LESSONS LEARNED

In Situ Biogeochemical Treatment Demonstration: Lessons Learned from ESTCP Project ER-201124

DECEMBER 2015

Hans Stroo
Stroo Consulting, LLC

John Wilson
Scissortail Environmental, LLC

Patrick Evans
CDM Smith

Carmen Lebrón
Private Consultant

Bruce Henry
Parsons Engineering

Drew Latta
University of Iowa

Rajat Ghosh
Alcoa, Inc.

Andrea Leeson
SERDP and ESTCP

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 09/12/2015	**2. REPORT TYPE** Final Report	**3. DATES COVERED** *(From - To)* April 2011 - April 2016

4. TITLE AND SUBTITLE In Situ Biogeochemical Treatment Demonstration: Lessons Learned from ESTCP Project ER-201124	**5a. CONTRACT NUMBER** W912HQ-11-C-0029
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Stroo, H.F., Wilson, J.T., Evans, P.J., Lebrón, C.A., Henry, B.M., Latta, D.E., Ghosh, R.S., and Leeson, A.	**5d. PROJECT NUMBER** ER-201124
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Stroo Consulting, LLC. 300 Skycrest Dr., Ashland, OR 97520 CDM Smith 14432 S.E. Eastgate Way, Suite 100, Bellevue, WA 98007	**8. PERFORMING ORGANIZATION REPORT NUMBER** ER-201124
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 17D08 Alexandria, VA 22350-3605	**10. SPONSOR/MONITOR'S ACRONYM(S)** SERDP
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER-201124

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The project was originally intended to demonstrate and update engineering guidance for the subsurface bioreactor technology, based on results from field-scale testing at the same site used for earlier column testing. The site was moved from the original location, however, and the engineering guidance has not yet been developed. Despite these logistical issues, the overall objective of testing the ability to enhance biogeochemical transformations at a field scale was still of interest, given the potential advantages of the technology.

Although the demonstration was not successful, it is important to understand the reasons for these disappointing results if this technology is to be used with confidence in the future. This document has been prepared to summarize the findings and capture any lessons learned from this effort to demonstrate biogeochemical transformation at a field scale.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**		78	Hans Stroo
					19b. TELEPHONE NUMBER *(Include area code)* 206-351-0228

Reset

Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

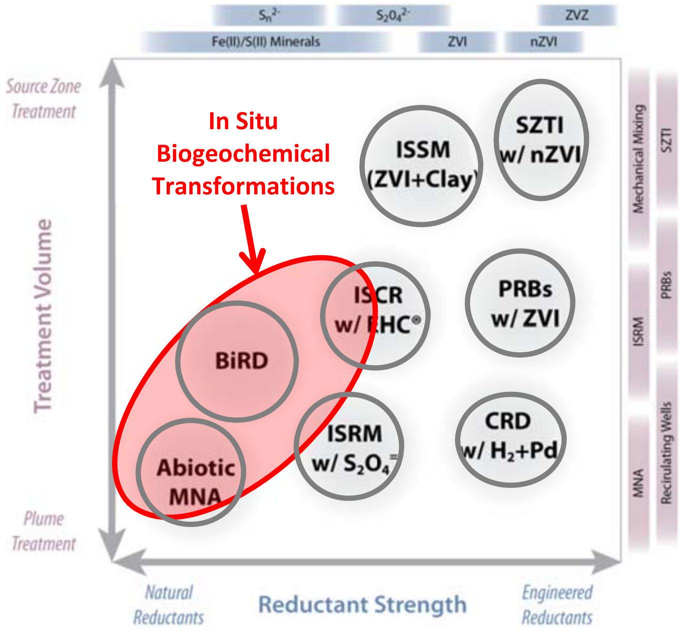
bgs	below ground surface
BiRD	biogeochemical reductive dechlorination
CRD	chemical reductive dechlorination
CVOC	chlorinated volatile organic compound
DCE	*cis*-dichloroethane
DO	dissolved oxygen
DOC	dissolved organic carbon
EHC	proprietary ISCR product (peroxychem)
EVO	emulsified vegetable oil
HRT	hydraulic residence time
ISCR	in situ chemical reduction
ISRM	in situ redox manipulation
ISSM	in situ soil mixing
MNA	monitored natural attenuation
NAVFAC	Naval Facilities Engineering Command
nZVI	nanoscale zero-valent iron
ORP	oxidation reduction potential
PCE	tetrachloroethene
PRB	permeable reactive barrier
SZTI	source zone targeted injection
TCE	trichloroethene

VC	vinyl chloride
VFA	volatile fatty acids
ZVI	zero-valent iron

1.0 BACKGROUND

In situ chemical reduction (ISCR) encompasses a broad range of technologies, ranging from those relying on naturally occurring minerals to those based on adding engineered reductants (Figure 1; Tratnyek et al., 2014). In situ biogeochemical transformation is one form of ISCR that includes “processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface” (AFCEE et al., 2008). This term also encompasses a range of technologies, from abiotic monitored natural attenuation (MNA) by reduced iron minerals (Ferrey et al., 2004) to strategies that rely on biological processes, notably iron and sulfate reduction, to create a reducing environment and form iron minerals (principally iron sulfides) that will reduce chloroethenes. More details are available from Naval Facilities Engineering Command (NAVFAC, 2014).

There are several ways to use in situ biogeochemical transformation to remediate contaminated sites, ranging from natural attenuation to engineered systems such as biowalls. The specific technology demonstrated in this project is enhanced in situ biogeochemical transformation of chloroethenes in a subsurface bioreactor. The enhancement is achieved by forming reactive iron minerals in the bioreactor, which is comprised of mulch, iron, and emulsified vegetable oil (EVO), with sulfate added to the influent. A webinar providing an overview of biogeochemical transformation and this project is available by visiting www.youtube.com/watch?v=wRuQSChkrDk.

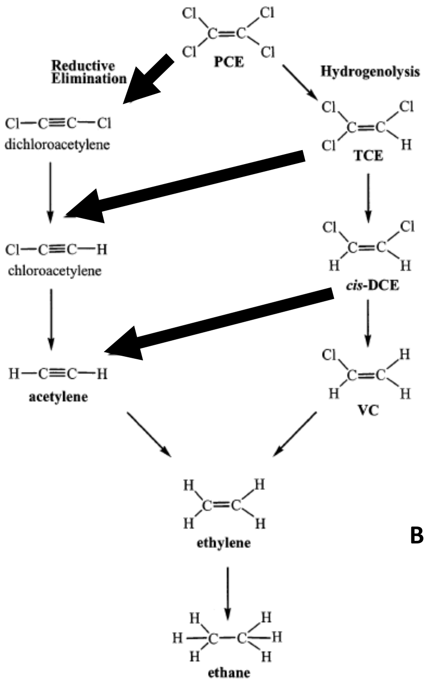


SZTI - Source Zone Targeted injection
ISSM - In Situ Soil Mixing
PRB - Permeable Reactive Barriers
ISCR - In Situ Chemical Reduction
BiRD - Biogeochemical Reductive Dechlorination
MNA - Monitored Natural Attenuation
ISRM - In Situ Redox Manipulation
CRD - Chemical Reductive Dechlorination
EHC - Proprietary ISCR Product (Peroxychem)
ZVI - Microscale Zero-valent Iron
nZVI - Nanoscale Zero-valent Iron

Figure 1. Map of ISCR technologies with range covered by in situ biogeochemical transformation (Modified from Tratnyek et al., 2014).

This technology relies on biological processes to generate reducing conditions and to form reactive iron minerals that are then capable of reducing chloroethenes. Reactive iron minerals are solid phases containing ferrous iron (also called divalent iron, expressed as Fe(II) or Fe^{2+}). They usually form under anoxic conditions, and can include iron sulfides as well as other iron minerals (e.g., green rusts or magnetite). Iron sulfides such as mackinawite and pyrite are common in the subsurface, and form readily under sulfate- and iron-reducing conditions. Bacteria reduce any oxidized ferric (Fe^{3+}) iron and sulfate to ferrous iron and sulfides, which then precipitate to form a range of iron minerals. These minerals can be very reactive to chloroethenes, and also can have relatively high surface areas, making them attractive for remediation (He et al., 2015). However, the minerals may also be passivated, or their reactivity reduced, as a result of several biological and chemical processes, therefore, the rate of formation must exceed any reductions in reactivity.

Abiotic reactions generally produce different intermediates than the biological reductive processes, so accumulation of intermediates such as *cis*-dichloroethene (DCE) and vinyl chloride (VC) may not be a limitation (a simplified pathway is shown in Figure 2). Zero-valent iron (ZVI) is capable of reducing all of the chloroethenes (and many other chlorinated solvents), but abiotic reduction by the divalent iron sulfides is more complex (Cwiertny and Scherer, 2010). For example, *cis*-DCE can be reduced at appreciable rates by freshly-generated precipitates of the common iron sulfide mackinawite (ferrous [Fe2+] monosulfide [FeS]) (Hyun and Hayes, 2015), but many forms of mackinawite will not reduce *cis*-DCE (Jeong et. Al, 2011; Figure 3).



Bold Arrows Identify the More Rapid Reactions

Figure 2. Major abiotic chloroethene degradation pathways and products (*trans*-DCE and others occur at lower levels). Modified from Lee and Batchelor (2002) and He et al. (2015).

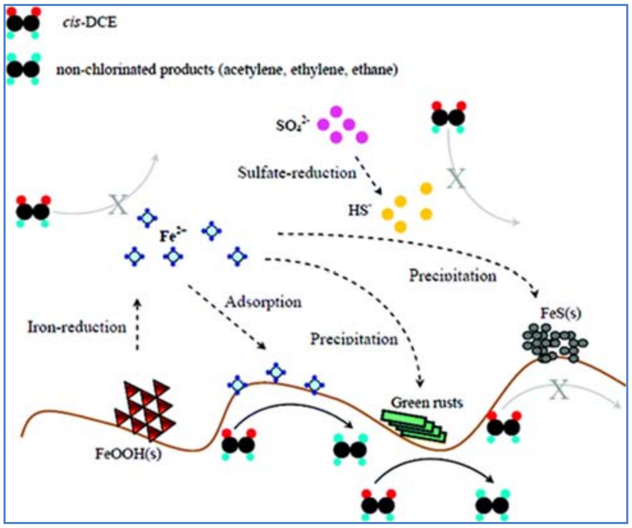


Figure 3. *cis*-DCE degradation by iron minerals (Jeong et al., 2011).

The technical basis for the subsurface reactor technology is similar to the BiRD technology (Kennedy et al., 2006), in which reactive iron sulfides are created by stimulating microbial sulfate reduction in the presence of iron. BiRD is based on injecting a carbon source, to ensure reducing conditions and stimulate sulfate- and iron-reducing bacteria, as well as sulfate and iron, if needed. Sufficient iron is often naturally present as iron minerals, and sulfate may be present in sufficient amounts in some aquifers. Iron-reducing bacteria may be added, although these are present in most soils and aquifers. In fact, some iron reducers (and other bacteria) can dechlorinate tetrachloroethene (PCE) and TCE, though degradation does not proceed past *cis*-DCE (Sung et al., 2006).

The biogeochemical basis for the BiRD technology has been adapted to other applications, most often as a barrier technology. PRBs based on biogeochemical treatment have generally been mulch biowalls modified with gypsum (calcium sulfate dihydrate, as a sulfate source), an iron source such as goethite (an iron oxyhydroxide mineral, FeOOH), and often EVO as a source of carbon. This application of biogeochemical remediation has been reportedly successful, and the technique has been proposed as a method to reactivate or improve mulch-based PRBs, since reactive iron sulfides will form naturally over time within mulch biowalls (He et al., 2008).

Despite more than a decade of research, applications of biogeochemical remediation have not been widely adopted, largely because of concerns about the ability to control the process reliably under field conditions. In addition, the major competing technologies are both robust and cost-effective. In situ bioremediation is a mature technology for plume treatment, so the primary incentive to use biogeochemical treatment is to avoid potential daughter product accumulation. The use of ZVI to form PRBs is also mature, so biogeochemical PRBs are most attractive for situations where ZVI is problematic (e.g., alkaline groundwater that can cause iron carbonate fouling) or where strictly biological remediation is not practical.

This ESTCP project (ER-201124) tested a more aggressive application of in situ biogeochemical remediation, a subsurface bioreactor designed to provide sufficient control of the environmental conditions to enhance biogeochemical degradation reliably and for long periods of time. For this application, groundwater is pumped through the subsurface bioreactor that is filled with materials designed to enhance biogeochemical transformation of chloroethenes. To create the bioreactor, contaminated soils are first excavated from the surface down into the upper saturated zone, and the removed volume is then replaced with mulch and an iron source. Contaminated groundwater is pumped through the bioreactor, with sulfate added as needed to the influent.

The reactor design was based on earlier successful column studies (Evans et al., 2014). This earlier testing showed rapid and sustainable abiotic dechlorination in columns amended with mulch and iron. Iron was effective when added as either magnetite (a partially oxidized iron oxide, Fe_3O_4) or hematite (a fully oxidized iron oxide, Fe_2O_3). In addition, sulfate was added to the influent (Whiting et al., 2014). Magnetite (but not hematite) also can directly reduce chloroethenes, and can in fact be the basis for natural attenuation in some cases (Ferrey et al., 2004). However, the main goal of adding iron minerals in this technology is to provide a source of iron for the formation of reactive iron minerals, particularly iron sulfides, the most stable of which is pyrite (iron disulfide, FeS_2).

The reactive iron minerals can form as coatings on the iron minerals or as separate precipitates formed from dissolved iron and sulfide, and can be highly reactive against chloroethenes (Butler and Hayes, 2001; Lee and Batchelor, 2002). Figure 4 provides conceptual models of different iron-based biogeochemical transformation processes.

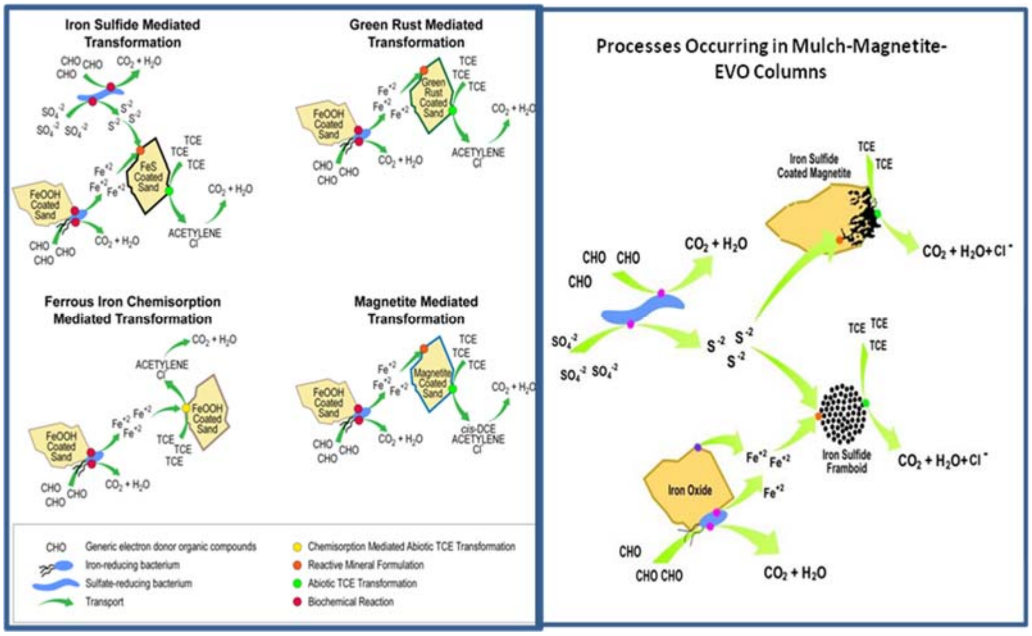


Figure 4. Biogeochemical transformation mechanisms. Left panel - AFCEE et al. (2008). Right panel - Conceptual model of this technology, based on abiotic mulch columns.

2.0 DEMONSTRATION SUMMARY

The following sections provide a brief summary of the subsurface bioreactor demonstration project funded by ESTCP (Project ER-201124). More detail is provided in the appendix, and an overview is available at https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201124/ER-201124.

2.1 Objectives

The project was originally intended to demonstrate and update engineering guidance for the subsurface bioreactor technology, based on results from field-scale testing at the same site used for earlier column testing (Whiting et al., 2014). The site was moved from the original location, however, and the engineering guidance has not yet been developed.

Despite these logistical issues, the overall objective of testing the ability to enhance biogeochemical transformations at a field scale was still of interest, given the potential advantages of the technology. The modified demonstration objectives were to:

1. Demonstrate that the key parameters controlling in situ biogeochemical transformation can be manipulated to enhance contaminant degradation.
2. Develop and test engineering guidance for in situ biogeochemical transformation
3. Document cost and performance of the technology.

The key parameters to consider when designing a subsurface bioreactor include: 1) the particular reduced iron minerals formed; 2) the iron oxide minerals used as a source of iron; 3) the volumetric sulfate consumption rate; and 4) the type and amount of organic material used to stimulate biological activities (Table 1). Specific performance objectives for this demonstration, and a summary of the ability to meet those objectives, are given in Table 2.

Although the demonstration was not successful, it is important to understand the reasons for these disappointing results, if this technology is to be used with confidence in the future. This document has been prepared to summarize the findings and capture lessons learned from this effort to demonstrate biogeochemical transformation at a field scale.

Table 1. Key Design Parameters for Enhancing In Situ Biogeochemical Transformations

Parameter	Optimal
Reduced iron phase minerology	Iron sulfides of mixed stoichiometry with high surface area. Forms can include iron sulfide particles, framboids, and/or iron sulfide coatings on iron oxides including magnetite.
Iron oxide minerology	Sufficient iron oxides are required to promote formation of iron sulfides. These iron oxides serve two purposes: 1) is to provide ferric iron that can complex with sulfide to form iron sulfides; and 2) is to provide a surface to which iron sulfides can attach.
Volumetric Sulfate Loading Rate	High to ensure constant renewal of reactive iron sulfides. This is accomplished through a combination of sulfate concentration and hydraulics necessary to generate a dynamic system.
Organic Carbon Content	Sufficiently high to promote anaerobic conditions and active sulfate reduction.

Table 2. Summary of Performance Metrics for Each Subsurface Bioreactor

Performance Metric	Biotic Mulch	Abiotic Mulch	Abiotic Soil	Goal Achieved?
Volumetric Sulfate Loading >10 mg/L/d	0.90	158	167	Yes
Oil and Grease Analysis: Sufficient to meet demand for 1 year (>100%)	114%	206%	143%	Yes
Effluent DOC not limiting (mg/L)	224	317	297	Yes
Sulfate Consumption >50%	98%	98%	81%	Yes
Methane Production > 5 mg/L	0.77	3.0	0.05	No
Sum of Ethene, Ethane, Acetylene <20% of Total CVOC Influent	ND	ND	ND	Yes
Effluent ferrous iron (mg/L)	107	267	125	Yes
Less than 10% formation of daughter products in abiotic reactors	66%	84%	63%	No

DOC	dissolved organic carbon
CVOC	chlorinated volatile organic compounds

2.2 Design

This field demonstration involved installing three side-by-side 8-foot diameter and 8-foot high columnar bioreactors in situ, to a depth of approximately 10 feet below grade at the Nike PR-58 site in North Kingstown, Rhode Island. Two of the reactors were intended to run under abiotic conditions and the third reactor was intended to run under biotic conditions, for use mostly as a control and for comparison between the biotic and abiotic transformations (Figure 5).

