions
- Monitoring limitations
- Competing electron acceptors
- Contaminant bypass
- Depth limitations
- Sustainability: Carbon limited
- More "Art" not "Science"
- Lack of "How to Manuals"
- Limited Site Selection Criteria
- On-going patent arguments
- Vendor claims and "over selling"
- High cost of mobilization
- High monitoring costs
- Need for Microcosms
- Regulatory Concerns
- Infrastructure issues
- Indoor vapor intrusion
- Increased interests in PBC
- Inaccurate CSMs

So then why the continued interests?

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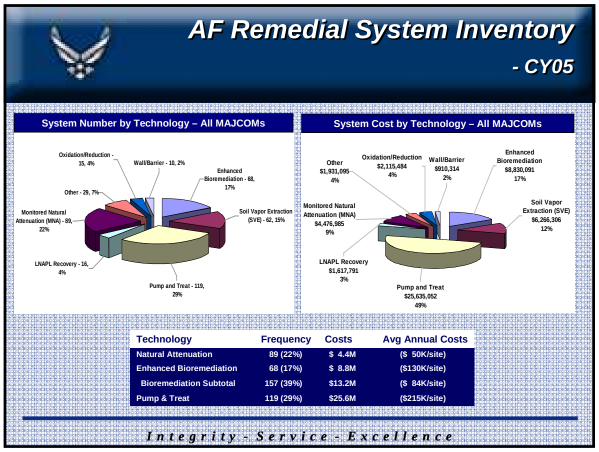

AF Remedial System Inventory
- CY05

Technology	Frequency	Costs	Avg Annual Costs
Natural Attenuation	89 (22%)	$ 4.4M	($ 50K/site)
Enhanced Bioremediation	68 (17%)	$ 8.8M	($130K/site)
Bioremediation Subtotal	157 (39%)	$13.2M	($ 84K/site)
Pump & Treat	119 (29%)	$25.6M	($215K/site)

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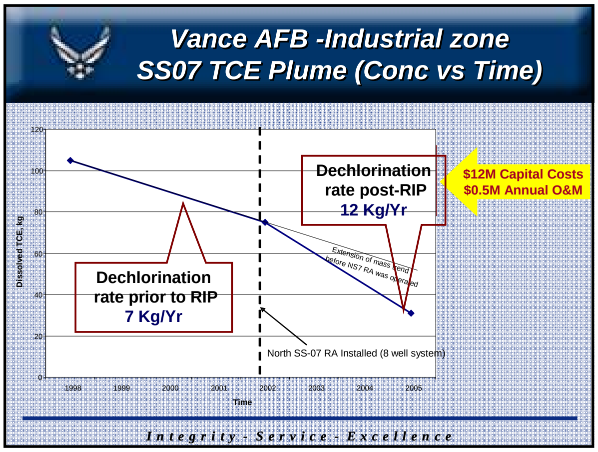

Vance AFB -Industrial zone SS07 TCE Plume (Conc vs Time)

Dechlorination rate prior to RIP
7 Kg/Yr

Dechlorination rate post-RIP
12 Kg/Yr

$12M Capital Costs
$0.5M Annual O&M

North SS-07 RA Installed (8 well system)

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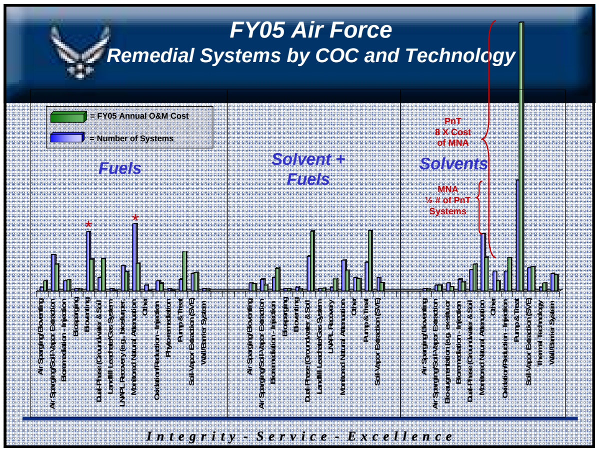

