Synergistic Treatment of Chlorinated VOCs Using Reductive Dechlorination and Zero Valent Iron

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ABSTRACT: Enhanced reductive dechlorination and micro-scale zero valent iron (ZVI) injections have been implemented to treat chlorinated volatile organic compounds (CVOCs) at a former dry cleaning facility in Cincinnati, Ohio. These remedial approaches, commonly implemented as stand alone technologies, were combined to achieve synergistic reductions to overcome the buildup of cis-1,2-dichloroethene (cis-1,2-DCE), resulting from the breakdown of tetrachloroethene (PCE). The property is situated on a thin veneer, approximately 10-12 feet (3.0-3.7m) thick of heterogeneous glacial material, overlying shale and interbedded limestone. The glacial material consists primarily of hard till with a thin sand seam of six to eight inches (15.2-20.3 cm) situated above the bedrock. The sand seam thickens towards an adjacent down-gradient property where CVOCs are present in a highly oxidized perched water-bearing zone. Site investigations have identified the soil source area as the former basement of the dry cleaning facility near a sewer drain, just above the soil/bedrock interface. Reductive dechlorination was stimulated in the source area by staging a series of injections at 18 points in the soil source area to enhance the anaerobic environment. Results of the injections have seen the reduction of PCE to below detection limits in two of the three source zone monitoring points; PCE concentrations in the remaining source area monitoring well monitoring location was 0.008 milligrams per liter (mg/L). Based on monitoring results, the cis-1,2-DCE and vinyl chloride continues to degrade, the subsurface remains anaerobic and sufficient nutrients are present to maintain the degradation.

INTRODUCTION

Tetrachloroethene (PCE) and trichloroethene (TCE) have been used widely as solvents and degreasers since the 1940s. The widespread use, in combination with improper handling and storage of PCE and TCE, for degreasing and dry cleaning, has resulted in impacted soil and ground water at facilities where these chemicals were used. Due to their toxicity and persistence in subsurface media, these volatile organic compounds (VOCs) have been studied extensively in order to develop remediation technologies to effectively remove these compounds from subsurface media.

The environmental chemistry of a site in part determines the rate of biodegradation of chlorinated solvents at that site. The initial metabolism of chlorinated solvents such as chloroethenes in ground water usually involves a biochemical process described as sequential reductive dechlorination. The occurrence of different types and concentrations of electron donors such as native organic matter, and electron acceptors such as oxygen and chlorinated solvents, determines to a large degree the extent to which reductive dechlorination occurs during the natural attenuation of a site.

Adding amendments to the subsurface media can stimulate the microorganisms. To accelerate the natural processes, ZVI and enhanced microbial dechlorination processes were utilized at the site. The utilization of coenzymes, oxygen scavengers and nutrients insured that little or no lag phase in the process was experienced and that the most efficient pathways were utilized. Treatment has been implemented at a site in southwestern Ohio using complementary injections to biologically and chemically reduce chlorinated ethenes.

Background

PCE and TCE were prevalent in the subsurface at a former dry cleaning facility in Cincinnati, Ohio. Soil and ground water sampling results prior to injecting the reductive dechlorination amendments indicated that cis-1,2-dichloroethene (cis-1,2-DCE) and vinyl chloride, daughter products of the breakdown of PCE and TCE, were also present in the soil and ground water. The presence of these breakdown products indicated that reductive dechlorination of the TCE and PCE was occurring.

Soils encountered at the site consist of silty clay with minor amounts and sand and gravel (glacial till), overlying interbedded shale and limestone bedrock. Bedrock was encountered across the site between 12 and 16 feet (3.7-4.9 m) below surface grade. A thin sand seam is present at the this interface. A source area in the soil and very low yielding ground water, above the soil/bedrock interface was identified, near a floor drain in the basement of the former dry cleaner. PCE concentrations ranged between 78.9 milligrams per kilogram (mg/kg) and 140 mg/kg in the soil source area. Ground water concentrations of PCE in the same area (prior to remediation) ranged between 2.5 milligrams per liter (mg/l) and 12 mg/L. The elevated ground water conditions are due in part to the low flow, low-yield nature of the water-bearing zone.

