August 2002

Bioremediation of Chlorinated Solvents in Fractured Bedrock: Characterization and Case Studies

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Prepared for
U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Arlington, VA
http://clu-in.org/fracrock

ADMIN RECORD

1/34

SW-A-006017

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Purpose

The objective of this paper is to present in situ bioremediation in fractured bedrock as an innovative technology for the treatment of chlorinated solvents. The heterogeneity of fractured bedrock and the persistence of chlorinated aliphatic hydrocarbons (CAHs) create a costly, remedial challenge in the subsurface. Due to the existence of microorganisms in the subsurface, bioremediation processes in fractured bedrock have proven to be a potentially successful remedial process due to attractive attributes, such as: low capital costs, no secondary waste, destruction of contaminants, low maintenance, minimal site disturbance, and decreased working hazards. This paper summarizes ten on-going case studies that are utilizing bioremediation of chlorinated solvent and will discuss the parameters of the projects as well as current findings. Major components of each site are tabulated. (Appendix 1)

1.0 Introduction

When a contaminant, in particular a dense non-aqueous phase liquid (DNAPL), is released in to the environment, the DNAPL migrates downward due to gravity until it is confined. In areas of fractured bedrock, DNAPL is capable of migrating through the subsurface to the lowest potential energy where it may collect, creating an ongoing contaminant source. So long as pure product chlorinated aliphatic hydrocarbons contaminants are in contact with water, the ability of the contaminant to dissolve into and migrate with the groundwater is sustained and continued contamination can occur. Properties associated with pure product DNAPL include high volatility, high density, low viscosity, low interfacial tension, low partitioning to soil material, low degradability, and high solubility relative to the concentrations that are harmful to human health. If the groundwater concentration of dissolved DNAPL exceeds 1% of the solubility, than it is probable that a DNAPL source zone is present (Pankow and Cherry, 1996). The recalcitrant properties of DNAPL make cleanup especially difficult particularly in areas of heterogeneity where pure product pools may reside for decades with slow dissolution.

Clean groundwater is crucial since approximately 50% of Americans get their drinking water from groundwater sources (The Groundwater Foundation, 2001).

Below the surface, microbial presence tends to decrease through the vadose zone as nutrients decrease and then tend to increases with the presence of water in the saturated zone. Microorganisms were once believed to be nonexistent in bedrock fractures (Pankow & Cherry, 1996), but new laboratory-and field-scale research indicates that microbial activity may be feasible. When contamination is introduced to a sub-surface environment and the conditions are permitting, the native microbes may be able to metabolize the contaminants into, water or carbon dioxide, a process known as mineralization. In some cases, the contamination can destroy or inhibit the microbes if the concentration is above the microbes' threshold; however, microbes tend to have the ability to adapt to their environment utilizing the predominant compounds for energy (i.e., facultative microbes have the ability to use oxygen or carbon dioxide or chlorinated solvents as an electron acceptor depending on the availability of each). Microbes under conditions with no oxygen can use chlorinated solvent as a source of energy with dissolved hydrogen as the electron acceptor. Other microbes can cometabolize compounds when more than one substrate or carbon source is available. This process involves the production of an enzyme by the microbe during the metabolic process. The enzyme then breaks down the substrate or contaminant.

As a means to speed degradation, nutrients and/or microorganisms can be added to a site to produce the optimum conditions for achieving dechlorination. The contaminants at the sites in this report includes, in order of oxidized state, tetrachloroethene (PCE) or trichloroethene (TCE) and daughter products dichloroethene (DCE), vinyl chloride (VC), and non-toxic ethene. This report includes several full scale and pilot scale site profiles along with an innovative biobarrier design. Also included in appendix of this report is a chart summarizing site characteristics and parameters. With each field study, the application of chlorinated solvent bioremediation in fractured bedrock is gaining recognition as a technology that has the potential to remediate DNAPL contaminated groundwater in fractured bedrock.

2.0 Bioremediation processes

2.1 Hydrogen Release Compound

Hydrogen Release Compound (HRC®) is an in situ, anaerobic dechlorination, process in which a hydrolysis chemical reaction and symbiotic microorganism relationships are utilized. HRC, through a series of redox reactions, dehalogenates organic compounds in groundwater; specifically chlorinated aliphatic hydrocarbons. HRC is a food-grade polylactate ester. Anaerobic microorganisms (acetogens) use the lactate to create dissolved hydrogen as part of the fermentation process (eq.1-3), where equation 3 is a secondary reaction to equation 2. Another group of anaerobic microbe (reductive dehalogenators) uses the hydrogen as an electron donor to metabolically dechlorinate the solvent to benign byproducts, cleaving off a chlorine atom through each step (eq 4, 5, 6, 7). Therefore, the polylactate ester is fermented into dissolved hydrogen, which then serves as the electron donor while the chlorinated solvent is the electron acceptor. The robustness to this process is the consistent, low concentration of dissolved hydrogen from the degradation of the lactate due to the slow time-release property of the HRC. HRC, as a viscous solid, is injected perpendicular to flow using a pressurized single or straddle packer delivery method. (Koenigsberg, 2000)

The fermentation of lactate follows one of three pathways (Martin, 2001):

$$lactate \rightarrow acetate,\ bicarbonate\ ion,\ hydrogen\ ion,\ dissolved\ hydrogen \quad \textbf{(eq 1)}$$

$$lactate \rightarrow 2\ propionate,\ acetate,\ bicarbonate\ ion,\ hydrogen\ ion \quad \textbf{(eq 2)}$$

$$propionate \rightarrow acetate,\ bicarbonate\ ion,\ dissolved\ hydrogen \quad \textbf{(eq 3)}$$

Dechlorination in the presence of hydrogen (H_2):

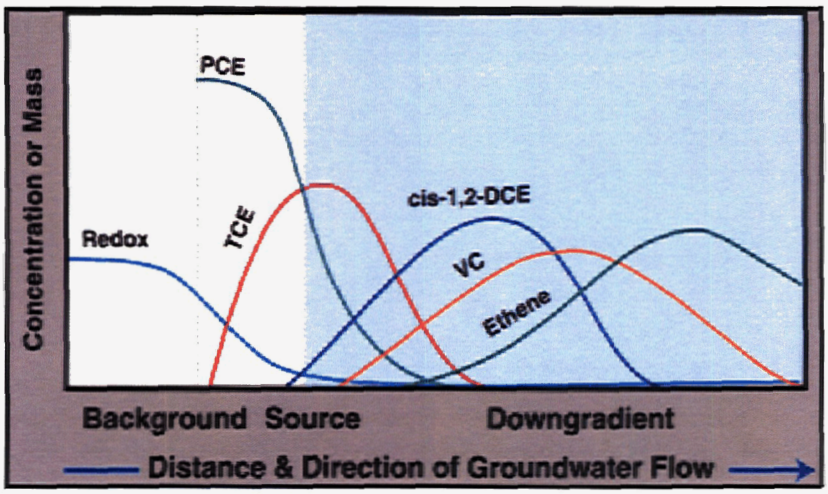
$$PCE(C_2Cl_4) + H_2 \rightarrow TCE(C_2HCl_3) + H^+ + Cl^- \quad \textbf{(eq 4)}$$

$$TCE(C_2HCl_3) + H_2 \rightarrow DCE(C_2H_2Cl_2) + H^+ + Cl^- \quad \textbf{(eq 5)}$$

$$DCE(C_2H_2Cl_2) + H_2 \rightarrow VC(C_2H_3Cl) + H^+ + Cl^- \quad \textbf{(eq 6)}$$

$$VC(C_2H_3Cl) + H_2 \rightarrow ethene(C_2H_4) + H^+ + Cl^- \quad \textbf{(eq 7)}$$

PCE has a higher rate of degradation than does TCE, VC, DCE down to ethene, sequentially. Due to the low reduction rate of DCE, some sites see an accumulation of DCE. In the source zone where the dissolved PCE concentrations are high, the concentration of the daughter compounds will be extremely low or non-detectable. As the groundwater flows downgradient the PCE concentration will decrease as the TCE concentration increases creating a reductive lag in daughter compounds (Figure 1). In Figure 1, groundwater distance is synonymous with time.



