AEROBIC AND ANAEROBIC BIOREMEDIATION OF cis-1,2-DICHLOROETHENE AND VINYL CHLORIDE

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ABSTRACT: This paper presents a comparative study of aerobic and anaerobic bioremediation of cis-1,2-dichloroethene (DCE) and vinyl chloride (VC). The study includes laboratory bench scale testing of anaerobic biodegradation followed by a side by side field pilot test comparing the effectiveness of aerobic and anaerobic biodegradation processes. Prior to initiating the pilot test, DCE and VC concentrations ranged from 220 to 5700 µg/L in the test wells. A proprietary time release oxygen and hydrogen source was utilized for the enhancement of aerobic and anaerobic degradation processes, respectively. The side by side field pilot tests consist of two 4-well application arrays with monitor wells located 20 ft (6.1 m) upgradient, 5 ft (1.5 m) downgradient and 25 ft (7.6 m) downgradient at both test areas. After six months of monthly post-application sampling, the data indicate that DCE and VC concentrations have been reduced significantly in both the aerobic and anaerobic field pilot tests. DCE and VC concentrations have been reduced in the two 25 ft (7.6 m) downgradient wells by an average of 78% in the aerobic test and 96% in the anaerobic test. Full-scale groundwater remediation of the entire 400 ft (122 m) by 600 ft (183 m) sandstone bedrock groundwater plume is planned for later this year.

INTRODUCTION

Objective. The objective of this study is to determine the feasibility of using either enhanced aerobic or anaerobic biodegradation to remediate DCE and VC contamination in groundwater at a site in Ohio, and to evaluate which approach is most cost-effective to complete the onsite groundwater remediation.

Scope. In order to develop the data necessary to successfully remediate the constituents of concern this remedial effort is structured in the following three phases:

- Phase I—Anaerobic Bench Scale Test
- Phase II—Aerobic/Anaerobic Comparative Study Field Pilot Test
- Phase III—Full Scale Implementation

Phase I activities include conducting an anaerobic bench scale test to determine how well the proposed hydrogen enrichment source would enhance the natural biodegradation process at the site. The results of the bench scale testing indicate that the naturally occurring bacteria at the site can significantly lower site volatile organic compound (VOC) contamination in the groundwater, and the rate of contaminant reduction can be increased by the proposed hydrogen enrichment material.

Phase II consists of conducting a comparative study field pilot test to confirm laboratory bench-scale results and provide information required to complete the final design of the full-scale remediation system. The objectives of the field pilot test include determining if the groundwater contamination in the VOC plume can be reduced more effectively aerobically (using oxygen enrichment material) or anaerobically (using hydrogen enrichment material). The Phase II field pilot testing activities include well installation, application, and groundwater sampling. The results of the field pilot test indicate that the site VOC groundwater contamination can be very effectively remediated by both aerobic and anaerobic processes. The currently available data collected from the pilot test indicate that anaerobic biodegradation may be the most cost-effective approach for site groundwater remediation.

Phase III activities will include the full-scale implementation of the in situ remediation effort planned for the entire 400 ft (122 m) by 600 ft (183 m) VOC groundwater plume, later this year.

Site Description. The site is located in Ohio, and manufacturing activities have been conducted at the site for over 100 years. The site is underlain by approximately five to eight ft of overburden, which is underlain by sandstone and shale bedrock of Mississippian age. The 30 ft (9.1 m) thick sandstone is fine to medium-grained, with interbedded siltstone and shale layers in the lower part of the formation. The sandstone is underlain by low permeable shale with some thin siltstone layers in the upper part of the formation.

A groundwater elevation contour map of wells screened in the sandstone bedrock is shown in Figure 1. The depth to water at the site generally ranges from 9.5 to 11.5 ft (2.9 to 3.5 m) below ground surface (bgs) and the overburden is unsaturated across most of the site. The average hydraulic conductivity (K) calculated from slug and pump tests in site wells is 4 ft/day (1.2 m/day). The horizontal groundwater gradient is 0.008 ft/ft in the northeast direction. Based on these data and an assumed effective porosity of 15%, the groundwater velocity is approximately 0.2 ft/day (0.06 m/day) in the pilot test area.

Soil vapor extraction (SVE) and soil removal efforts were used to remediate TCE soil contamination, which was the source of the DCE and VC groundwater contamination. Groundwater contamination now consists almost entirely of DCE and VC. The general absence of elevated TCE concentrations in the groundwater demonstrates that significant biologic degradation processes are present in the sandstone water bearing unit and that the soil source reduction efforts were effective.

