Ground Water Monitoring&Remediation

Trichlorofluoroethene: A Reactive Tracer for Evaluating Reductive Dechlorination in Large-Diameter Permeable Columns

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Abstract

Trichlorofluoroethene (TCFE) was used as a reactive tracer to determine the in situ rate of reductive dechlorination in treatment zones impacted by three large-diameter permeable columns (LDPCs) that were installed at a trichloroethene (TCE)–contaminated site. The LDPCs were part of a pilot study to evaluate the effectiveness of hydrogen, lactate, and zero-valent iron for remediating TCE-contaminated ground water. The rate of TCFE reductive dechlorination was determined for each LDPC by means of push-pull tests conducted in each treatment layer. In addition, the distribution of TCFE's lesser chlorinated transformation products was determined. The rates of TCFE reductive dechlorination ranged from 0.05/d to 0.20/d and corresponded to half-lives ranging from 3.5 to 13.9 d. *cis*-Dichlorofluoroethene was the dominant transformation product detected in all the tests, which is consistent with the findings from pilot tests conducted in the LDPCs prior to the TCFE push-pull tests. *cis*-Chlorofluoroethene (CFE) and 1,1-CFE also were detected and indicate the potential for vinyl chloride to form under all treatment regimes. Significant production of fluoroethene (FE), the analog of ethene, was observed for only one of the hydrogen treatments. Unambiguous and sensitive detection of the lesser chlorinated products, such as CFE and FE, is possible because TCFE and its transformation products are not found in the background ground water at contaminated sites. Good agreement between the rates and transformation product profiles for TCFE and TCE in both field and laboratory experiments indicates the suitability of TCFE as a surrogate for predicting the rates of TCE reductive dechlorination.

Introduction

Trichloroethene (TCE) is the most frequently detected organic contaminant in ground water (Domenico and Schwartz 1990) and is detected in one-half to one-third of the Superfund sites in the United States (Richtel 2003), and several in situ remediation strategies are being used to clean up TCE-contaminated ground water. Anaerobic transformation of TCE by indigenous or introduced microorganisms is one commonly used approach (Bellapragada et al. 1997; Major et al. 2002). Under anaerobic conditions, TCE is transformed to one or more less-chlorinated products following a well-defined pathway (Figure 1).

The microbially mediated transformation of TCE may result in the accumulation of *cis*-dichloroethene (*cis*-DCE) or vinyl chloride (VC), with no ethene production (Middeldorp et al. 1999; McCarty 1997). The accumulation of VC is particularly problematic as it is a known neurotoxin and has the lowest drinking water standard (2 µg/L) of all the TCE transformation products (U.S. EPA 1996; Squillace et al. 1999). It is important to establish the likelihood of VC production when evaluating or selecting remedial approaches because the persistence of VC and *cis*-DCE may determine the acceptability of a remedial design (Arnold and Roberts 2000).

Anaerobic transformations of TCE have been observed in a wide variety of laboratory and field studies. A variety of chemical amendments have been investigated in laboratory and field studies as a means for enhancing the rates of reductive dechlorination (Lee et al. 1998). Electron donors including lactate (Fennel et al. 1997; Song et al. 2002) and hydrogen (Bellapragada et al. 1997; Cupples et al. 2004; Haston and McCarty 1999; Pon et al. 2003) were used successfully in laboratory studies to promote reductive dechlorination. However, the rate and extent of dechlorination reactions and the distribution of transformation products appear to vary from site to site and with the type, concentration, and method of delivery of the selected electron donor(s).

Permeable reactive barriers containing zero-valent iron are another approach for remediating TCE-contaminated ground water (Johnson et al. 1996; Orth and Gillham 1996;