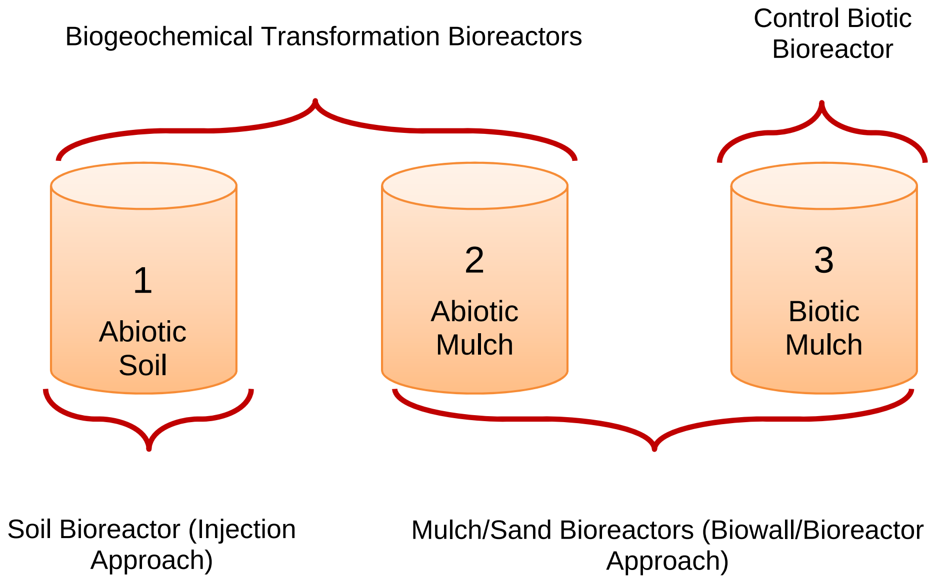
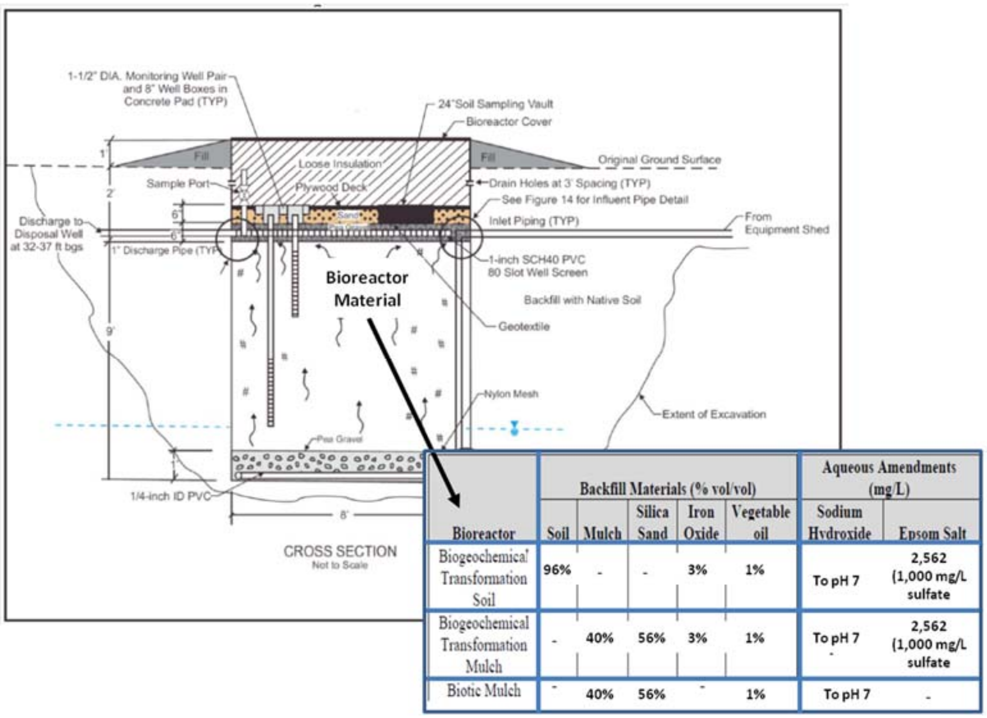


Figure 5. Subsurface bioreactors tested.

Of the two abiotic reactors, Reactor # 1 (*Abiotic Soil*) contained native soil from the site amended with iron oxides at 3% concentration, electron donors, and sulfate (1,000 mg/L) to simulate an injection strategy for biogeochemical transformation. Reactor # 2 (*Abiotic Mulch*) contained sand, mulch, vegetable oil (1%), iron oxides (3%), and sulfate (to simulate a bioreactor or biowall strategy). Reactor # 3 (*Biotic Mulch*) was the biotic reactor (reductive dechlorination) and contained sand, mulch, and vegetable oil.

Groundwater from the site was extracted, adjusted for pH control, and injected into the reactors. The groundwater distribution system was installed at the bottom and piping to a reinjection well was installed near the surface (Figure 6). The hydraulic residence time (HRT) in each bioreactor was about 11 days, with a combined flow rate of about 0.16 gpm. The original intent was to run the reactors for one year while monitoring water quality, solid phase chemistry, mineralogy, and microbiology. However, no abiotic transformation was observed over the first 8 months, despite several efforts, and there were ongoing operational problems (notably recurring fouling of the reinjection well), so the demonstration was terminated.



Bioreactor	Backfill Materials (% vol/vol)					Aqueous Amendments (mg/L)	
	Soil	Mulch	Silica Sand	Iron Oxide	Vegetable oil	Sodium Hydroxide	Epsom Salt
Biogeochemical Transformation Soil	96%	-	-	3%	1%	To pH 7	2,562 (1,000 mg/L sulfate
Biogeochemical Transformation Mulch	-	40%	56%	3%	1%	To pH 7	2,562 (1,000 mg/L sulfate
Biotic Mulch	-	40%	56%	-	1%	To pH 7	-

Figure 6. Subsurface bioreactor designs.

Groundwater geochemistry indicated a reducing environment. Dissolved oxygen (DO) was below saturation and the oxidation reduction potential (ORP) was negative. The pH varied historically from approximately 5 standard units in 2008 to near neutral (7.3 standard units) in 2010. Depth to groundwater varies seasonally between 5 and 15 feet below ground surface (bgs), and can vary throughout the site by up to 6.5 feet. The groundwater velocity was relatively high, approximately 0.85 feet/day. Historical geochemistry data indicated that iron- and sulfate-reducing conditions were present.

The major contaminant in the site groundwater was TCE, at 7.4 mg/L (Table 3). Other contaminants were also present, including the major breakdown product *cis*-DCE (at 1.3 mg/L), suggesting the presence of bacteria capable of partial dechlorination. Vinyl chloride was not detectable; however, indicating dechlorination beyond DCE was not occurring. In addition, chloroethanes were also present as well as lower levels of *trans*-DCE.

Table 3. Groundwater Chlorinated Volatile Organic Concentrations at Demonstration Site

Parameters	Extraction Well (µg/L)
1,1,2,2-Tetrachloroethane	1,400
1,1,2-Trichloroethane	70
cis-1,2-Dichloroethene	1,300
Tetrachloroethene	320
trans-1,2-Dichloroethene	850
Trichloroethene	7,400
Vinyl chloride	<100

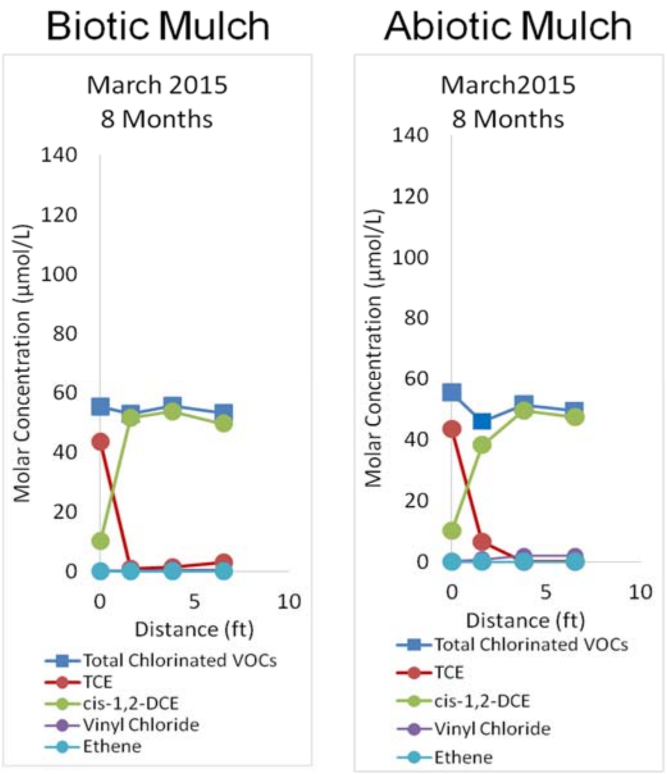
2.3 Results

The results are described briefly below, including the chlorinated ethene transformations observed in all three reactors, the key geochemical conditions during the test, a discussion of the issues that arose during the demonstration, and identification for the disappointing results.

2.3.1 Chloroethene Removal

The chloroethene degradation results from all three reactors were similar. TCE was reduced rapidly and almost entirely to *cis*-DCE, but little to no further degradation was measured. Figure 7 shows VOC concentration trends for the mulch reactors (the abiotic soil reactor was similar). Greater detail on the results and project is available in the project summary presentation, attached as Appendix A.

These results indicate that biotic reduction by bacteria capable of partial degradation was the dominant mechanism for TCE removal in all of the reactors, and abiotic reduction contributed little to the overall removal. The test was terminated after 8 months due to the lack of evidence for abiotic transformations. A summary of the calculated degradation rates and abiotic contributions to the overall removal (Table 4) confirmed that most of the TCE removal was due to biodegradation in all three reactors. After 4 months, the rates were near 1.0 per day (100% removal) in all three reactors, indicating that most of the TCE reduction was being done by bacteria in all three reactors. Unfortunately, these bacteria were apparently capable only of partial degradation of TCE to *cis*-DCE, and any FeS formed could not degrade the DCE.


Biotic Mulch

Abiotic Mulch

Figure 7. Results from subsurface bioreactors containing mulch after 8 months.

Table 4. Degradation Rate Constants Over Time in Each Reactor

Parameters	Units	Abiotic Mulch			Biotic Mulch			Abiotic Soil		
		2 mo.	**4 mo.**	**6 mo.**	**2 mo.**	**4 mo.**	**6 mo.**	**2 mo.**	**4 mo.**	**6 mo.**
Influent TCE	µmole/L	49.47	41.1	52.52	49.47	41.1	52.52	49.47	41.1	52.5
Effluent TCE	µmole/L	1.6	0	4.57	15.22	1.83	1.98	9.89	5.37	5.58
Residence Time	days	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Rate Constant	per day	-1.56	-	-1.11	-0.54	-1.41	-1.49	-0.73	-0.93	-1.02

As mentioned, magnetite can directly reduce chloroethenes, or it can provide a base for reactive iron sulfides to form. However, there was no evidence that either of these processes played a significant role in the subsurface reactors. Although earlier column tests did show excellent abiotic removal of chloroethenes by iron sulfides, under similar conditions with a similar mix of amendments, any iron sulfides formed in the abiotic reactors did not degrade the parent TCE or the biotic daughter product *cis*-DCE.

A separate estimate of the potential contribution of direct reduction by the magnetite in the reactor was performed using data from the site and from literature values for magnetite reduction of TCE. Using the most credible value for the surface area-normalized rate constant for TCE reduction by magnetite (Lee and Batchelor, 2002; Ferrey et al., 2004), magnetite could have degraded only about 1% of the influent TCE mass in the abiotic reactors (Table 5).

Finally, the results were used to estimate the rate constant that would be expected for abiotic degradation on FeS (Table 6). The amount of FeS formed over the first 4 months (at 1,000 mg/L sulfate in the influent) and over the next 2 months (at 3,000 mg/L) were estimated using literature values and the Rickard's equation (Rickard and Luther, 2007). The results from either method were similar. After 4 months, the estimated rate constant was approximately 0.06 per day (roughly 6% of the biotic rate). After 6 months, with the last 2 months at an influent sulfate concentration of 3,000 mg/L, the estimated rate constant for TCE reduction was approximately 0.14 per day: 14% of the biotic rate constant.

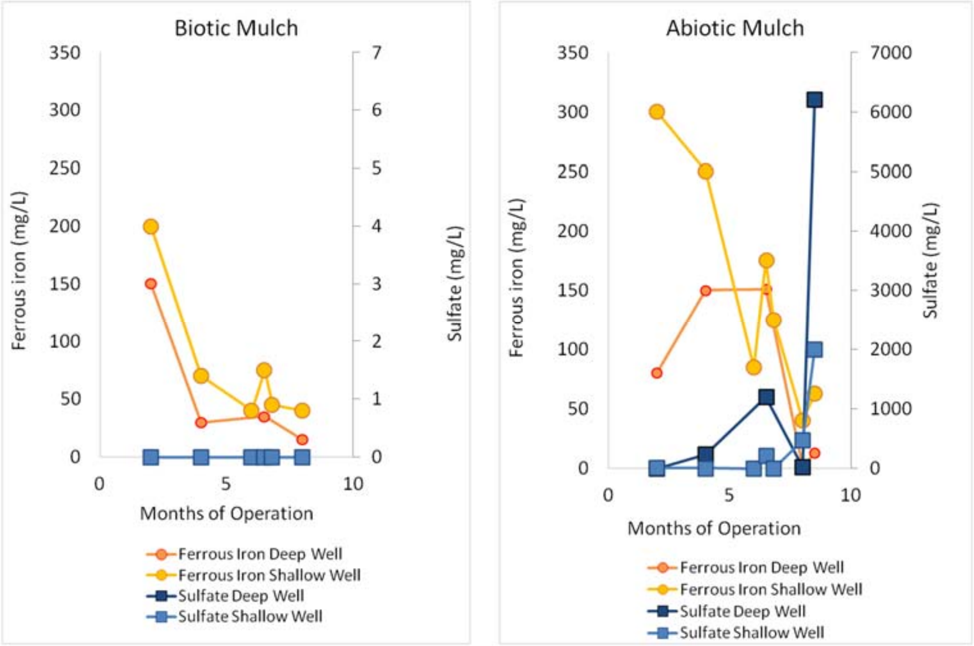
These estimates suggest that if there had not been any biological degradation, the abiotic removal of TCE on FeS at 6 months of operation would have been nearly 80% of the influent concentration (14% per day at an 11-day HRT). Instead, the TCE was biologically transformed to *cis*-DCE, and FeS does not degrade *cis*-DCE at appreciable rates. Note that any abiotic treatment system can use similar spreadsheets to estimate the potential contribution of abiotic degradation, and practitioners should include such calculations during both system design and data analysis.

2.3.2 Geochemistry

The geochemical conditions in the abiotic mulch reactor (Figure 8) were considered favorable for effective abiotic treatment. The pH was near neutral and the ORP was negative, although not as low as desired. Ferrous iron was initially elevated, and even though it declined over time, the initial goal of ensuring a surplus of ferrous iron was achieved. Sulfate was rapidly reduced in the first foot of the reactor, but the dissolved sulfide concentrations remained low throughout the reactor, suggesting that iron sulfides were indeed being formed, though they were likely present only in the lower portion of the reactor, within the first foot of the inlet.

Though it is likely that reactive iron sulfides were being formed, it is not known what types of iron minerals were present, their sizes and surface areas, or to what extent they may have been passivated. Subsequent testing of frozen core samples from the abiotic mulch reactor could provide some information for a relatively low cost, though such testing may not be definitive. More definitive information would require restarting the reactor for weeks to months prior to sampling, for considerably more cost.

Iron (II) and Sulfate Concentrations During Treatment



Geochemical Conditions
Abiotic Mulch Reactor (8 months)

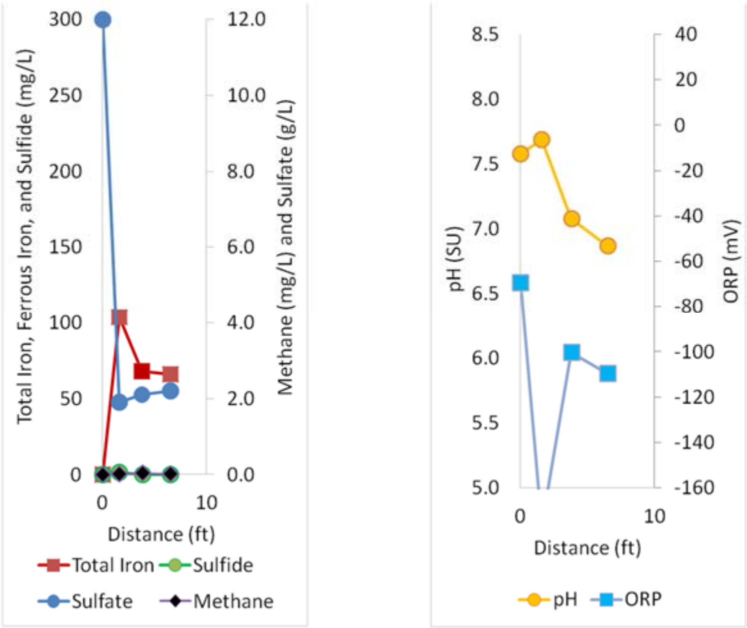


Figure 8. Summary of geochemical conditions, showing ferrous iron and sulfate levels over time in the mulch reactors and the pH and ORP at the end of treatment in the abiotic mulch reactor.

2.3.3 Operational Issues

After 6 months of operations, and three rounds of sampling, biogeochemical processes had not been established yet and continued operation was becoming expensive. Initially the team increased the influent sulfate dose to precipitate excess ferrous iron, which had been observed in the effluent and was also causing iron fouling in the reinjection well. This iron fouling caused additional expense as the team had to rehabilitate the well several times. After the second sampling event (after 4 months of operation), the team increased the influent sulfate concentration in the two abiotic reactors from 1,000 mg/L to 3,000 mg/L. Even with SO_4 at 3,000 mg/L, there was still no sulfide in the effluent, although eventually there was some sulfate breakthrough.

The increase in the influent sulfate concentration (from 1,000 to 3,000 mg/L) was calculated to be in excess of the stoichiometric requirement to consume ferrous iron measured at the reactor effluent. The iron flux was likely too great, and dominated the system. Iron fouling caused unexpected maintenance (therefore cost) and the team reported it to the Program Office. The next plan was to increase residence time, and to discharge the effluent into the pea gravel layer between the bioreactor housing and an exterior corrugated steel caisson. However, the test was terminated after 8 months, on March 30, 2015.

2.3.4 Differences From Prior Column Tests

The conditions within these abiotic reactors differed in several key characteristics from the earlier successful column tests of this technology (Evans et al., 2014). The key operational factors that differed during this demonstration include:

> **Increased Reduced Iron**: The total iron and ferrous iron concentrations were higher than in the column testing. Higher amounts of magnetite were added, and the magnetite used was from a different source (Davis Colors Synthetic Iron Oxide) than the one used during the column study (magnetite grit from magnetic iron core). This change may have resulted in greater bioavailable iron concentrations, and possibly reduced FeS reactivity. As a comparison, the synthetic magnetite used in the column studies had a much higher surface area. No treatability tests or analyses of any potential passivation were done for the product used in the subsurface reactors, although this magnetite was used successfully at a site with high sulfates/sulfides (Bruce Henry, personal communication).
>
> **Insufficient Sulfate:** Most of the sulfate was consumed at or near the reactor inlet, thereby resulting in less distribution across the reactors than desired; no sulfides were detected in the effluent. Balance between the iron and the sulfur must be maintained, but it seems difficult to balance the Fe and the S fluxes at a field scale. Even though the Fe^{2+} concentrations in the abiotic and biotic systems were on the same order of magnitude, the rate of sulfide production was greater in the abiotic systems (about two orders of magnitude greater). This

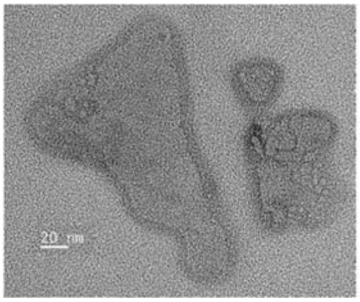
sulfide was apparently bound to most of the magnetite iron being reduced to Fe^{2+} in the abiotic system.

Lower pH: The groundwater pH at the site was initially 6.5 but had to be amended upon extraction. The vegetable oil fermentation to volatile fatty acids (VFA) also likely reduced the pH and this change could have reduced the FeS reactivity.

2.3.5. Potential Technical Issues

Other possible reasons for the disappointing performance are more speculative. One possibility is chemical and/or biological passivation of any iron minerals that were formed. Another is that the surplus of iron throughout most of the reactor could have maintained the ORP at a level too high (near -100 mV) to allow abiotic reduction of chloroethenes. Another possibility is that iron sulfides may have been consumed by other processes. These issues are potentially important to practitioners, and are briefly discussed below.

Inorganic Coatings: Perhaps the FeS produced was coated by inorganic coatings, rendering the FeS less effective. Under conditions of excess Fe^{2+}, inorganic coatings like siderite ($FeCO_3$) or calcite ($CaCO_3$) could coat the FeS/FeS_2 and render it inactive. The picture at right shows an example of an armoring texture of a secondary Fe (darker contrast) on a pre-existing FeS_x mineral shows possible deactivation.



ORP Changes: Supplying enough sulfate will ensure sulfate-reducing conditions, but one speculative possibility is that the excess iron could poise the ORP in a less favorable range; however, that is unlikely to completely prevent abiotic degradation. In any case, preventing a ferrous iron surplus is desirable for other reasons.

Consumption of Iron Sulfides by Other Processes: Magnetite exposed to ambient air is oxidized, and this process consumes sulfide. One possibility is that the added magnetite was oxidized to maghemite, which is deficient in Fe^{2+}, and less reactive than magnetite (Drew Latta, personal communication). The sulfide could have played a role in reducing maghemite to magnetite (i.e., if the system in fact had maghemite). Further, it is also possible that sulfide was sorbing to or binding the magnetite, or it was precipitating with the dissolved reduced iron being produced.

These issues may have occurred, but what can be concluded from the data so far is that the biotic reduction was so fast that any abiotic contribution could not be detected. The high biological activity resulted from adding high amounts of degradable organic carbon. The rate of FeS formation was limited by the sulfate supply, which was considerably less than the supply of reduced iron.

2.3.6 Summary

Iron sulfides were likely present under these conditions although their form and reactivity are not known. However, over 8 months, the predominantly biotic conversion of TCE to *cis*-DCE could not be overcome by the desired abiotic reduction of TCE to acetylene. Abiotic degradation in the reactors was not measurable because the biotic reduction of TCE to *cis*-DCE was considerably more rapid than any abiotic reduction, and the *cis*-DCE accumulated because it was not degradable by the bacteria present in the soil and groundwater, or by the iron minerals formed in the reactors.

