

Evaluating TCE Abiotic and Biotic Degradation Pathways in a Permeable Reactive Barrier Using Compound Specific Isotope Analysis

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Abstract

A pilot-scale zero valent iron (ZVI) Permeable Reactive Barrier (PRB) was installed using an azimuth-controlled vertical hydrofracturing at an industrial facility to treat a chlorinated Volatile Organic Compound (VOC) plume. Following ZVI injection, no significant reduction in concentration was observed to occur with the exception of some multilevel monitoring wells, which also showed high levels of total organic carbon (TOC). These patterns suggested that the zero valent iron was not well distributed in the PRB creating leaky conditions. The geochemical data indicated reducing conditions in these areas where VOC reduction was observed, suggesting that biotic processes, associated to the guar used in the injection of the iron, could be a major mechanism of VOC degradation. Compound-Specific Isotope Analysis (CSIA) using both carbon and chlorine stable isotopes were used as a complementary tool for evaluating the contribution of abiotic and biotic processes to VOC trends in the vicinity of the PRB. The isotopic data showed enriched isotope values around the PRB compared to the isotope composition of the VOC source confirming that VOC degradation is occurring along the PRB. A batch experiment using site groundwater collected near the VOC source and the ZVI used in the PRB was performed to evaluate the site-specific abiotic isotopic fractionation patterns. Field isotopic trends, typical of biodegradations were observed at the site and were different from those obtained during the batch abiotic experiment. These differences in isotopic trends combined with changes in VOC concentrations and redox parameters suggested that biotic processes are the predominant pathways involved in the degradation of VOCs in the vicinity of the PRB.

Introduction

Chlorinated solvents, such as trichloroethene (TCE), are used in a wide range of industrial processes. The historical handling and disposal practices have led to the formation of plumes of dissolved Volatile Organic Compounds (VOCs). A variety of site remediation strategies have been developed to address these problems. Passive groundwater remediation using zero-valent iron permeable reactive barriers (ZVI PRBs) has been established as an effective in situ treatment technology for chlorinated solvent plumes (Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994; Orth and Gillham 1996; O'Hannesin and Gillham 1998). Although the concept is relatively straightforward, placing a vertical zone of ZVI across a contaminant plume

can be a somewhat complex exercise, as results can be confounded by issues such as flow bypassing, desorption of contaminants from the downgradient aquifer, or the use of carbon-based, biodegradable fluids during construction (Crane et al. 2004).

As part of a comprehensive remedial program adopted for an industrial facility, a pilot-scale ZVI PRB was installed at the downgradient property boundary to prevent off-site migration. Due to the local site conditions, azimuth-controlled vertical hydrofracturing was selected for the pilot PRB installation. This methodology consists on inducing fractures at controlled directions within the aquifer media created by pneumatic pressure. During the installation procedure, seven injection strings were installed along the PRB alignment aiming to create a 30.5 m long system. Iron filings were injected in a highly viscous guar gum gel, which propagated along the fractured pathway, which supposedly will create a homogeneous iron treatment zone. An enzyme was added to the gel during injection to promote its breakdown following emplacement.

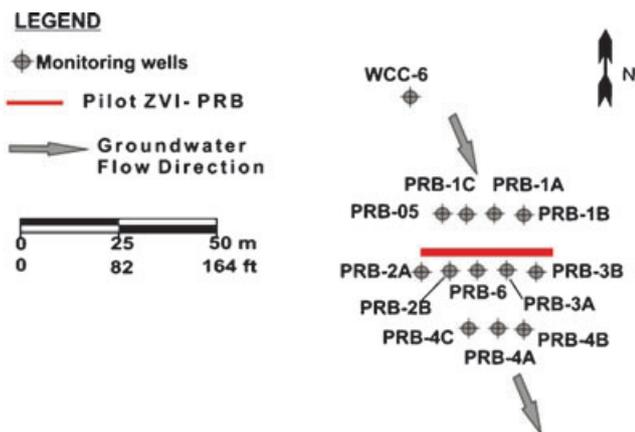


Figure 1. Monitoring wells location.

As part of the site-monitoring program, multilevel wells located upgradient and downgradient from the PRB (Figure 1) were pre-installation and periodically sampled post-PRB installation for VOCs and inorganic compounds to evaluate long-term PRB performance.

Data collected during the monitoring program indicated that VOCs concentrations were still high post-PRB injection with the exception of areas where reducing conditions were observed. Also an increase in Total Organic Carbon (TOC) accompanied by a concurrent decrease in terminal electron acceptors, particularly sulfate, was observed in some of the wells, suggesting that biotic processes could be acting as the main mechanisms for VOC degradation rather than the expected ZVI-driven abiotic processes. These observations were made about three months after the PRB installation in the monitoring wells near the PRB and after seven months in monitoring wells located further away from the PRB (Fiorenza and Christie 2008). The use of guar gum biopolymers typically used in the installation of PRBs may result in elevated guar-derived Dissolved Organic Carbon (DOC) levels that have been shown to persist in groundwater systems for periods of many months (Vidumsky et al. 2002; Crane et al. 2004; Johnson et al. 2008). An increase of sulfate-reducer bacteria population in the vicinity of the studied PRB was suggested to occur either as a function of iron corrosion or guar-derived carbohydrates, which could be acting as potential electron donors. An increase in *Dehalococcoides* sp., as determined by qPCR, was also detected in some of the wells, along with an increase in volatile fatty acids and ethene and ethane, suggesting that anaerobic reductive dechlorination was occurring (Fiorenza and Christie 2008).

Compound Specific Isotope Analysis (CSIA) is a recently developed tool that may be used to evaluate the role of biotic and abiotic processes in PRB settings. Laboratory experiments (Bill et al. 2001; Dayan et al. 1999; Slater et al. 2002; Schuth et al. 2003a; Vanstone et al. 2004) and field studies have been used to evaluate reductive dechlorination using zero-valent iron (Vanstone et al. 2005). Similarly, CSIA has been used successfully during biodegradation studies of VOCs in groundwater (Hunkeler et al. 1999; Bloom et al. 2000; Sherwood

Lollar et al. 2001; Slater et al. 2001; Song et al. 2002). The method is based on the differences in reaction rates between molecules with light (^{12}C , ^{35}Cl) and heavy (^{13}C , ^{37}Cl) isotopes. Normally, molecules with light isotopes are transformed faster than molecules with heavy isotopes. Consequently, the reactant becomes increasingly enriched in heavy isotopes while the product is initially depleted in heavy isotopes relative to the reactant. This unequal distribution of isotopes between product and reactant is denoted as isotope fractionation.