In May 2005 (Figure 1) and again in December 2005 (Figure 2), ZVI and other chemical amendments were injected into the soil and ground water to enhance the reductive dechlorination rates and stimulate the indigenous microbes to breakdown concentrations of PCE and TCE at the property. A total of 18 injection points were utilized to distribute the reductive dechlorination amendments during the May 2005
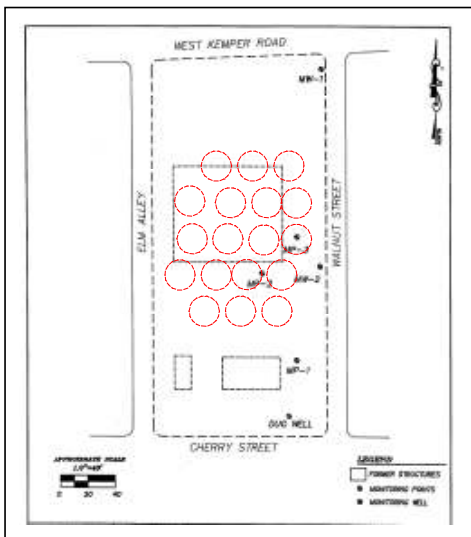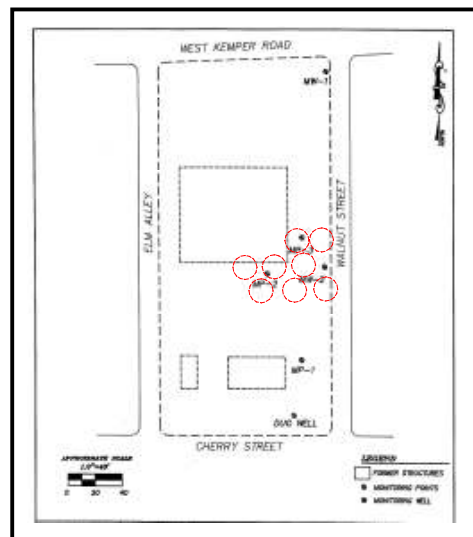

FIGURE 1

FIGURE 2

injection event. Six injection points were advanced during the December 2005 event, which targeted the source area after the nutrients from the initial injections were depleted.

The objective of the injections was to treat the dissolved and sorbed phase chloroethenes at and down gradient of the source area. By adding the amendments, reductive dechlorination of PCE and its daughter products was accomplished by biotic and abiotic processes.

MATERIALS AND METHODS

In order for the rate of reductive dechlorination to increase, it was necessary to establish conditions in situ that could accelerate the dechlorination process by providing nutrients to the indigenous microbial population. Injection points were plotted on the property to supply essential microbial nutrients necessary for the dechlorination process to be stimulated and to introduce ZVI which would accelerate chemical reduction of the chlorinated volatile organic compounds (CVOCs), acting synergistically with the anaerobic process. . A sequence of task-specific compounds, including ZVI and HRC$^{®}$, were injected through the perforated rod using a patent-pending, compressed nitrogen gas delivery system. The stepwise injection process and intended effects are as follows:

Compressed Nitrogen Gas. Nitrogen gas was delivered to the subsurface by injection at 175 pounds per square inch (psi) to open up delivery pathways in the subsurface. The pressure was maintained at a constant rate and pathway development was verified by observing a substantial pressure drop at the point of application, once the pathways formed. Nitrogen was used in this step to establish and maintain the anaerobic conditions in the subsurface. The goal of this step was to open pathways similar to those along which the CVOCs would have migrated.

Sodium Sulfite Solution. Injecting a solution of food-grade sodium sulfite immediately followed the nitrogen injection. Sodium sulfite was used to scavenge residual oxygen from the subsurface to: 1) ensure anaerobic conditions and further reduce the oxidation/reduction potential (ORP) in the range favorable to the anaerobic microorganisms; and 2) to prevent dissolved oxygen from reacting with the subsequently injected ZVI. Nutrients such as orthophosphate and organic ammonia (nitrogen) were injected with the sodium sulfite to enhance the growth of the microbial population and help them maintain their metabolic pathways.

Micro-scale ZVI. ZVI was injected immediately following the sodium sulfite/nutrient slurry. A primary goal of the ZVI was to rapidly reduce the high concentrations of dissolved phase PCE in the source area. The corrosion of the ZVI by ground water also produces hydrogen that can be utilized by the indigenous microbial population metabolizing PCE while maintaining pH. Approximately 55 pounds (24.9 kg) of ZVI was injected into each location during both injection events.