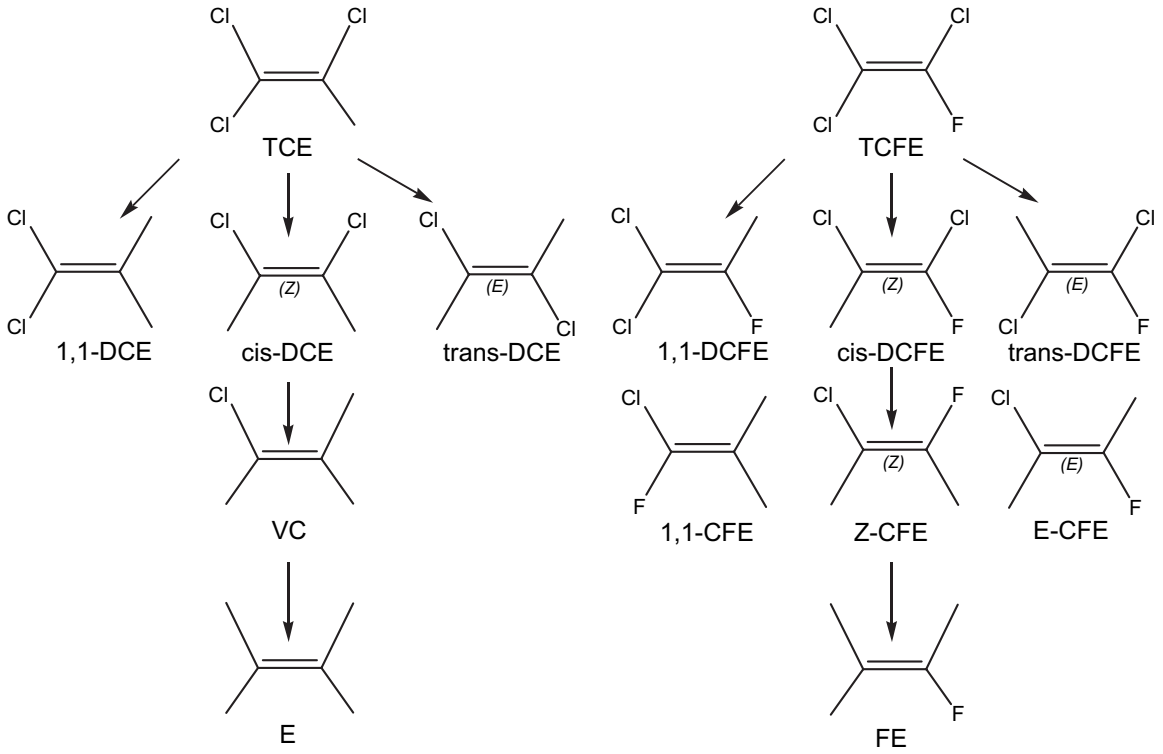

Figure 1. Analogous reductive dechlorination pathways for TCFE and TCE.

Vogan et al. 1999; Puls et al. 1999; Farrell et al. 2000; Scherer et al. 2000; Arnold and Roberts 2000). Zero-valent iron mediates TCE reductive dechlorination primarily by β elimination (Roberts et al. 1996; Arnold and Roberts 2000), which involves the production of chloroacetylene and acetylene as intermediates that are further transformed to ethene and ethane. In addition, TCE transformation in the presence of zero-valent iron also occurs, although to a lesser extent, by hydrogenolysis to form *cis*-, *trans*-, and 1,1-DCE, and VC (Arnold and Roberts 2000; Orth and Gillham 1996). Due to the dominance of the β-elimination reaction pathway, the formation and accumulation of lesser chlorinated products such as *cis*-DCE and VC is minimized (Arnold and Roberts 2000).

Regardless of the selected remediation approach, field methods are needed to monitor the progress of these reactions. In particular, there is a need for methods that may be used to quantify the in situ rates of these reactions so that overall treatment effectiveness can be evaluated, as well as the potential for the formation of unwanted transformation products. The conventional approach for quantifying transformation rates is to monitor changes with time in the concentration of TCE and its less-chlorinated transformation products along ground water flowpaths through the treatment layer (Buscheck and Alcantar 1995; Wiedemier et al. 1996). However, this approach may give ambiguous or misleading information because, in addition to potential chemical or microbially mediated reactions, the observed concentration changes may be caused by a combination of confounding factors including high and spatially variable initial concentrations of contaminants and their transformation products; poorly defined pore water velocities, flowpath lengths, and poorly defined dispersion coefficients; and the release of contaminants from poorly characterized nonaqueous phases (if present) (e.g., Martian et al. 2003).

Alternative methods are needed to obtain rates of biotransformation processes in the field. The concept of using stable carbon isotope ratios of TCE and transformation products was developed in laboratory (Bloom et al. 2000; Slater et al. 2001) and applied toward field studies where it was used to obtain qualitative evidence for TCE reductive dechlorination (Hunkeler et al. 1999; Song et al. 2002). While the use of stable carbon isotopes is appealing due to the structural similarity between the contaminant and its isotope, stable carbon isotopes have not been used to determine in situ rates of transformation.

Alternatively, reactive tracers or surrogates of TCE can be injected into contaminated ground water that flows through treatment layers. Chlorofluoroethenes (CFEs) such as trichlorofluoroethene (TCFE) are not widely used in industry and have not been reported as background contaminants in TCE-contaminated ground water. The presence of the fluorine "label" in TCFE and each of its transformation products allows for their unambiguous detection by gas chromatography/mass spectrometry (GC/MS) at trace levels (μM) in the presence of high (mM) and variable background concentrations of TCE and its transformation products. Unlike stable carbon isotopes that are prohibitively expensive, which precludes their injection into aquifers, TCFE is relatively inexpensive.

Laboratory microcosm studies (Vancheeswaran et al. 1999) indicated that under anaerobic conditions, the microbial transformations of TCE and TCFE proceed by an analogous series of reductive dechlorination reactions to form an analogous series of lesser chlorinated products

(Figure 1). Vancheeswaran et al. (1999) also reported that the rates for TCFE reductive dechlorination were within a factor of 0.3 to 2 of the rates for perchloroethene and TCE.

Hageman et al. (2001) performed a series of field push-pull tests with TCFE at a former chemical-manufacturing plant site. A push-pull test consists of the injection of a prepared test solution into an existing monitoring well, followed by the recovery of the test solution/ground water mixture from the same location. With the push-pull tests, they confirmed the findings of Vancheeswaran et al. (1999) by demonstrating that TCE and TCFE formed analogous transformation products in a well in which both TCE and TCFE were injected. Not only did TCFE and TCE form analogous products but the ratio of *cis*-DCE and *trans*-DCE was similar to that of *cis*-dichlorofluoroethene (DCFE) and *trans*-DCFE (Hageman et al. 2001). TCFE underwent reductive dechlorination at a sixfold higher rate than TCE. The higher observed rate obtained for TCFE may be due its higher concentration, which was 25 times greater than that of TCE (Hageman et al. 2001). Hageman et al. (in press) further demonstrated the utility of TCFE by using it at the same field site to quantify increases in the in situ reductive dechlorination rates after the sequential addition of fumarate as a chemical amendment.