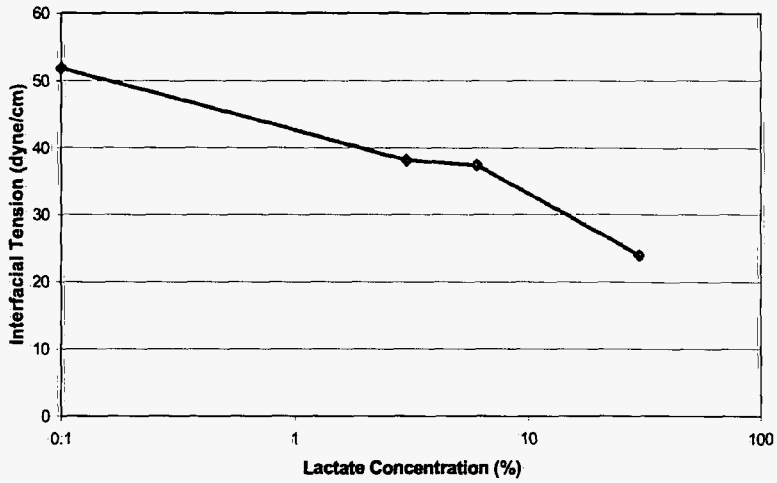
Source: http://www.clu-in.org/conf/itrc/natatt_043002/prez/800x600/ppframe.cfm?date=82&simul=1

Figure 1: Anaerobic dechlorination pathway concentration versus distance.

Anaerobic dechlorination using HRC can be predicted by analyzing certain groundwater parameters including: dissolved oxygen (DO), oxidation-reduction potential (ORP), organic acid, hydrogen, and methane concentrations. A low DO concentration for anaerobic processes and negative ORP values are desired for anaerobic, reducing environments. The release of lactate in water (lactate + proton = lactic acid) produces high concentrations of organic acids: lactic acid, pyruvic acid, and acetic acid. The presence of methane suggests either methanogens are using excess hydrogen to complete the anaerobic dechlorination process or carbon dioxide is being reduced (Kozar, 2002).

2.2 Anaerobic Reductive Dechlorination—Sodium Lactate

Anaerobic Reductive Dechlorination (ARC) is a bioremediation process that attacks the contaminant source in addition to the groundwater. ARC is similar to HRC in that a lactate source is used so the metabolic dechlorination pathway is analogous; however, ARC uses liquid sodium lactate as opposed to a viscous solid polylactate ester. The lactate concentration released by HRC in the groundwater is about 100 mg/L, whereas the lactate concentrations achieved using ARC are considerably higher, up to 4,500 mg/L. The high lactate concentrations decrease the interfacial tension of the free product to the aqueous phase, which allows the microbes to easily respire the dissolution contaminant; ARC increases bioavailability by increasing dissolution. With a percent weight increase of sodium lactate in solution from 0.1% to 3%, the interfacial tension decreases by 26%, with an increase from 0.1% to 30% the interfacial tension decreases by 47% (Figure 2).

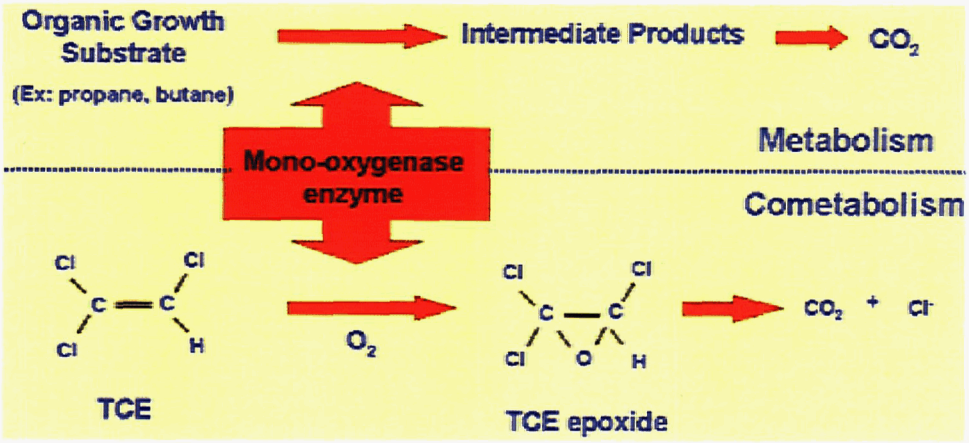


Source: Sorenson, in press

Figure 2: DNAPL/water interfacial tension in the presence of sodium lactate

2.3 Aerobic cometabolism

Aerobic cometabolism bioremediation is the process of utilizing a microbe's capacity to metabolize a carbon source while producing an enzyme that degrades halogenated hydrocarbons.



Source: http://wrhsrc.orst.edu/projects/aerobic/
Figure 3: Cometabolism process of TCE

This process involves the addition of a substrate for a carbon source such as propane, ethane, etc. The microorganism then respires the carbon source resulting in innocuous byproducts including carbon dioxide and water. During this process, an enzyme is created that has the capability to oxidize the contaminant creating a less stable epoxide variation. Ideally, the chlorinated compound will be mineralized. Figure 3 shows the aerobic metabolic pathway of TCE.

2.4 Bioaugmentation

Bioaugmentation is the process of seeding a contaminated site with microorganisms capable of degrading a contaminant. Nutrient injection or biostimulation is usually used in conjunction with bioaugmentation. The microorganisms can be taken from their native environment, cultivated, and then reinjected or a non-native species can be purchased and injected.

2.5 Biostimulation

Biostimulation is the process of adding a substrate to a site for the purpose of activating the native microorganism. For the purpose of this paper, biostimulation is the technology developed by the Department of Energy and licensed to Earth Tech Inc. The process involves injecting a gas mixture of air, nutrients, and methane to a contaminated site

where methanogens and other groups of microbes degrade the contaminant into less hazardous compounds (Gallardo, 2002).

3.0 Site profiles

This section is an overview of several case studies utilizing various bioremedial technologies: anaerobic dechlorination, bioaugmentation, biostimulation and aerobic cometabolism. This section briefly discusses site characterization and current status. Due to the remedial stages of the site profiles, this document contains as much information as was available due to contract agreements and releasable public information.