As shown by Liang et al. (2007) and Elsner et al. (2008), different isotopic fractionation patterns are expected to occur during abiotic and biotic processes, making it possible to use CSIA as a complementary tool to distinguish between these two degradation processes.

The main objective of this research is to evaluate the role of abiotic and biotic processes on VOCs reduction within the pilot PRB using a combined approach of VOCs and inorganic data evaluation and CSIA.

Site Background

A heterogeneous mixture of fine-grained continental, marine, and windblown sediments, which comprise the overburden materials beneath the site, extends to a depth of approximately 34 m to 40 m. These materials are defined by interbedded layers of clays, silts and sands (Parsons 2007). Two lateral continuous silty sand horizons, approximately 1.5 m thick, occur at 9 and 15 m below grade and define the local groundwater bearing zones, here classified as shallow and intermediate aquifer horizons. The regional horizontal groundwater flow for the shallow and intermediate aquifer horizons is preferentially toward the southeast (Figure 1) and the horizontal groundwater velocity ranges from 7 to 17 m/year for these aquifer horizons.

The primary chlorinated solvent detected at the site is trichloroethene (TCE) (>60 mg/L) and its associated daughter products, cis-1,2-dichloroethene (cis-1,2-DCE) (>4 mg/L) and vinyl chloride (VC) (>0.2 mg/L) are present in minor concentrations. PCE and TCE were both used as source chemicals at different times during the facility's history. Elevated TCE concentrations were historically detected at the site in the southern portion of the property, upgradient from the PRB alignment. The PRB was completed in August 2003 and was designed as a continuous wall, 30 m long by 25 m deep. The monitoring network is shown in Figure 1. One shallow monitoring location is downgradient from a potential TCE source area and upgradient from the PRB, comprising the "source area well." Monitoring wells screened in the shallow aquifer horizon (9 m) are named by a code followed by the letter "A" (e.g., PRB-1A) or by a number (WCC-06). These wells are located both upgradient (WCC-06 and PRB-1A) and downgradient (PRB-2A, PRB-3A, and PRB-4A) from the PRB. Monitoring wells associated with the intermediate aquifer horizon (15 m) are named by a code followed by the letter "B" (e.g., PRB-1B) and are located upgradient (PRB-1B) and downgradient (PRB-2B, PRB-3B, PRB-4B) from the PRB (Figure 1). Monitoring data at the site have been obtained on a semi-annual basis since 2003.

Methods

The sampling strategy for the present study consisted of two groundwater sampling rounds, conducted in July 2007 and July 2008, and included the collection of samples for analysis of VOCs, dissolved gases, inorganic parameters, and carbon and chlorine isotopes of TCE and cis-1,2-DCE. The groundwater sampling procedure consisted of removing a minimum of three casing volumes from each monitoring well using a submersible Grundfos pump. Upon completion of purging, groundwater samples were collected from each well using a disposable bailer for VOCs and CSIA analyses. All VOA (VOCs and CSIA) containers were filled from a disposable bailer fitted with a small diameter drain into 40 mL vials. The VOA vial was tilted so as to fill by slowly allowing water to flow with minimal turbulence along the side of the VOA vial. All other containers used for geochemical parameters were filled from the discharge line of the submersible pump set at a reduced rate of flow.

A batch experiment was conducted in order to obtain the isotopic fractionation factor for the abiotic reduction of VOCs using site groundwater in the presence of ZVI. Four liters of groundwater were collected in the monitoring well WCC-6, located downgradient from a potential TCE source area and upgradient from the PRB. All sampling bottles collected for CSIA and VOCs samples were stored in coolers packed with ice and after shipping kept in fridges until analyzed.

Once in the laboratory, the collected 4-L groundwater sample was first homogenized and then added to 200 mL glass bottles containing 55 g of reactive ZVI material used in the PRB installation (Connelly-GPM). The vials were filled by gravity flow, leaving no headspace, and then sealed immediately with caps with Teflon®-lined septa. The test bottles were filled in sequence and placed on a rotating disc, allowing for complete mixing without agitation at room temperature (23 °C). At pre-determined time intervals (sampling more frequently at early times), the bottles were removed from the rotating disc and samples were extracted for VOCs, dissolved gases, acetylene and CSIA analyses.

VOCs analyses were performed using a Hewlett Packard 5890 gas chromatograph equipped with an Hnu Photoionization detector (PID) and an Hnu NSW-plot capillary column. Dissolved gases and acetylene were analyzed using a Hewlett Packard 5790 gas chromatograph equipped with a Flame ionization detector (FID) and a GS-Q plot capillary column.

Carbon isotope ratios of PCE, TCE, and cis-1,2-DCE were obtained using a gas chromatograph combustion isotope ratio mass spectrometer (GC-C-IRMS). The GC-C-IRMS system consisted of an Agilent 6890 GC (Agilent, Palo Alto, California) with a split/splitless injector, a Micromass combustion interface operated at 850 °C, a cold trap cooled to -100 °C using liquid nitrogen, and a Micromass IsoPrime isotope-ratio mass spectrometer (IsoPrime, Micromass, Manchester, UK). Solid Phase Micro Extraction (SPME) technique was used to extract and inject the contaminants. The SPME uses a fiber assembly and a holder equipped with a 75 µm Carboxen PDMA black fiber, which can effectively adsorb VOC at room temperature and desorb VOC at high temperature.

Chlorine isotope ratios were analyzed by a continuous flow-isotope ratio mass spectrometer equipped with gas chromatograph and a CTC analytics CombiPAL SPME autosampler as described by Shouakar-Stash et al. (2006).