Monitoring well installations and subsurface investigations began at the former chemical-manufacturing site in the early 1980s, and TCE and tetrachloroethene were detected in the deeper (C zone) layer at high concentrations (up to 3.1 mM). Measured contaminant concentrations, geochemical indicator data (Buscheck et al. 1997; Bennett et al. 2003c), and previous push-pull tests with TCFE (Hageman et al. 2001 in press) indicate that TCE transformations in the C zone are slow, electron donor limited, and may be inhibited by high sulfate concentrations. For these reasons, three large-diameter permeable columns (LDPCs) were installed as part of a pilot study in the deep layer in order to evaluate three in situ treatment approaches. Each LDPC was used to evaluate a separate remedial treatment including lactate, zero-valent iron, and hydrogen. The objective of this study was to quantify the rate and extent of TCFE transformation in each LDPC. No additional electron donor (e.g., lactate or hydrogen) was added to the LDPCs during the push-pull tests. The information obtained from these tests was then compared with information on the rate and extent of TCE transformations obtained from the pilot tests during which TCE and its transformation products were determined for samples from the test cells.

Materials and Methods

Site Description

Field tests were conducted at the site of a former chemical-manufacturing plant (Hageman et al. 2001). The water table lies within 3 m of the ground surface. There are two main water-bearing layers including the A zone (0 to 3 m below land surface) and the C zone (3 to 24 m below land surface). The C zone is characterized by alluvial fan deposits and is hydrologically isolated from the A zone because it underlies the bay mud. Within the C zone, a confined aquifer consisting of two silty-sand layers is present between 6.3 to 7.5 m (upper layer) and 8.5 to 10.4 m (lower layer) below land surface.

Large-Diameter Permeable Columns

The design of the LDPCs and pilot study involving the LDPCs is described in greater detail in Bennett et al. (2003a, 2003b, 2003c). The pilot study used three 0.9-m-diameter borings, each containing three 20.3-cm-diameter dual-screened wells, and eight 2.5-cm-diameter polyvinyl chloride (PVC) piezometers. The borings and inside materials are referred to as the LDPCs (Figure 2). The LDPCs were installed in a row perpendicular to ground water flow on 1.5-m centers. The LDPC concept was based on the findings of Wilson and Mackay (1995), who showed that

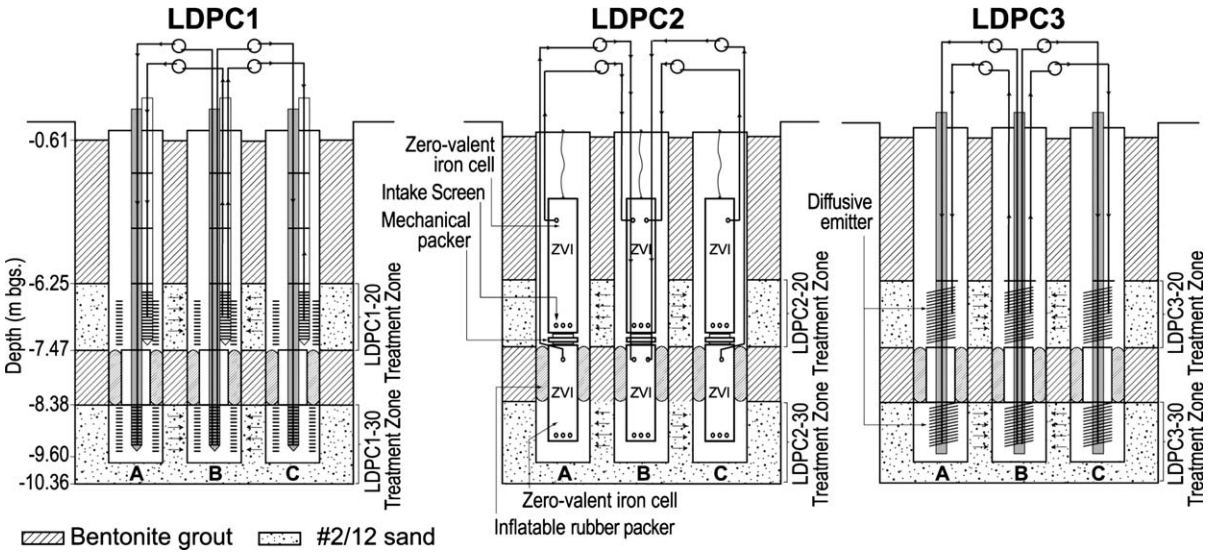

Figure 2. Typical construction details for LDPCs used in pilot study.

wells closely spaced in transects perpendicular to ground water flow could be used to create a permeable reactive barrier. Each LDPC contained two separate 0.9-m-diameter treatment layers that intercepted the two silty-sand layers of the C zone, one from ~6.3 to 7.5 m below ground surface and the other from ~8.4 to 10.4 m below ground surface. Annular seals made of bentonite and inflatable packers within each LDPC aid in minimizing mixing between the two treatment layers.