FY05 Air Force Remedial Systems by COC and Technology

PnT
8 X Cost
of MNA

MNA
½ # of PnT
Systems

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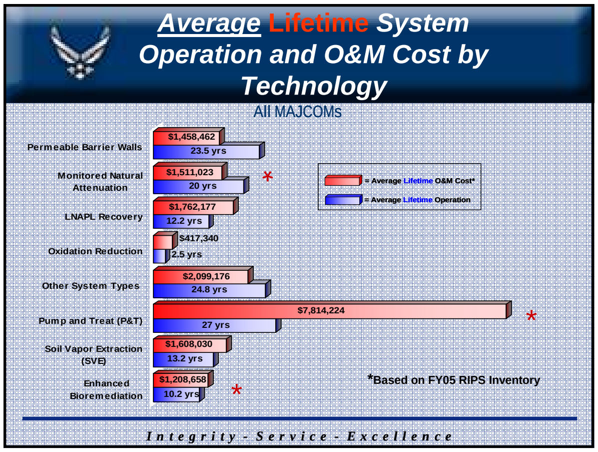

Average Lifetime System Operation and O&M Cost by Technology

All MAJCOMs

*Based on FY05 RIPS Inventory

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Questions?

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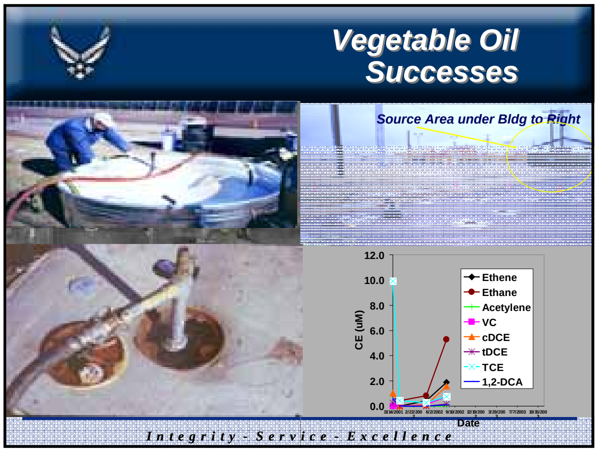

Vegetable Oil Successes

Source Area under Bldg to Right

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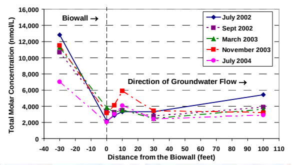
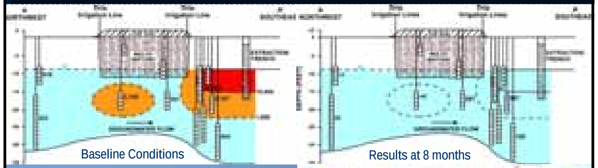
Biowall Successes