All $^{13}\text{C}/^{12}\text{C}$ and $^{37}\text{Cl}/^{35}\text{Cl}$ ratios were reported in the delta notation ($\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$) referenced to the Vienna Peedee Belemnite (VPDB) and the Standard Mean Ocean Chloride (SMOC) standard, respectively.

The delta notation is defined as $\delta = (R_{\text{sample}}/R_{\text{reference}} - 1) \times 1000$, where R_{sample} and $R_{\text{reference}}$ are the carbon and chlorine isotope ratios of the aqueous sample and the respective standard. The precision for carbon and chlorine isotope analyses are ± 0.5 and $0.1 \pm \%$.

Isotope fractionation during VOC degradation under abiotic and biotic processes can be assessed using the Rayleigh equation. The equations for ^{13}C and ^{37}Cl are defined by:

$$1000 \cdot \ln \frac{\delta^{13}\text{C}_s + 1000}{\delta^{13}\text{C}_0 + 1000} = \varepsilon \ln f; 1000 \cdot \ln \frac{\delta^{37}\text{Cl}_s + 1000}{\delta^{37}\text{Cl}_0 + 1000} = \varepsilon \ln f$$

where $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ are the carbon and chlorine isotope ratios of the reactant at a remaining fraction f and $\delta^{13}\text{C}_0$ and $\delta^{37}\text{Cl}_0$ are the initial carbon and chlorine isotope ratios of the reactant.

Results and Discussion

Batch Experiment—VOCs Patterns

TCE was the main compound present in the groundwater used in the experiment (19.2 mg/L) along with concentrations of PCE (3.5 mg/L), cis-1,2-DCE (2.0 mg/L) and VC (0.12 mg/L). An initial decrease in TCE, PCE, cis-1,2-DCE and VC concentration was observed during the first 9 h of the experiment (Figure 2). However, the production of lower chlorinated compounds, ethene or ethane was not observed, suggesting that VOC adsorption onto the iron fillings (Figure 2) was the initial removal mechanism. After 9 h, changes in both concentrations and molar distribution were observed, including generation of products such as cis-1,2-DCE, ethene and ethane. Cis-1,2-DCE concentrations increased during the interval of 12 to 50 h, as a function of TCE degradation. After a period of 50 h, cis-1,2-DCE started to degrade, producing mainly ethene and ethane. Vinyl chloride also degraded over time with no apparent production from TCE and cis-1,2-DCE degradation. The main degradation products observed during the experiment were ethene and ethane. Ethene was produced over the first 120 h of experiment and then decreased, likely because of its conversion to ethane. Ethane was the final reaction product obtained and tended to be produced throughout the experiment. No acetylene was detected in any of the samples analyzed throughout the experiment.

Although acetylene was not detected during the experiment, β -elimination and hydrogenation were suggested to be the dominant degradation pathways, as ethene and ethane were formed concomitantly with the decrease of PCE, TCE, and cis-1,2-DCE (Arnold and Roberts 2000). It is suggested that acetylene was formed by the degradation of TCE and cis-1,2-DCE and rapidly transformed to ethene and ethane. Hydrogenolysis was also inferred to be acting as a minor pathway, as cis-1,2-DCE was produced due to TCE degradation.