HRC ^{TM}. The ZVI injection was followed by the injection of HRC ^{TM} and vitamins B-2 and B-12. The HRC ^{TM} was heated to approximately 180 degrees (F) to enhance the flow ability of the material during injection. The HRC ^{TM} provides an electron

donor for the anaerobic microbes which degrade the PCE. Approximately 30 pounds (13.6 kg) of HRC was injected at each location.

Vitamins B-12 and B-2. Injected with the HRC ^{TM}. Vitamin B-12 helps maintain the accelerated reductive dechlorination process and lowers the activation energy for electron transfer of the terminal electron to cis-1,2-DCE, while the core element, cobalt, catalyzes the surface action of the ZVI in reducing the dissolved phase CVOCs. Without B-12, sulfate also acts competitively with the CVOCs as an electron acceptor. Vitamin B-2 allows for more efficient microbe utilization of the hydrogen, increasing the overall kinetics.

These injections were followed by another injection of the sodium sulfite/nutrient slurry to clear the injection lines and provide for in situ mixing and penetration of the HRC into the formation. Lastly, the injection lines were then cleared of all injected materials with additional nitrogen gas.

RESULTS AND DISCUSSION

In the development and implementation of a monitoring and evaluation program for the project, critical field and laboratory parameters were selected. The components of the monitoring program required that the efficacy of the applied technology be valued based on target compound concentration reduction, appearance and disappearance of daughter products, pH control, dissolved gas evolution and degradation products of the organic hydrogen donor. The objectives of the implemented monitoring program were: 1) the assessment of the delivery technology, 2) the valuation of individual components of the remedial program and 3) the treatment efficiency of the program.

Ground water sampling occurred on May 22, 2005, immediately prior to the first injection event to establish the baseline concentrations of the targeted chlorinated compounds. A total of six ground water monitoring events were performed between the baseline-sampling event and March 2006.   In order to control the analytical costs associated with the project, the initial sampling events did not include dissolved gas analysis, field parameters or the analysis of the breakdown products of the organic hydrogen donor. Beginning with the October 2005 sampling event, all parameters of the monitoring program were included so as to value the biological component of the program and to allow for the scheduling of the second injection event. Scheduling of the second injection was based on the residual levels of the volatile fatty acid precursors (acetate, butyrate, formate, lactate, propionate and pyruvate) and dissolved gas levels.

In order to assess the efficacy of the delivery process the evaluation program has focused on the analytical and field results from MW-2. No injection occurred within twenty to twenty-five feet of MW-2, a cross gradient monitoring well which historically exhibited moderate levels of PCE and its daughter products. The analytical data obtained from MW-2 supports the design basis of the injection program. The area of influence achieved by the injections exceeded a twenty-foot (6.1 m) radius based on the decrease in chlorinated compounds after the first injection event (Figure 3) and is confirmed by the fatty acid compound appearances (Figure 4) following the second injection event.
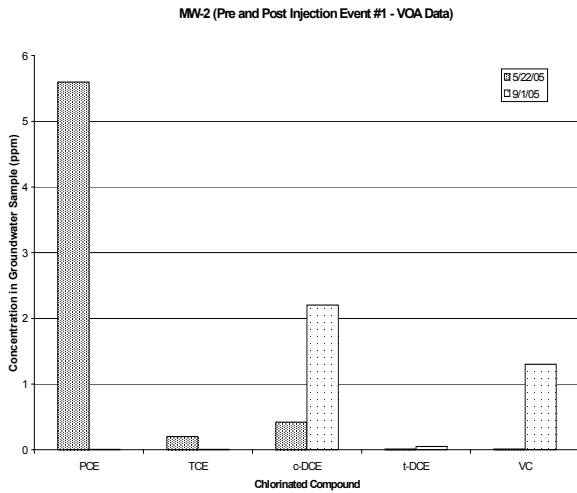
MW-2 (Pre and Post Injection Event #1 - VOA Data)

MW-2(Pre and Post Second Injection Event Fatty Acids)