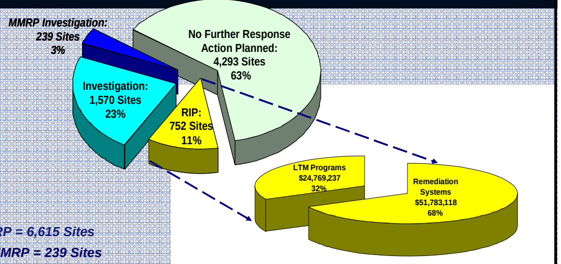


Bioreactor Successes


Baseline Conditions

Results at 8 months

Program Status Percent of Program by Phase



IRP = 6,615 Sites

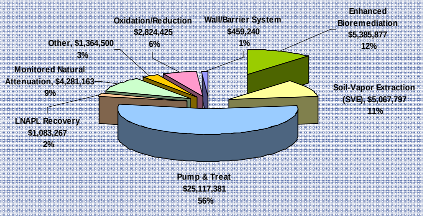
MMRP = 239 Sites

ERA Cleanup Total = 6,854 Sites

74% PROGRAM COMPLETE

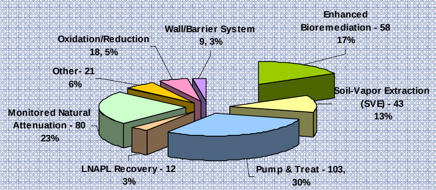
FY06 Air Force Remedial Systems Types

Remediation System Cost and Percentage by System Type



FY06 Air Force

Number of Remediation Systems by Type



Vance AFB Extraction System Effectiveness

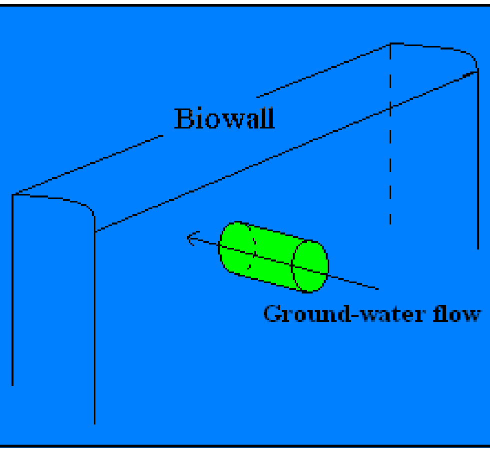
Extraction Well	TCE Mass Removal Rate (kg/yr)
EW7-7	0.0235
EW7-8	0.0556
EW7-9	0.2035
EW7-10	0.8441
EW7-11	0.5026
NS7-ICT1	0.0644
NS7-ICT2	0.0427
NS7-ICT3	0.1397
TOTAL	**1.88**

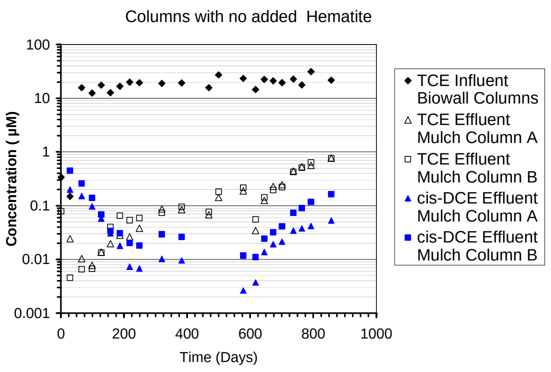
John T. Wilson
Rick Wilkin
Cherri Adair
Summit on Biogeochemical Processes
in the Degradation of Chlorinated Solvents
School of Aerospace Medicine, Brooks City-Base, Texas
25 – 26 April 2007

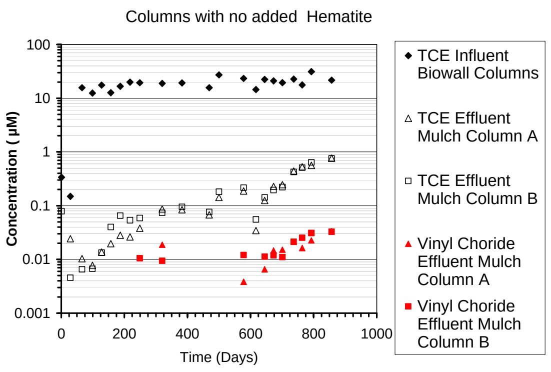
Trichloroethylene Removal from Ground Water in Flow-through Columns Simulating a Permeable Reactive Barrier Constructed with Plant Mulch (Supporting Information)