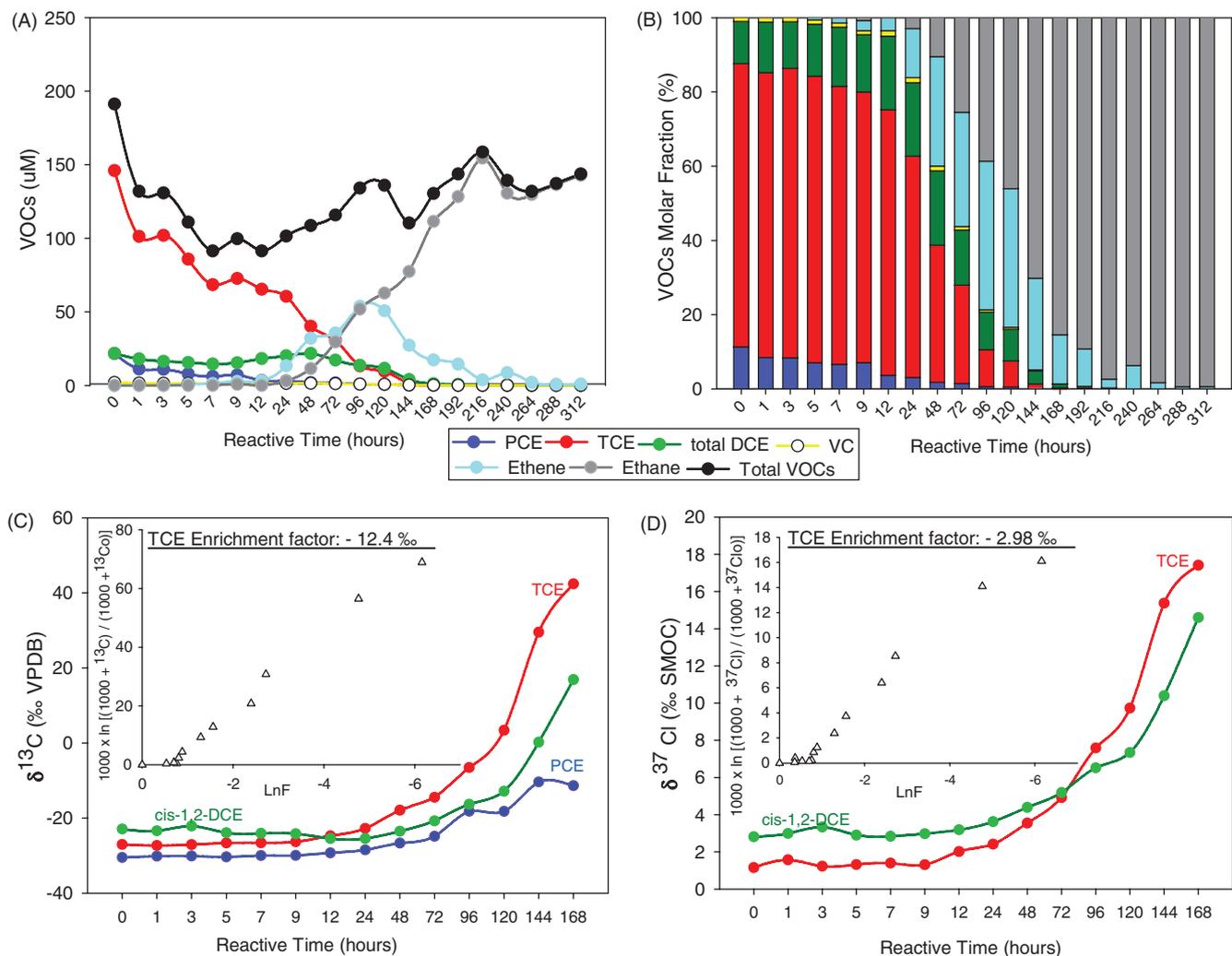


Figure 2. Laboratory study results. (A) VOCs (µM) over time; (B) VOC's molar fraction (%) over time; (C) $\delta^{13}\text{C}$ of TCE, PCE and cis-1,2-DCE over time and TCE enrichment factor "ε" calculation; (D) $\delta^{37}\text{Cl}$ of TCE, PCE and cis-1,2-DCE over time and TCE enrichment factor "ε" calculation.

Batch Experiment— $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ Data

No significant isotopic fractionation was observed for TCE, PCE, and cis-1,2-DCE during the first 9 h of the experiment, where a decrease in VOCs concentration was also observed (Figure 2). This early time pattern confirms VOC adsorption into the iron fillings during the early phase of the experiment (Slater et al. 2000; Schüth, et al. 2003a, 2003b).

A significant $\delta^{13}\text{C}$ enrichment pattern changing from -30.5 to -10.4 ‰ was observed for PCE. A $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ enrichment of 69.4 and 16.5 ‰, respectively, was observed during the abiotic reduction of TCE. A carbon isotope enrichment factor of -12.4 ‰ was calculated for the TCE using the Rayleigh equation, which is consistent with other values reported in the literature for abiotic reduction of TCE with ZVI (-10.1 ‰ by Schüth et al. 2003a and -16 ‰ by Slater et al. 2002). Regarding ^{37}Cl data, an enrichment factor of -2.98 ‰ for TCE was calculated during the abiotic reaction. To our knowledge, this is the first paper to report a $\delta^{37}\text{Cl}$ enrichment factor during abiotic degradation with ZVI.

Regarding cis-1,2-DCE, an enrichment of 39.8 and 11.8 ‰ for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$, respectively, was observed during the experiment. As presented in Figure 2C, over the first 9 h (i.e., where sorption only occurred), the $\delta^{13}\text{C}$ signature of cis-1,2-DCE was found to be more enriched than TCE, which represents the isotope composition of the site groundwater near one of the VOC sources. After 9 h, as the initial abiotic reduction of TCE started, the produced cis-1,2-DCE becomes more depleted in $\delta^{13}\text{C}$ than the TCE. As the reaction proceeded and cis-1,2-DCE was also degraded, the ^{13}C enrichment trend followed a parallel trend to the TCE $\delta^{13}\text{C}$ pattern, but the cis-DCE was always more depleted in ^{13}C than the TCE. Similar trends were observed for the $\delta^{37}\text{Cl}$ data of TCE and cis-1,2-DCE, during a period of 72 h. This parallel ^{13}C enrichment pattern, where the cis-DCE is more depleted than the TCE, has been reported previously during abiotic reduction of TCE and cis-1,2-DCE (Elsner et al. 2008).

In contrast, as demonstrated by several authors (Hunkeler et al. 1999; Bloom et al. 2000; Sherwood Lollar et al. 2001), during sequential biodegradation, the ^{13}C signature of

cis-1,2-DCE (sequential product) is initially more depleted compared to TCE (reactant). If the sequential degradation is incomplete (i.e., stalling at cis-1,2-DCE), cis-1,2-DCE will tend to get more enriched in ^{13}C over time, approaching the original isotope composition of TCE. On the other hand, if the degradation reaction proceeds beyond cis-1,2-DCE (generating VC), the carbon isotope composition of cis-1,2-DCE would become more enriched with respect to the original TCE signature. As no biodegradation microcosm experiment was carried out with aquifer materials from the study site, it is important to mention that the absolute value

of the carbon isotope fractionation factors for biodegradation of TCE and cis-DCE can change from site to site but the isotope trends typical of biodegradation between TCE and cis-DCE does not change (Hunkeler et al. 1999; Bloom et al. 2000; Slater et al. 2001).

Field Results

Upgradient from the PRB

Table 1 summarizes the VOC concentrations and the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ data collected during two events at the site.