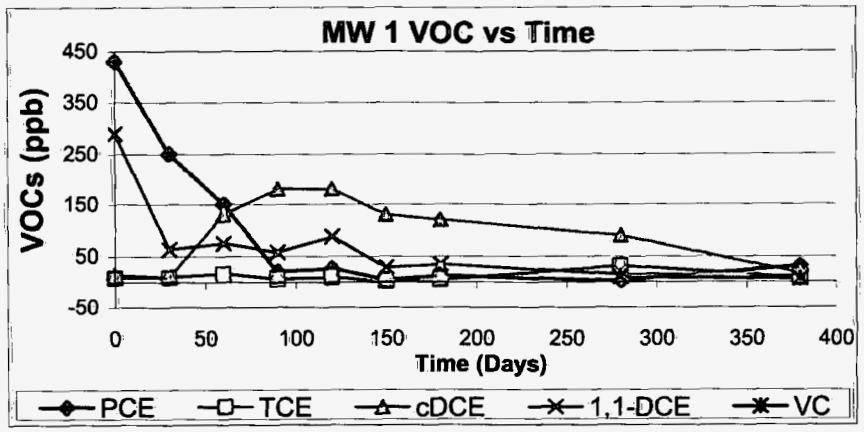
3.1 Hydrogen Release Compounds

3.1.1 Former manufacturing site in New Jersey

The former manufacturing site in New Jersey is a relatively small site, approximately 183 meters x 61 meters with site activity including industrial well pumping for process water. The Passaic bedrock formation of red-brown shale/siltstone is 1.2 meters to 22.9 meters below ground surface with overburden covering the top 1.2 meters. Groundwater depth is 6.7 meters below ground surface. There are 6 monitoring wells on site.

The groundwater under the former manufacturing site is primarily contaminated with PCE including some reduced forms: TCE, 1,1-DCE, and cis-1,2-DCE (cDCE). No residual contaminant source was ever identified. A field test, in progress since November 2000, was implemented to determine if HRC is a viable bioremediation technology in shallow fractured bedrock. From a depth of 6.7 meters to 12.8 meters, HRC was injected into 9 injection points, perpendicular to groundwater flow, using straddle-packer injection, single-packer injection, and gravity feeding through the overburden and into the bedrock. High-pressure injection using water filled packers was determined to be the best method for injecting HRC into the formation. A total of 693 liters of HRC was injected. Figure 4 displays the results of the injection for monitoring well 1, which is

laterally in the vicinity of the injection point or "in-field" (i.e. a monitoring well within 3 m of injection well, or a monitoring well neither upgradient nor downgradient of the injection well).



Source: McIlvaine, 2002

Figure 4: NJ monitoring well VOC (μg/L) vs time

Following injection, the following reductive anaerobic conditions were observed:

- The DO concentrations dropped
- The ORP values reduced significantly; 3 wells produced negative values
- Ferrous iron concentrations increased reinforcing the evidence of redox conditions (i.e., iron reduction)
- The pH decreased due to the presence of organic acids.
- The hydrogen concentrations increased
- Methane was produced either by methanogenesis or due to the reduction of carbon dioxide from bicarbonate.

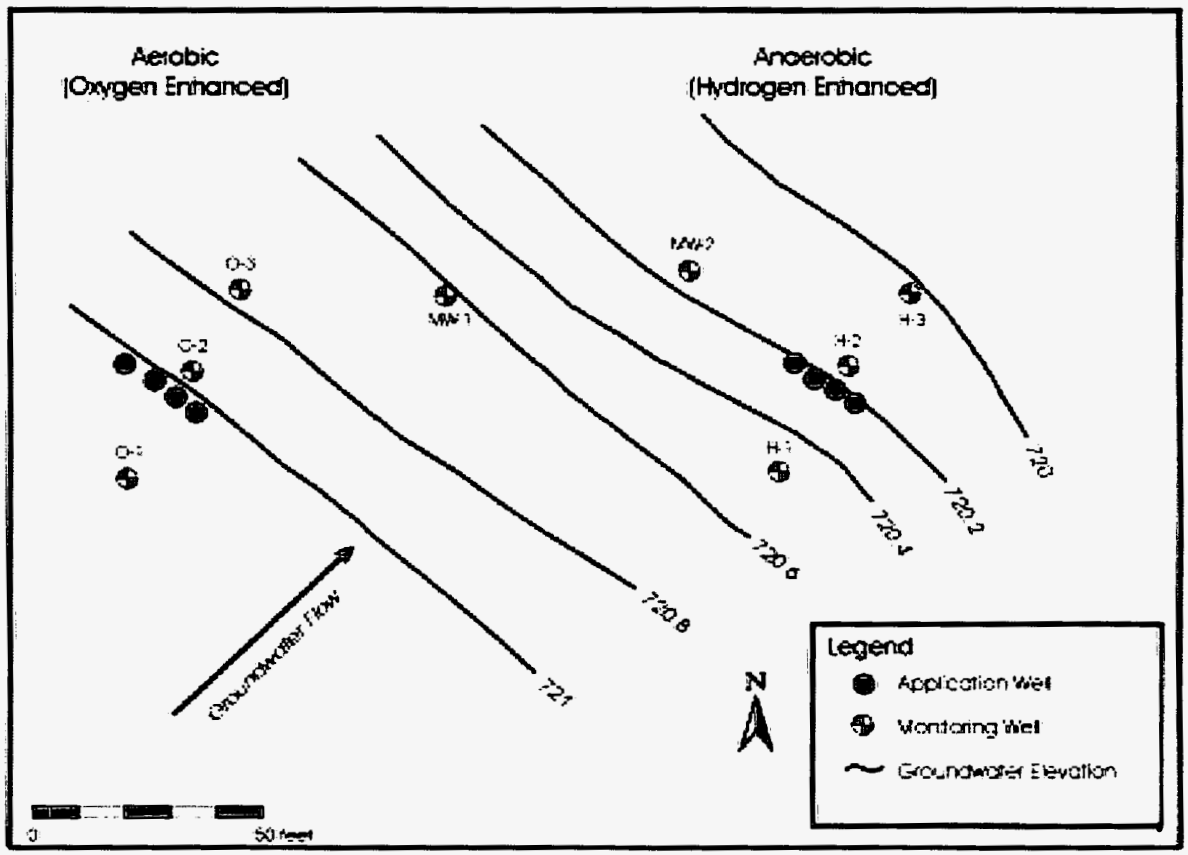
The concentration of PCE decreased over 90% within 90-days of treatment; conversely, the cDCE daughter compound increased as would be expected (VC appeared around day 280), but the decrease of cDCE was stalled until April of this year. This could be due to the lack of microbial population capable of degrading the cDCE or the mere degradation difficulty of cDCE reduction because cDCE reduces at a slower rate than PCE and TCE (Kozar, 2002).

Although the reduction process stalled at cDCE, VC was present in various wells. Methane concentrations were high, which is a result of methanogens competing for the dissolved hydrogen ultimately slowing the dechlorination process. Despite dechlorination occurrence, altering site conditions may provide desired results such as bioaugmenting with a proficient cDCE-reducing microbe.

3.1.2 Industrial Facility, Ohio Site

The manufacturing site in Ohio has been in operation since 1800's. The groundwater at the fractured Mississippian sandstone bedrock site is contaminated with cDCE and VC and underlain by low permeability shale. The plume covers 122 meters by 183 meters with initial cDCE and VC concentrations ranging from 220 to 5700 μg/L. The site has 1.5 to 2.4 meters of unsaturated overburden, which is underlain by 9.1 m of sandstone containing interbedded siltstone and shale layers in the lower area of the formation. Low permeable shale underlies the sandstone. The depth to water ranges from 2.9 to 3.5 m. The injection wells within the pilot area have a hydraulic conductivity of 1.2 m/day, with a porosity of 15%, and a velocity of approximately 6 cm/day. TCE was the original source of the DCE and VC contaminated groundwater, however, the TCE has since been removed from the soil via soil vapor extraction, excavation, and naturally occurring degradation (Cornuet et al, 2000).