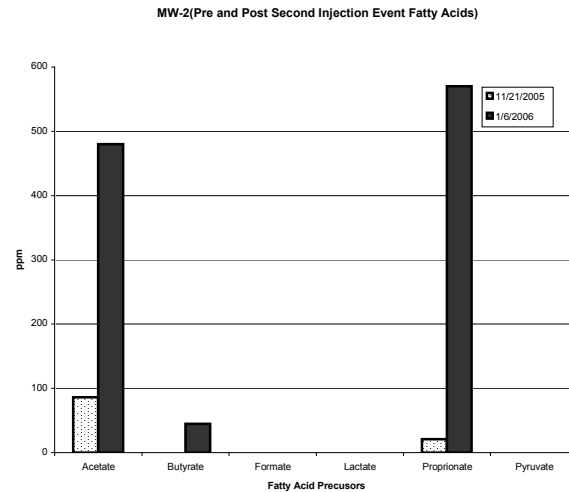**FIGURE 3**   **FIGURE 4**

Valuation of the individual components of the remedial program consisted of the evaluation of the effects of the zero valent iron component and the biological component of the remedial program. The corrosion of the zero valent iron component was valued by-way of the influence of the ferrous iron on pH at MP-1 and MP-2 following the second injection event. The valuation of the biological component was valued by-way of the appearance of dissolved gasses at monitoring points MP-2 and MP-3 before and after the second injection event (Figures 5-7).
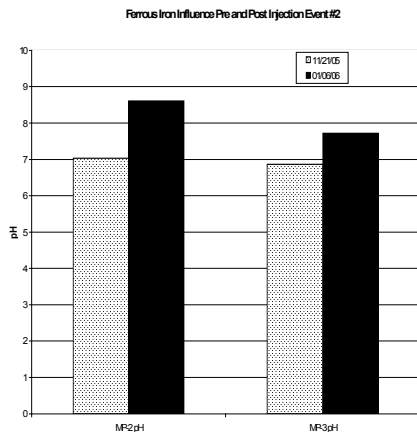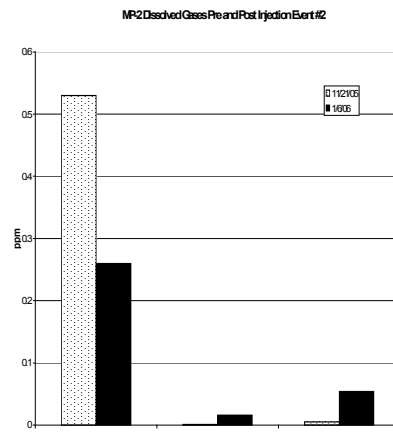
Ferrous Iron Influence Pre and Post Injection Event #2

MP-2 Dissolved Gases Pre and Post Injection Event #2

MP-3 Dissolved Gases Pre and Post Injection #2

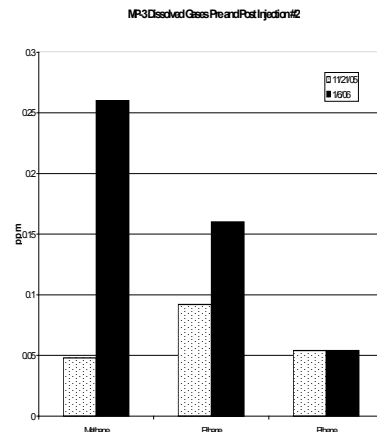**FIGURE 5**   **FIGURE 6**   **FIGURE 7**

The evidence of the ZVI corrosion is seen in the effect of the ferrous iron species on the pH in both MP-2 and MP-3.   With the corrosion of the iron component dissolved chlorinated compounds are converted to ethane and the ferrous iron provide hydroxyl species as a pH buffer.

The evolution of dissolved gases following the second injection event provides further evidence of the effectiveness of the in-situ program. The dissimilar dissolved gas

profiles in MP-2 and MP-3 reflect the differences in the target compound concentrations in these areas. The ability of the injection program to control the competition for microbial resources between the dehalogenators present at the site and the homoacetogens and methanogens is seen in the dissolved gas distribution in the wells MP-2 and MP-3. As compared to alternative organic hydrogen donors, which exhibit rapid release of hydrogen, the HRC product effectively controls methanogenesis from out competing the dehalogenators for microbial resources until the dissolved chlorinated compounds are mineralized.

The treatment efficacy of the program is demonstrated by the significant reductions in the targeted chlorinated compounds (Figures 8-11). Unlike programs that utilize only organic hydrogen donors, this remedial approach had no lag phase between the injection event and the mineralization of the chlorinated compounds. As a result, the ground water sampling indicates that concentrations of PCE and TCE have decreased in all wells and monitoring points since the initial injections in May 2005. The highest PCE concentration remaining in the source area ground water after the March 2006 sampling was 0.008 mg/L in monitoring point MP-2; the highest TCE concentration was 0.005 mg/L in the same well. Concentrations of cis-1,2-DCE and vinyl chloride however, have increased at various times as a result of the breakdown of the PCE and TCE on site.