The treatment layers intercepted TCE-contaminated ground water, and three different treatment technologies were assessed during the LDPC pilot study: lactate addition in LDPC1 (Bennett et al. 2003b), zero-valent iron in LDPC2 (Bennett et al. 2003c), and direct hydrogen addition using diffusive emitters in LDPC3 (Bennett et al. 2003a). For the lactate treatment in LDPC1, three additions of yeast extract (~30 g per addition) and lactate were added to LDPC1 on January 29, 2002 (52 g lactic acid in 1 L); on March 4, 2002 (460 g lactic acid in 1 L); and on April 24, 2002 (1235 g lactic acid in 3 L) (Bennett et al. 2003b). The lactic acid and yeast extract were added quickly and mixed within each test cell. The test cells were then monitored for 100 d for TCE and its reductive dechlorination products.

LDPC2 consisted of six separate zero-valent iron cells, which were prepared and inserted into each of the three 20-cm casings, two cells per casing, the lower cell isolated by a packer from the upper cell (Connelly-GPM Inc., Chicago, Illinois) (Bennett et al. 2003c). The three cells in the shallow LDPC2 layer contained 35.8 kg of zero-valent iron each, and the cells in the deep layer of LDPC2 contained 19.8 kg each. The average residence time for the shallow layer in LDPC2 cell was calculated to be 170 min and for the deep layer in LDPC2 to be 94 min. The pH in LDPC2 was measured periodically in the effluent from the zero-valent iron cells and ranged from 6.4 to 8.1 in the shallow layer and 6.8 to 7.7 in the deep layer (January 31, 2002, to May 9, 2002). The pH of the sample with the highest measured concentration of Fe^{2+} (2 mM) was 6.8. Pretest pH was near neutral (6.7 and 6.9) in the LDPC2 shallow and deep layers, respectively. The increase in pH normally observed in the zero-valent iron barriers was not observed here, probably because the LDPC cells contained a lower mass of zero-valent iron relative to the mass of water and TCE pumped through the system. These low residence times, initial natural buffering capacity of the water, and high influent concentrations of TCE (which would have contributed protons from reduction) likely mitigated the pH increase from zero-valent iron corrosion.

For the hydrogen treatment in LDPC3, Waterloo Emitters™ were used for the controlled release of hydrogen into cells (Wilson and Mackay 1995). Yeast extract (63 g) was added to the LDPC3 test cells, and then the emitters were pressurized with 100% H_2 gas to 2.7 atm (Bennett et al. 2003a). The H_2 pressure was increased to 5.4 atm on day 85, and lactic acid also was added on day 85 to the lower layer of LDPC3.

Geochemical data collected during the LDPC pilot tests (December 2001 to May 2002) indicated that the remedial treatments were effective in changing ground water chemistry within both sand layers (Bennett et al. 2003a, 2003b, 2003c). In LDPC1, released lactate was rapidly used and production of acetate, propionate, and formate was observed; in LDPC3, hydrogen concentrations rapidly increased from ~4 to 120,000 nM; and in LDPC2, Fe(II) concentrations increased from ~1 to 110 mg/L (0.02 to 2.0 mM). Concentrations of TCE and its transformation products were also monitored during the pilot test in wells located upgradient and downgradient of each LDPC (Bennett et al. 2003a, 2003b, 2003c). Monitoring for the pilot study ceased after ~100 d of operation, ending on May 5, 2002.

Push-Pull Tests

Push-pull tests were conducted at the end of May 2002 in each LDPC. Prior to conducting the push-pull tests, ground water samples were collected from PVC piezometers that had been installed in both layers. The concentrations of TCE and its degradation products as well as electron acceptors in the background ground water are summarized in Table 1. For each push-pull test, concentrated aqueous solutions (250 L) of TCFE (100 μM) and bromide (1.3 mM) were injected into each single LDPC piezometer using a piston pump (Fluid Metering Inc., Oyster Bay, New York) and then recirculated (by injecting and extracting from piezometers at two depths within the sand layer) for ~24 h to obtain an approximately uniform initial TCFE concentration. Note that lactate was not added to the test solutions for LDPC1 tests, and no hydrogen was actively being injected into LDPC3 during the push-pull tests. Lactate (<0.11 mM) and hydrogen (0.12 to 0.23 mM) concentrations were low 3 weeks prior to the push-pull tests (Table 1). Samples of the test solution/ground water mixture were collected weekly for 12 weeks from one piezometer. Five replicate 40-mL samples were collected from each treatment zone using a peristaltic pump, without headspace in glass vials, and preserved with 0.75% (v/v) concentrated HCl for analysis of TCFE and its transformation products. Samples were shipped on ice and stored at 4°C until analyzed.

Analytical Methods

TCFE (97% minimum purity); 1,2-dichlorofluoroethene (DCFE; 98%, with a composition of 14% *cis*-DCFE and 86% *trans*-DCFE); 1,1-CFE (98%); and 1-chloro-2-fluoroethene (97% purity composed of 54% of *cis*-CFE and 46% of *trans*-CFE) were obtained from SynQuest Laboratories Inc. (Alachua, Florida) for use in field experiments or as external standards for laboratory analyses.