Controlling this biotic-abiotic competition is critical for successful biogeochemical treatment, and must be considered in the selection, design, and operation of these systems. For biogeochemical treatment to be effective, the biological transformation of TCE should be limited until appreciable amounts of FeS have accumulated. One approach to limiting biotic reduction is to use carbon substrates that do not provide high concentrations of molecular hydrogen or acetate. The plant mulch used in prior successful biowalls likely had this property, and other slowly degradable materials such as propylene glycol also may work. Sugars or lactic acid probably provide too much hydrogen and acetate. If vegetable oil is used, it is probably best to omit the lactate that is commonly injected with it.

Bacteria capable of partial dechlorination of TCE (possibly including iron reducers) are abundant in most soils and groundwater, particularly under anoxic conditions, but bacteria capable of complete biological reduction are less common and require a lower ORP than iron-reducers (i.e., sulfate-reducing or methanogenic). As a result, biogeochemical treatment may work better in environments that are aerobic prior to treatment, as suggested by practitioner experience (Bruce Henry, personal communication).

It is likely that reactive iron minerals did form under these conditions, given the sulfate consumption and elevated ferrous iron present, but these minerals (likely FeS) had little activity against the *cis*-DCE that was formed biologically. It is not clear how abiotic activity against *cis*-DCE can be enhanced in a biogeochemical treatment system designed to maximize iron sulfide formation, though other forms of reduced iron can degrade *cis*-DCE (Jeong et al., 2011).

These results have important implications for future applications of the technology and for future research in this area. Although there are remaining questions, particularly regarding the forms and amounts of the iron minerals present, there are important lessons from this work, and the other SERDP- and ESTCP-funded work on biogeochemical treatment in recent years. The lessons learned to date and the current recommendations are described in the following sections.

3. LESSONS LEARNED

The overarching lesson is that this technology has proven to be complex and unreliable to date. Despite over a decade of research, and some effective field-scale applications, it remains difficult to implement the technology with confidence. The availability of robust and cost-effective alternatives (bioremediation and ZVI reduction) suggests that this technology should be considered only for sites where biotic or abiotic treatment is not effective, or for relatively unique sites (i.e., high sulfate groundwater with dominantly aerobic conditions prior to treatment).

The other general lesson is that operating a biogeochemical remediation system is more complicated than operating solely biotic or abiotic systems. To operate a biotic treatment system, it is important to ensure that the organisms are capable of complete dechlorination to ethene and beyond (i.e., that *Dehalococcoides mccartyi* are present and active). To operate a solely abiotic treatment system, it is important to use reductants (such as ZVI) that are capable of complete dechlorination and to ensure these remain active. However, practitioners attempting biogeochemical remediation are faced with the difficult task of controlling both biotic and abiotic processes.

Some specific lessons include:

1. **Limit biological activity.** Bacterial activities are needed to form the dissolved mineral precursors (sulfide and ferrous iron), but stimulating these bacteria can also stimulate partial dechlorinators that can prevent abiotic degradation reactions from occurring. Stimulating biological activities can also lead to serious iron fouling of wells, making subsurface bioreactor operations more costly and less reliable. Use of slowly-degraded carbon substrates may be helpful in limiting biotic reduction until appreciable levels of FeS minerals can accumulate.

2. **Establish abiotic reduction early, before biotic processes dominate.** In practice, it is probably best to start with an aerobic system. It can be difficult to overcome the biotic reduction after these processes have already become established. For example, the Nike site used in this demonstration already exhibited some signs of an active biotic system, including the presence of daughter products, particularly *cis*-DCE. The initial goal of operating the system should be to form reactive FeS minerals as rapidly as possible. One possible approach considered was to precondition the reactor to form iron sulfide minerals quickly without adding contaminated water or high levels of degradable carbon.

3. **Perform site-specific testing**. Prior treatability testing with the specific groundwater and materials to be used (mulch, iron sources, gypsum, etc.) is essential at this point

given the complexities, the unknowns, and the number of problems encountered to date with this technology.

4. **Balance the Fe and S fluxes.** Balancing the two mineral precursors is critical for effective operations. If too much Fe^{2+} is produced, it causes iron fouling issues, as occurred in this demonstration at the reinjection well, increasing costs and downtime. If too much sulfide is produced, it transforms the active FeS to much less active FeS_2, a fatal flaw. A slight sulfide excess may be the optimal situation, but a significant excess of either can be detrimental.

5. **Ensure the reactivity of the iron minerals.** First, the reactivity of the minerals formed should be tested directly to ensure they will reduce the target contaminants under the intended conditions (ORP, pH, precursor concentrations). In particular, reactivity against daughter products such as *cis*-DCE should be verified, as well as against parent compounds. Second, it is important to limit the formation of inorganic coatings like siderite ($FeCO_3$) or calcite ($CaCO_3$) that can render the sulfides non-effective. Finally, in some cases, it may be preferable to stimulate production of reduced iron minerals that are capable of degrading *cis*-DCE, such as the reduced iron coatings that can accumulate on hematite.

6. **Carefully consider the size, concentration, and composition of iron sources.** Particle size is a critically important parameter. The goal is to balance competing objectives - maximizing the surface area available for reactive iron sulfide formation while allowing sufficient flow velocities through the reactor or PRB. The applied concentration, the method of application, and the site conditions are also important variables. In this case, applying less of the iron material (say 0.3% vs. the 3% applied) could have resulted in more effective treatment by ensuring a better balance between the Fe and S fluxes. Finally, hematite appears to be a better source of iron for these treatment systems than magnetite. If the iron is provided as hematite or some other purely Fe(III) oxide, excess ferrous iron should not be a problem, because the sulfide produces the amount of Fe^{+2} that is needed by chemical reduction of the Fe(III). The rate of abiotic iron reduction is therefore limited by the supply of sulfide.

4. RECOMMENDATIONS

Recommendations are provided in the following sections for both the current project and for future applications of active biogeochemical remediation.

4.1 Current Project

Further evaluation of the subsurface reactors is needed, particularly the abiotic mulch reactor. The recommended option is the relatively inexpensive alternative, even though it may not provide definitive results. The post-mortem evaluation involves collecting frozen cores for several analyses, including:

- Analyses for magnetite (if so, in which form), goethite, mackinawite, and pyrite
- Tests to determine the reactivity of these minerals
- Reassess ORP to confirm that the system is not oxidized
- Electron microscopic analysis to look for other minerals such as siderite
- Sulfur ratios in the iron sulfide minerals
- Surface areas of the iron species present
- Biogeochemical parameters that could have compromised the reactivity of the magnetite
- Potential column or laboratory incubations of the material to determine rate constants (a more costly option.

4.2. Future Research and Demonstration Projects

This technology has proven complex and difficult to implement with confidence. A better fundamental understanding is needed before conducting further demonstration projects. Any field demonstrations should be preceded by microcosm testing to verify abiotic treatment can be established and the conditions needed for effective treatment. The impacts of the Fe:S ratio should be established, and in general, the optimal conditions for establishing and maintaining abiotic reduction need to be understood with appropriate diagnostic performance tests. The tables provided in this document (Tables 5 and 6) should allow practitioners to quantitatively optimize the design and evaluate the operations of a range of abiotic reactors.

Importantly, the specific mineralogy desirable for effective treatment, and the changes in mineral species over time and in response to changes in the operating conditions needs to be established. The impacts of pH and Eh need to be better understood and modeled. Finally, the relationships between biotic and abiotic processes should be studied to determine the specific operating conditions needed to optimize and sustain effective treatment when using biogeochemical transformations as an active remediation technology.

Table 5. Estimated Contributions of Magnetite to TCE Reduction

		Reactor		
Parameter	**Units**	**Abiotic Mulch**	**Abiotic Soil**	**Basis**
Reactor diameter	ft	7.5	7.5	Design
Reactive media height	ft	6.75	6.75	Design
Bulk reactive media volume	L	8439	8439	Calculation
Porosity	-	0.40	0.25	Assumed
Void volume	L	3376	2110	Calculation
Specific reactive media volume (not incl. void)	L	5064	6329	Calculation
Water volume	L	3376	2110	Calculation
Magnetite concentration	volume %	3%	3%	Design
Magnetite volume	L	253	253	Calculation
Magnetite bulk density	g/cm^3	4.6	4.6	Vendor data
Magnetite mass	kg	1165	1165	Calculation
Magnetite exposed to water	kg/L	0.34	0.55	Calculation
Magnetite exposed to water	g/L	344.51	551.22	Calculation
Specific surface area of magnetite	m^2/g	5.83	5.83	Calculation assuming sphere with diameter 0.2 µm
Surface area of magnetite exposed to water in reactor	m^2/L	2.01×10^3	3.21×10^3	Calculation
Surface area normalized abiotic rate constant for TCE degradation on magnetite	$L/(m^2*day)$	7.21×10^{-7}	7.21×10^{-7}	Lee and Batchelor, 2002
Abiotic degradation rate constants for TCE	per day	1.45×10^{-3}	2.32×10^{-3}	Calculation
Fraction TCE removed	$1-(C/C_0)$	1.4%	2.3%	Calculation
Abiotic degradation rate constants for TCE in presence of Fe^{+2}	per day	1.45×10^{-2}	2.32×10^{-2}	Calculation
Fraction TCE removed in presence of Fe^{+2}	$1-(C/C_0)$	13.3%	20.5%	Calculation

Prepared by John Wilson, Scissortail Environmental Solutions, LLC

Table 6. Estimated Contribution of FeS to TCE Reduction in Abiotic Reactors

Parameter	Unit	Output	Output
		(1,000 mg/L SO_4^{2-})	(3,000 mg/L SO_4^{2-})
Length of flow path in reactor	ft	8	8
Residence time in column	days	11	11
Seepage Velocity of Groundwater	ft per year	265.45	265.45
Distance from points with lowest to highest sulfate levels	ft	8	8
Concentration sulfate in influent	mg/L	1000	3000
Concentration sulfate in effluent	mg/L	0	0
Concentration of soluble sulfide in influent	mg/L	0	0
Concentration of soluble sulfide in effluent	mg/L	0	0
Time since groundwater first reached the top of the reactor	years	0.33	0.28
Yearly production of FeS along flow path	moles FeS/ liter	0.23025	0.69074
Average pH		7.00	7.00
Average total soluble sulfide	mg/L	0.10	0.10
1st order rate constant, FeS inactivation (Rickard's Equation)	per year	0.006	0.006
1st order rate constant, FeS inactivation (Literature value)	per year	0.162	0.162
Reactive iron sulfide that is accumulated calculated from Rickard's equation based on pH and soluble sulfide	moles FeS/L groundwater	7.59E-02	1.93E-01
Reactive Iron Sulfide that is accumulated based on the first order rate constant for inactivation of FeS	moles FeS/L groundwater	7.40E-02	1.89E-01
Rate Constants for Attenuation of TCE by Reactive FeS:			
1st order rate constant, FeS inactivation (Rickard's Equation)	per day	5.65E-02	1.44E-01
1st order rate constant for FeS inactivation (Literature value)	per day	5.50E-02	1.41E-01

Prepared by John Wilson, Scissortail Environmental Solutions, LLC

REFERENCES

AFCEE, NAVFAC ESC and ESTCP (2008). Workshop on in situ biogeochemical transformation of chlorinated solvents. Prepared by CDM Smith. www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA501302 AFCEE, Brooks City-Base, TX.

Butler, E.C. and K.F. Hayes, 2001 Factors influencing rates and products in the transformation of trichloroethylene by iron sulfide and iron metal. *Environmental Science & Technology* 35:3884–3891.

Cwiertny, E.M. and M.M. Scherer, 2010. Abiotic Processes Affecting the Remediation of Chlorinated Solvents. Chapter 4 (pages 69-108 in Stroo HF and CH Ward (Editors). *In Situ* Remediation of Chlorinated Solvent Plumes. Springer. New York, NY. 786 p.

Evans, P.J., D. Nguyen, R.W. Chappell, K.S. Whiting, J. Gillette, A. Bodour, and J.T. Wilson, 2014. Factors controlling in situ biogeochemical transformation of trichloroethene: Column study. *Groundwater Monitoring & Remediation* 34:65–78.

Ferrey, M.L., R.T. Wilkin, R.G. Ford, and J.T. Wilson, 2004. Non-biological removal of cis-dichloroethylene and 1,1-dichloroethylene in aquifer sediment containing magnetite. *Environmental Science & Technology* 38:1746–1752.

He, Y.T., J.T. Wilson, and R.T. Wilkin, 2008. Transformation of reactive iron minerals in a permeable reactive barrier (biowall) used to treat TCE in groundwater. *Environmental Science & Technology* 42:6690–6696.

He, Y.T., J.T. Wilson, C. Su, and R. Wilkin, 2015. Review of abiotic degradation of chlorinated solvents by reactive iron minerals in aquifers. *Groundwater Monitoring & Remediation* (Available online). doi: 10.1111/gwmr.12111.

Hyun, S.P., K.F. Hayes, 2009. Feasibility of using in situ FeS precipitation for TCE degradation. *Journal of Environmental Engineering* 135:1009–1014.

Hyun, S.P., K.F. Hayes, 2015. Abiotic reductive dechlorination of cis-DCE by ferrous monosulfide mackinawite. *Environmental Science and Pollution Research* 21:16463-16474. DOI 10.1007/s11356-015-5033-2.

Jeong, H.Y., K. Anantharaman, Y-S Han, and K.F. Hayes, 2011. Abiotic reductive dechlorination of cis-dichloroethylene by Fe species formed during iron-or sulfate-reduction. *Environmental Science & Technology* 45:5186-5194.

Kennedy, L.G., J.W. Everett, E. Becvar, and D. DeFeo, 2006. Field-scale demonstration of induced biogeochemical reductive dechlorination at Dover AFB, Dover, Delaware. *Journal of Contaminant Hydrology* 88:119–136.

Lee, W. and B. Batchelor, 2002. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and magnetite. *Environmental Science & Technology* 36:5147–5154.

Naval Facilities Engineering Command, 2014. Fact Sheet: In Situ Biogeochemical Transformation Processes for Treating Contaminated Groundwater. https://clu-in.org/download/techfocus/bio/bio-insitubiogeochem-FS.pdf. 6 p.

Rickard, D. and G.W. Luther III, 2007. Chemistry of iron sulfides. *Chemical Reviews* 107:514–562.

Sung, Y., K.E. Fletcher, K.M. Ritalahti, R.P. Apkarian, N. Ramos-Herndandez, R.A. Sanford, N.M. Mesbah, and F.E. Löffler, 2006. *Geobacter lovleyi* sp. nov. Strain SZ, a Novel Metal-Reducing and Tetrachloroethene-Dechlorinating Bacterium. *Applied and Environmental Microbiology* 72:2775-2782.

Tratnyek, P.G., R.L. Johnson, G.V. Lowry, and R.A. Brown, 2014. *In Situ* Chemical Reduction for Source Remediation. Chapter 10 (pages 307-351) in Kueper BK, HF Stroo, C Vogel, and CH Ward (Editors). Chlorinated Solvent Source Zone Remediation. Springer, New York, NY. 716 p.

Whiting, K., P.J. Evans, C. Lebrón, B. Henry, J.T. Wilson, and E. Becvarc 2014. Factors controlling in situ biogeochemical transformation of trichloroethene: Field survey. *Groundwater Monitoring & Remediation* 34:79–94.

Report prepared by Patrick Evans (CDM Smith), Rajat Ghosh (Alcoa, Inc.), Bruce Henry (Parsons Engineering), Drew Latta (University of Iowa), Carmen Lebrón (independent consultant), Hans Stroo (Stroo Consulting, LLC), and John Wilson (Scissortail Environmental, LLC); reviewed by Paul Tratnyek (Oregon Health Sciences University).

Appendix A: ER-201124 Final Project Summary Presentation

SERDP & ESTCP February 2015 IPR

In Situ Biogeochemical Transformation of Chlorinated Solvents

ER-201124
Dr. Patrick Evans
CDM Smith

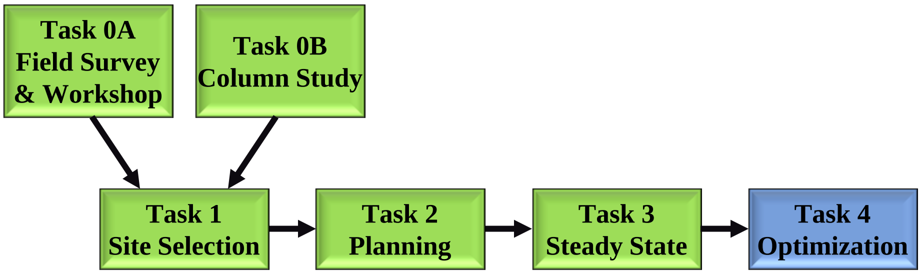
Revised for May 8, 2015 Expert Panel

Project Team

- Patrick Evans, Ph.D., CDM Smith (PI)
- Jennifer Hooper, P.E., CDM Smith
- Kent Whiting, L.G. CDM Smith
- Bruce Henry, P.G., Parsons
- John Wilson, Ph.D., Scissortail Environmental Solutions

Technology Background Leading to the ESTCP Demonstration

Technical Approach



Task 0A
Field Survey & Workshop

Task 0B
Column Study

Task 1
Site Selection

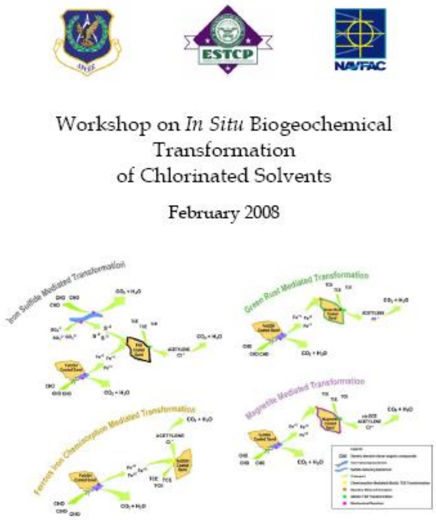
Task 2
Planning

Task 3
Steady State

Task 4
Optimization

In Situ Biogeochemical Transformation

Processes where contaminants are degraded by abiotic (chemical) reactions with naturally occurring and biogenically-formed minerals in the subsurface.

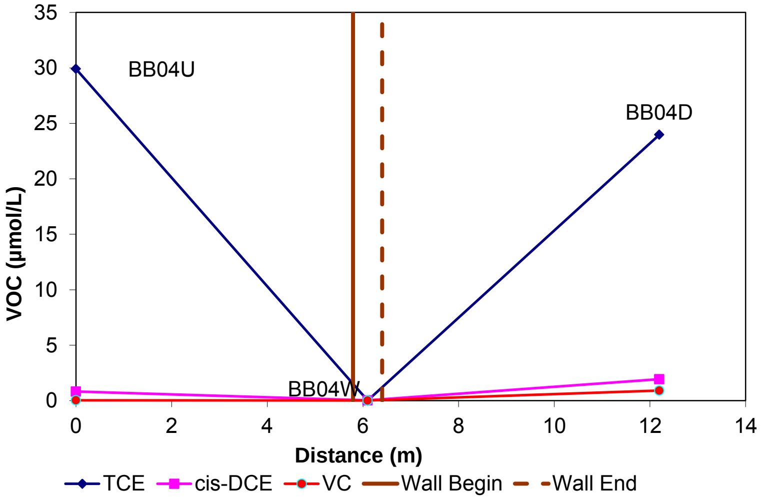


Workshop on *In Situ* Biogeochemical
Transformation
of Chlorinated Solvents

February 2008

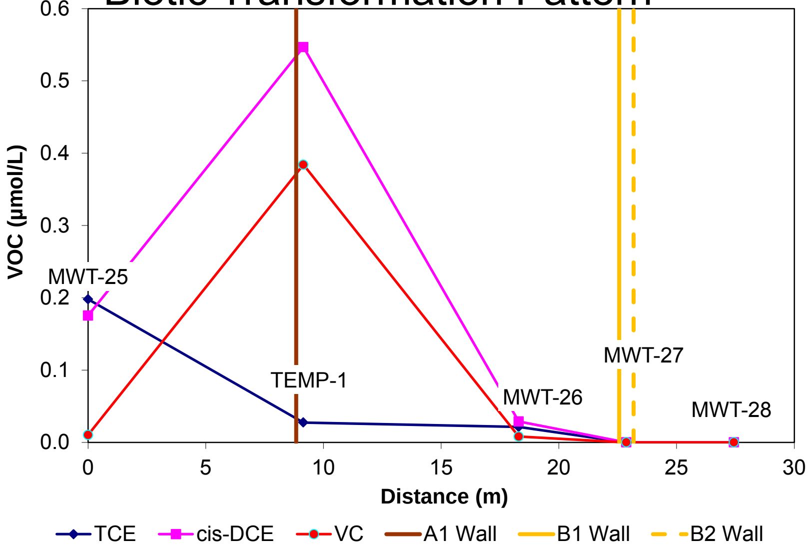
AFCEE, NAVFAC ESC, and ESTCP. 2008. Workshop on in situ biogeochemical transformation of chlorinated solvents. Prepared by CDM Smith. www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA501302

Altus AFB SS-17
Abiotic Transformation Pattern



Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

Seneca Army Depot
Biotic Transformation Pattern



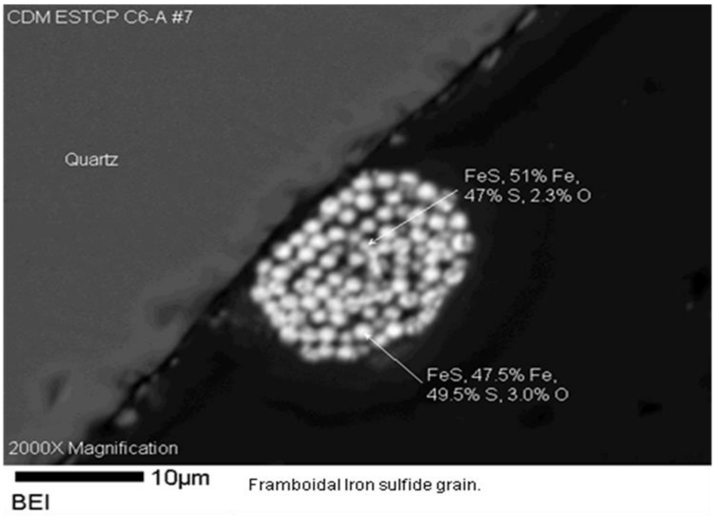
Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

VOC Destruction and Sulfate Consumption

Site	$f_{abiotic}$	First-Order VOC Rate Constant (d^{-1})	Volumetric Sulfate Consumption Rate ($mg\ L^{-1}\ d^{-1}$)
Altus AFB OU-1	0.83	0.15	150
Altus AFB SS-17 West Transect	1.0	0.25	24
Altus AFB SS-17 East Transect	0.98	0.26	12
USEPA Column B3	0.98	0.25	44
Dover AFB North Transect – DG Wall	- 0.30	0	0.058
Dover AFB South Transect – DG Wall	- 0.05	0	- 0.10

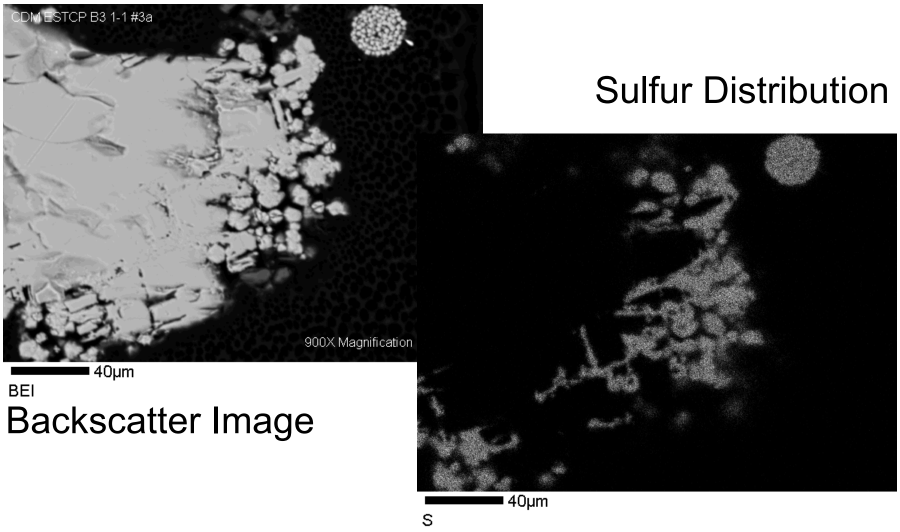
Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

Framboidal Pyrite
Altus AFB OU1 Site



Framboidal Iron sulfide grain.