Shallow aquifer horizon										
Parameters	Upgradient ¹						Downgradient ¹			
	WCC-6		PRB-1A		PRB-2A		PRB-3A		PRB-4A	
	2007	2008	2007	2008	2007	2008	2007	2008	2007	2008
TCE ($\mu\text{g/L}$)	30,000	30,000	20,000	8,800	28,000	50,000	5,000	13,000	45,000	6,200
TCE $\delta^{13}\text{C}$ (‰)	-27.1	-27.0	-27.1	-26.7	-27.2	-25.7	-25.5	-25.4	-27.1	-26.9
Average TCE $\delta^{13}\text{C}$ (‰)	-27.1		-27.0		-26.5		-25.5		-27.0	
TCE $\delta^{37}\text{Cl}$ (‰)	2.0	2.9	1.7	0.7	2.1	1.0	2.0	2.2	1.9	1.74
Average TCE $\delta^{37}\text{Cl}$ (‰)	2.5		1.2		1.6		2.1		1.8	
c-DCE ($\mu\text{g/L}$)	1,500	2,200	1,700	2,100	2,900	9,800	4,000	5,400	1,400	340
c-DCE $\delta^{13}\text{C}$ (‰)	-24.6	-24.1	-25.4	-24.6	-22.7	-20.0	-19.4	-18.3	-24.5	-21.9
Average c-DCE $\delta^{13}\text{C}$ (‰)	-24.4		-25.0		-21.4		-18.9		-23.2	
c-DCE $\delta^{37}\text{Cl}$ (‰)	3.9	3.3	3.4	3.4	4.6	4.2	5.7	4.9	3.7	3.4
Average c-DCE $\delta^{37}\text{Cl}$ (‰)	3.6		3.5		4.6		5.4		3.5	
Vinyl Chloride ($\mu\text{g/L}$)	38	98	210	130	150	1,800	1,600	2,400	86	29
TOC (mg/L)	NA	NA	19	12	4.6	14	6.8	18	4.8	1.4
Intermediate aquifer horizon										
Parameters	Upgradient ¹				Downgradient ¹					
	PRB-1B		PRB-2B		PRB-3B		PRB-4B			
	2007	2008	2007	2008	2007	2008	2007	2008		
TCE ($\mu\text{g/L}$)	1,200	7,400	330	220	17,000	10,000	19,000	22,000		
TCE $\delta^{13}\text{C}$ (‰)	-26.5	-27.1	-24.5	-24.3	-23.9	-26.7	-27.9	-28.3		
Average TCE $\delta^{13}\text{C}$ (‰)	-26.8		-24.4		-25.6		-28.1			
TCE $\delta^{37}\text{Cl}$ (‰)	2.0	1.7	2.8	2.2	2.6	1.5	1.7	1.7		
Average TCE $\delta^{37}\text{Cl}$ (‰)	1.9		2.5		2.1		1.7			
c-DCE ($\mu\text{g/L}$)	620	2,900	310	130	5,900	3,300	440	820		
c-DCE $\delta^{13}\text{C}$ (‰)	-22.5	-17.7	-16.2	-16.2	-30.5	-17.6	-23.3	-22.2		
Average c-DCE $\delta^{13}\text{C}$ (‰)	-20.1		-16.2		-24.1		-22.7			
c-DCE $\delta^{37}\text{Cl}$ (‰)	4.1	5.0	5.8	4.5	3.1	4.1	4.9	4.5		
Average c-DCE $\delta^{37}\text{Cl}$ (‰)	4.5		5.1		3.6		4.67			
Vinyl Chloride ($\mu\text{g/L}$)	480	1,600	470	190	340	860	ND	ND		
TOC (mg/L)	52	54	100	59	8.0	55	3.0	2.1		

NA, not analyzed; ND, not detected.

¹Position related to the PRB.

Well WCC-6, which represents a shallow upgradient well near one of the VOC sources at the site, contained 30 mg/L TCE concentration, along with cis-1,2-DCE, 2.2 mg/L and VC, 0.098 mg/L (Figure 3A and Table 1). The TCE is characterized by $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of -27.1 and 2.5‰ (mean values), respectively (Table 1). These values seem to be enriched when compared to typical values published in literature for TCE (van Warmerdan et al. 1995), indicating that TCE has been partially affected by natural biodegradation in this part of the aquifer. The $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ signatures of cis-1,2-DCE (-24.3 and $+3.6\text{‰}$, respectively) in the upgradient groundwater are more enriched than TCE, indicating that TCE biodegradation extends beyond cis-1,2-DCE, generating VC. This pattern is in agreement with the VOC molar distribution.

The groundwater collected in monitoring well PRB-1A, which should represent shallow groundwater reaching the PRB, is characterized by high TCE and cis-1,2-DCE concentrations (TCE—8.8 mg/L and cis-1,2-DCE—2.1 mg/L) (Table 1). The geochemical data (Figure 3B) indicated aerobic conditions in this area (high nitrate), suggesting that the local redox conditions are not suitable for complete

biodegradation of TCE. The $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of -27 and $+1.2\text{‰}$, respectively, indicated also that TCE was not affected significantly by biodegradation (Figure 3C and 3D). However, similar to well WCC-6, the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ signatures of cis-1,2-DCE (-25.0 and $+3.4\text{‰}$) were found to be more enriched than those observed for TCE. This pattern was observed by the VOC's molar distribution (Figure 3A), where a slight increase of daughter products (cis-1,2-DCE and VC) were found to occur indicating that even though limited conditions for TCE reductive dechlorination exist, degradation products are found and probably caused by biodegradation upgradient of the area where PRB-1A is located.

In the intermediate aquifer (Figure 4A), VC and ethene were detected in well PRB-1B, representing over 60% of the total VOC concentrations. High concentrations of TOC (>50 mg/L), ferrous iron and methane and low concentrations of nitrate and sulfate were detected when compared to the other wells, suggesting that sulfate-reducing to methanogenic geochemical conditions were occurring upgradient from the PRB (Figure 4B). Moreover, enriched $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ signatures of TCE (-26.9 and 1.9‰) were