Concentrations of TCFE, DCFE, CFE, and fluoroethene (FE) in ground water samples were determined by purge-and-trap analysis, followed by detection and quantitation by GC/MS. The purge-and-trap system consisted of a Tekmar-Dohrmann 3100 Sample Concentrator and Aqua-Tek 70 Liquid Autosampler (Tekmar-Dohrmann, Cincinnati, Ohio). The system was operated with a 131.7-kPa system pressure, a 30.4-kPa trap pressure, a 6-min purge time, and a 3-min drying time. Analytes were desorbed from a Supelco Purge Trap K (Vocarb 3000; Supelco, Bellefonte, Pennsylvania) at 250°C for 1 min. The GC/MS system consisted of a Hewlett-Packard (Palo Alto,

Table 1
Background Constituent Concentrations in the LDPCs at the Conclusion of the Pilot Study[a]

	LDPC1 (shallow)[b]	LDPC1 (deep)[b]	LDPC2 (shallow)[c]	LDPC2 (deep)[c]	LDPC3 (shallow)[d]	LDPC3 (deep)[d]
TCE (μM)	7.2	28.2	8.4	312.0	159.8	327.3
cis-1,2-DCE (μM)	340.4	371.4	113.5	226.9	340.4	526.1
VC (μM)	2.4	1.1	0.9	1.8	3.4	5.6
Ethene (μM)	0.001	0.0004	0.043	0.139	0.001	0.001
Nitrate (mM)	ND[e]	ND	ND	ND	ND	ND
Sulfate (mM)	<0.02	0.20	5.2	6.04	3.20	3.02
Lactate (mM)	<0.01	<0.11	NA[f]	NA	<0.01	0.02
Hydrogen (mM)	2.7×10^{-4}	2.9×10^{-3}	2.0×10^{-5}	NA	0.12	0.23

[a]The push-pull tests were started 3 weeks after the conclusion of the pilot study.
[b]LDPC1 received lactate in both the shallow and deep zones.
[c]LDPC2 contained zero-valent iron in both the shallow and deep zones.
[d]LDPC3 received hydrogen in both the shallow and deep zones.
[e]ND = $<6 \times 10^{-4}$ mM.
[f]NA, not analyzed.

California) model 5890 GC and 5972 series Mass Selective Detector. Chromatographic separations were performed on an Agilent Technologies (Folsom, California) GS-Gaspro 60-m × 0.32-mm × (film thickness is proprietary) column. The MS was operated in selected ion-monitoring mode. The ions used for analyte quantitation and confirmation are given in Table 2; 1-chlorobutane served as the internal standard. For selected samples, the identities of TCFE and its degradation products were confirmed by comparing their spectra obtained in full-scan mode to that of authentic standards. The quantitation limit for all analytes determined by purge-and-trap GC/MS (defined as the concentration that gave signal/noise $\geq$10) was 0.005 μM.

Data Analysis

Concentration data for TCFE and its transformation products were interpreted using the "forced mass balance" data processing technique described by Hageman et al. (2003). In this technique, measured CFE concentrations are multiplied by their corresponding organic matter/water distribution coefficients (K_{om}), the fraction of organic matter (0.01), and the volume of aquifer solids to compute an estimated sorbed concentration. It should be noted that rate estimates reported subsequently were not sensitive to the fraction of organic matter used in these calculations (Hageman et al. 2003).

Table 2
Quantitation and Qualifier Ions Used for the Analysis of TCFE and its Transformation Products

Analyte	Quantitation Ion	Qualifier Ions
TCFE	148	113, 152
cis-, *trans*-, and 1,1-DCFE	114	81, 116
E-, Z-, and 1,1-CFE	80	45, 82
FE	46	26, 45
1-Chlorobutane (internal standard)	56	27, 41

K_{om} values of 90.5, 33.5, and 12.2 were obtained for TCFE, DCFE, and CFE, respectively, from the Estimation Program Interface Suite (Syracuse Research Corporation 2000). The total (aqueous plus sorbed) concentration of each analyte was then divided by an adjustment factor, which is defined as the sum of the total concentration of TCFE and its transformation products divided by the total TCFE in the injected test solution. Rates of TCFE transformation to DCFE over the 80-d test period were calculated by nonlinear regression. Additional details are in Hageman et al. (2003).

Results and Discussion

LDPC1–Lactate Addition

Reductive dechlorination in the LDPC1 shallow and deep treatment layers was demonstrated by the TCFE push-pull tests. Transformation of TCFE to lesser chlorinated products was detected in both the shallow and deep depths in all the three LDPCs. In LDPC1, which received lactate during the pilot study, TCFE was transformed to DCFE, CFE, and FE in the tests conducted in the shallow and deep sand layers (Figure 3). The predominant transformation products in the shallow layer were *cis*-DCFE (37.6%), followed by E-CFE (36.2%) and 1,1-CFE (15.6%), while only 2.1% consisted of FE (Table 3). In the deep layer, *cis*-DCFE (62.2%) was the dominant product, followed by Z-CFE (15.6%) and only 0.2% of FE (Table 3). The rate of TCFE disappearance was 0.05/d for the push-pull tests in the shallow and deep levels, and the estimated half-life was 13.9 d (Table 4).