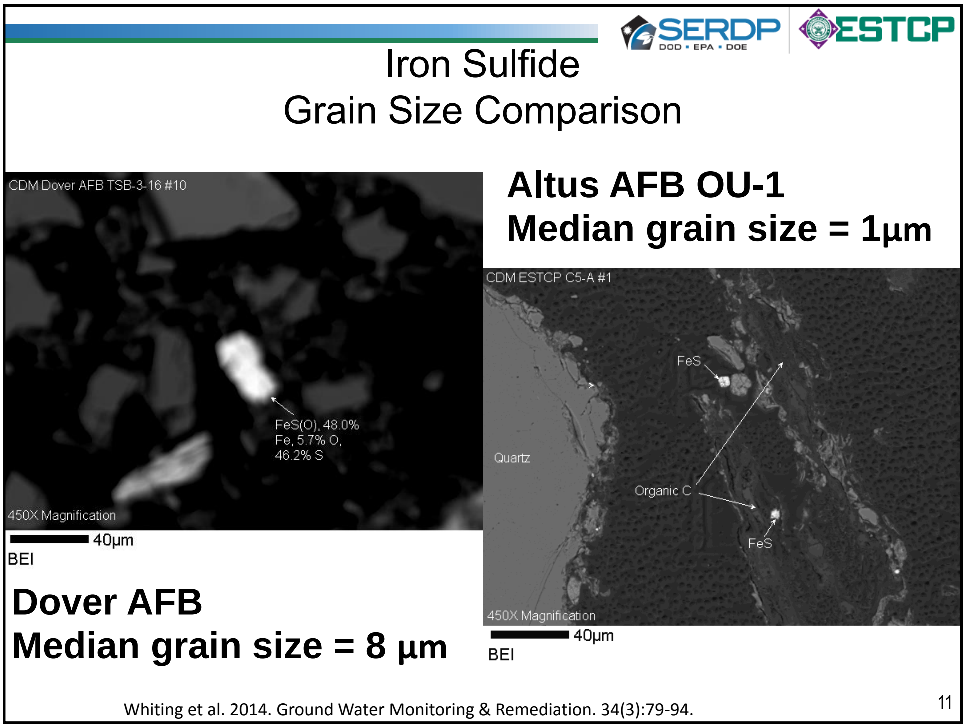
Iron Sulfide-Coated Magnetite
EPA Column Study Samples



Sulfur Distribution

Backscatter Image

Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

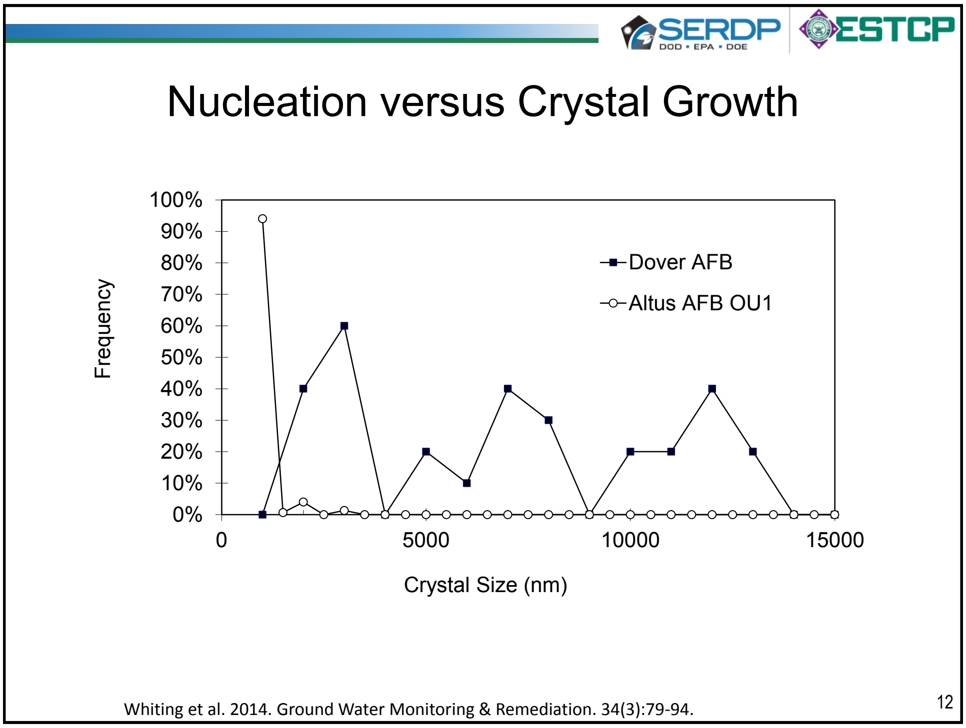


Iron Sulfide Grain Size Comparison

Altus AFB OU-1
Median grain size = 1µm

Dover AFB
Median grain size = 8 µm

Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.



Nucleation versus Crystal Growth

Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

Factors Affecting Reactive Iron Sulfide Production

- Reduced iron phase mineralogy
- Iron oxide mineralogy
- Organic carbon content
- Eh/pH conditions
- Ionic strength
- Dissolved oxygen
- Microbiology
- Volumetric sulfate loading rate
- Iron sulfide surface area
- Residence time

$$Fe^{+2} + S^{-2} \xrightarrow{k_1} FeS_{ACTIVE}$$

$$FeS_{ACTIVE} \xrightarrow{k_2} FeS_{INACTIVE}$$

We want $k_1 > k_2$

Column Study: Factorial Experimental Design

Factor	Low Level	High Level
Iron oxide coated sand	Absent	Present (35%)
Magnetite	Absent	Present (5%)
Hematite	Absent	Present (5%)
pH	6.0	7.5
Groundwater sulfate (mg/L)	18 to 62	1,200 to 2,100
Gypsum	Absent	Present (2.5%)
Seepage velocity (cm/day)	1.5	7.4
Vegetable oil	Absent	Present (1.25%)

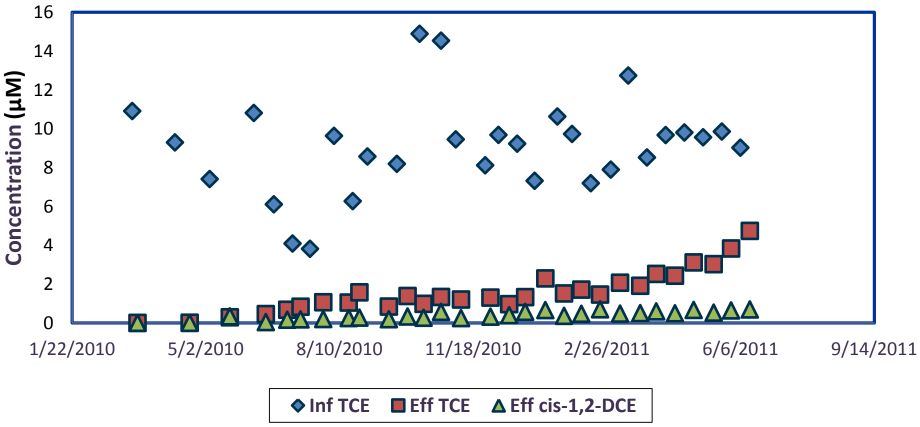
Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

Column Study Setup

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

Column #31 Example:

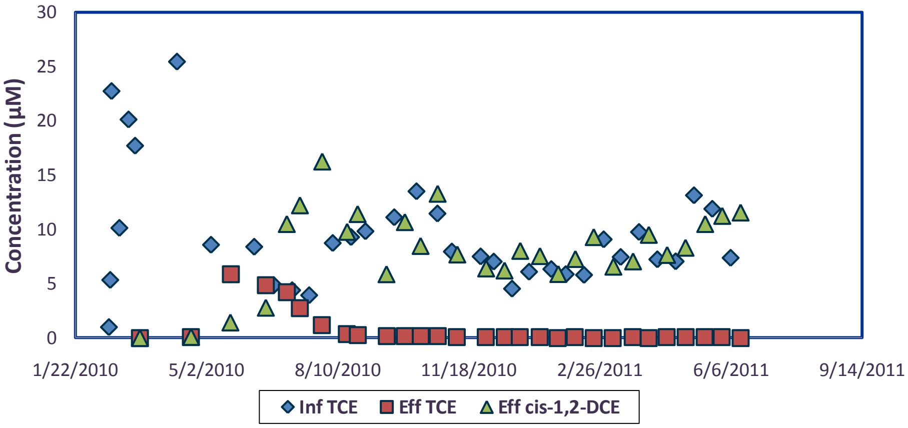
VOC Removal w/ Minimal cis-1,2-DCE Accumulation



Present: Magnetite, Hematite & Oil; Low: Flow; High: GW SO_4 & pH; Hard Wood

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

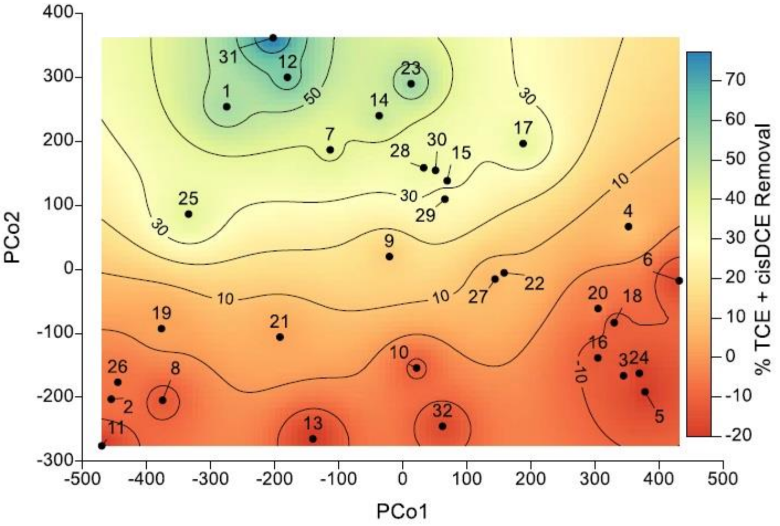
Column #6 Example:
Significant cis-1,2-DCE Accumulation



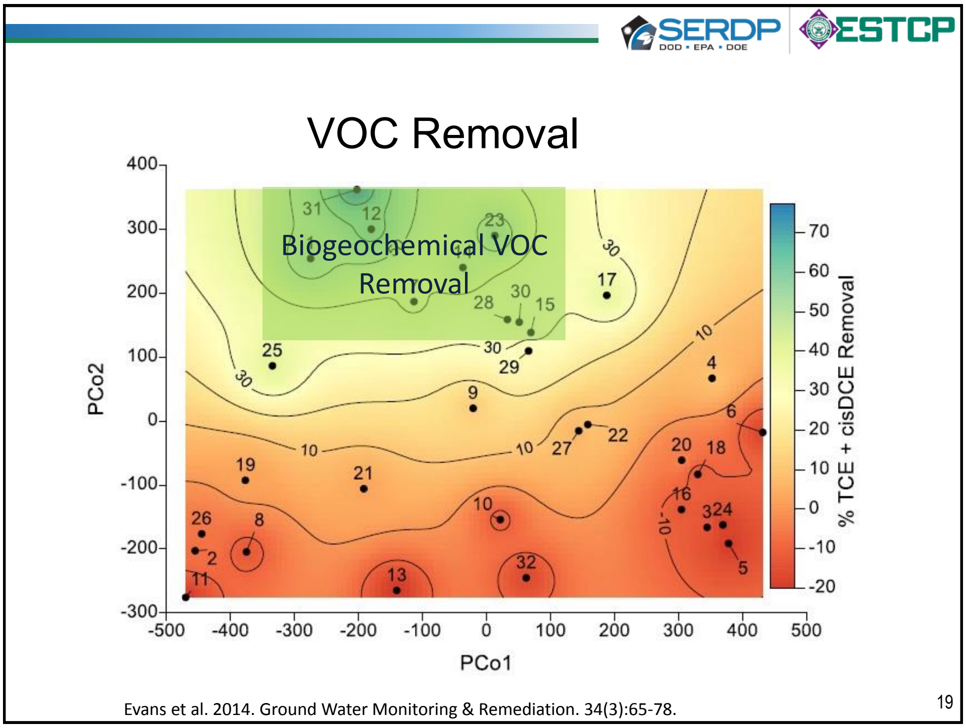
Present: Fe Sand, Hematite, Gypsum & Mulch; Low: GW SO$_4$, pH, & Flow

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

VOC Removal



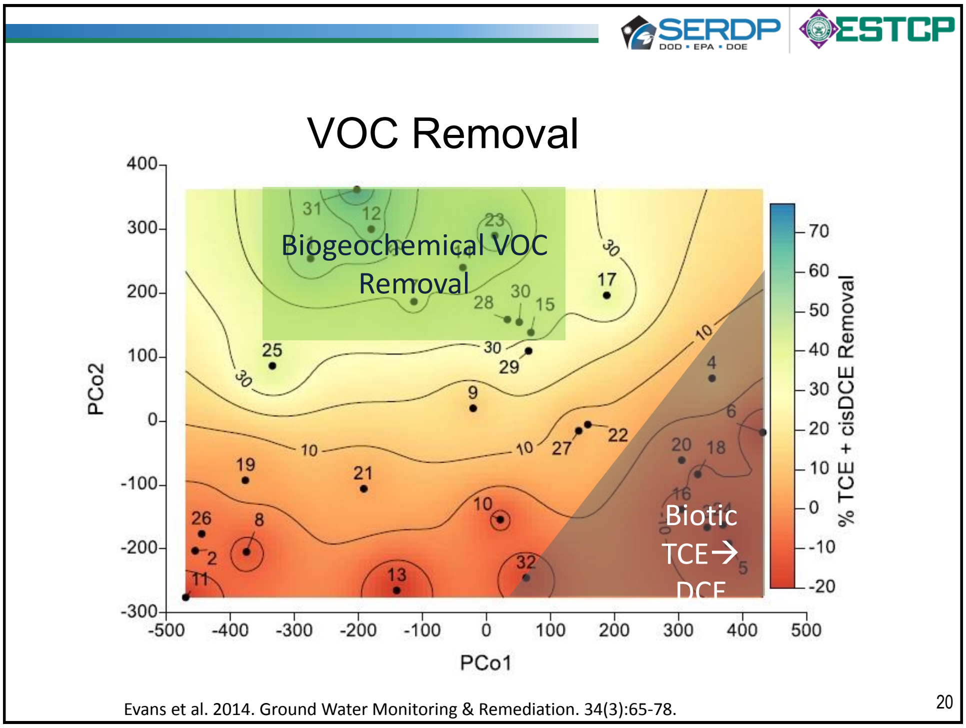
Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.



VOC Removal

Biogeochemical VOC Removal

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.