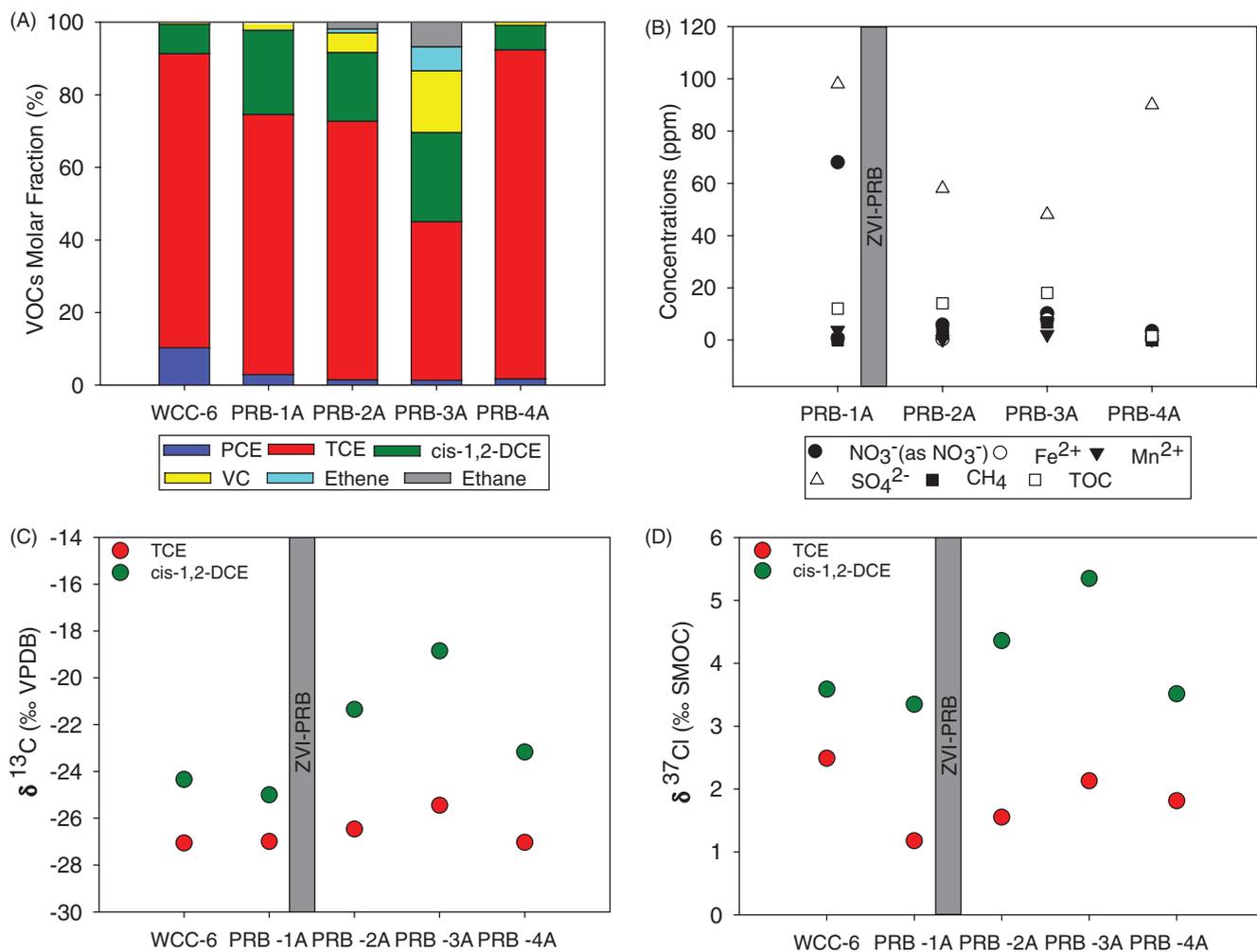


Figure 3. Field results—shallow aquifer. (A) VOC's molar fraction (%) (July 2008); (B) REDOX parameters (mg/L) (July 2008); (C) $\delta^{13}\text{C}$ (‰ VPDB) mean values (July 2007 and 2008) of TCE and cis-1,2-DCE; (D) $\delta^{37}\text{Cl}$ (‰ SMOC) mean values (July 2007 and 2008) of TCE and cis-1,2-DCE; *PRB-1 is located 12 m upgradient from the PRB, PRB-2A and PRB-3A are located 3 m downgradient and PRB-4A is located 25 m downgradient from the PRB.