The study for this site included anaerobic bench scale tests, which determined that native bacteria were capable of reductive dechlorination. The study also included Oxygen Release Compounds (ORC)-aerobic and Hydrogen Release Compounds (HRC)-anaerobic field pilot tests for the purposes of determining which process would be the most efficient at reducing cDCE and VC. A pilot test base map is shown in Figure 5. The pilot test results showed that ORC and HRC were both successful at degrading the contaminants, but the HRC treatment provided the most significant and sustained cDCE and VC reduction during the test. Table 1 presents the aerobic and anaerobic pilot test sampling results.



Source: Cornuet et al, 2002

Figure 5: Ohio Pilot Test Base Map

Table 1: DCE and VC Sampling Results (ug/L) and Percent Reduction

Aerobic Test		DCE			VC		
Well	**Location**	**Baseline**	**180 days**	**Percent Reduction**	**Baseline**	**180 days**	**Percent Reduction**
O-1	**6 m upgradient**	740	675	9%	1,100	553	50%
O-2	**1.5 m downgradient**	420	339	19%	1,700	1,040	39%
O-3	**7.6 m downgradient**	2,500	448	**82%**	800	275	**66%**
Anaerobic Test		**DCE**			**VC**		
Well	**Location**	**Baseline**	**180 days**	**Percent Reduction**	**Baseline**	**180 days**	**Percent Reduction**
H-1	**6 m upgradient**	5,700	5,600	2%	450	290	36%
H-2	**1.5 m downgradient**	2,600	1,640	37%	1,200	253	79%
H-3	**7.6 m downgradient**	590	20	**97%**	210	12	**94%**

Source: Cornuet et al, 2000

A full-scale HRC program was implemented across the 120 by 180 m plume based on the laboratory and field pilot tests. The site is currently 1 year into its 3 year predicted full-scale remedial project plan. Pilot test and full scale sampling results have shown a

significant decrease in dissolved oxygen and ORP, and a significant increase in total organic carbon (TOC) and ethene. One year of full-scale bimonthly sampling results have shown that the cDCE plume mass has been reduced by more than 60% and the VC plume mass has been reduced by more than 30%.

3.1.3 Industrial facility, Virginia

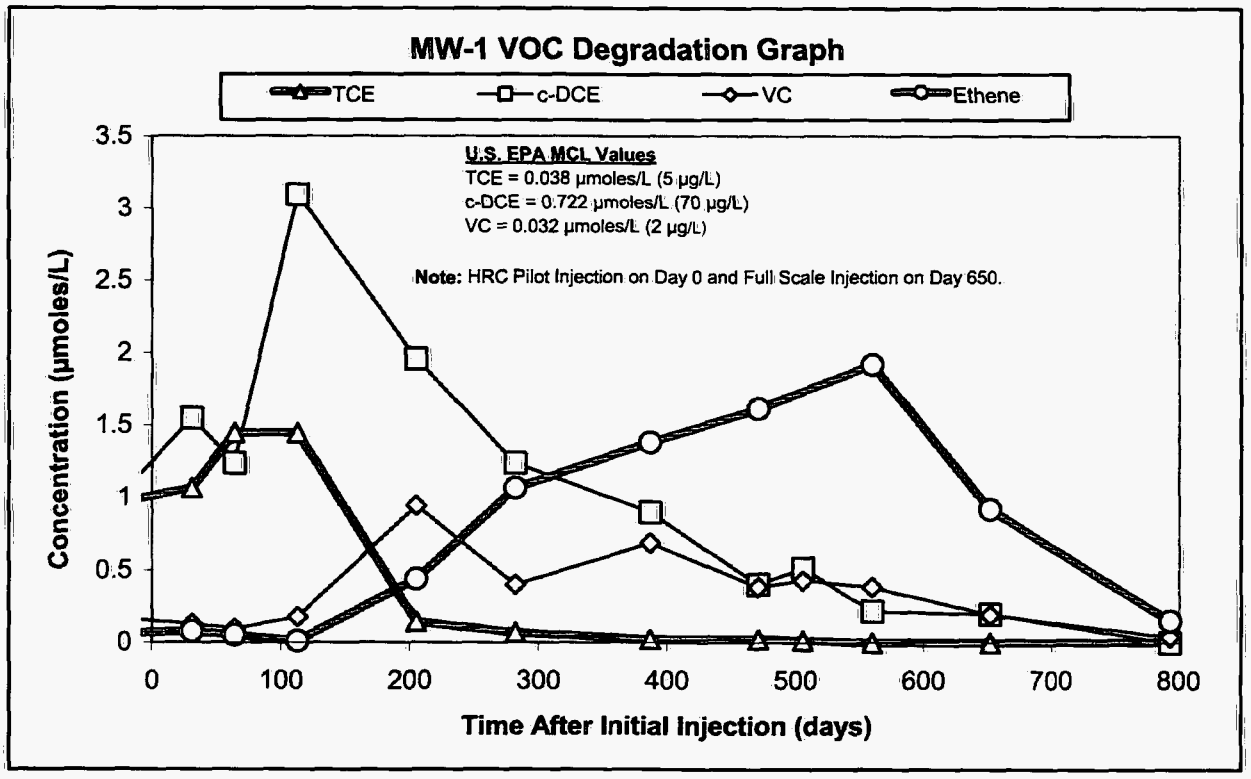
The industrial facility located in the Blue Ridge physiographic province of Virginia has been in operation for over 30 years. The fractured greenstone, crystalline bedrock contains a contaminated TCE plume (61 m x 91 m x 9.1 m) ranging from 22 to 220 μg/L and includes the daughter products. The depth to the groundwater is 3 m below the surface; the top of the bedrock is approximately 2.4 m below the surface (Cornuet et al 2000b).

Before HRC was injected, borehole logging and down-hole photography was implemented for site characterization. The characterization study determined that the main fractures controlling the groundwater flow were located at 6.7 meters and 9.8 meters below the surface. Characterization also determined that 2 of the 3 injection wells and the downgradient monitoring well were hydraulically connected via fractures.

The 3 HRC injection wells, 2.5 meters apart and 3 meters from the downgradient monitoring well, acted as a biological barrier to the flow of contaminated water. Additional monitoring was also conducted 60 m downgradient of the injection. A single packer was used to inject HRC in to the 9.8-meter deep fracture and straddle packers were used to inject the HRC into the upper fracture zone of 6.7 to 8.5 meter below the surface. A total of 38 to 120 liters of HRC was injected into each injection well for a total of 253 liters of HRC injected during the bedrock pilot test (Cornuet et al, 2000b).

TCE concentrations were dramatically reduced throughout the project while the cDCE increased and then decreased with the reductive dechlorination process (Figure 6). The VC peak followed the cDCE peak approximately 100 days later, and the ethene peak

followed approximately 350 days after the VC peak. The data show that anaerobic reducing conditions were maintained for more than 560 days after the pilot test injection.