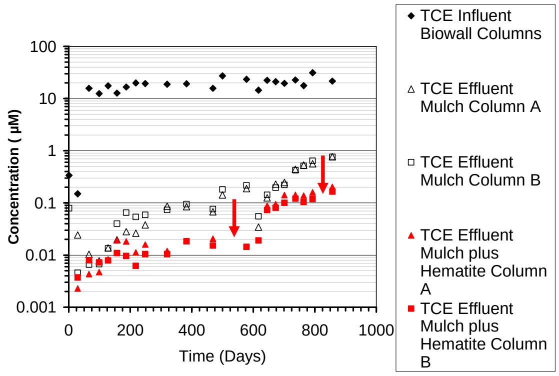
Hai Shen and John T. Wilson

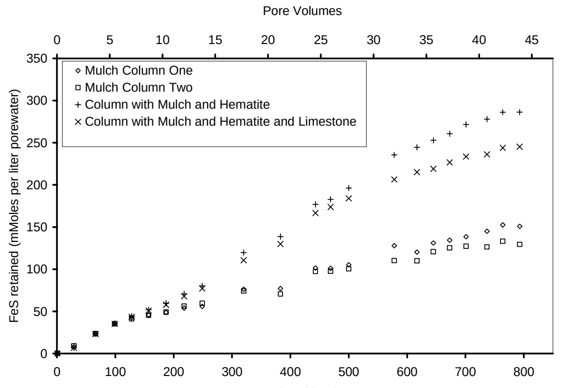
In Press, Environmental Science & Technology











Butler, E.C., and K.F. Hayes. 1999.
Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide.
Environ. Sci. Technol. 33:2021-2027.

Rate = 5.0 x 10^{-4} per hour at pH 7 in presence of 10 g/L FeS

Rate = 0.067per day in presence of 1.0 FeS in contact with 1.0 liter of water (M*)

Time of Operation (d)	Column with Mulch and Hematite	Column with Mulch and Hematite and Limestone
normalized rate constant associated with FeS ($d^{-1}M^{-1}$)		
383	1.6	1.8
578	2.3	1.6
793	0.53	0.90
0.067 (Butler and Hayes)		

Permeable Mulch Biowall at Landfill 3, Operable Unit 1, Altus Air Force Base, Oklahoma. Table 4

Appendix D2 in

Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls and Bioreactors

2007, Version 1

Air Force Center for Environmental Excellence

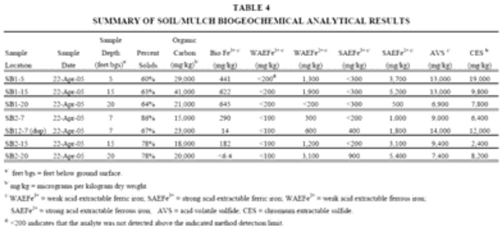


TABLE 4

SUMMARY OF SOIL/MULCH BIOGEOCHEMICAL ANALYTICAL RESULTS

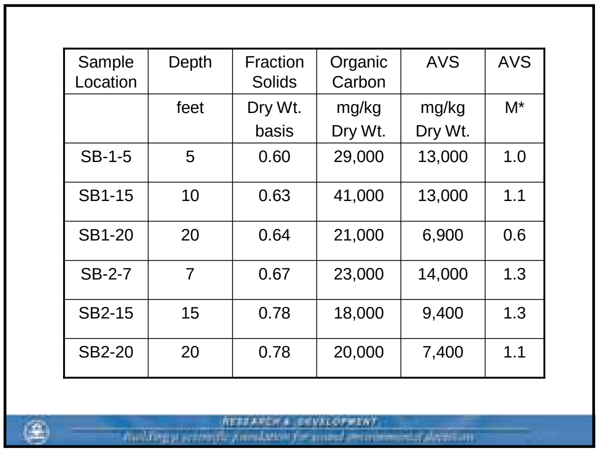
Sample Location	Sample Date	Sample Depth (feet bgs)[a]	Percent Solids	Organic Carbon (mg/kg)[b]	Bio Fe^{3+} [c] (mg/kg)	$WAEFe^{3+}$ [c] (mg/kg)	$WAEFe^{2+}$ [c] (mg/kg)	$SAEFe^{3+}$ [c] (mg/kg)	$SAEFe^{2+}$ [c] (mg/kg)	AVS [c] (mg/kg)	CES [c] (mg/kg)
SB1-5	22-Apr-05	5	60%	29,000	441	<200[d]	1,300	<300	3,700	13,000	19,000
SB1-15	22-Apr-05	15	63%	41,000	622	<200	1,900	<300	5,200	13,000	9,800
SB1-20	22-Apr-05	20	64%	21,000	645	<200	<200	<300	500	6,900	7,800
SB2-7	22-Apr-05	7	86%	15,000	290	<100	300	<200	1,000	9,000	6,400
SB12-7 (dup)	22-Apr-05	7	67%	23,000	14	<100	600	400	1,800	14,000	12,000
SB2-15	22-Apr-05	15	78%	18,000	182	<100	1,200	<200	3,100	9,400	2,400
SB2-20	22-Apr-05	20	78%	20,000	<4.4	<100	3,100	900	5,400	7,400	8,200