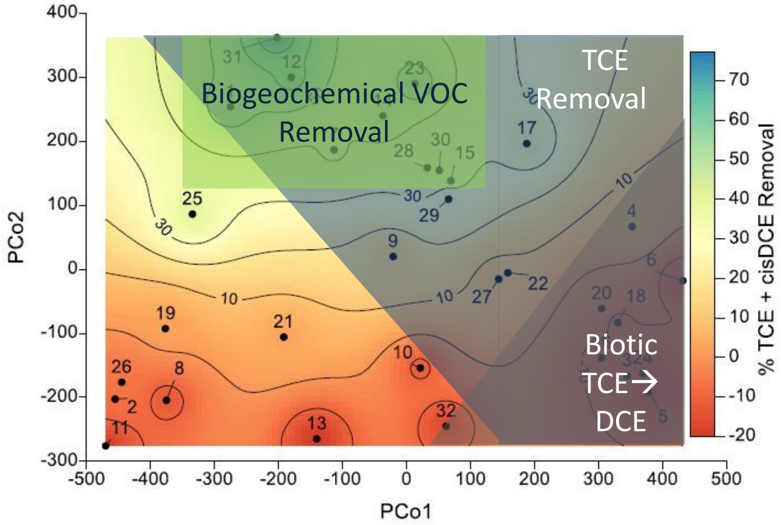
VOC Removal

Biogeochemical VOC Removal

Biotic TCE→ DCE

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

VOC Removal

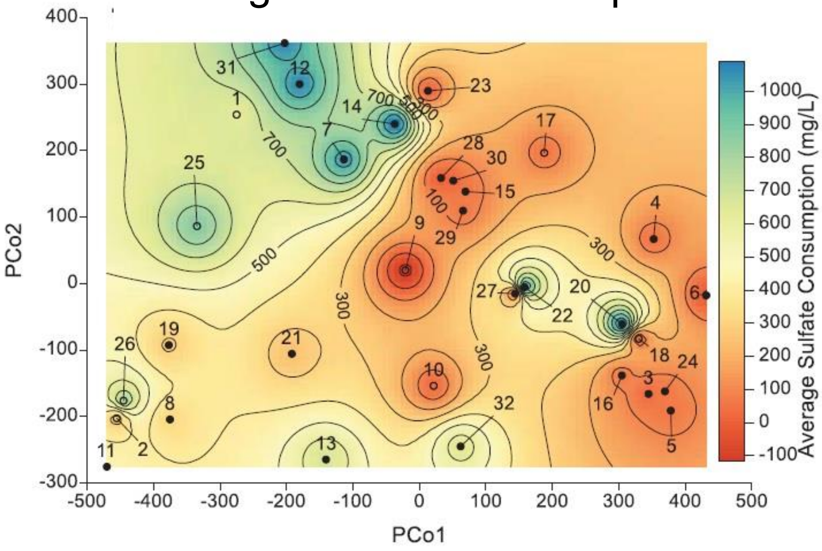

Biogeochemical VOC Removal

TCE Removal

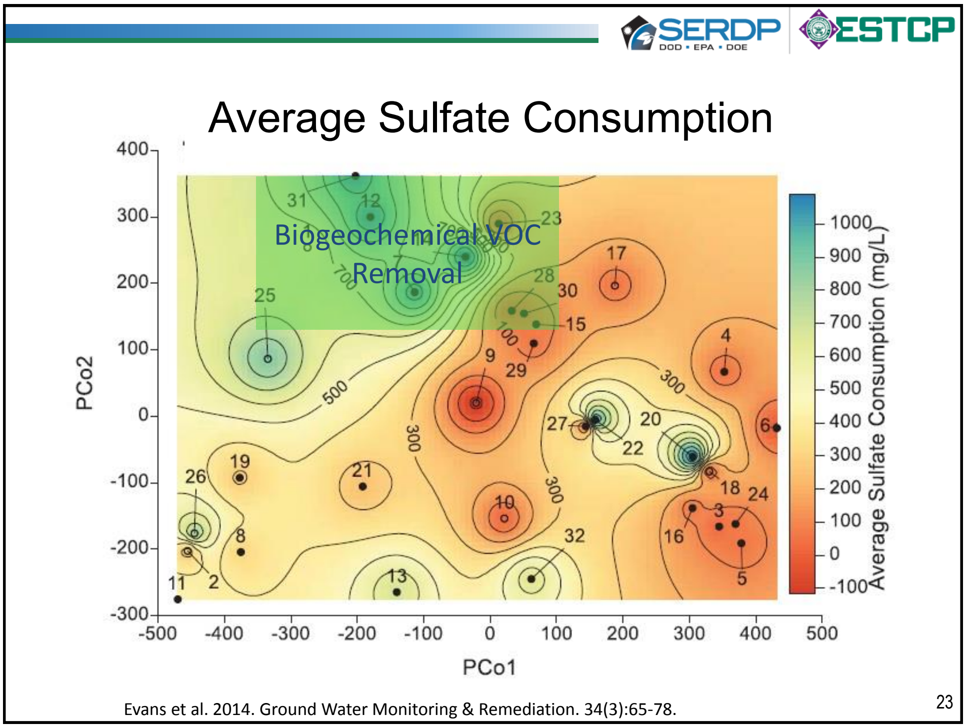
Biotic TCE→ DCE

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

Average Sulfate Consumption

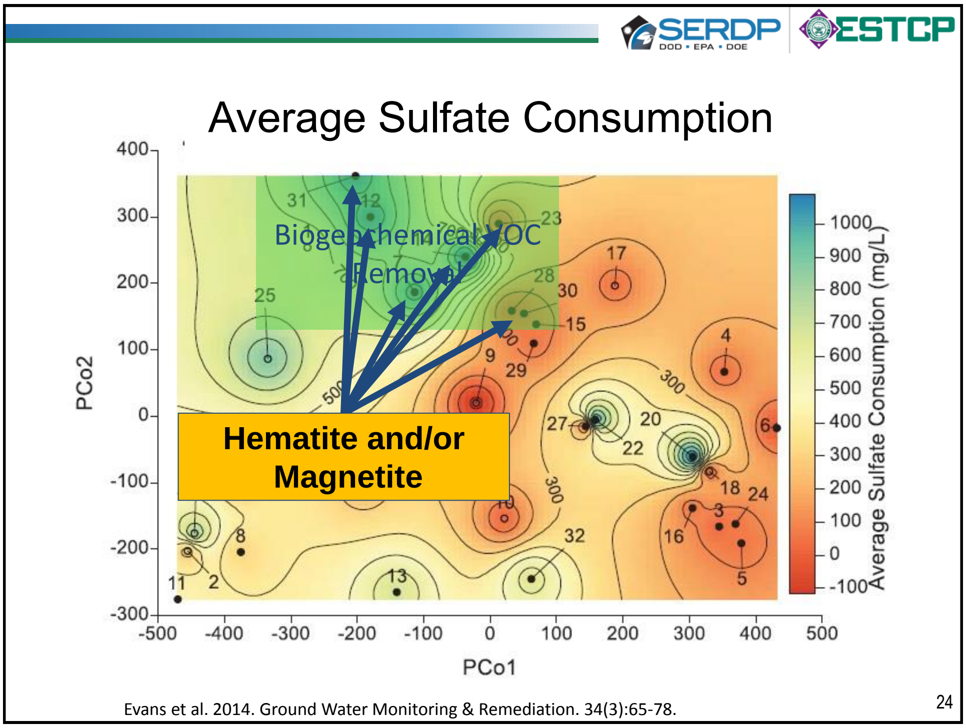


Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.



Average Sulfate Consumption

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.



Average Sulfate Consumption

Evans et al. 2014. Ground Water Monitoring & Remediation. 34(3):65-78.

Critical Factors

- Volumetric sulfate consumption rate (flux)
- Presence of magnetite or hematite
- Excess electron donor (vegetable oil)
- Sufficient residence time

Identification of these critical factors and our understanding at the time drove the design of the ESTCP demonstration.

ESTCP Project ER-201124

Technical Objectives

- Demonstrate that *in situ* biogeochemical transformation is capable of destroying TCE without significant accumulation of cis-DCE and VC.
- Confirm the critical factors identified in the AFCEE column study are important.
- Document technology cost and performance.

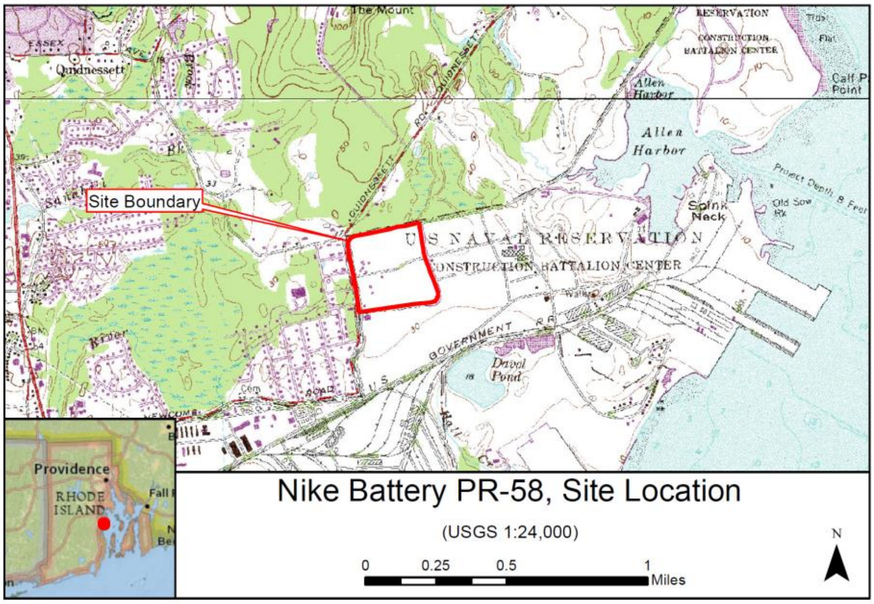
Technology Performance Objectives*

- Remediation Effectiveness (TCE and VOC removal)
- Attain geochemical conditions that are supportive of and consistent with biogeochemical transformation
- Sustainability/ Longevity
- Technology controllability
- Assess tools to distinguish between biotic and abiotic degradation mechanisms
- Applicability to multiple site conditions

*See Backup Slides for Details

Site Description

Site Location



Nike Battery PR-58, Site Location

(USGS 1:24,000)

Groundwater VOC Composition

Parameters	Units	Extraction Well
1,1,2,2-tetrachloroethane	µg/L	1,400
1,1,2-trichloroethane	µg/L	70
cis-1,2-dichloroethene	µg/L	1,300
tetrachloroethene	µg/L	320
trans-1,2-dichloroethene	µg/L	850
trichloroethene	µg/L	7,400
vinyl chloride	µg/L	<100

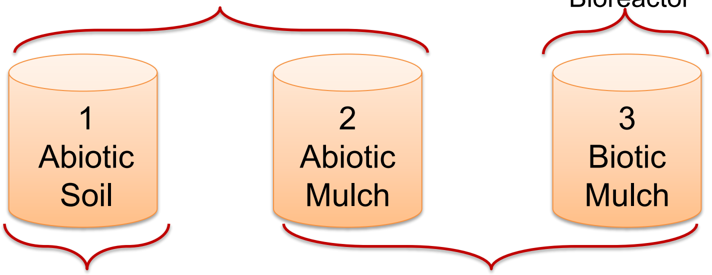
**Sample collected in March 2014 during start-up*

Chemistry/Hydrogeology

Parameter	Data Range	Units
Groundwater Chemistry		
Sulfate	9 - 11	mg/L
Ferrous Iron	**< 0.02 to 11**	**mg/L**
ORP	-4 to -14.9	mV, SHE
Dissolved Oxygen	2 to 48	% of saturation
Alkalinity	21 to 71	mg/L as $CaCO_3$
pH	**4.9 to 7.3**	**std units**
Soil Chemistry and Hydrogeology Data		
Depth to water	5 to 15	ft bgs
Groundwater Velocity	0.85	ft/d
Hydraulic Conductivity	0.26 to 0.2	ft/d
Total Iron	**10,000 to 13,000**	**mg/kg**
Bioavailable Ferric Iron	525±32	mg/kg
Organic Carbon	7,760	mg/kg

Test Design

Experimental Design Concept



Biogeochemical Transformation Bioreactors

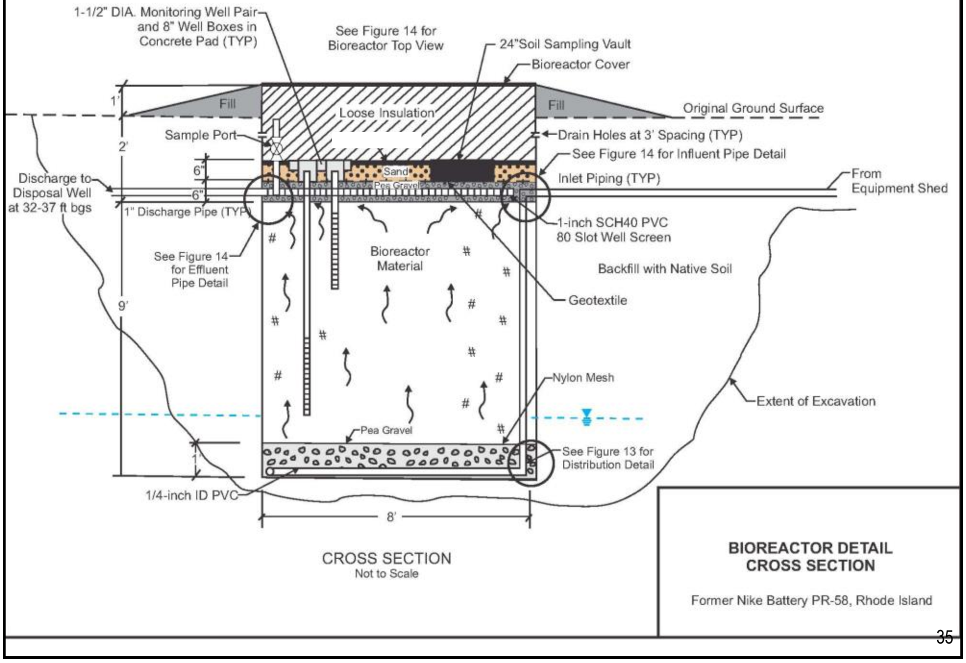
Control Biotic Bioreactor

Soil Bioreactor
(Injection Approach)

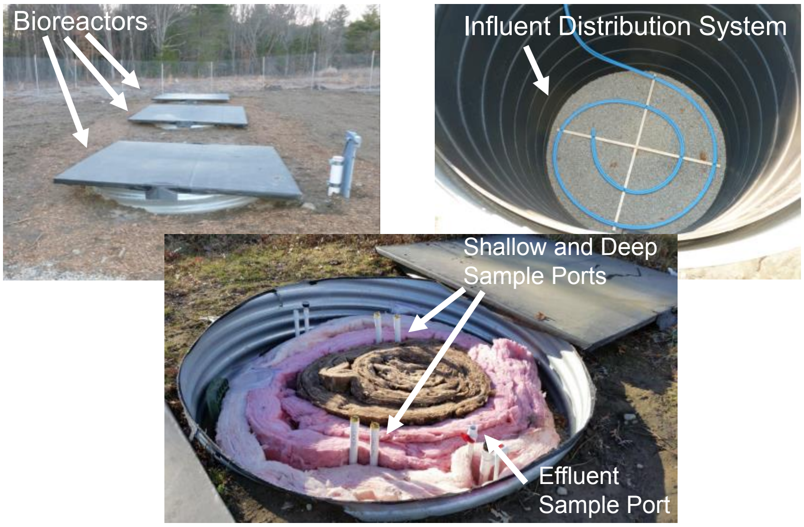
Mulch/Sand Bioreactors
(Biowall/Bioreactor Approach)

Reactor	Media	Magnetite (3%)	Sulfate (1000 mg/L)	Veg. Oil (1%)
1	Soil	Yes	Yes	Yes
2	Mulch/Sand	Yes	Yes	Yes
3	Mulch/Sand	No	No	Yes

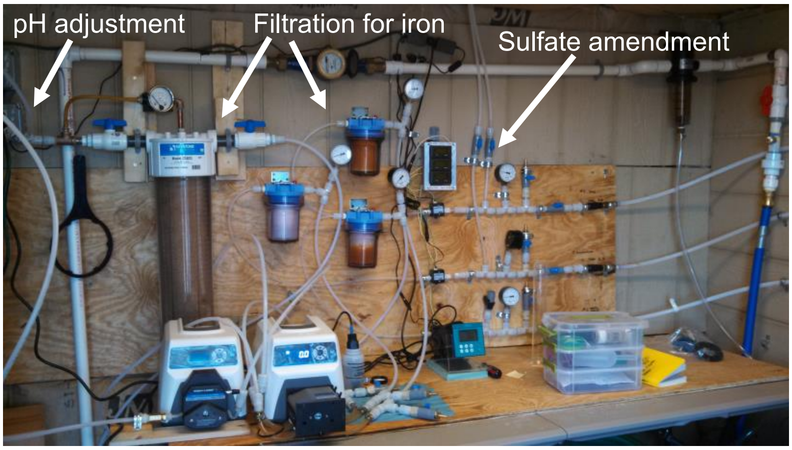
Bioreactor Cross Section



Bioreactors

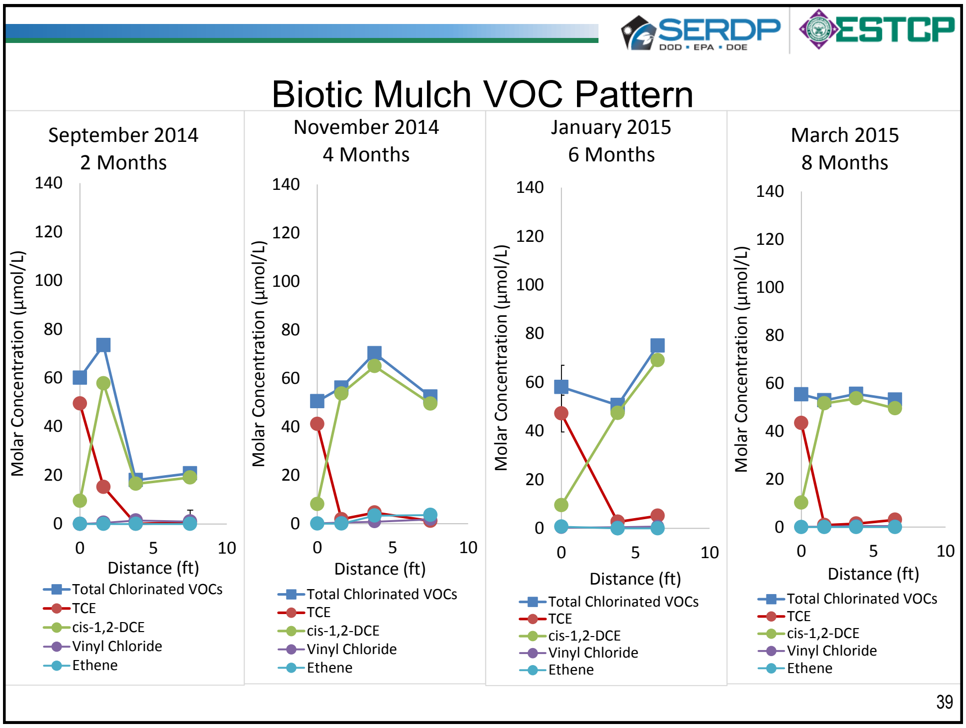


Bioreactor Influent Process Flow



Process Flow

Performance Assessment



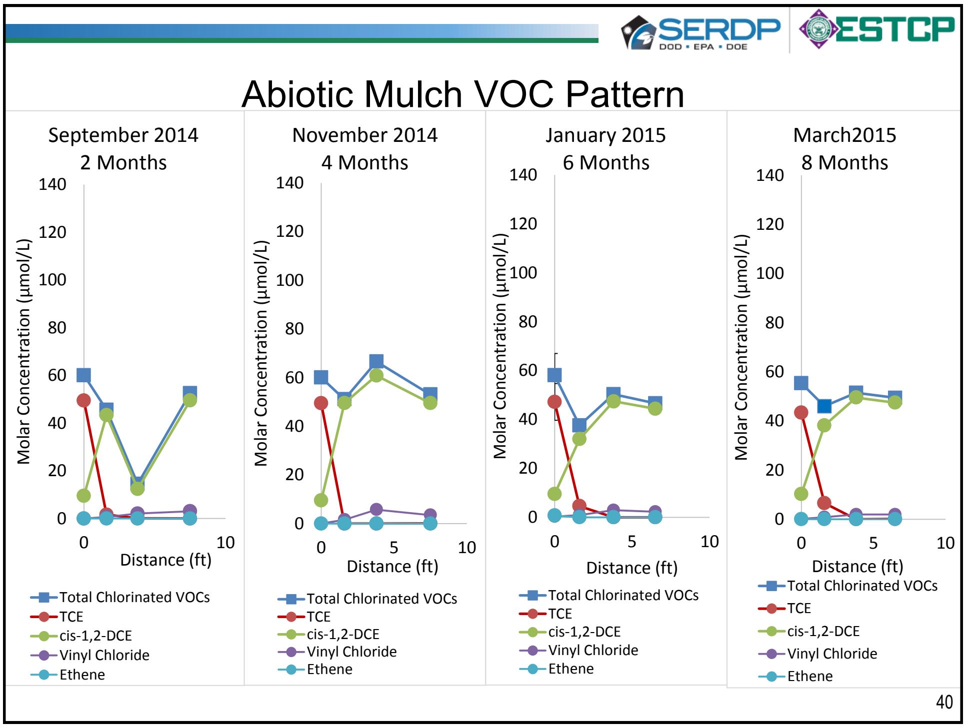
Biotic Mulch VOC Pattern

September 2014
2 Months

November 2014
4 Months

January 2015
6 Months

March 2015
8 Months



Abiotic Mulch VOC Pattern

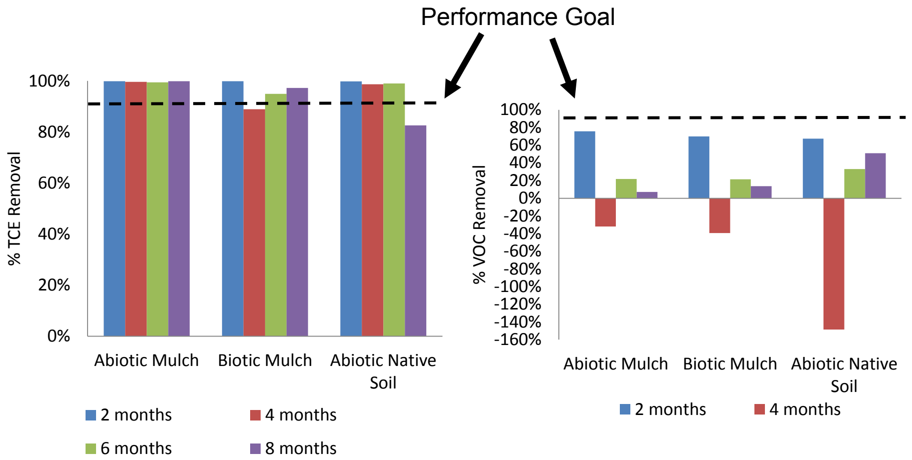
September 2014
2 Months

November 2014
4 Months

January 2015
6 Months

March2015
8 Months

Percent TCE and VOC Removal*



*Based on samples collected from the shallow well.

Quantifying the Abiotic/Biotic Pattern

$$f_{abiotic} = \frac{\sum VOC_I - \sum VOC_E}{\sum VOC_I}$$

$f_{abiotic}$ = Abiotic fraction (1 = Abiotic pattern, 0 = Biotic pattern)

ΣVOC_I = Total influent VOCs & ethene/ethane

ΣVOC_E = Total effluent VOCs & ethene/ethane

Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

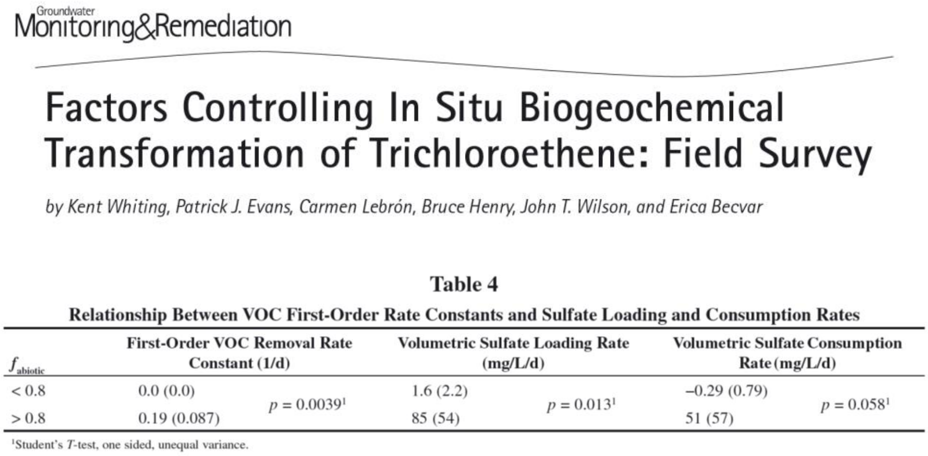
Relationship of Rates and VOC Patterns

Reactor	First-Order TCE Rate Constant* (d^{-1})	First-Order VOC Rate Constant* (d^{-1})	$f_{abiotic}$*
Biotic Mulch	0.23±0.07	0.05±0.05	0.16±0.42
Abiotic Mulch	0.25±0.04	0.04±0.04	0.003±0.095
Abiotic Native Soil	0.39±0.11	0.02±0.003	0.24±0.49

- $f_{abiotic}$ <<1
- High removal of TCE
- TCE → cis-1,2 DCE
- Why?