Since the initial sampling event, cis-1,2-DCE and vinyl chloride concentrations in monitoring well MW-2 increased from 0.420 mg/L and 0.009 mg/L, respectively, to 11.0 mg/L and 0.440 mg/L.
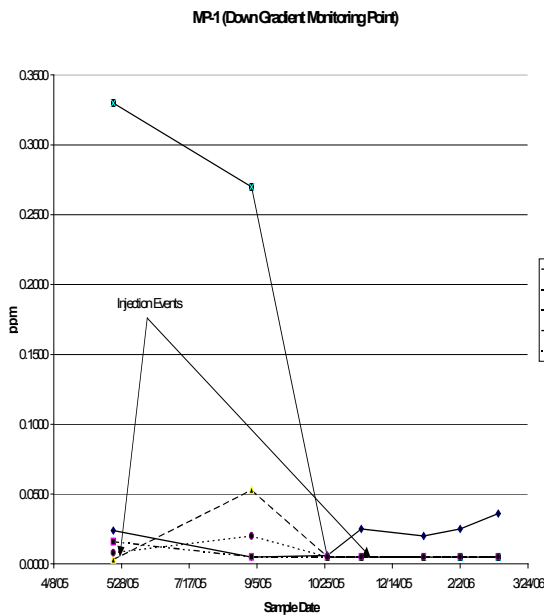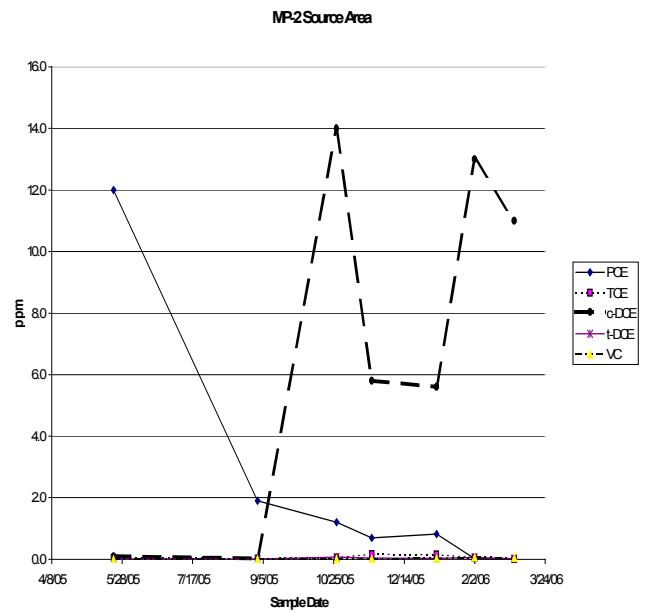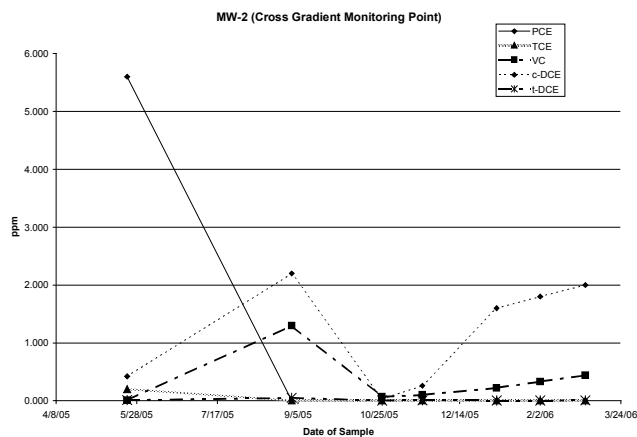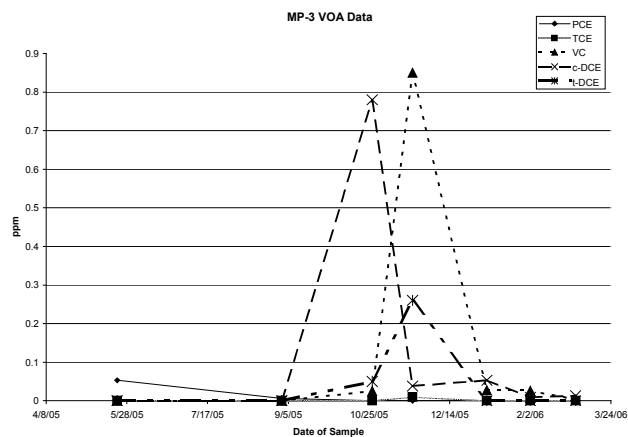

FIGURE 8

FIGURE 9

FIGURE 10

FIGURE 11

CONCLUSIONS:

The biological activity and the rates of dechlorination appear to vary across the injection area based on the concentrations of the targeted compounds and the sorbed mass. It is clear that the polylactate ester and its degradation products have provided prolonged hydrogen for the enhanced attenuation phase. The effects of the second injection are clearly seen in MP-3 where the rapid disappearance of the daughter products of the PCE occurred.