[a] feet bgs = feet below ground surface.

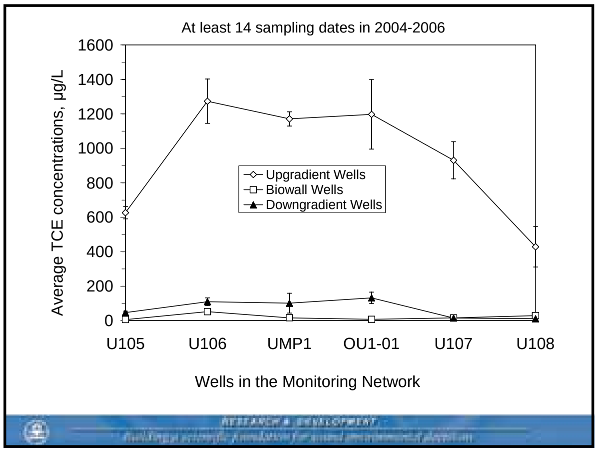
[b] mg/kg = micrograms per kilogram dry weight.

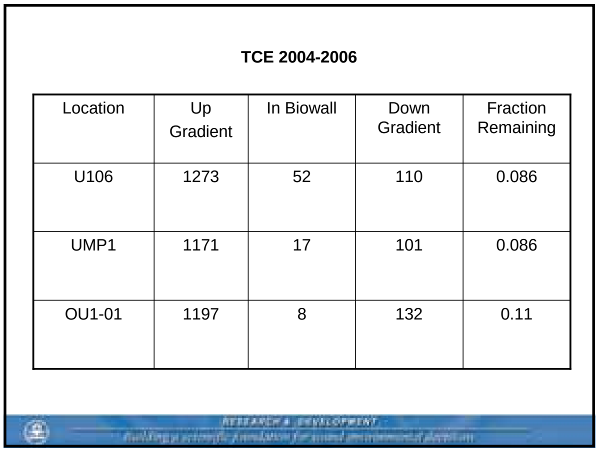
[c] $WAEFe^{3+}$ = weak acid extractable ferric iron; $SAEFe^{3+}$ = strong acid extractable ferric iron; $WAEFe^{2+}$ = weak acid extractable ferrous iron; $SAEFe^{2+}$ = strong acid extractable ferrous iron. AVS = acid volatile sulfide; CES = chromium extractable sulfide.

[d] <200 indicates that the analyte was not detected above the indicated method detection limit.



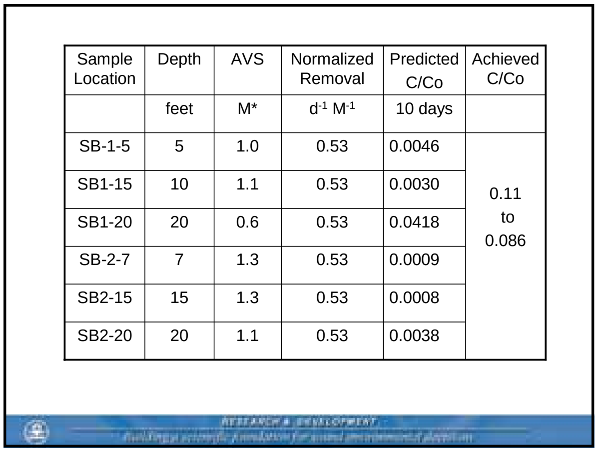
Sample Location	Depth	Fraction Solids	Organic Carbon	AVS	AVS
	feet	Dry Wt. basis	mg/kg Dry Wt.	mg/kg Dry Wt.	M*
SB-1-5	5	0.60	29,000	13,000	1.0
SB1-15	10	0.63	41,000	13,000	1.1
SB1-20	20	0.64	21,000	6,900	0.6
SB-2-7	7	0.67	23,000	14,000	1.3
SB2-15	15	0.78	18,000	9,400	1.3
SB2-20	20	0.78	20,000	7,400	1.1