Source: Cornuet et al 2000b with updated data Cornuet, 2002

Figure 6: Dechlorination process of Virginia Site

A 25-well full-scale injection was conducted across the 60 by 90 m plume 650 days after the initial pilot test injection. Sampling data collected 800 days after the initial injection show that TCE, cDCE, and VC concentrations have all been reduced below US EPA MCLs and that there was no accumulation of VC at the site (see Figure 6). Following HRC injection, TOC and ferrous iron concentrations increased concurrent with significant decreases in DO and ORP in both the 3 m and 60 m downgradient monitoring wells.

3.1.4 Piedmont, SC

In the Piedmont physiographic province, two HRC pilot tests were conducted for the bioremediation of TCE: one in a saprolite aquifer where the water table is located within the saprolite and another in Paleozoic fractured, crystalline bedrock where the water table

is located below the top of the bedrock. After HRC injection, the fractured bedrock site was found to have a greater reducing environment for dechlorination than the saprolite site. This could be because of the difference in pre-existing microbe populations and groundwater chemical characteristics.

The site was characterized by analyzing rock core and pressure test data, which was then used to determine the optimum distribution of the HRC. The 6 injection wells were placed 3 meters apart, perpendicular to the water flow. A total of 1,136 liters of HRC was injected using pneumatic packers and high-pressure pumps to a depth of 15 meters after groundwater characterization. Three monitoring wells were utilized for sampling: one located 6 meters upstream of the HRC injections, one located 3 meters downstream from the injections, and one located 6 meters downstream from the injections. Aside from the up-gradient monitoring well, the concentration of TCE had decreased as the concentration of cDCE increased, which suggests a reducing environment (Table 2). The increase in TCE in the up-gradient well from increased DNAPL dissolution is attributed to a change in water levels and drilling disturbance. A reducing environment was observed within 5 weeks of HRC injection. The most active well site was the in-field injection well. (Klutz, 2002)

Table 2: Well comparison of Piedmont, SC site

contaminant (mg/L)	up-gradient well		in-field well		down-gradient well	
	before injection	Day 300	before injection	Day 300	before injection	Day 300
TCE	8.8 - 5.4	20	30	0.6	8.8	0.1
cDCE	0.38	0.8	1	44	0.24	13
VC	*	0.04	*	*	0.018	0.017
ethene	<0.01	<0.01	*	0.03	*	0.03
ethane	*	0.03	*	<0.01	*	0.021

* denotes non-detect levels
Source: George Maalouf, 6/2002

Groundwater samples were analyzed prior to the pilot-test to determine baseline parameters and then monitored throughout the project for common parameters. For reductive measurement, analysis of HRC indicators (total organic carbon and chemically reductive acids: lactic, acetic etc.) and biological indicators (carbon dioxide, alkalinity,

and methane) were measured and compared along with solvent concentrations. The baseline pH measured at 6.8 and as low as 5.1 after HRC injections.

This pilot study suggests that HRC injections shifted the bedrock environment to reducing conditions, thereby accelerating the degradation of TCE to ethene. A possible concern for the site is the accumulation of cDCE without reduction to VC, however; an increase in VC was detected as of day 390 (Maalouf, 2002). The VC was at 17 μg/L at day 300, now it is up to 1.3 mg/L. The site is currently undergoing monitoring to determine the final results of the pilot study.

3.2 Cometabolism

3.2.1 ITT Industries Night Vision

ITT Industries Night Vision (ITTNV) is a manufacturing company that produces night vision products. The manufacturing plant has been in operation since 1958 (EPA Region 3 GPRA Baseline RCRA Corrective Action Facility, 2001). The initial release of contamination occurred from leaking tanks containing chlorinated and non-chlorinated cleaning solvents. The solvents eventually contaminated the groundwater 1.5 to 4.6 m below ground surface reaching the clay overburden and eventually the fractured shale and limestone bedrock under the site. Groundwater flow is primarily through fractures in the bedrock in two different zones: the upper zone, 3 to 11 m below ground surface and the lower zone, 12.2 to 15.2 m below ground surface. The hydraulic conductivity ranges from 10^{-2} to 10^{-4} cm/s (Gallardo, 2002).

In 1992, contamination from ITTNV was first discovered in the groundwater beneath the Tinker View Trailer Park in Roanoke, VA located down gradient, south, of ITTNV. A field demonstration was conducted under the Environmental Protection Agency's Superfund Innovation Technology Evaluation (SITE) program in 1998.

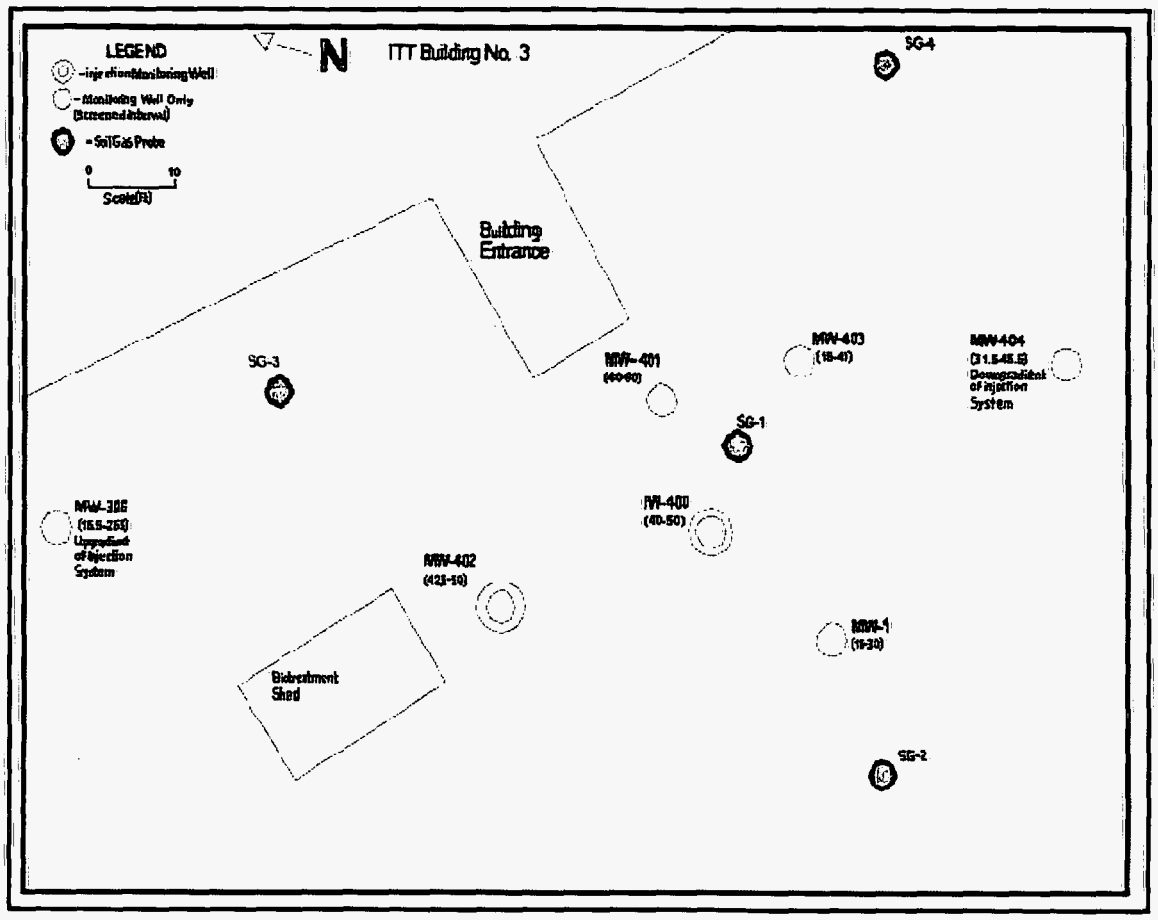
The contaminants identified at the site include: TCE, 1,1,1-trichloroethene (TCA), cis-1,2-DCE, cis-1,1-DCE, 1,1-dichloroethane (DCA), VC, chloroethane (CA), acetone, and isopropanol. Biostimulation for cometabolic dechlorination was chosen for remediation. This involves a continuous gas injection of air, triethyl phosphate (TEP), nitrous oxide, and a pulse injection of methane. Methanotophic bacteria aerobically oxidize the methane while cometabolically creating an enzyme to degrade the solvent. The triethyl phosphate is the phosphorous source, the nitrous oxide is the nitrogen source and the methane is the carbon source for the microbes. This remediation method was chosen with the idea that methanotrophic bacteria producing an enzyme to degrade chlorinated solvents in unsaturated soil could also work in the saturated zone under the right conditions.