*calculated as average values over 2, 4, and 6 months

Field Survey (ER-200316; C. Lebrón PI)



Groundwater Monitoring&Remediation

Factors Controlling In Situ Biogeochemical Transformation of Trichloroethene: Field Survey

by Kent Whiting, Patrick J. Evans, Carmen Lebrón, Bruce Henry, John T. Wilson, and Erica Becvar

Table 4

Relationship Between VOC First-Order Rate Constants and Sulfate Loading and Consumption Rates

$f_{abiotic}$	First-Order VOC Removal Rate Constant (1/d)		Volumetric Sulfate Loading Rate (mg/L/d)		Volumetric Sulfate Consumption Rate (mg/L/d)	
< 0.8	0.0 (0.0)	$p = 0.0039$[1]	1.6 (2.2)	$p = 0.013$[1]	–0.29 (0.79)	$p = 0.058$[1]
> 0.8	0.19 (0.087)		85 (54)		51 (57)	

[1] Student's *T*-test, one sided, unequal variance.

Whiting et al. 2014. Ground Water Monitoring & Remediation. 34(3):79-94.

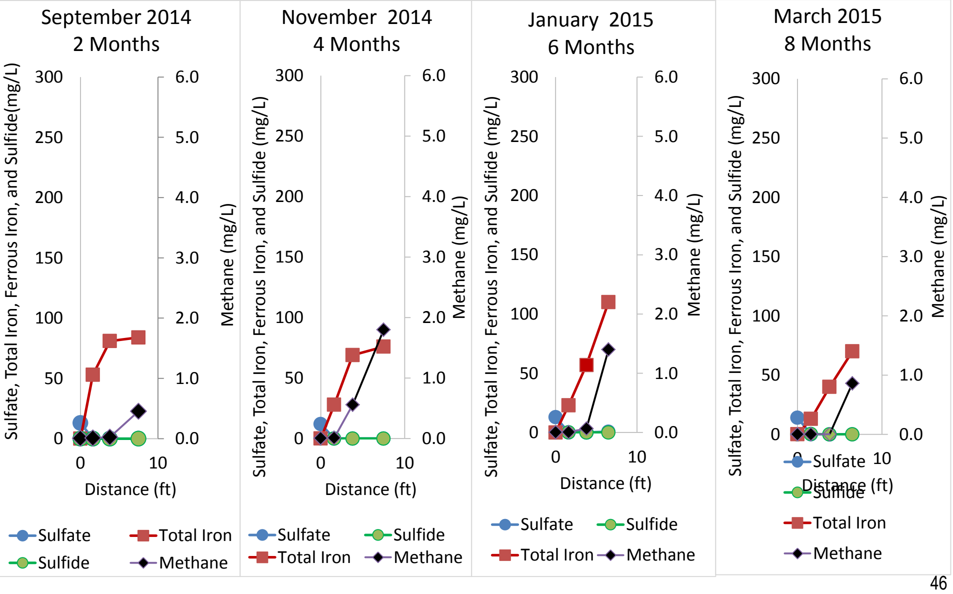
Sulfate Consumption Rate

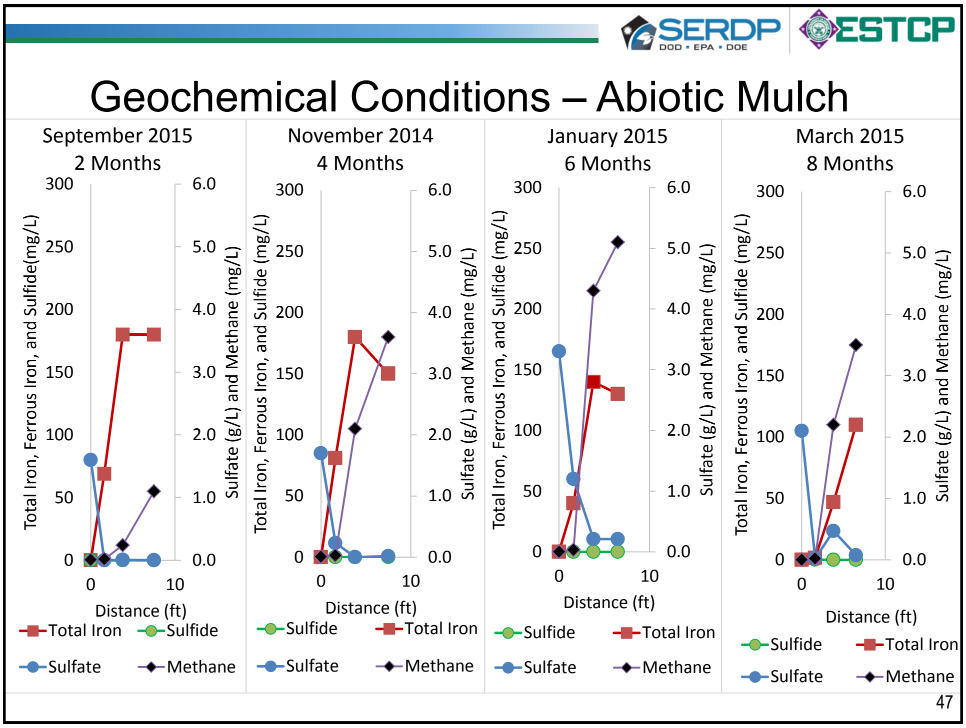
Reactor	First-Order TCE Rate Constant* (d^{-1})	First-Order VOC Rate Constant* (d^{-1})	$f_{abiotic}$*	Sulfate Rate* (mg/L/d)
Biotic Mulch	0.23±0.07	0.05±0.05	0.16±0.42	0.9±0.1
Abiotic Mulch	0.25±0.04	0.04±0.04	0.003±0.095	160±70
Abiotic Native Soil	0.39±0.11	0.02±0.003	0.24±0.49	170±30

- $f_{abiotic}$ <<1
- High removal of TCE
- TCE → cis-1,2 DCE
- Factors in addition to sulfate rate/flux are in play
- What about iron?

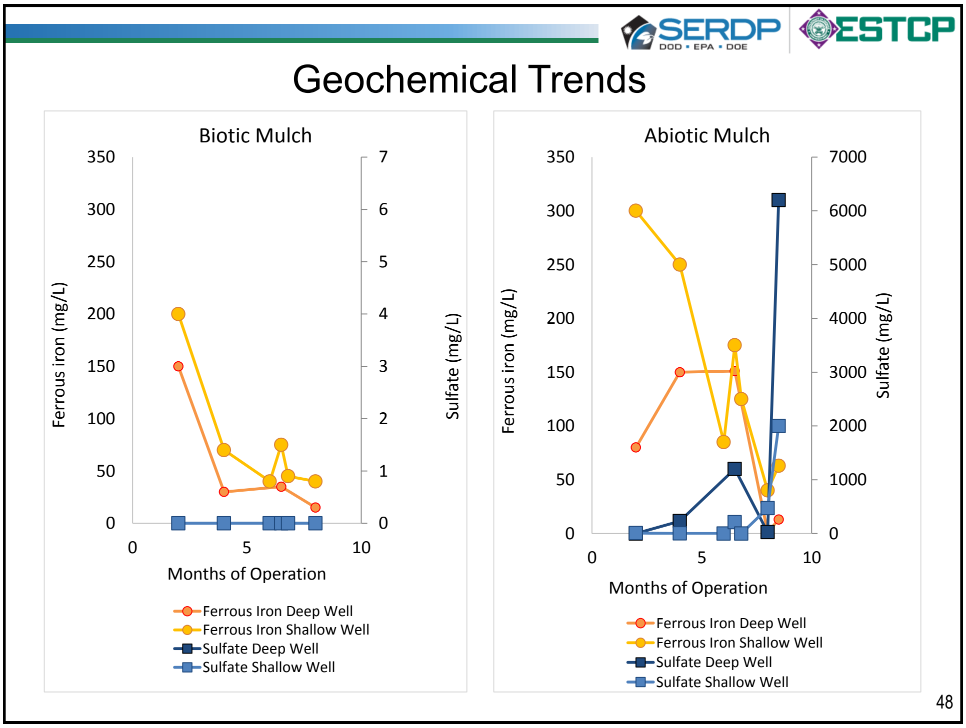
**calculated as average values over 2, 4, and 6 months*

Geochemical Conditions – Biotic Mulch





Geochemical Conditions – Abiotic Mulch



Geochemical Trends

Performance Objective:

Attain Geochemical Conditions that Support Biogeochemical Transformation

Performance Metric	Biotic Mulch	Abiotic Mulch	Abiotic Soil	Goal Achieved?
Volumetric sulfate loading rate >10 mg/L/d	0.90	160	170	Yes
Oil and grease analysis: Sufficient to meet demand for 1 year (>100% of Demand)	110%	210%	140%	Yes
Effluent DOC not limiting (mg/L)	220	320	300	Yes
Sulfate consumption >50%	98%	98%	81%	Yes
Methane production > 5 mg/L	0.77	3.0	0.05	No
Ethene, ethane, acetylene < 20% of total CVOC influent	ND	ND	ND	Yes
Effluent ferrous iron	110 mg/L	270 mg/L	130 mg/L	Yes
Less than 10 percent formation of daughter products in abiotic reactors	66%	84%	63%	No

**calculated as average values over 2, 4, and 6 months*

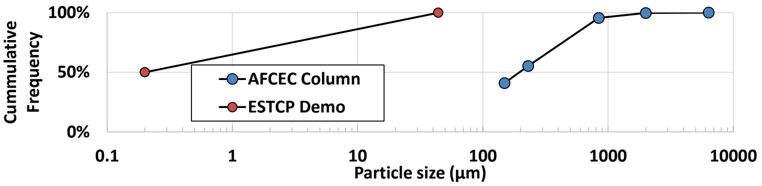
Differences between the Column Study and the ESTCP Demonstration

Attribute	AFCEC Column Study	ESTCP Demonstration
Magnetite	5% Reade magnetite from ore	3% Davis Colors synthetic magnetite
Vegetable oil	1.25% Soybean oil	1.0% Soybean oil
Mulch	Living Earth double ground hardwood mulch (similar to that used at Altus AFB)	Hopedale Trucking hardwood mulch
Hydraulic residence time	5 or 20 days	11 days
Sulfate concentration	1,000 to 2,000 mg/L	1,000 to 2,000 mg/L

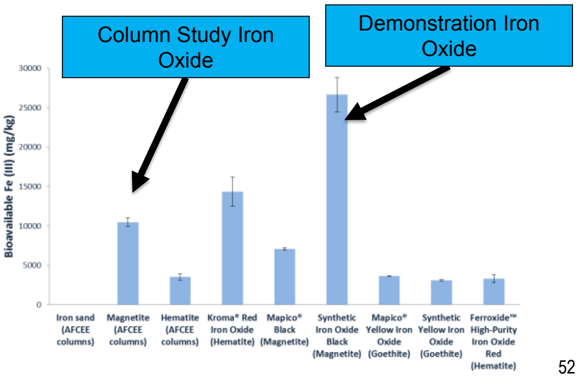
Magnetite Comparison

	AFCEC Column Study	ESTCP Demonstration
Supplier	**Reade Advanced Materials**	**Huntsman**
Product	**Magnetite grit**	**Davis Colors^{TM} Synthetic Iron Oxide Black 860**
Source	**Magnetic iron ore**	**Unidentified synthetic process**
Additives	**None**	**3 to 4% Al_2O_3 and SiO_2**
Reported trace elements	**Al, As, Ca, Cu, Mg, Mn, Na, P, K, Si, S**	**As, Sb, Cd, Cr(III), Cu, Pb, Hg, Ni, Se**

Magnetite Particle Size Distribution



Magnetite	Median size (µm)	Specific surface area (m^2/g)
AFCEC Column	200	0.0063
ESTCP Demo	0.2	6.5


Column Study Iron Oxide

Demonstration Iron Oxide

Comparison to Previous Studies

Study	FeS Concentration	First-order VOC Rate Constant (d^{-1})	Second-Order VOC Rate Constant ($M^{-1}\ d^{-1}$)	Effluent
Abiotic Mulch	**15,000 mg/kg[a]**	**0.04±0.04**	**0.0**	**130 mg/L Fe^{+2}**
Biotic Mulch	**88 mg/kg[a]**	**0.05±0.05**	**0.0**	**270 mg/L Fe^{+2}**
Shen and Wilson 2007[b]	**4,700 mg/kg[a]**	**0.22**	**1.6**	**13 mg/L S^{-2}**
Kennedy et al 2006	**59 mg/kg[c]**	**0.023**	**4.6**	**Not reported[d]**
He, Wilson, and Wilkin 2010	**20 g/L**	**0.17**	**0.75**	**NA**

[a] Calculated using a mass balance on sulfur
[b] Hematite and mulch column sampled at 383 days.
[c] Measured as acid volatile sulfide
[d] Likely sulfide present in groundwater

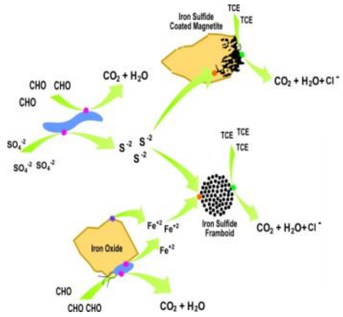
VOC Destruction

- Performance objective of 90% destruction of TCE was achieved
- Biotic degradation pathways dominated with accumulation of cis-DCE
- Biogeochemical transformation was not observed

Data Synthesis

- **Iron was in excess**
  - High bioavailability
  - High surface area (powder)
  - Synthetic vs. natural magnetite
  - Impurities
  - May affect FeS reactivity/deactivation
- **Sulfate was limiting**
  - Most is consumed near reactor inlet
  - Effective HRT is less than desired
  - No sulfide in effluent
  - Iron sulfide reactive zone is short (HRT < 5 days?)
  - Increases in sulfate led to reduced Fe in effluent
- **pH was initially low then increased**
  - Initially about 6.5
  - Vegetable oil fermentation to VFAs
  - Lower FeS_x reactivity

Need to balance iron and sulfur!



Critical Factors - Revised

- Volumetric sulfate consumption rate (flux)
- Presence of magnetite or hematite
- Balanced iron and sulfur flux
- Source of magnetite
- Sufficient ~~Excess~~ electron donor ~~(vegetable oil)~~
- Balanced electron donor
- Sufficient residence time

Lessons Learned

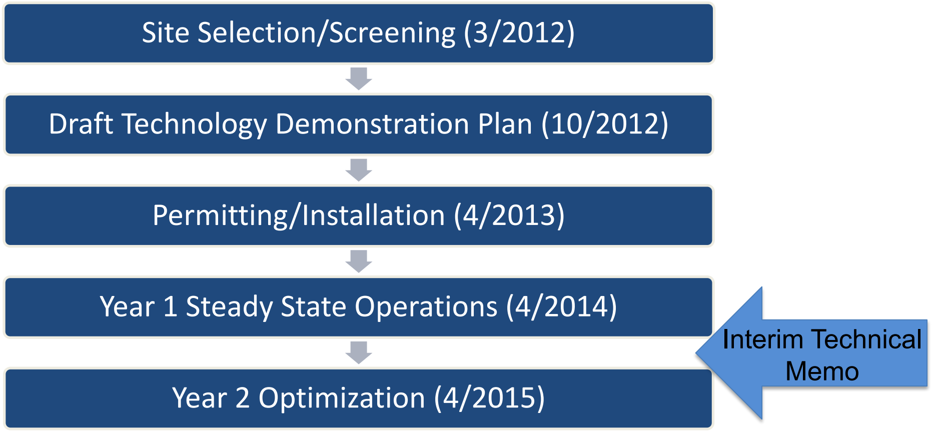
- All magnetite is not created equal
  - Surface area
  - Composition
  - Source
- An excess of iron is not necessarily good
- It is better to have S^{-2} present in groundwater than Fe^{+2}
- Electron donor type and delivery is important
- Balancing iron and sulfur flux is critical

BACKUP MATERIAL

Particle Size and Surface Area

Median Grain Diameter (µm)	Specific Surface Area (m^2/g)	Notes
0.004	360	4 nm "nanoparticles"
0.004	298	4 nm "nanoparticles"
0.7	1.7	Approximate size of framboid microcrystals in OU-1 and the USEPA column samples
1	1.2	Median for the OU-1 samples
1	1.4	Median for the OU-1 samples
8	0.149	Median for the Dover AFB samples

Original Plan



Site Selection/Screening (3/2012)

Draft Technology Demonstration Plan (10/2012)

Permitting/Installation (4/2013)

Year 1 Steady State Operations (4/2014)

Year 2 Optimization (4/2015)

Interim Technical Memo

Revised Plan

**per April 2013 White Paper*

- Site Selection/Screening (3/2012)
- Technology Demonstration Plan (6/2013)
- Permitting/Installation (3/2014)
- Field Demonstration (7/2015)
- Decommissioning (8/2015)
- Final Report (2/2016)

⇨ *One year demonstration*

⇨ *Reduced monitoring plan*

⇨ *Interim technical memo will not be completed*

Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Remediation effectiveness	• Pre- and post-treatment TCE concentrations in groundwater • Pre- and post-treatment VOC concentrations	• 90 percent reduction in TCE concentration • 90 percent reduction in total chlorinated VOCs on a molar basis

Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Attain geochemical conditions that are supportive of and consistent with biogeochemical transformation	• Volumetric sulfate loading • Sulfate consumption • Electron donor concentration • Methane production • Ethene, ethane, and acetylene concentrations • Electron microprobe analysis of soil/mulch samples • Ferrous iron in groundwater effluent; • Influent water chemistry for geochemical modeling • VOC concentrations	• > 10 mg/L/d • > 50 percent consumption of sulfate • Oil and grease analysis sufficient to meet electron acceptor demand for at least 1 year • Dissolved methane > 5 milligrams per liter (mg/L) • Dissolved ethane and ethene in effluent stoichiometrically < 20 percent of influent VOCs • Electron microprobe analysis shows presence of iron sulfides and/or green rusts • Ferrous iron present in effluent if sulfate is limiting • Geochemical modeling results are supportive of biogeochemical transformation • < 10 percent formation of daughter products in biogeochemical reactors

---

Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Sustainability/ Longevity	• Pre- and post-treatment TCE concentrations in groundwater • VOC concentrations in groundwater • Electron donor concentration	**Remediation effectiveness demonstrated for at least 1 year** (e.g. 90 percent reduction in TCE concentration and 90 percent reduction in total chlorinated VOCs on a molar basis without daughter product formation). Oil and grease analysis sufficient to meet electron acceptor demand.

Note: Red text no longer applicable based on April 2013 White Paper Project Plan Changes

Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Qualitative Performance Objectives		
Technology controllability	• Design conditions • Operating records including data on electron donor supplementation • Concentrations of VOCs • Sulfate concentrations • Flow rate • Methane, sulfide, ferrous iron, dissolved methane, ethene, ethane, and acetylene, sulfate, pH, and ORP	• Factors identified in the AFCEE column study as being capable of enhancing biogeochemical transformation are demonstrated as being effective in the field • **Process changes implemented at the end of Year 1 result in expected performance changes**.

Note: Red text no longer applicable based on April 2013 White Paper Project Plan Changes

---

Performance Objectives

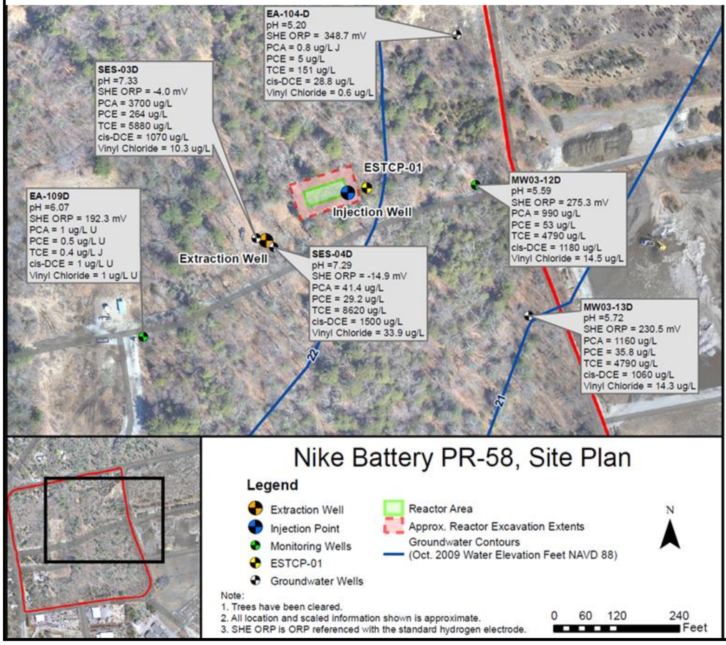
Performance Objective	Data Requirements	Success Criteria
Qualitative Performance Objectives		
Assess tools to distinguish between biotic and abiotic degradation mechanisms	• Molar concentrations of VOCs and daughter products throughout the bioreactor (e.g. influent, mid-points, and effluent), including TCE, cis-DCE, VC, ethane, ethane • **CENSUS for microbial populations present** • Compound stable isotope analysis (CSIA) • Chromate reducible sulfide (CrRS) and acid volatile sulfide (AVS) • Electron microprobe analysis • **Sequential extractions of iron** • Volatile fatty acids	• One or more methods can provide sufficient data to statistically distinguish between dominant degradation pathways in the mulch bioreactor designed for enhanced biodegradation and the mulch bioreactor designed for biogeochemical transformation.