The rate of TCFE reductive dechlorination and the transformation product distribution obtained for the push-pull tests conducted in the LDPCs was compared to those obtained in previous studies of other C-zone wells. The rates obtained for the lactate pretreated LDPC1 layers (0.05/d) were similar to those achieved after three successive additions of fumarate to three C-zone wells (0.05/d to 0.15/d) (Hageman et al. 2004), which was above the

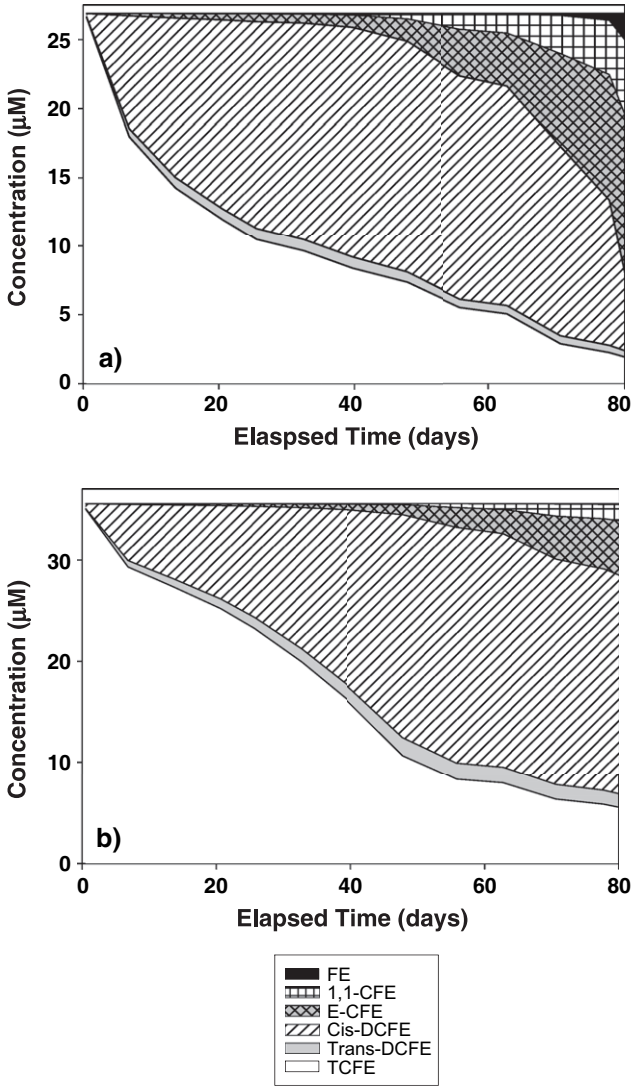

Figure 3. In situ transformation of the injected TCFE in upper (a) and lower (b) silty-sand layers in LDPC1 (lactate addition).

highest background rate (0.017/d) determined for C-zone wells in the vicinity of the LDPCs (Hageman et al. 2001). Lactate pretreatment of LDPC1 resulted in the conversion of TCFE to a greater number of lesser chlorinated transformation products (e.g., CFE and FE) beyond that observed for the background tests (Hageman et al. 2001) or after fumarate additions (Hageman et al. 2004). This finding that lactate treatment increases apparent rates of in situ TCFE reductive dechlorination is consistent with the observation of Song et al. (2002), who found an increase in the in situ TCE transformation due to lactate addition.

In the pilot study (Bennett et al. 2003b) conducted prior to the push-pull tests, the half-life estimates for TCE in the LDPC1 wells receiving lactate ranged from 2.8 to 3.5 d (the rates were not reported for the individual layers). Note that rate estimates for the pilot study were determined from temporal changes in TCE concentrations in the test cells. The transformation of TCE resulted in a statistically significant increase in *cis*-DCE. However, VC and ethene concentrations did not increase significantly compared to pretest concentrations. Stable carbon isotope data also indicated that *cis*-DCE was not further transformed in the LDPC1 (Bennett et al. 2003c).

The half-life calculated for TCFE from push-pull tests in the upper and lower treatment layers was 13.9 d (Table 4), and the TCE half-life was 2.8 to 3.5 d during the pilot test (Bennett et al. 2003c). The rate determined for TCFE in the LDPC1 treatment layers was four to five times slower than that for TCE determined from the pilot tests. The slower rate for TCFE may be due to the fact that no lactate was added during the push-pull tests but was actively added to LDPC1 during the pilot study.

Hageman et al. (2001) reported a sixfold higher in situ reductive dechlorination rate for TCFE relative to TCE in a push-pull test conducted at this site but in an A-zone well, which is above the treatment layers of LDPC1. However, the TCFE concentration in the Hageman et al. (2001) push-pull test was 25 times higher than that of TCE. In addition, laboratory experiments indicated that the TCE rate was 0.2 to 3 times that of TCFE and varied over the time course of the experiments (Vancheeswaran et al. 1999). While the rates of TCFE and TCE are variable, as evident in both field and laboratory experiments, they are in reasonable agreement and indicate the suitability of TCFE as a surrogate for TCE.