MATERIALS AND METHODS

Biochemistry. This study utilizes a proprietary time release oxygen or hydrogen source for the enhancement of aerobic or anaerobic degradation processes, respectively. The aerobic pilot test utilizes Oxygen Release Compound (ORC®) as an oxygen enrichment material to stimulate the aerobic degradation of the DCE and VC contamination. The anaerobic pilot test utilizes Hydrogen Release Compound (HRC™) as a hydrogen enrichment material to stimulate anaerobic reductive dechlorination of the DCE and VC contamination. Both of these products are manufactured by Regenesis Bioremediation Products.

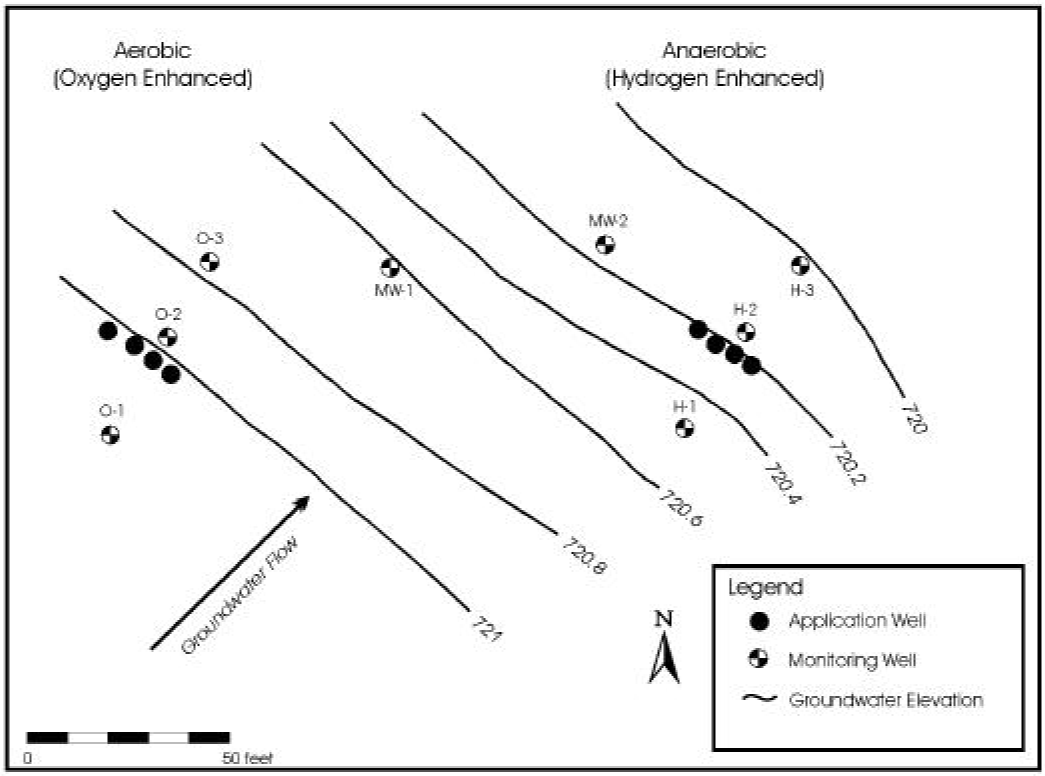

Figure 1. Site Map

The oxygen enhancement material used in the aerobic pilot test is a unique formulation of magnesium peroxide that releases oxygen slowly when hydrated. The compound releases oxygen while being converted to ordinary magnesium hydroxide in accordance with the following equation:

$$MgO_2 + H_2O \dashrightarrow 1/2\ O_2 + Mg(OH)_2$$

Magnesium peroxide and magnesium hydroxide are both environmentally benign and actually safe enough to ingest. They are both recognized as medical antacids, magnesium hydroxide is known as milk of magnesia. Aerobic degradation of DCE and VC can occur by two processes including direct metabolism or cometabolism. Direct metabolism is an intracellular process in which DCE and VC serve as a primary substrate for oxygen dependent microbial growth. Cometabolism is an extracellular degradation process that requires an enzyme-inducing substrate (Koenigsberg and Sandefur, 1999).

The hydrogen enhancement material used in the anaerobic test is a proprietary, environmentally safe, food-quality polylactate ester specially formulated for the slow release of lactic acid upon hydration. The lactic acid is converted to several other acids and produces hydrogen along the way. The hydrogen produced by this process is used by reductive dechlorinators, which are capable of dechlorinating DCE and VC (Koenigsberg and Farone, 1999).