Note: Red text no longer applicable based on April 2013 White Paper Project Plan Changes

Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Qualitative Performance Objectives		
Applicability to multiple site conditions	• Compare designs, operating conditions, and performance data between the biogeochemical transformation mulch bioreactor and soil bioreactor.	• Factors identified as being important for biogeochemical transformation can be applied to multiple configurations (e.g., biowalls and injection systems)

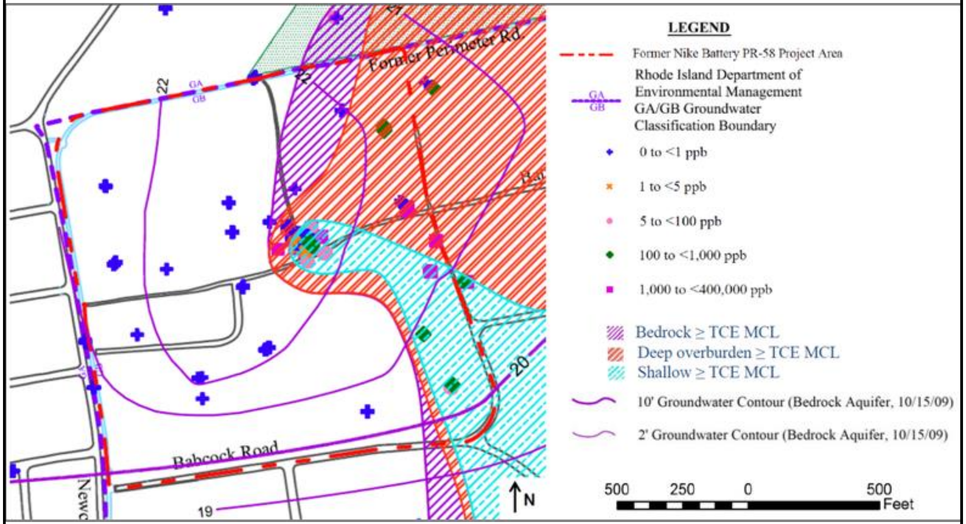
Site Description – VOC Concentrations & pH



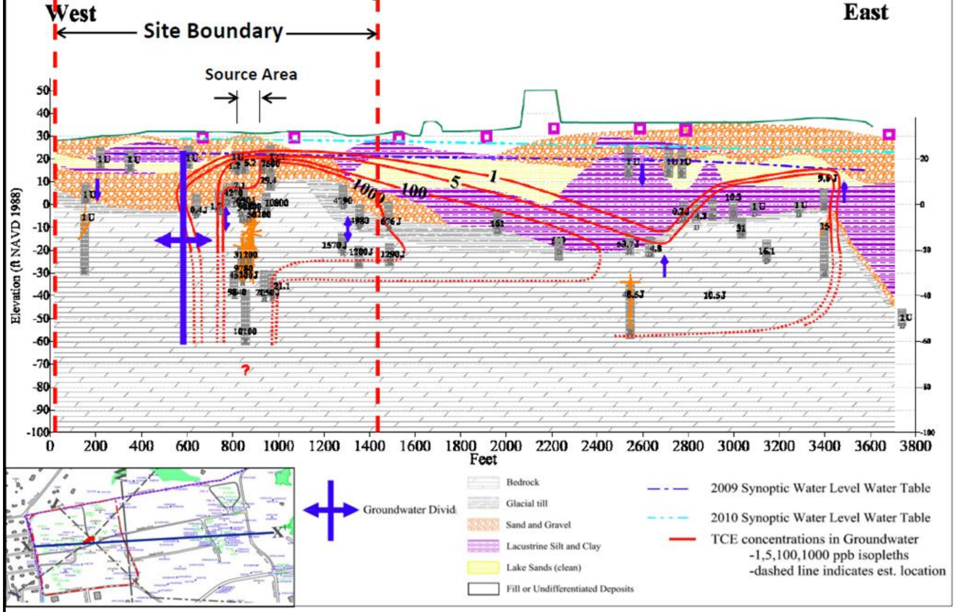
Note:
1. Trees have been cleared.
2. All location and scaled information shown is approximate.
3. SHE ORP is ORP referenced with the standard hydrogen electrode.

- Mostly TCE and cis-DCE in source
- Trace VC
- PCA downgradient
- pH as low as 5

TCE Plume



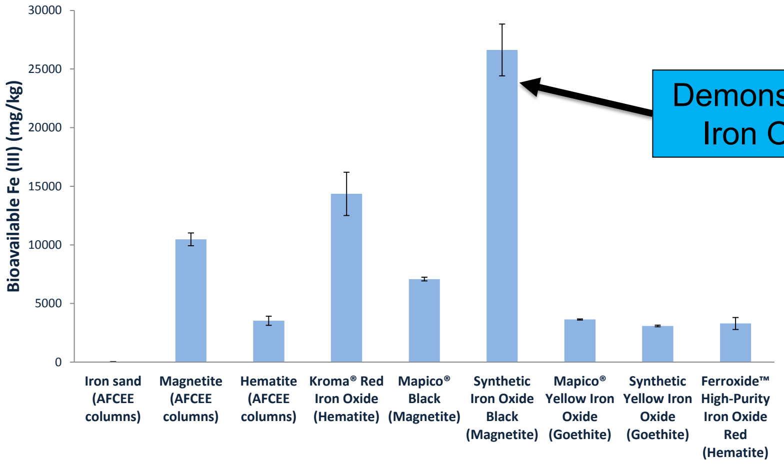
Site Description – Cross Section



Test Design – Bioreactor Media

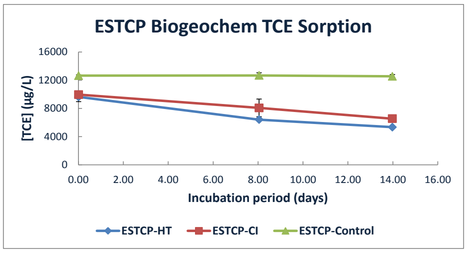
Bioreactor	Mechanism	Backfill Materials (% vol/vol)				
		Soil	Mulch	Silica Sand	Iron Oxide	Vegetable oil
1 Abiotic Soil	Biogeochemical Transformation	96%	-	-	3%	1%
2 Abiotic Mulch	Biogeochemical Transformation	-	40%	56%	3%	1%
3 Biotic Mulch	Biotic	-	40%	59%	-	1%

Iron Oxide Selection



Demonstration Iron Oxide

Mulch Selection



Hopedale Trucking mulch selected based on:

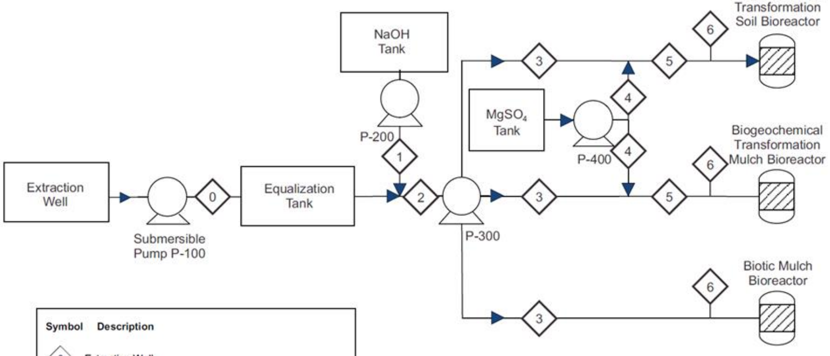
- Less TCE sorption
- Greater CO_2 Evolution
- Smaller particle size

Test	Hopedale Trucking 1	Hopedale Trucking 2	Castle Island 1	Castle Island 2
Solids	47	47	33	31
Organic Matter (dry wt)	95.6	95.3	65.5	66.3
CO_2 evolution ($mgCO_2$-C/gOM/d)	0.3	0.3	0.2	0.2
CO_2 evolution ($mgCO_2$-C/gTS/d)	1.1	1.2	0.5	0.5
Ammonia evolution (gNH_3-N/kg/d)	0.5	0.3	0.3	0.6

Test Design – GW Amendments

		Aqueous Amendments		
Bioreactor	**Mechanism**	**NaOH**	**Sulfate (mg/L)**	**Vegetable oil**
1 Abiotic Soil	Biogeochemical Transformation	pH = 7.0	1,000	If needed after 1 year
2 Abiotic Mulch	Biogeochemical Transformation	pH = 7.0	1,000	If needed after 1 year
3 Biotic Mulch	Biotic	pH = 7.0	0	If needed after 1 year

Process Flow Diagram



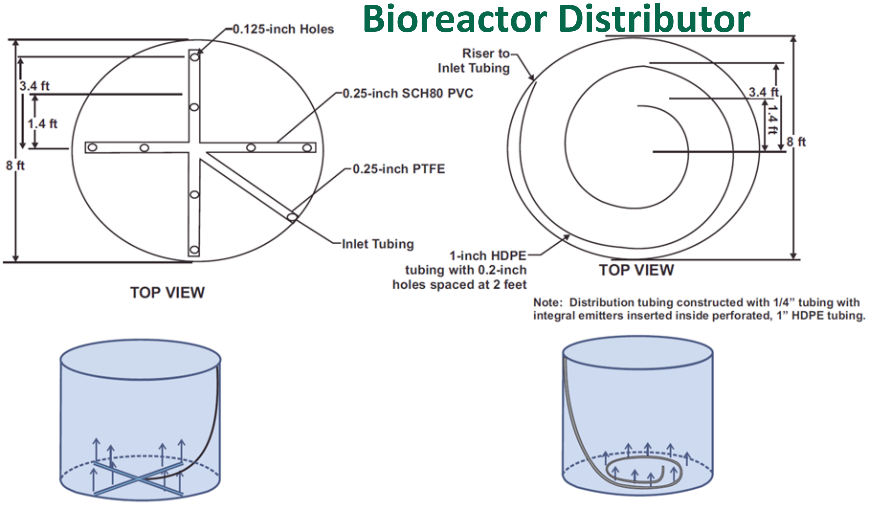
Symbol	Description
0	Extraction Well
1	NaOH Tank
2	Post pH Adjustment
3	Header
4	MgSO$_4$ Tank
5	Post pH Adjustment and Sulfate Addition
6	Injection Port for Emulsified Vegetable Oil

Note: Stream IDs shown above are used in design calculations.

BIOREACTOR SYSTEM
PROCESS FLOW DIAGRAM

Former Nike Battery PR-58, Rhode Island

Bioreactor Distributor



TOP VIEW

TOP VIEW

Note: Distribution tubing constructed with 1/4" tubing with integral emitters inserted inside perforated, 1" HDPE tubing.

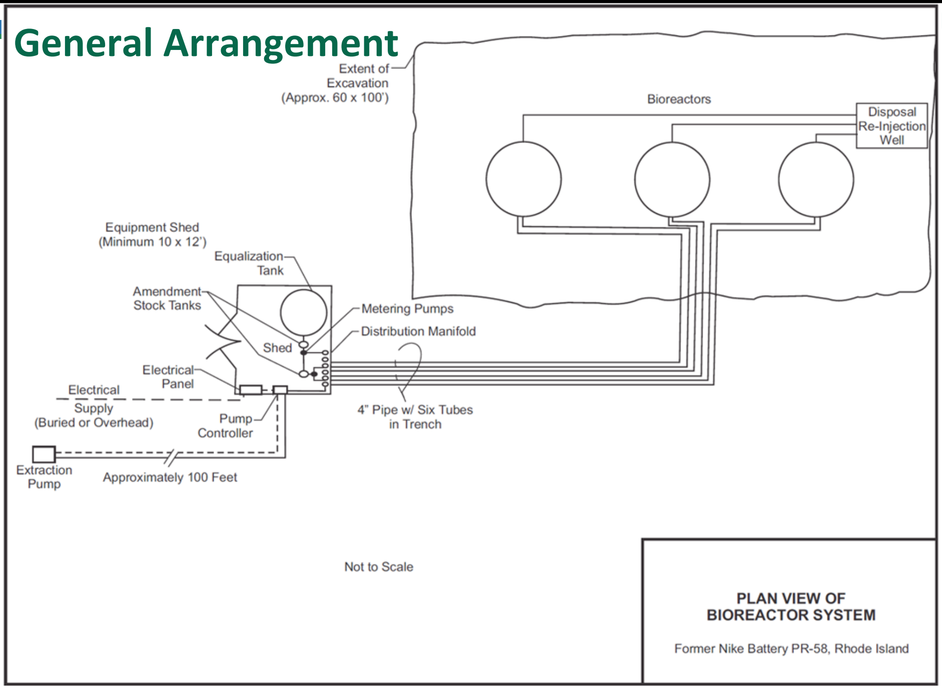
PRIMARY DISTRIBUTION SYSTEM
Not to Scale