The transformation product profiles obtained from the TCFE and pilot tests in LDPC1 were consistent in that *cis*-DCFE and *cis*-DCE were the principal transformation products formed from TCFE and TCE, respectively.

Table 3
Distribution of TCFE Transformation Products at the End of 80-d Push-Pull Tests

	LDPC1 (shallow)[a]	LDPC1 (deep)[a]	LDPC2 (shallow)[b]	LDPC2 (deep)[b]	LDPC3 (shallow)[c]	LDPC3 (deep)[c]
TCFE	6.6	13.6	2.2	38.6	2.2	1.3
trans-DCFE	1.9	3.9	0.6	4.8	2.9	0.5
cis-DCFE	37.6	62.2	54.7	36.0	87.4	1.2
E-CFE	36.2	15.6	9.0	3.6	3.5	2.7
Z-CFE	0	0	0.5	0.4	0	0.1
1,1-CFE	15.6	4.5	32.5	15.8	3.0	6.7
FE	2.1	0.2	0.5	0.9	1.0	87.5

[a]LDPC1 received lactate during the pilot study in both the shallow and deep zones.
[b]LDPC2 contained zero-valent iron in both the shallow and deep zones.
[c]During the pilot study, LDPC3 received hydrogen in both the shallow and deep zones, and lactate was added to the deep layer 2 weeks before the end of the pilot study.

Table 4
Calculated TCFE Transformation Rates and Half-Lives for the Push-Pull Tests

	LDPC1 (shallow)[a]	LDPC1 (deep)[a]	LDPC2 (shallow)[b]	LDPC2 (deep)[b]	LDPC3 (shallow)[c]	LDPC3 (deep)[c]
Rate (d^{-1})	0.05	0.05	0.20	0.02	0.20	0.10
Half-life (d)	13.9	13.9	3.5	34.7	3.5	6.9

[a]LDPC1 received lactate during the pilot study in both the shallow and deep zones.
[b]LDPC2 contained zero-valent iron in both the shallow and deep zones.
[c]During the pilot study, LDPC3 received hydrogen in both the shallow and deep zones, and lactate was added to the deep layer 2 weeks before the end of the pilot study.

trans-DCFE formed, but was a factor of 10 lower in concentration compared to *cis*-DCFE. Higher concentrations of the *cis*-isomer relative to the *trans*-isomer were observed for DCFE and DCE during earlier push-pull tests conducted at this site by Hageman et al. (2001). Although no VC and ethene were detected in the pilot study, CFE and a small amount of FE were observed in the TCFE push-pull tests. This difference may be due to the fact that there is no CFE and FE in the background ground water such that the detection of CFE and FE is determined solely by the analytical method detection limit (0.005 μM). In contrast, VC and ethene production during the pilot study could only be detected if the concentrations of VC and ethene had increased significantly above the temporally variable, pretest background concentrations.

LDPC2–Zero-Valent Iron

Transformation of TCFE also was observed upon contact with zero-valent iron in LDPC2 (Figure 4). At the end of the 80-d test, the major TCFE transformation products were *cis*-DCFE (36% to 54%) and 1,1-CFE (16% to 32%), but only a small proportion was present as FE (0.5% to 0.9%) (Figure 4, Table 3). The rate of TCFE transformation in the shallow layer was 0.20/d, while in the deep layer it was an order of magnitude slower at 0.02/d (Table 4). The half-lives were estimated at 3.5 and 34.7 d for the shallow and deep layers, respectively.

The transformation rate obtained for TCFE in the shallow LDPC2 layer (0.20/d) was a factor of 10 above the only background rate (0.02/d) reported for C-zone well 15C (Hageman et al. 2001). On the other hand, the rates obtained for TCFE in the zero-valent iron test cells in LDPC2 were within the range of rates obtained for all three C-zone wells after stimulation of activity by the addition of fumarate (0.05/d to 0.15/d) (Hageman et al. 2004). Zero-valent iron yielded a larger number and higher concentrations of lesser chlorinated transformation products, including *cis*-DCFE, CFE, and a small amount of FE, which is in contrast to the study by Hageman et al. (2004), where fumarate additions promoted primarily *cis*-DCFE, with very small amounts of CFE and no FE.

TCFE clearly underwent transformation in the zero-valent iron of LDPC2 as indicated by the detection of *cis*-DCFE, *trans*-DCFE, and CFE isomers. To the best of our knowledge, this is the first use of TCFE for interrogating the performance of zero-valent iron under field conditions. Additional research is needed to fully characterize the mechanism and transformation products of TCFE for zero-valent iron systems because no laboratory tests have yet been reported for TCFE and zero-valent iron. Arnold and Roberts (2000) reported small concentrations of *cis*-DCE and 1,1-DCE in a TCE/zero-valent iron system, and Roberts et al. (1996) reported the formation of VC from DCE isomers. TCE is known to be transformed by β elimination to form chloroacetylene and acetylene, which can be