Anaerobic Bench Scale Test. The purpose of the anaerobic laboratory bench-scale test was to determine how well the proposed hydrogen enrichment source would enhance the natural biodegradation process at the site. Existing site data indicate that in situ bioremediation is already occurring naturally at the site. The focus of the bench scale test was to determine whether the bedrock groundwater contains a population of bacteria that is suitable to perform the remediation and respond to an increase in both the carbon compound biochemical energy and the hydrogen generated from the proposed hydrogen enrichment source material.

In situ rock and groundwater samples were collected at the site to conduct four laboratory bench-scale tests. One test was conducted using bedrock chips and groundwater. Three additional tests were conducted using groundwater samples collected from well MW-2, one additional upgradient well, and well O-3. The test using bedrock chips and site groundwater is considered to be the best representation of biodegradation occurring at the site. Varying concentrations of trichloroethene (TCE) were added to the bench-scale test tubes and subsequent samples were collected for analysis of target VOCs and lactic acid. At the conclusion of the test, the water was plated to determine the actual bacterial concentrations. The bench scale test was conducted by William Farone at Applied Power Concepts, Anaheim, California (as outlined in Farone and Koenigsberg, 1999).

TCE concentration reductions were observed during the first week of all four bench scale tests. TCE concentrations were significantly reduced in all four tests after four weeks, and the tests were terminated at that time. The bedrock chip test showed that the concentrations had decreased from initial concentrations of 25 and 10 mg/l to final concentrations of 4.41 and 1.63 mg/L, respectively. The test samples were also analyzed for DCE and VC. These data showed that DCE and VC were generated during the test from the breakdown of TCE. After four weeks, the bedrock chip bench-scale test indicated significant degradation of DCE and VC. The results of the bench scale testing indicate that the naturally occurring bacteria at the site can significantly lower site VOC contamination in the groundwater, and the rate of contaminant reduction can be increased by the proposed hydrogen enrichment material.

Pilot Test Design. This comparative study consists of two side by side field pilot tests. Both tests consist of two 4-well application arrays with monitor wells located 20 ft (6.1 m) upgradient, 5 ft (1.5 m) downgradient and 25 ft (7.6 m) downgradient. The application wells are spaced 5 ft (1.5 m) apart. The two test areas are located in the same 30 ft (9.1 m) thick sandstone bedrock water bearing unit and are separated by approximately 150 ft (46 m) in a cross gradient direction. The sandstone unit is underlain by very low permeability shale. Figure 1 shows a general layout of the two pilot tests. Wells O-3, H-3, MW-1, and MW-2 were installed 6 years before the pilot test and groundwater samples were collected from them 6 years, 3 years, and 1 year prior to the test. The additional pilot test wells O-1, O-2, H-1, H-2, and all of the application wells were installed 1 month before the pilot test. The test wells were installed to a depth of approximately 35 ft (10.7 m) bgs. The aerobic test application wells are 8-inch (20 cm) diameter wells and the anaerobic test application wells and all monitor wells are 5-inch (13 cm) diameter wells. Both sets of pilot test wells were drilled using water rotary drilling techniques in order to limit the amount of aeration during drilling.

Application of the oxygen and hydrogen enhancement material was conducted on the same day. The aerobic pilot test consists of stacking four PVC screened canisters containing five 'socks' of material per canister across the entire saturated thickness in each of the four aerobic test application wells. Each filled 'sock' contains 11 pounds of material amounting to a total of 220 pounds (100 kg) of applied material into each of the four aerobic test application wells. The rate of canister application was approximately one application well per hour.

The anaerobic pilot test consists of completely filling the saturated thickness of the open-hole bedrock application wells with the hydrogen enhancement material. Thirty gallons of the material were applied into each of the four anaerobic application wells. The application rate was approximately one to two gallons per minute. Both of these tests simply consisted of filling each application well up with one well volume of bioremediation enhancement material. This application had minimal affect on the surrounding water levels, which dissipated shortly after application, and was not enough material to either spread or block the natural movement of the plume.

Groundwater Sampling and Analysis. Baseline groundwater samples were collected from all upgradient and downgradient monitor wells prior to application. Groundwater samples were also collected from wells O-3 and H-3 prior to the test 6 years, 3 years, and 1 year before the application. Following application, groundwater samples were collected monthly (approximately every 30 days), to monitor the effectiveness of the aerobic and anaerobic pilot tests. Groundwater samples were collected using low flow sampling techniques. Laboratory samples collected during the pilot test included VOCs, inorganics, total organic carbon (TOC), and acids. Field parameters collected throughout the sampling period included dissolved iron, pH, temperature, Eh, specific conductance, and dissolved oxygen.