The field demonstration of the site work began in late winter in 1998 of and continued into August 1999. A breakdown of demonstration schedule is shown below:

- March 4 – 12: Baseline samples were taken
- March 13 – April 3: Air was injected into IW 400L
- April 4 – May 1: Second sampling
- May 2 – July 12: Air, nitrous oxide, and TEP injection
- July 13 – 16: Sampling
- July 16 – January 1999: Air, nutrient, and methane injection
- Januray - February: MW-402L was made into an injection well to reach the lower bedrock
- February 2 – April: Air, nutrient, and methane injection
- April: Operational problems in MW-402L
- May – July 26: Air, nutrients, and methane injection
- July 27 – August 3: Final sampling

The contaminant concentrations were random, except 4 wells that were "within the expected zone of influence:" MW-1, IW-400L, MW-4001L, and MW-403 (Figure 7). Each of the 4 "critical" wells contained elevated concentrations of CA, DCA, cDCE, and

VC. The primary focus of the demonstration was to compare the baseline samples with the final samples for the compounds of interest in the "critical" wells (Gallardo, 2002).



Source: Gallardo, 2002

Figure 7: ITTNV site layout

From a helium tracer test, several fractures were determined to hydraulically connect MW-403 to IW-400L and MW-401 (Figure 7). Detailed location of the hydraulic fractures remains unknown. The natural bedrock environment prior to and shortly after gaseous injection was found to be reducing with anaerobic degradation. The system may be both aerobic and anaerobic occurring simultaneously in different areas due to the inability of the gaseous mixture to distribute evenly.

The upper monitoring wells had significantly greater contaminant reduction perhaps due to the property of gas to elevate out of liquid – i.e., the upper zone microbes were exposed to more gas than the lower zone microbes. The lower zones had lower than expected degradation perhaps due to the brevity of gas in the groundwater. In the lower

zones, anaerobic conditions encouraged reductive dechlorination reactions. While the biodegradation pathways are not fully understood, contaminant reduction did occur.

The percent reduction for the four elevated compounds in the "critical wells" was averaged at 90 percent confidence intervals with lower and upper confidence limits (Table 3).

Table 3: ITTNV - Average percent reduction of critical compounds

contaminant	Lower confidenct limit	Upper confidence limit
CA	4%	54%
DCA	71%	86%
cis-1,2-DCE	95%	98%
VC	92%	98%

Source: Gallardo, 2002

Extrapolating from the results of the 17-month field demonstration, a full-scale project life would be a minimum of 2 years with 16 groundwater wells and 4 injection wells required to reduce contamination to undisclosed "acceptable regulatory levels." The site area is predicted to be approximately 2100 m^2 with an average injection depth of 13.1 m to the primary fracture zone. Results from the field demonstration, indicate that a full-scale implementation would sufficiently clean up the site. (Gallardo, 2002)

3.3 Anaerobic Reductive Dechlorination-Sodium Lactate

3.3.1 Idaho National Engineering Environmental Laboratory Test Area North

The Idaho National Engineering & Environmental Laboratory (INEEL) is a Department of Energy site located on 2300 km^2 in Idaho Falls. Test Area North (TAN) is a small, contaminated area of that site. Activities within TAN during the 1950s through the 1980s includes: nuclear power airplane testing, nuclear power reactor safety testing, and Three-Mile Island material testing after the accident. Along with radioactive contamination, organic sludge from municipal wastewater facilities and industrial process wastewater were injected into an injection well leading to the Snake River aquifer from 1953 to 1972.

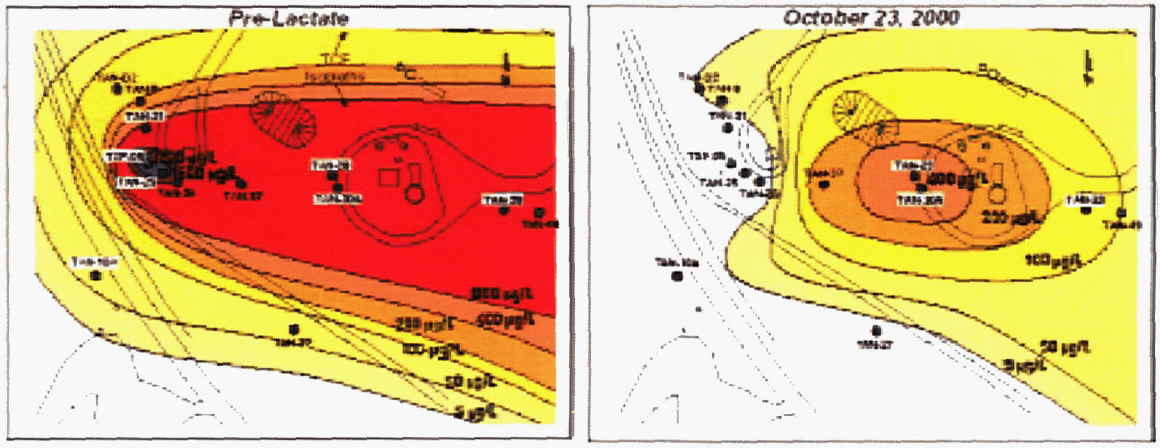
An estimated 132,500 kg of TCE was pumped 61 m below ground surface into the aquifer. From this activity, a plume 3 km long and 0.8 km wide developed (Strzelecki, 2002).

The site consists of 64 m of a fractured basalt vadose zone underlain by 61 m of a fractured basalt aquifer and confined by impermeable silty clay. The interflow zones within the basalt fractures controls the horizontal groundwater flow (Sorenson, 2000-Melbourne). The evaluation of five innovative technologies was written into the 1995 Record of Decision along with the implementation of a pump-and-treat for immediate groundwater cleanup and containment. A pump-and-treat program began in November 1995 and continued until May 1997. After which an enhanced bioremediation project was studied and then applied to the test area for the treatment of groundwater and the source area.

In November 1998, baseline parameters were determined. Sodium lactate was injected weekly into the former waste injection well beginning in January 1999 and continued until September at concentrations ranging from 3% to 60%. TCE dechlorination to ethene was found just 5 months after the injections and up to 15 m away from the injection point. The main metabolic pathway that followed during these injections was lactate fermentation (shown in Equation 2). This was determined by the 2:1 propionate to acetate ratio-for every mol of lactate, 2 propionate moles and 1 acetate mol are formed. From September 1999 to February 2000, injections ceased due to electron donor buildup. Monitoring occurred bi-weekly in 8 wells and monthly in 3 additional wells. The propionate to acetate ratio dramatically decreased and the pathway changed to equation 3 via propionate fermentation. TCE dechlorination rapidly increased and ethene concentrations increased. The reaction described by Equation 3 is more efficient than the process shown in Equation 2, thus with the addition of lactate, equation 2 will be more predominate and the ARD will be lower than with no lactate addition (Martin, 2001).