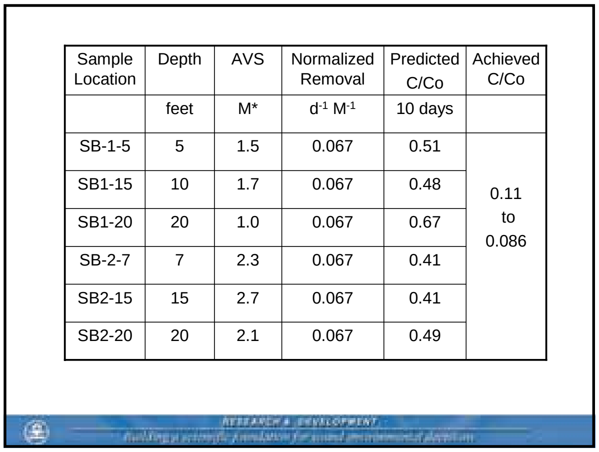


TCE 2004-2006

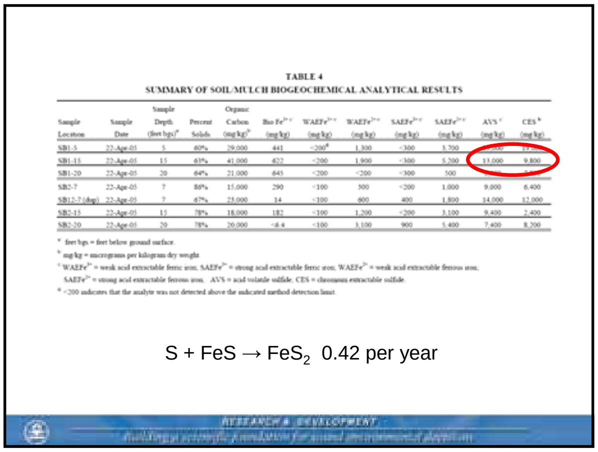
Location	Up Gradient	In Biowall	Down Gradient	Fraction Remaining
U106	1273	52	110	0.086
UMP1	1171	17	101	0.086
OU1-01	1197	8	132	0.11



Sample Location	Depth	AVS	Normalized Removal	Predicted C/Co	Achieved C/Co
	feet	M*	d^{-1} M^{-1}	10 days	
SB-1-5	5	1.0	0.53	0.0046	0.11 to 0.086
SB1-15	10	1.1	0.53	0.0030	
SB1-20	20	0.6	0.53	0.0418	
SB-2-7	7	1.3	0.53	0.0009	
SB2-15	15	1.3	0.53	0.0008	
SB2-20	20	1.1	0.53	0.0038	



Sample Location	Depth	AVS	Normalized Removal	Predicted C/Co	Achieved C/Co
	feet	M*	d^{-1} M^{-1}	10 days	
SB-1-5	5	1.5	0.067	0.51	0.11 to 0.086
SB1-15	10	1.7	0.067	0.48	
SB1-20	20	1.0	0.067	0.67	
SB-2-7	7	2.3	0.067	0.41	
SB2-15	15	2.7	0.067	0.41	
SB2-20	20	2.1	0.067	0.49	



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SB1-20	22-Apr-05	20	64%	21,000	645	<200	<200	<300	500	[illegible]	[illegible]
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SB12-7 (dup)	22-Apr-05	7	67%	23,000	14	<100	600	400	1,800	14,000	12,000
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$S + FeS \rightarrow FeS_2$ 0.42 per year