RESULTS AND DISCUSSION

After six months of monthly post application sampling, the data indicate that DCE and VC concentrations have been reduced significantly in both the aerobic and anaerobic field pilot tests. The two downgradient wells in the anaerobic test area (H-2 and H-3) were sampled for acids every month following the application. Sampling results for well H-2 are presented in Table 1 and indicate that acids were detected in that well during every monthly post-application sampling event. Lactic acid was detected in well H-2 five months after the application indicating that the lactic acid lasted at least five months in the treatment area. The data indicate that propionic acid was still present at a concentration of 273 mg/L in well H-2 six months after application, indicating that hydrogen will continue to be produced beyond the six month pilot test sampling effort. Propionic and acetic acid were detected in well H-3 120 days after application at concentrations of 12 and 21 mg/L, respectively, indicating that acids migrated at least 25 ft (7.6 m) in the sandstone bedrock water bearing unit.

Sulfate, dissolved iron, TOC and pH data for well H-2 are also presented in Table 1. The general decrease in sulfate (with the exception of the 120 and 150 day samples) and increase in iron are geochemical indicators that anaerobic conditions favoring reductive dechlorination were developed. The elevated TOC and decreased pH indicate that the hydrogen enrichment material migrated to well H-2. These same trends were also observed in well H-3. Conversely, the downgradient aerobic test wells O-2 and O-3 exhibited increasing sulfate and decreasing iron and no significant changes in TOC and pH.

Table 1. Well H-2 Sampling Results (mg/L) – Anaerobic Application

Analyte	Baseline	30 days	60 days	90 days	120 days	150 days	180 days
Lactic Acid	<100	571	6900	3830	279	214	<1
Pyruvic Acid	<100	1.2	10.4	4.2	0.4	2.1	<0.1
Butyric Acid	<1	166	309	313	156	103	52
Propionic Acid	<1	208	434	146	142	211	273
Acetic Acid	<1	284	566	272	131	243.0	272
Sulfate	310	29	7	29	420	860	62
Iron, dissolved	24	44	311	486	142	183	53
TOC	9	880	300	670	520	570	310
pH	6.45	5.74	4.53	5.1	NA	5.15	5.62

Table 2: DCE and VC Concentration (ug/L) 25 ft (7.6 m) Downgradient

	Prior Historical Data			**Baseline**	Post Application					
	6 years	3 years	1 year	**0 days**	30 days	60 days	90 days	120 days	150 days	**180 days**
Aerobic: Well O-3										
DCE	2900	990	1900	**2500**	1800	1700	930	613	181	**448**
VC	1300	1300	1300	**800**	570	490	560	736	64	**275**
DCE + VC	4200	2290	3200	**3300**	2370	2190	1490	1349	245	**723**
Anaerobic: Well H-3										
DCE	2700	1100	1400	**590**	690	1600	120	88	23	**20**
VC	230	320	1300	**210**	160	420	220	248	50	**12**
DCE + VC	2930	1420	2700	**800**	850	2020	340	336	73	**32**

Historical VOC sampling data are available from wells O-3 and H-3. The DCE and VC data collected from these wells 6 years, 3 years, and 1 year before application is summarized in Table 2. These data show that some contaminant reduction occurred during that time period but the rate of reduction was relatively slow. Extrapolation of these data show that it would take several decades for the DCE and VC concentrations to be naturally lowered to the U.S. EPA Maximum Contaminant Levels (MCLs) of 70 and 2 ug/L, respectively. The pilot test was conducted to determine if adding oxygen and hydrogen enrichment products could increase these natural degradation rates.

Table 2 also shows the DCE, VC, and total (DCE + VC) concentrations for the baseline and the 6 monthly post-application sampling events. These data show that while some fluctuations occurred during the six-month sampling period, a significant trend of reduced DCE and VC concentrations was observed in wells H-3 and O-3. Most notably in the anaerobic test, the DCE concentration in well H-3 was reduced from 590 ug/L during the baseline sampling to 20 ug/L (significantly below the MCL of 70 ug/L) 180 days later. The VC concentration was also reduced in well H-3 from 210 ug/L during the baseline sampling to 12 ug/L (much closer to the MCL of 2 ug/L) 180 days later. The aerobic test well O-3 also exhibited significant DCE and VC concentration reductions during the 180 day pilot test, although slightly less on a percentage basis than the anaerobic test.