The accelerated reductive dechlorination was preferred over the historic pump-and-treat process because of its ability to treat the contaminant source, thereby decreasing the

length of the remediation project and in time saving resources and money (Figure 8). The estimated savings of utilizing accelerated reductive dechlorination over pump-and-treat is $23 million over a 30-year period (Sorenson, 2000 Toronto).



a) **b)**

Source: Sorenson, 2000, Toronto.

Figure 8: TAN plume
a) Concentrations of TCE after 18 months of pump-and-treat.
b) Concentration after approximately 2 years of lactate injection.

Injections continued twice a month into 2001. Currently, 5000 L of lactate are injected every 2 months (Strzelecki, 2002). The plume is shrinking. The current challenge is associated with distributing the sodium lactate into areas that are hard to reach. Due to the high microbial population around the injection well, the lactate is often consumed before it has an opportunity to travel downgradient. A possible solution for this is to inject sodium lactate downgradient of the initial injection well to enhance distribution. Another possibility would be to inject a slow-release sodium lactate solution to prevent the microorganisms from consuming the entire electron donor at one time.

The Record of Decision was amended and signed in September 2001. In situ bioremediation was selected as the remedial technology with monitored natural attenuation to replace pump-and-treat for most of the plume area. The project design will be finished and submitted in October 2002 for the 2003 fiscal year.

3.4 Bioaugmentation

3.4.1 Caldwell Trucking

The Caldwell Trucking site is 44,550 square meters located in Fairfield Township, NJ. The site is within the 100-year floodplain of the Passaic River and within the vicinity of Deepavaal Brook and many wetlands. Caldwell Trucking was started in 1946 for the purposes of cleaning residential septic tanks. The waste from the septic tanks was dumped in unlined lagoons at the far end of the property without permits. In the mid-1950s industry began around the area. The site became contaminated from Caldwell dumping industrial waste mixed with septic waste on site, solvents disposal directly on-site, other trucking disposal facilities disposing their septic and hazardous waste in Caldwell's lagoons, and/or leaking steel tanks used to hold waste. Among the sludge dumped into the lagoons includes TCE, chloroform, PCBs, and lead. (ROD, 1986, 1989, 1995)

Since 1981, approximately 300 private wells have been contaminated and taken off line. Those of the affected 500 residential homes living within 1 mile of the site were placed on the municipal water system. The groundwater flowing north of the site discharges into the Passaic River, which is a drinking water source as well as a recreational area (EPA, National Priority Site Fact Sheet, 2002).

A fractured basalt zone is located just below the sand and gravel overburden at 30.5 to 38 m below ground surface. The hydraulic conductivity is 0.25 cm/s and groundwater travels half through the sand/gravel aquifer and half in the fractured basalt. The size of the plume is hundreds of meters long and eventually discharges into the Passaic River. The natural attenuation at the site is approximately 3,000 kg of contaminant per year as indicated by a study (Permeable Reactive Barriers Action Team, 2001).

In 1998, a full-scale permeable reactive barrier wall system was installed 914 m downgradient of the source zone in sand and fractured basalt. The wall is using zero-valent iron as the reactive metal for decontamination of groundwater. As of June 2001,

the permeable wall was reducing the TCE contaminated groundwater from 7,000 μg/L to less than 3,500 μg/L (Permeable Reactive Barriers Action Team, 2001). The decontamination did not meet the expectations of TCE concentrations below 50 μg/L so bioaugmentation was implemented in May 2001.

The project involves an ongoing large-scale pilot test that includes a large portion of the suspected source area. As a goal set by the Environmental Protection Agency, the project must prove that complete TCE degradation to ethene occur in areas of no previous degradation. The first microbial augmentation occurred May 31, 2001, which also included electron donor addition. A mixture of methanol, lactate, and acetate was injected to create a reducing environment, and then the addition of the KB-1 culture was augmented. This KB-1 culture includes strict anaerobes of the dehalococcoides species. The 3 injection points are located upgradient from the source and are spaced 15.2 to 18.5 m apart. The monitoring wells are located approximately 12 m downgradient from the injection wells (Major, 2002).

The result of the large-scale pilot test dechlorinated TCE to ethene. Also, reduction of the parent compound was significant in that the dissolution of the source would accelerate the bioremediation. This site is still in early phases to testing. The concentration values were not readily available.

3.4.2 Rockville, Maryland site

The Rockville site was formerly commercial property, which consisted of a dry cleaner, a casket manufacturer, a restaurant, and an auto shop. The site is contaminated with PCE and daughter components either from contaminated sewer pipes or a release into the soil, which has since been excavated. The PCE free product was predicted to have sorbed to the rock matrix. The overburden consists of fine-grained soils; the saprolitic metamorphic bedrock is fractured schist and phyllitic. The fractures have low hydraulic conductivity due to clay corking or plugging the fractures as depth increases. The groundwater velocity is 7.6 to 22.9 cm/day and depths greater than 9.1 meters.

To date, this site has been subject to 2 enhanced oxidation remediation processes: one with Fenton's Reagent and another with sodium permanganate to obtain the Maryland risk-based on site cleanup goal of 253 μg/L. The Fenton's Reagent was first implemented after successful bench and field tests, which confirmed the Reagent's rapidity of remediation. The PCE concentrations dramatically decreased following the treatment but then, with time, began to increase. This was speculated to be caused by desorption of the source material from the sorbed or free product matrix into the dissolved phase in the groundwater as heat was produced from the Fenton's Reagent. The PCE concentrations following the Fenton addition averaged 8.5 mg/L. The next remedial process was injection of sodium permanganate. Late January 2001, nearly 5,000 kg of 20% sodium permanganate solution was injected into 50 different areas around the site. The PCE concentration decreased to an average concentration of 909 μg/L over 17 sampling points by late February 2001. This constituted an 89.3% reduction (Werner, 2001).

March 6, 2002 following the period of permanganate addition, the site was augmented with 3-55 gallon drums of CL-OUT, a cometabolic aerobic bacterial culture containing dextrose as an energy source (Werner, June 13, 2002). Most of the site is currently aerobic and oxidative; however, the middle of the plume is anaerobic with an oxidation-reduction potential (ORP) of -120. Another 45 kg of dextrose was added and monitored for chloride. Iron, sulfate, and residual manganese from the permanganate addition are the electron acceptors; dextrose is the electron donor.

Approximately $350,000 was spent on the full-scale chemical oxidation program. Bioaugmentation is the polishing step. Monitored natural attenuation is currently taking place for the off site plume. The site is expected to reach its 253 μg/L limit 2 years from now (Werner, July 1, 2002). An additional 43 kg of dextrose was added in July 2002. New data, yet to be released, has revealed that bioremediation is very effective at treating chlorinated solvent contamination at the site (Werner, July 17, 2002).