SECONDARY DISTRIBUTION SYSTEM
Not to Scale

BIOREACTOR
DISTRIBUTION SYSTEM

Former Nike Battery PR-58, Rhode Island

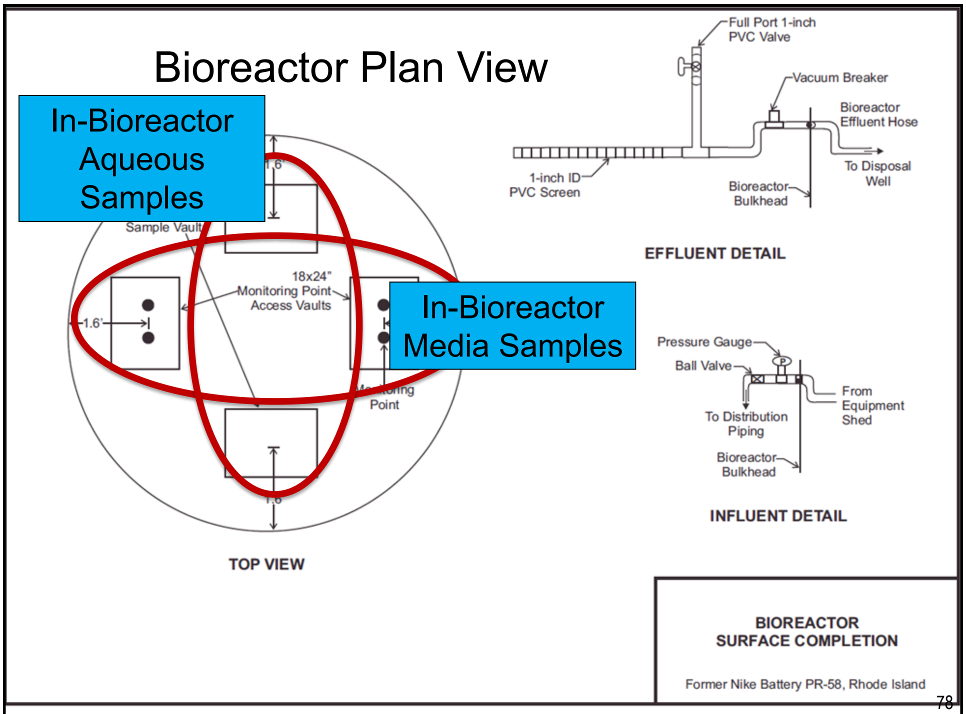
General Arrangement



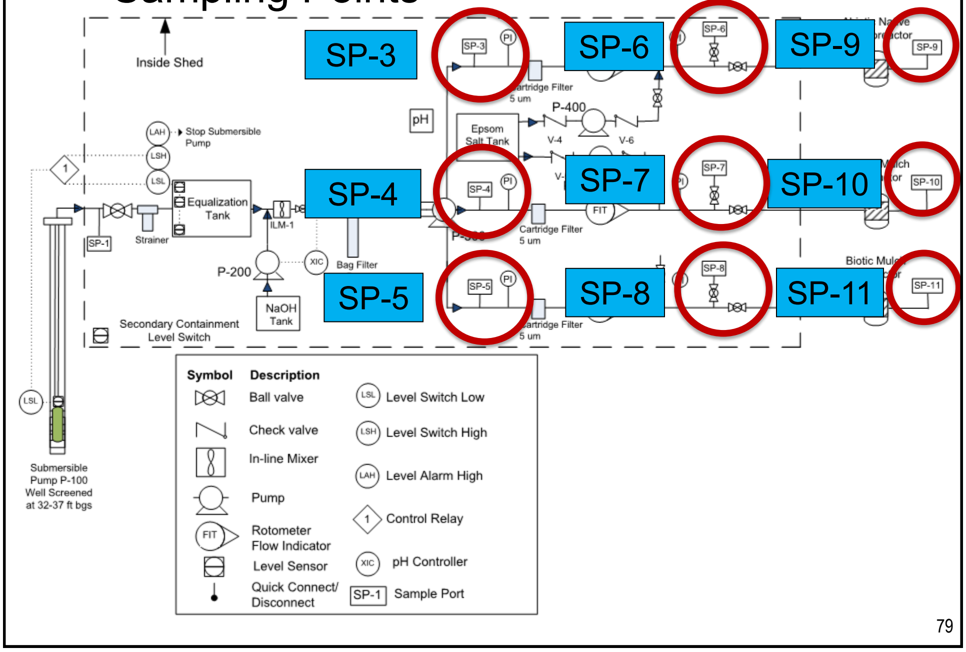
Bioreactor Plan View

In-Bioreactor Aqueous Samples

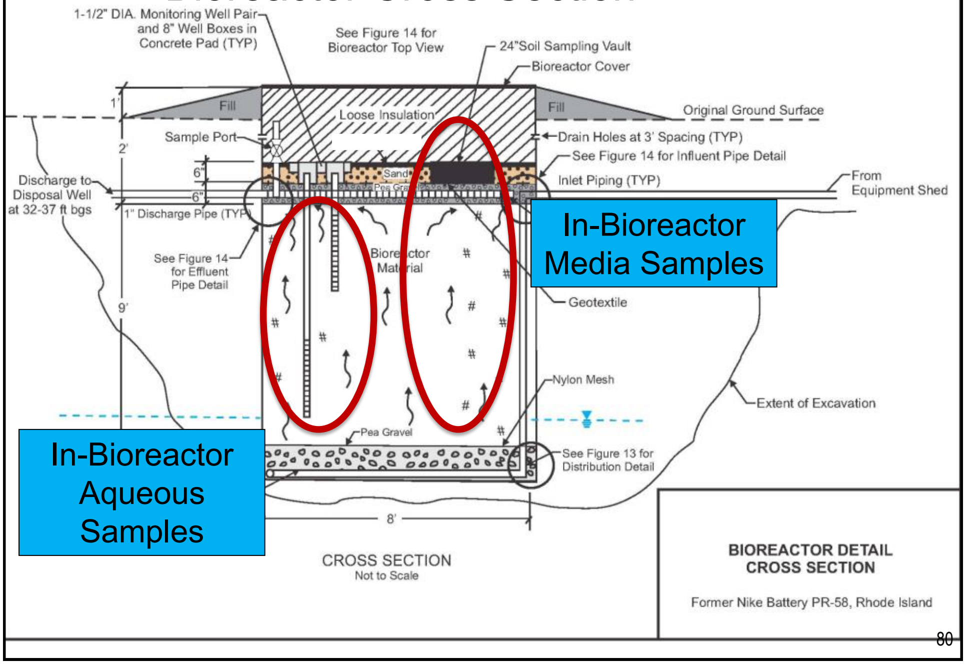
In-Bioreactor Media Samples



Sampling Points

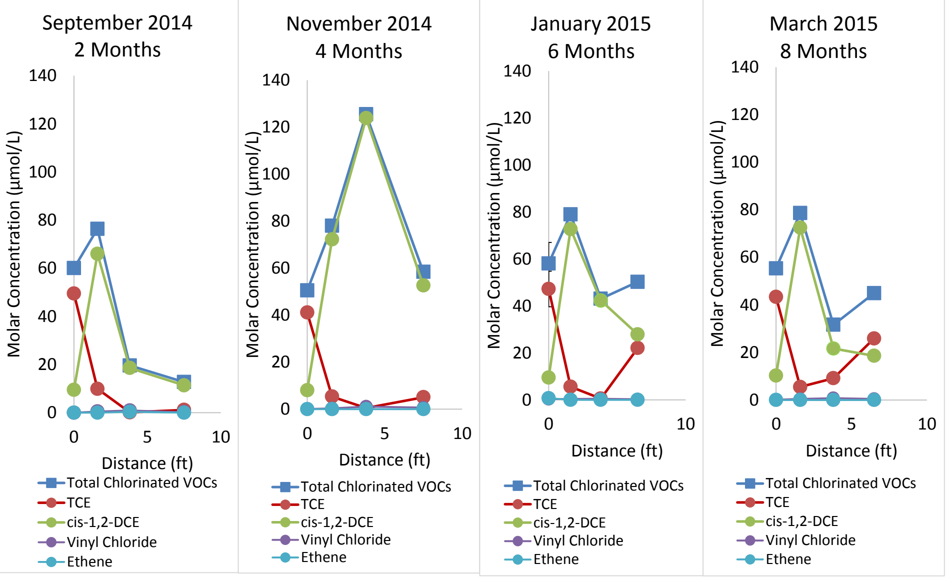


Bioreactor Cross Section



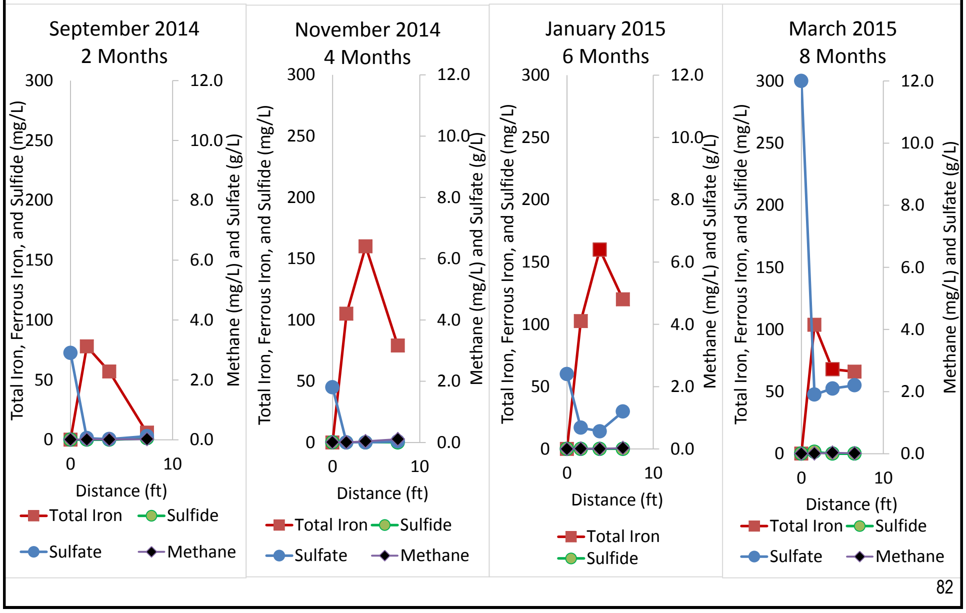
SERDP DOD • EPA • DOE ESTCP

Abiotic Soil VOC Pattern

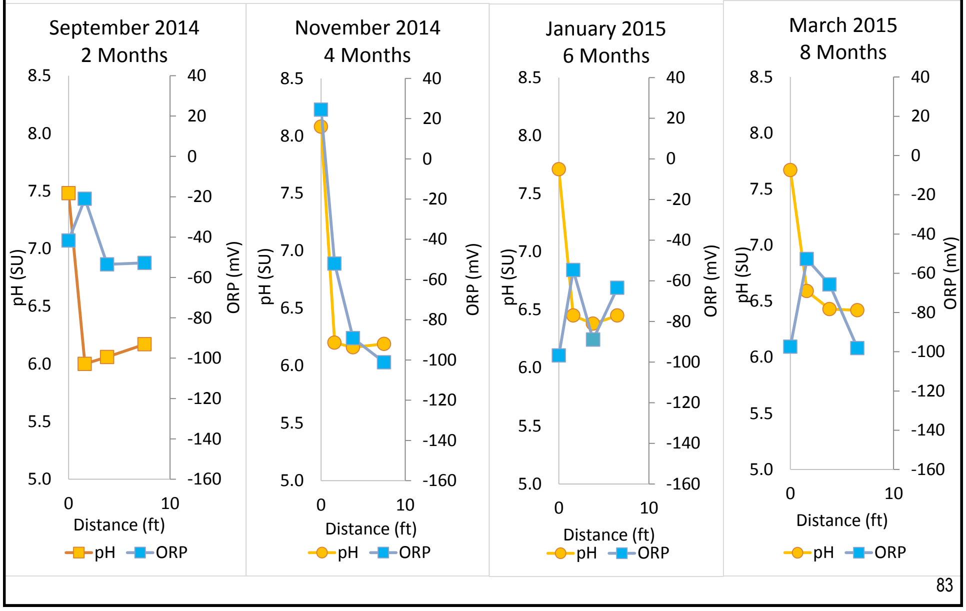


SERDP DOD • EPA • DOE ESTCP

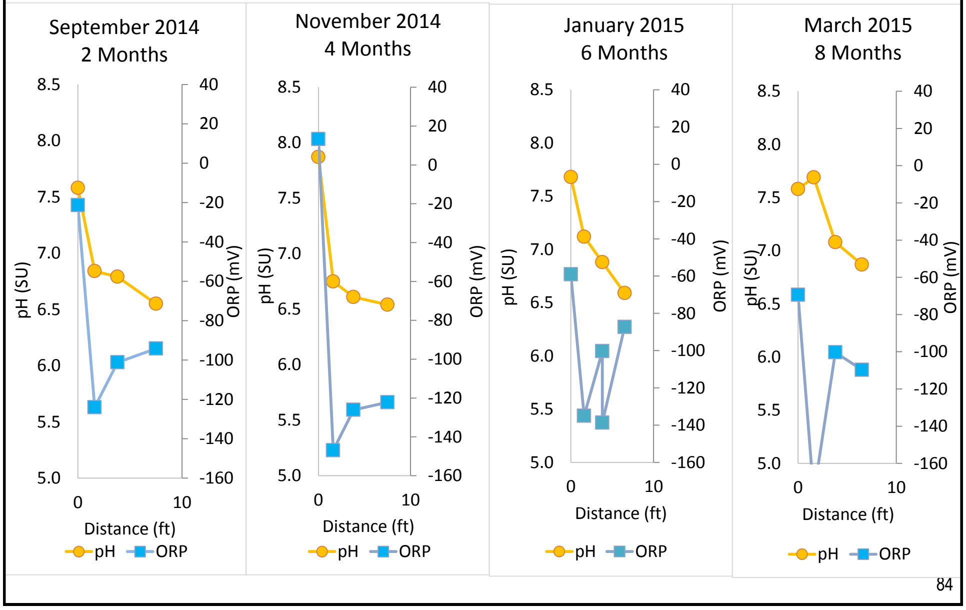
Geochemical Conditions – Abiotic Soil



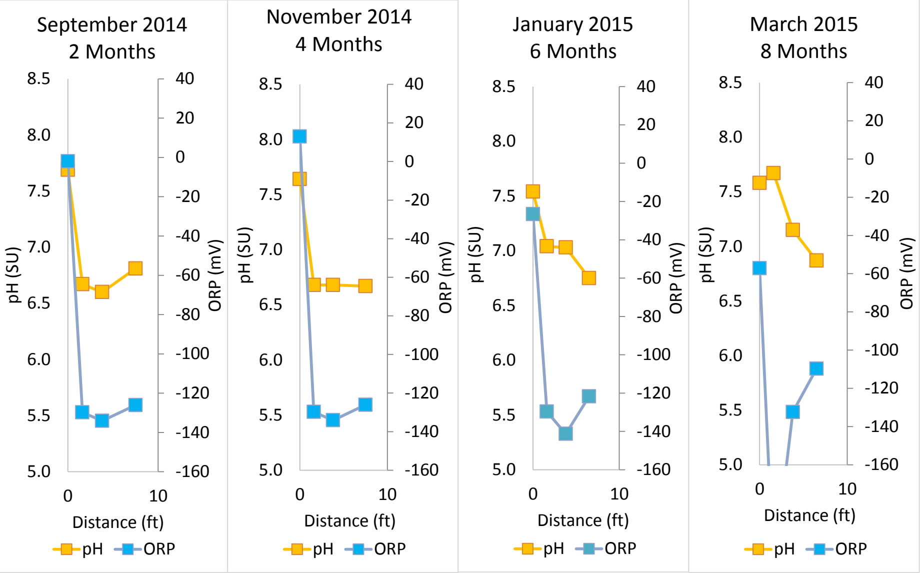
Geochemical Conditions Biotic Mulch Profile



Geochemical Conditions Abiotic Mulch Profile



Geochemical Conditions Abiotic Native Soil Profile



Iron Mass Balance*

Parameter	Abiotic Mulch	Biotic Mulch	Abiotic Soil
Initial Iron (mg/kg)	**60,000**	**7,000**	**75,000**
Initial Iron (kg)	**510**	**67**	**1,000**
Average Iron in effluent (mg/L)	**270**	**130**	**110**
Volume water (L)	**33,500**	**33,500**	**33,500**
Iron mass in effluent (kg)	**8.9**	**4.2**	**3.6**
Percent iron discharged	**1.7%**	**6.3%**	**0.35%**

**After 6 months of operation*

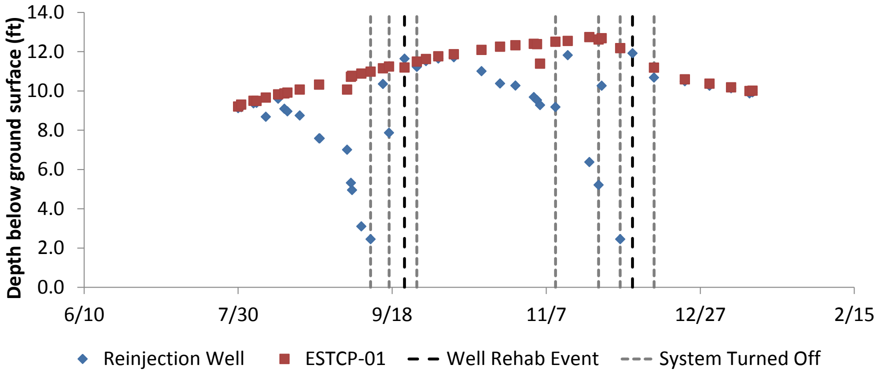
Reported Magnetite Impurities

Element	AFCEC Column Study	ESTCP Demonstration
Al_2O_3	0.62%	3 to 4%
SiO_2	3.03%	
As	Trace	< 5 mg/kg
Sb	NA	< 5 mg/kg
Ca	0.57% as CaO	NA
Cd	NR	< 1 mg/kg
Cr (III)	NR	< 400 mg/kg
Cu	190 mg/kg	< 400 mg/kg
Mg	1.07% as MgO	NA
Pb	NR	< 10 mg/kg
Mn	190 mg/kg	NR
Hg	NR	< 2 mg/kg
Ni	NR	< 100 mg/kg
P	200 mg/kg	NR
K	0.143% as K_2O	NR
Se	NR	< 2 mg/kg
Na	0.132% as Na_2O	NR
S	3150 mg/kg	NR

Issues

- **AFCEE Engineering Guidance**
  - AFCEE has de-scoped development of guidance from CDM Smith contract
  - A workshop is scheduled for Nov 14 where development of guidance will be discussed.
  - ESTCP proposal involved validation of guidance
  - Currently there is no guidance to validate
  - Updating guidance is not currently scoped or budgeted as described in white paper
- **Site-Specific Water Quality**
  - System influent iron concentrations from extracted groundwater was higher than anticipated and necessitated more frequent O&M support to mitigate iron fouling.
- **Bioreactor Effluent Discharge**
  - The bioreactors discharged to a reinjection well. This well became fouled three times during 6 months of system operations, likely from a combination of excess iron precipitation and biofouling. We have successfully rehabilitated the well, but there is uncertainty in how long the well can be rehabilitated.
  - We have implemented system modifications including pH optimization for iron removal and a modification to the bioreactor effluent discharge has been implemented to mitigate these issues.

Injection Well Fouling and Rehabilitation



Field Demonstration Modifications Since Last IPR

As discussed in the April 2013 and January 2015 White Papers, the following changes have been made:

- Duration for system operations modified from 2 years to 1
- Six water sampling events rather than 13
- One bioreactor matrix sampling event would occur at the end of the project rather than 3 events
- The following analyses were removed: microbial gene analysis (CENSUS), bioavailable ferric iron, and iron extractions (weak acid, citrate dithionite bicarbonate, and ammonium oxalate)

Milestone Updates

- The following milestones need to be removed from SEMS:
  - **Interim Technical Memo** - the scope was revised to not include preparation of this memo in the April 2013 White Paper (per Option 2)
  - **Optimization** – the scope was revised to include one year of the field demonstration rather than two years in the April 2013 White Paper (per Option 2)
  - **Draft Engineering Guidance** and **Final Engineering Guidance** - AFCEE did not fund preparation of the Guidance so there is no guidance to update. We communicated this in the November 2012 IPR and the January 2015 White Paper.
- The following milestones need to be modified
  - **Steady State Operation (Year 1)** - revise to **Year 1 Operations** with a completion date of 7/2015.
  - **Draft Final Report** – revise completion date to 9/2015
  - **Final Final Report** – revise completion date to 2/2016
  - **Draft Cost and Performance Report** – revise completion date to 3/2016
  - **Final Cost and Performance Report** – revise completion date to 4/2016

Action Items from Fall 2012 IPR

- Please note that FY13 funds will not be released at this time. There appears to be sufficient funds from FY11 and FY12 to last through calendar year 2013. If the project teams believes these funds are not sufficient, please provide an estimate and rational for FY13 funds by 31 January 2013.

- ***RESPONSE:*** *CDM Smith prepared a White Paper with options for moving the project forward which was submitted in January 24, 2013 and then revised and resubmitted on April 29, 2013. We requested $290K of FY13 funds and received $327K.*

Action Items from Fall 2012 IPR

- The reactivity of iron sulfide depends strongly on the formation pathways and post-formation geochemical environments. The key to this technology is to come up with a robust way to maintain the FeS reactivity that can be implemented in soils of various geochemical characteristics. Please discuss this issue in the next Quarterly Progress Report (due 15 January 2013).

- ***RESPONSE:*** *We agree with the comment. The AFCEE column study was intended to identify factors that result in creating and maintaining FeS reactivity. We were successful in identifying volumetric sulfate loading rate, sufficient electron donor and hydraulic residence time to promote consumption of the loaded sulfate (i.e., translating into a high volumetric sulfate consumption rate), and presence of suitable iron oxide minerals including magnetite and hematite. The ESTCP demonstration is based on validation of these factors in the field. Our design includes these factors in two different configurations (i.e., a bioreactor/biowall configuration containing mulch and a injection/recirculation configuration without mulch) to validate applicability of these factors to a variety of systems rather than just mulch-based systems. The demonstration is also phased where the first year is focused on testing whether the factors do indeed promote biogeochemical transformation and the second year is focused on optimization and robustness testing of the technology. in summary, we believe the technology demonstration plan contains an experimental design that addresses the issue raised by ESTCP.*

Action Items from Fall 2012 IPR

- In the next Quarterly Progress Report (due 15 January 2013), please clarify the issues associated with the Guidance Document. Will AFCEE be supporting preparation of a Guidance Document and if not, how does that impact this project?

- ***RESPONSE****: AFCEE has not supported preparation of a Guidance Manual. This project will not be updating the guidance since there is no guidance to update.*

Action Items from Fall 2012 IPR

- It would have been useful to be aware of the cost implications before selecting the Nike site. Given current budget limitations, it may not be possible to provide additional funding. Please provide a white paper that provides options for scope reductions to offset the additional costs. Include an option that shows how much additional funding is required to complete the project within the original scope (due 31 January 2013).

- ***RESPONSE:*** *CDM Smith prepared a White Paper with options for moving the project forward which was submitted in January 2013 and then revised and resubmitted on April 29, 2013. The White Paper included three options for project continuation: moving forward with the original scope of work from the proposal (Option 1), modifying the duration of the field demonstration from two years of operation to one and reducing some monitoring analyses (Option 2), and reducing the sampling and analysis frequency and number of analyses with a two-year project duration. ESTCP elected to move forward with Option 2.*

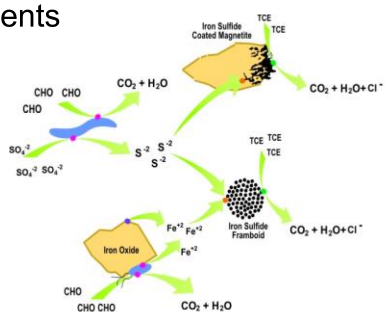
Publications

- Evans et al. 2015. Optimization of Biogeochemical Transformation of Chlorinated Solvents. REMTEC
- Evans et al. 2015. Biogeochemical Transformation of Chlorinated Solvents. 25th AEHS Foundation Conference on Soil, Water, Energy, and Air.
- Evans et al. 2015. Biogeochemical Transformation in Engineered Iron Sulfide Systems. Battelle Annual Conference.
- Smith, J.L., et. al. 2014. Field Demonstration of a Monitoring Toolbox for In Situ Biogeochemical Transformation. Battelle Symposium.
- Whiting et al. 2014. Factors Controlling In Situ Biogeochemical Transformation of Trichloroethene: Field Survey. Ground Water Monitoring and Remediation.
- Evans et al. 2014. Factors Controlling In Situ Biogeochemical Transformation of Trichloroethene: Column Study. Ground Water Monitoring and Remediation
- Smith et al. 2014. Pilot-Scale Demonstration of In Situ Biogeochemical Transformation for Treatment of Chlorinated Solvents. Battelle Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds
- Evans et al. 2014. Biogeochemical transformation design, implementation, and optimization. Battelle Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds.
- Evans et al. 2014. Biogeochemical Transformation for Chlorinated Compound Degradation. Presentation to EPA Region III.
- Evans et al. 2014. Innovative Treatment Technologies for Remediation of Chlorinated Solvents, 1,4-Dioxane, and Perchlorate. Presentation to EPA Region II.
- Evans et al. 2014. Biogeochemical Transformation for In Situ Remediation of Chlorinated Solvents. Contaminated Site Management: Sustainable Remediation & Management of Soil. Sediment, and Water (CSM-2014)
- Evans et al. 2014. Field Demonstration of a Monitoring and Control Toolbox for In Situ Biogeochemical Transformation. NGWA Groundwater Summit.
- Evans et al. 2014. In Situ Biogeochemical Transformation of Chlorinated Solvents. SERDP Chlorinated Solvents in Groundwater Technical Exchange Meeting.
- Evans et al. 2014. Biogeochemical Transformation of Chlorinated Solvents. EOS Webinar Series

Publications

- Wymore et al. 2013. Guidance for Biogeochemical Transformation: Site Selection, Design, and Monitoring. Battelle Conference.
- Smith, J. L, et al. 2013. Field Demonstration of In Situ Biogeochemical Transformation for Treatment of Chlorinated Solvents: Technology Evaluation and Design. Battelle Symposium.
- Whiting, K. et al., 2012. Factors Affecting *In Situ* Biogeochemical Transformation of Chlorinated Ethenes. Manuscript in preparation.
- Wymore, R. 2012. Field Demonstration of a Monitoring Toolbox for In Situ Biogeochemical Transformation. International Petroleum Environmental Conference (IPEC).
- Wymore, R. et al. 2012. Guidance for Biogeochemical Transformation: Site Selection, Design, and Monitoring. Battelle Symposium.
- Evans, P. et al. 2012. Engineering Guidance for Biogeochemical Transformation. Air Force ESOH Training Symposium.
- Evans, P. et al. 2011. Monitoring In Situ Biogeochemical Transformation, Performance. Air Force Restoration & Technology Transfer Workshop.
- Evans, P. et al. 2011. Design and Optimization of Biogeochemical Transformation. Battelle Bioremediation Symposium.
- Evans, P. 2011. Field Applications: Enhancing Biogeochemical Processes. Panel Session. Battelle Bioremediation Symposium.
- Evans, P. et al. 2011. In Situ Biogeochemical Transformation. Partners Workshop.

ER-201124: *In Situ* Biogeochemical Transformation of Chlorinated Solvents



Performers: Dr. Patrick Evans (PI), CDM Smith
Bruce Henry (co-PI), Parsons

Technology Focus

- *Biogeochemical transformation for removal of chlorinated solvents using three in situ bioreactors.*

Demonstration Site

- *Nike PR-58 Site in North Kingstown, RI*

Demonstration Objectives

- *Remediation effectiveness - greater than 90% removal of TCE and greater than 90% removal of total VOCs*
- *Attain geochemical conditions supportive of biogeochemical transformation*
- *Sustainability and longevity – consistent removal of greater than 90% of TCE and VOCs*
- *Technology controllability – field validation of factors identified to enhance formation of reactive minerals*
- *Assess tools to distinguish between biotic and abiotic mechanisms*

Project Progress and Results

- *Demonstrated greater than 90% removal of TCE in the three bioreactors, but total VOCs have not been reduced indicating anaerobic bioremediation processes are dominating. Several optimization methods including enhancing sulfate loading, increasing the hydraulic residence time, and increasing the pH are being implemented.*

Implementation Outlook

- *Balancing iron and sulfur in the system appears to be critical to success. Further research is needed.*
- *Field demonstration is expected to be complete in Summer 2015.*

Social Media Content

- Solutions IES Webinar on Biogeochemical Transformation given on July 9, 2014 www.youtube.com/watch?v=wRuQSChkrDk