The incorporation of the vitamins and nutrients into the enhancement program has effectively allowed for robust microbial growth without significant cis-1,2-DCE or vinyl chloride accumulation. The inclusion of the zero valent iron has allowed for pH control and enhanced remediation of the site. The anaerobic component of the program appears to be effective in addressing the chloroethenes.

The vitamin B-12 and to a lesser degree the vitamin B-2, appears to mediate the reductive dechlorination of the PCE. In most biological systems, the rate-limiting step to complete dechlorination to ethene is the last stage conversion of vinyl chloride. The rate of that process has been found to be significantly enhanced by the presence of vitamin B-12, which acts as an electron carrier. It is the core of B-12, which contains cobalt, and it is the various oxidation states of cobalt, which allows for the electron transfer intra-cellularly within the microbial population. The presence of the cobalt core has also been seen to catalyze the surface reaction of the iron lowering the necessary activation energy required for the electron transfer.

The accelerated reduction of PCE, TCE and cis-1,2-DCE to vinyl chloride (Figure 12) and ethene, has continued as expected as hydrogen is generated by the slow releasing polylactate ester and the effects of the ferrous compounds which formed as a result of the corrosion of the ZVI. The appearance of ethane in the dissolved gas evaluation also indicates that the zero valent iron species has contributed to the overall efficacy of the synergistic integration of these technologies.

Sample ID	Date	PCE	TCE	Vinyl Chloride	cis-1,2-DCE	trans-1,2-DCE
MW-2	5/22/05	5.600	0.200	0.009	0.420	0.011
	9/1/05	<0.050	<0.050	1.30	2.200	<0.050
	10/27/05	<0.005	<0.005	0.068	0.029	<0.005
	11/21/05	<0.005	<0.005	0.10	0.26	0.008
	1/6/06	<0.005	<0.005	0.220	1.60	<0.005
	2/2/06	<0.005	<0.005	0.330	1.80	<5
	3/2/06	<0.005	<0.005	0.440	2.00	0.006
MP-2	5/22/05	12.0	0.039	<0.002	0.100	<0.005
	9/1/05	1.90	0.016	<0.005	0.020	<0.005
	10/27/05	1.20	0.050	0.004	14.0	0.070
	11/21/05	0.690	0.160	0.016	5.80	0.041
	1/6/06	0.820	0.150	0.032	5.60	0.025
	2/2/06	0.020	0.047	0.061	13.00	0.060
	3/2/06	0.008	0.005	0.052	11.00	0.015
MP-1	5/22/05	0.024	0.016	0.003	0.330	0.008
	9/1/05	<0.005	<0.005	0.053	0.270	0.020
	10/27/05	0.006	<0.005	<0.002	<0.005	<0.005
	11/21/05	0.025	<0.005	<0.002	<0.005	<0.005
	1/6/06	0.02	<0.005	<0.002	<0.005	<0.005
	2/2/06	0.025	<0.005	<0.005	<0.005	<0.005
	3/2/06	0.036	<0.005	<0.005	<0.005	<0.005
MP-3	5/22/05	0.053	<0.005	<0.002	<0.005	<0.005
	9/1/05	0.006	<0.005	<0.002	<0.005	<0.005
	10/27/05	<0.005	<0.005	0.025	0.780	0.050
	11/21/05	<0.005	0.009	0.850	0.038	0.260
	1/6/06	<0.005	<0.005	0.028	0.053	<0.005
	2/2/06	<0.005	<0.005	0.026	0.009	<0.005
	3/2/06	<0.005	<0.005	0.003	0.013	<0.005

FIGURE 12

Ground water monitoring will continue until the cis-1,2-DCE has been degraded and the vinyl chloride concentrations reach the proposed cleanup goals. Once that has been accomplished, confirmatory soil sampling will be performed to determine if the PCE and TCE adsorbed onto the soil grains has also been effectively reduced or whether another injection to finish the process is required.