3.5. Natural Biodegradation

3.5.1 Manufacturing Facility, Niagara Falls, NY

The manufacturing facility located 8 km east of Niagara Fall was initially contaminated with TCE, methyl chloride, and acetone from aircraft propellant, which was placed in a neutralizing pond during the 1950s and 1960s and was eventually filled and capped in 1987. In 1990, a 1200 x 190 m plume of dissolved chlorinated solvents, mainly TCE, was determined from groundwater samples. The plume extended southeastward from a neutralizing pond. The 52 m thick fractured dolomite of the Lockport Group was found to contain gypsum and metal sulfides from a petroliferous (containing petroleum hydrocarbon) dolomite. The fracture zones are the main source of hydraulic movement, which discharges into the Niagara River, 5 km south of the facility. The site is categorized into 4 different zones of slightly varying hydogeological character. Zone 1 refers to the contaminated area and has a velocity of 0.2 to 0.9 m/d and a porosity of 3%. Zone 2 is contaminated with DNAPL on the surface and underlies zone 1 followed by zones 3 and 4. An off site treatment well began pumping in 1993, which changed the flow of the groundwater from moving southward to moving vertically upward (Yager, 1997).

Groundwater samples were tested in January 1995. The site was found to be anaerobic with iron reducing conditions in the area of the TCE plume. DCE, VC, and small amounts of ethene were present in the exterior of the plume. Samples taken in areas surrounding the plume turned up negative for ethene concentrations suggesting the presence of ethene within the plume was from reductive processes. Dechlorination of TCE became evident for two additional reasons: one because neither DCE nor VC was ever discharged into the neutralizing pond and two, because DCE and VC concentrations are spatially related to TCE dechlorination (Figure 1) (Yager, 1997).

A small test revealed the addition of bicarbonate encourages dechlorination of TCE down to the nontoxic ethene (Yager, 1997). The determination of the natural biodegradation

process, on the other hand, is still unclear. A laboratory microcosm study was implemented with the use of the site specific, petroliferous dolomite. The dolomite was either autoclaved at 120°C or autoclaved and then cooked at 500°C. The microcosm involved the addition of lactate, hexadecane, H_2, microbes within the plume, and either combusted dolomite or noncombusted dolomite as the electron donor. The combusted dolomite resulted in no reduction of TCE while the noncombusted dolomite degraded TCE into VC. When the sulfur-transforming microbes, as opposed to the dechlorinating microbes within the plume, taken outside of the plume area were used in the experiment, no dechlorination took place suggesting the microbes within the plume were adapted to TCE degradation.

The goals of the laboratory tests were to determine the source of the electron donor. The electron donor source was identified as one of the following: dissolved organic carbon, methane, or hydrocarbons in the petroliferous dolomite. The hydrocarbons were the most plausible hypothesis; however, the hydrocarbons did not prove to aid in dechlorination in lab tests so a new hypothesis was concluded: the electron source remains unidentified (Hohnstock-Ashe, 2001).

Pump-and-treat is being utilized for containment of the groundwater. The main curiosity of the site is the naturally occurring, adapted reductive dechlorination in the presence of an unknown electron donor. This site is being studied to further characterize the microbial metabolism in the subsurface.

3.6 Site Progression for Bioremediation Development

3.6.1 Oak Ridge National Laboratory Y-12

The Y-12 site in Oak Ridge Tennessee is contaminated with carbon tetrachloride (CCl_4), PCE, and TCE from accidental release. The CCl_4 has migrated as deep as 150 m below the ground surface. The site contains low permeability carbonate-dominant and siliciclastic-dominant limestone fracture bedrock. The flow path in the siliciclastic areas

is mainly through the fractures, whereas the flow path in the carbonate is through cavities and small passages enlarged by water flow.

The metabolic reduction pathway of carbon tetrachloride (CCl_4) breaks down into chloroform ($CHCl_3$), which breaks down into dichloromethane (CH_2Cl_3), then into chloromethane (CH_3Cl), and ultimately into methane (CH_4). Biodegradation of CCl_4 has been observed by various microbes including methanogens, sulfate-reducing, nitrate-reducing, and fermentative. CCl_4 can also be degraded into chloroform, carbon disulfide, and carbon dioxide via an abiotic degradation pathway. The process at Y-12 has been evaluated in microcosm studies and has yet to be implemented in a field study (Kelley, 2001).

Pump-and-treat has been utilized at the edge of the plume to prevent contaminated water from leaving the site. Until funding becomes available the bioremediation project is on hold despite microbial dechlorination in biogeochemical laboratory studies. (Hansley, 2002)

3.7 New Technology

3.7.1 Biobarriers

Biobarriers are biological fences made of biofilms that are used to decrease the hydraulic conductivity in groundwater. Biofilms are gel-like, slime layers residing in liquid that are composed of exopolymeric substances (EPS) and bacteria growing in a fixed film. EPS, with cohesive properties, are excreted from bacteria to assistance in attaching to surfaces. Biobarriers, composed of biofilm, may be used in the subsurface for hydraulic containment by plugging pores and fractures to prevent groundwater flow, and more even substantial: to prevent the distribution of contamination (Ross, 2002 Remediation). The injection of a simple carbon source has the potential to form a containment layer in the subsurface (Ross, Battelle 2002).

Thus far, biobarriers have demonstrated the retardation of groundwater flow in porous media, in laboratory fractured bedrock models, and currently in a fractured bedrock field application. In the porous media field experiment, where permeability was reduced by >99%, it was found that ultra small EPS producing microbes (ultramicrobacteria—diameter ≤ 0.3 μm) have a greater ability to form a biobarrier due to their ability to transport within the tight places. The larger microbes were retarded in the media in the top 1.2 to 1.8 m. The ultramicrobacteria are either naturally small or they are fed to normal size after a starvation period (Ross et al., 2001).

A biobarrier field trial is currently underway at an uncontaminated fractured bedrock site located 1.5 km north of Lake Ontario in Ontario, Canada. The site consists of 3 m of clay-sand overburden underlain by 20 m of shale bedrock with limestone interbeds. The water level is approximately 2.5 meters below the surface.

Biobarriers are a new concept in areas of fractured bedrock. The field trial in Ontario will provide information necessary to determine if biowalls are feasible in areas of fractured bedrock. Information including fracture bioclogging and reducing hydraulic conductivity for containment will be necessary to determine the success of biobarriers.

4.0 Conclusions

Microbial degradation of chlorinated solvents within the subsurface is on the cutting edge of innovative technology within fractured bedrock. Bioremediation accelerates the natural cleaning of the Earth. Not only is bioremediation cleaning up sites, it is doing so with speed, lower energy input, and fewer resources. There is still much to learn from biogeochemical processes but the technology is rapidly progressing. Each of the case studies presented are in the developmental stage (<5 years), yet promising results are surfacing. Bioremediation is a viable alternative to the expensive, default pump-and-treat system with attributes including low capital costs, no secondary waste production, destruction of contaminants in situ, low maintenance, minimal site disturbance, and decreased working hazards.

Accelerated anaerobic dechlorination appears to be most proficient at bioremediation due to the ability of the sodium lactate to dissolution the source zone while stimulating microbial growth. The process may become more efficient with a time-release feature to methodically distribute the nutrient loading. The remedial results of the presented bioremediation projects will become evident with time.

In conclusion, time is necessary to fully understand bioremediation technology. To understanding microbial dechlorination processes in fracture bedrock, implementation and corresponding results of full-scale remediation must be achieved. Classification of optimal site characteristics, classification of optimal microbial respiration, and implementation of new microbial technologies, like biobarriers, are important factors to be revealed.

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