A graph of the DCE + VC concentrations in wells H-3 and O-3 is shown in Figure 2. The DCE and VC concentrations for the three historical sampling events are also listed on this figure for comparison. This figure shows that the rate of DCE and VC contaminant reduction was significantly increased after the application of the oxygen and hydrogen enrichment material. The figure also shows that the DCE and VC concentrations steadily declined in the aerobic test well O-3 during the first five months of the test but started to rebound during the sixth month. This rebound may have been due to the depletion of the oxygen enhancement material. Conversely, the DCE and VC concentrations continued to decrease in the sixth month and it is anticipated that this reduction will continue due to the remaining presence of butyric and propionic acids in well H-2.

The percent reduction in DCE, VC, and DCE + VC was calculated for the aerobic and anaerobic monitor wells and is summarized on Table 3. This table shows that the DCE and VC concentrations were reduced in the aerobic test well O-3 by 82% and 66%, respectively at the end of the 180 day pilot test. The table also shows that the DCE and VC concentrations were reduced in the anaerobic well H-3 by an even more significant amount 97% and 94%, respectively. The data summarized in Table 3 and Figure 2 show that the DCE and VC concentrations were significantly reduced in both pilot tests and that the reductions were higher and more sustained in the anaerobic pilot test.

Future Work. Additional data collection will be used to confirm the results of the 180 day aerobic and anaerobic comparative study pilot tests and to design a full-scale groundwater bioremediation program for the entire 400 ft (122 m) by 600 ft (183 m) groundwater plume.

Table 3: 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	**20' upgradient**	740	675	9%	1,100	553	50%
O-2	**5' downgradient**	420	339	19%	1,700	1,040	39%
O-3	**25' 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	**20' upgradient**	5,700	5,600	2%	450	290	36%
H-2	**5' downgradient**	2,600	1,640	37%	1,200	253	79%
H-3	**25' downgradient**	590	20	**97%**	210	12	**94%**

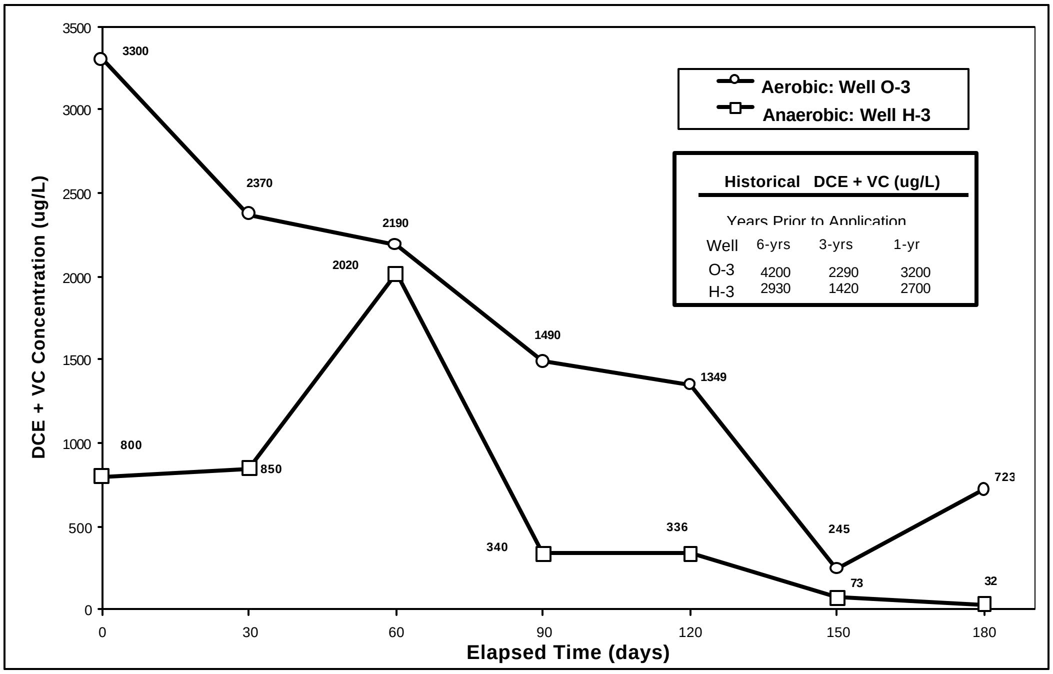

Figure 2. Summary of Results 25 ft (7.6 m) Downgradient of Application

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