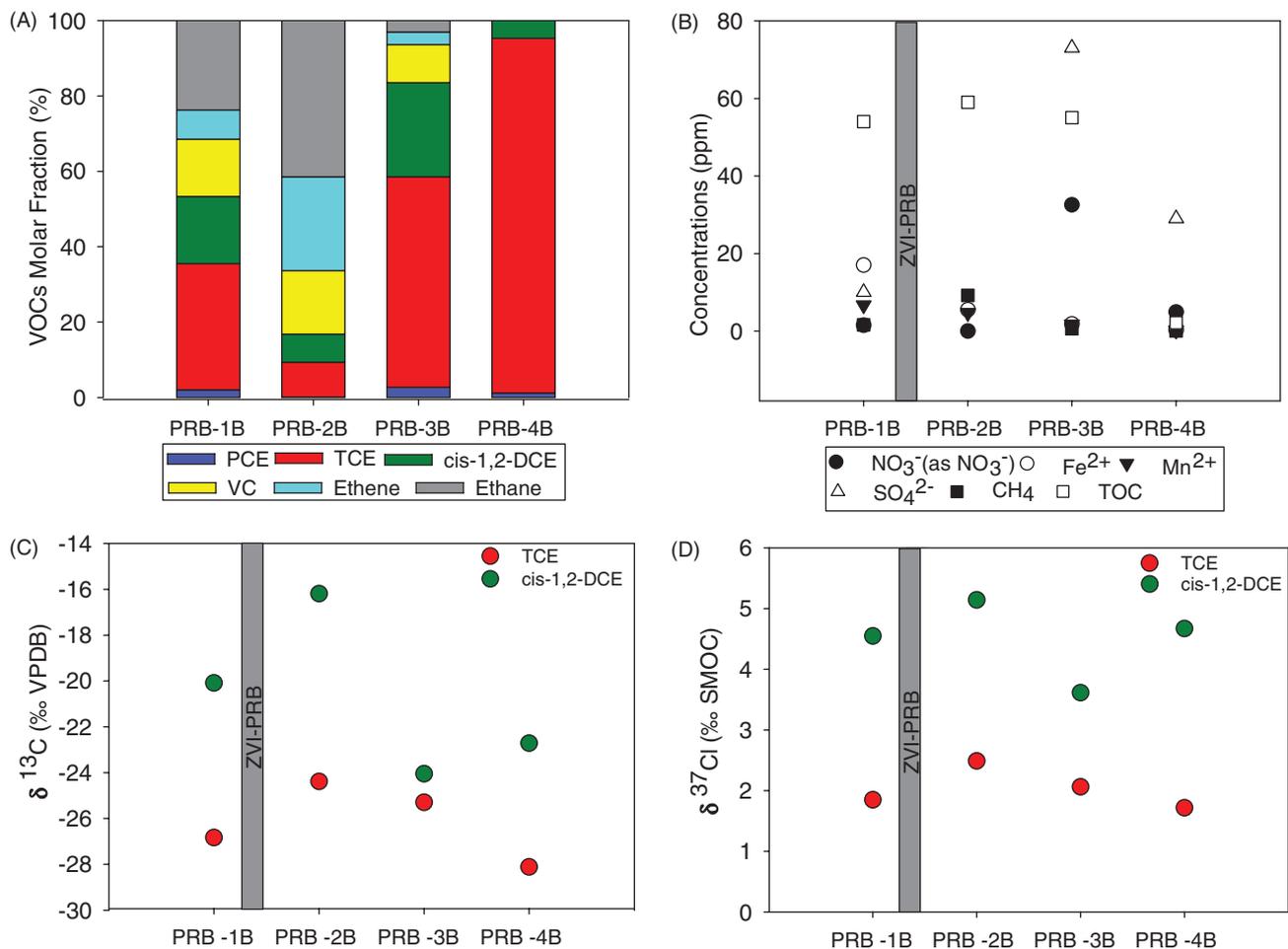


Figure 4. Field results—intermediate aquifer. (A) VOC's molar fraction (%) (July 2008); (B) REDOX parameters (mg/L) (July 2008); (C) $\delta^{13}\text{C}$ (‰) mean values (July 2007 and 2008) of TCE and cis-1,2-DCE; (D) $\delta^{37}\text{Cl}$ (‰) mean values (July 2007 and 2008) of TCE and cis-1,2-DCE; *PRB-1B is located 12 m upgradient from the PRB, PRB-2B and PRB-3B are located 3 m downgradient and PRB-4B is located 25 m downgradient from the PRB.

also observed to occur (Figure 4C and 4D) corroborating the concentration patterns previously observed. Following the same trend, very enriched values of $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ of cis-1,2-DCE (−20.1 and 4.54‰, respectively) were also observed to occur in the well PRB-1B, when compared to TCE. This pattern is in agreement to the molar fraction distribution, where the degradation pathway continued through VC, ethene and ethane. Therefore, based on the cross-evaluation of the VOCs, inorganic and CSIA data, it is suggested that some of the biodegradable guar gum carrier may have deviated from its planned azimuth, following more permeable pathways upgradient of the PRB, reaching the area of the well PRB-1B.

Downgradient from the PRB

Although high TCE concentrations were persistent downgradient from the PRB (PRB-2A—50 mg/L; PRB-3A—13 mg/L; PRB-2B—0.2mg/L; PRB-3B—10mg/L) (Table 1), the VOC's molar fraction showed an increase in the degradation products of TCE for both shallow and intermediate aquifer horizons (Figures 3A and 4A).

On the basis of the geochemical data, reducing conditions are found to exist in the shallow aquifer horizon, as

presented in Figure 3B. High concentrations of TOC, ferrous iron and methane and low concentrations of nitrate and sulfate were detected in the groundwater collected in well PRB-3A, indicating that at least sulfate-reducing geochemical conditions likely exist. Iron-reducing conditions are inferred to occur in the vicinity of well PRB-2A. As shown in Figure 3A, TCE represents about 20% of the total VOCs in well PRB-3A and 75% for well PRB-2A. This is strong evidence that TCE was likely degrading and suitable geochemical conditions for microbial reductive dechlorination exist in this area. Furthermore, an enrichment of the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ of TCE and cis-1,2-DCE was detected in monitoring wells PRB-2A (TCE: −26.5 and +1.6‰; cis-1,2-DCE: −21.4 and +4.4‰) and PRB-3A (TCE: −25.5 and +2.1‰; cis-1,2-DCE: −18.9 and +5.4‰), when compared to the upgradient well PRB-1A (Figure 3C and 3D). This pattern also supports VOC concentration data, indicating that TCE biodegradation was likely occurring downgradient of the PRB. In agreement with the VOC molar distribution (Figure 3), the fact that the isotope signatures of cis-1,2-DCE were more enriched than TCE in both wells is strong evidence that TCE degradation is extending beyond cis-1,2-DCE. These indicate that biotic processes are the

predominant pathways involved in degradation of VOCs in the shallow aquifer, downgradient from the PRB.

It is suggested that the input of high concentrations of TOC, that is, the breakdown product of the guar used for the iron fluid emplacement, could have enhanced the microbial activity in the vicinity of monitoring wells PRB-2A and PRB-3A. The abundance of additional electron donors in the aquifer could have increased the activity of the local microbial community responsible for degradation of TCE. Relative high concentration of TOC associated to guar has been reported in the literature (Vidumsky et al. 2002; Crane et al. 2004).

Further downgradient of the wells near the PRB, significant concentrations of TCE were detected in well PRB 4A (6.2 mg/L) and no evidence of TCE degradation was observed to occur based on the VOC molar distribution (Figure 3A) and the inorganic data (Figure 3B). Very similar $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ signatures of TCE and cis-1,2-DCE were observed between monitoring wells WCC-6 and PRB-4A (located near the known source area and further downgradient from the PRB). This pattern indicates that the VOCs observed in the downgradient well PRB-4A have not undergone any degradation process associated with the PRB installation. Since a heterogeneous distribution of the iron fillings occurred (Fiorenza and Christie 2008), hydraulic bypass around the PRB is suggested and the VOCs were not affected by either biotic or abiotic degradation processes associated with the PRB. An alternative hypothesis is that due to the very low horizontal hydraulic gradients that are found to exist in the area, the effects of the PRB could still not be observed far downgradient from the PRB in the time frame of sample collection following construction. This hypothesis assumes that the groundwater travel time which crosses the PRB is slower than the 6 years of existing monitoring data and therefore, more time would be needed in order to observe concentrations changes over 20 m downgradient from the PRB. However based on estimated groundwater velocity of 7 to 17 m/year at the study site, this hypothesis tends to be discarded. Finally, a third hypothesis is suggested, which involves back-diffusion from aquifer matrix in the established downgradient well, which could also explain the observed isotopic pattern. An analysis of sorbed VOC's in the aquifer sediments will be a good test of this hypothesis.

Strong evidence of TCE and cis-1,2-DCE degradation was also observed in the intermediate aquifer. Well PRB-2B exhibited a large decrease in TCE concentrations followed by a large increase of VC, ethene and ethane. Additionally, similar to well PRB-1B, high concentrations of TOC (>50 mg/L), ferrous iron and methane and low concentrations of nitrate and sulfate were observed to occur, therefore indicating that sulfate-reducing to methanogenic geochemical conditions are locally occurring. Increased levels of TCE reductase and VC reductase were detected in the downgradient PRB wells (S. Fiorenza, personal communication) as compared to the upgradient wells, further supporting the conclusion that increased electron donor concentration (guar) increased the activity of dechlorinating microorganisms.

In agreement with the VOC and inorganic data, the isotope data showed enriched $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values for TCE

(-24.4 and +2.5‰) and cis-1,2-DCE (-16.2 and +5.1‰) (Figure 4D and 4E). The large enrichment observed for both $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ of cis-1,2-DCE, when compared to TCE, is also indicative that cis-1,2-DCE is largely degraded, which is agreement with the relative high percentage of VC in the total VOC mass. A different trend was observed at well PRB-3B, located 3 m downgradient from the PRB, parallel to well PRB-2, where high TCE concentrations were still found to persist. TCE daughter products were also detected, accounting for approximately 40% of the total VOCs (Figure 4A). Although high TOC concentrations were detected (Figure 4B), more aerobic conditions were assumed to exist since high concentrations of nitrate and sulfate and low concentrations of manganese, ferrous iron and methane were detected (Figure 4B). These conditions are however, not assumed to be suitable for the complete microbial reductive dechlorination of TCE and cis-1,2-DCE.

An enrichment of TCE values of $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ (-25.6 and +2.1‰) was observed to occur (Figure 4C and 4D), when compared to the upgradient well PRB-1B and therefore, indicating some TCE degradation. Since VC, ethene and ethane were detected in these wells and very reducing geochemical conditions are needed for the complete reductive dechlorination of TCE, abiotic processes are assumed to be potentially affecting TCE degradation. An unpublished study documented the presence of acetylene in well PRB-3B and the upgradient well PRB-1B. This pattern could not, however, be confirmed by changes in groundwater pH or other geochemical tracers, such as decreasing alkalinity.

Regarding the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ signatures of cis-1,2-DCE for well PRB-3B, a different pattern was observed, as shown in Figure 4D. According to the data, the mean $\delta^{13}\text{C}$ value of cis-1,2-DCE was found to be more depleted when compared to other wells, and slightly enriched than the TCE. High data variability was observed between sampling rounds. During the groundwater sampling event conducted in July 2007, the $\delta^{13}\text{C}$ of cis-1,2-DCE was approximately 7‰ more depleted than TCE. In July 2008, however, a change in the pattern was observed, where the $\delta^{13}\text{C}$ of cis-1,2-DCE was already 9‰ more enriched than $\delta^{13}\text{C}$ of TCE. A high variability of the $\delta^{37}\text{Cl}$ was also observed to occur, however, the pattern was always found to be more enriched than the TCE.

Based on the evaluation of VOCs and inorganic results, it is suggested that the more depleted signatures of $\delta^{13}\text{C}$ of cis-1,2-DCE detected in July 2007 could be associated with the abiotic degradation of TCE. The shift in the isotopic composition, could however, be associated with the mass flux of enriched cis-1,2-DCE biotically originated upgradient. An alternative hypothesis relies on the fact that cis-1,2-DCE could have been still formed as a consequence of biodegradation in July 2007, and already degrading in July 2008, enhanced by the increasing of TOC concentrations (Table 1).

Further downgradient, no significant evidence of TCE degradation was found based on the VOCs and inorganic results (Figure 4A and 4B). This scenario is also supported by the more depleted values of $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ signatures of TCE and cis-1,2-DCE observed between PRB-4B and the other wells.

Conclusions

The role of abiotic and biotic processes on the degradation of TCE at the study site was evaluated comparing the isotope pattern obtained in the field with the isotope pattern obtained in abiotic laboratory experiments and biotic data reported in the literature. The abiotic experiment performed using the site groundwater showed $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of cis-1,2-DCE consistently more depleted than the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of TCE during the entire experiment when both compounds were present. This is in agreement with data reported in similar abiotic experiments (Elsner et al. 2008). In the field data, large differences between the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ of TCE and cis-1,2-DCE were observed. In the majority of the wells where TCE was found to be degrading and a large amount of degradation products were detected, the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ of cis-1,2-DCE were much more enriched to those observed for TCE. These patterns are not in agreement to those observed during the abiotic experiment and based on the observed field redox parameters and biodegradation isotopic trends for TCE and cis-DCE (Hunkeler et al. 1999; Bloom et al. 2000; Sherwood Lollar et al. 2001; Slater et al. 2001), it is suggested that microbial reductive dechlorination of TCE is playing a major role of TCE degradation upgradient and downgradient of the PRB.

The results obtained in this study indicated that significant biodegradation is likely to be occurring at the study site in addition to the expected abiotic degradation. It is suggested that high levels of TOC, produced by the breakdown of the injected gel, could have persisted in the local aquifer, maintaining high concentrations of electron donors over a long period of time. As a consequence, an enhancement of the microbial community is suggested to have occurred, increasing the biodegradation capacity in the local aquifer in the vicinity of the PRB. The aquifer geochemistry supported this hypothesis, since suitable reducing conditions for VOC's degradation were detected in some of the areas where TCE was degraded. CSIA field results, when compared to the expected site-specific abiotic pattern, have also shown strong evidence to support the role of biodegradation as a major process involved in the attenuation of TCE in the vicinity of the PRB.

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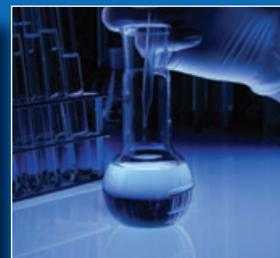
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