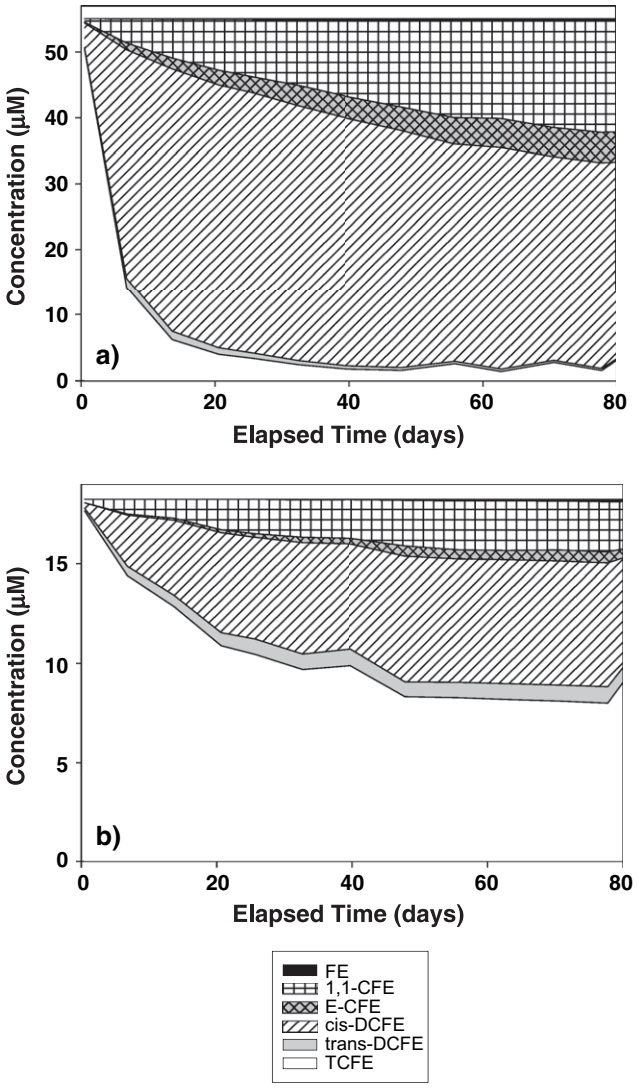

Figure 4. In situ transformation of the injected TCFE in upper (a) and lower (b) silty-sand layers in LDPC2 (zero-valent iron).

further transformed to ethene and ethane (Arnold and Roberts 2000; Roberts et al. 1996). TCFE may react in an analogous manner to form acetylenes; however, acetylene compounds as well as ethane were not measured for the TCFE push-pull tests.

For the pilot study, the estimated TCE half-lives were 0.9 to 7.2 d and 6.2 to 22.5 d in the shallow and deeper layers, respectively (Bennett et al. 2003c). This difference in half-life is consistent with the shorter half-life for TCFE found in the upper treatment layer. Bennett et al. (2003c) reported that the concentrations of *cis*-DCE and VC initially decreased and then increased during the pilot study. In addition, they reported 20% to 50% conversion of TCE to ethene and ethane over the course of the pilot test in LDPC2. Stable carbon isotope data also indicated that complete conversion of TCE to ethene and ethane was occurring. In the TCFE push-pull tests, *cis*-DCFE was the principal product detected, with lesser amounts of CFE and FE. It is not known whether FE can be further reduced to fluoroethane in the presence of zero-valent iron.

LDPC3–Hydrogen Addition

In the tests conducted in hydrogen pretreated LDPC3 layers, the TCFE transformation rate was higher in the shallow layer (0.20/d) compared to the deep layer (0.10/d) (Table 4). The TCFE half-life was 3.5 and 6.9 d in the shallow and deep layers, respectively. These half-lives were in the same range as those estimated for TCE from the pilot study (Bennett et al. 2002c), which included TCE half-lives of 4.3 to 21 d in the shallow layer and 8.3 to 19 d in the deeper layer. In the shallow layer, the principal product was *cis*-DCFE (87.4%), with <5% of the other products, while FE was 1% of the final mixture (Figure 5, Table 3). In the deep layer, FE comprised 87.5% of the final mixture of TCFE and its transformation products (Figure 5, Table 3). All other constituents were 7% or less of the final mixture, and only 1.3% consisted of TCFE.

The lactate pretreatment of the lower layer in LDPC3 during the pilot study may be responsible for the significant difference in the percent conversion of TCFE to FE between the upper (Figure 5a) and lower (Figure 5b) layers. During the pilot study, the lower treatment layer in LDPC3 also received lactate on day 85, which was ~5 weeks before the onset of the TCFE push-pull tests. The sulfate concentration determined 3 weeks before the push-pull tests was 3 mM (Table 1), and it had decreased to 0.2 mM during the 3-week period between the conclusion of the pilot test and onset of the push-pull test. A decrease in sulfate was probably due to the consumption by electron donors, including propionate (8.9 mM) and acetate (6.1 mM), which were produced by the injected lactate. High sulfate concentrations (>1 mM) have been shown to inhibit the transformation of TCE to ethene (Nelson et al. 2002; Smatlak et al. 1996). In contrast, the sulfate concentration in the shallow layer was initially ~3 mM and remained at that level throughout the push-pull test. Therefore, high sulfate concentrations may have inhibited the transformation of TCFE to FE in the shallow layer, while the lower sulfate concentrations in the lower layer may have permitted FE formation.

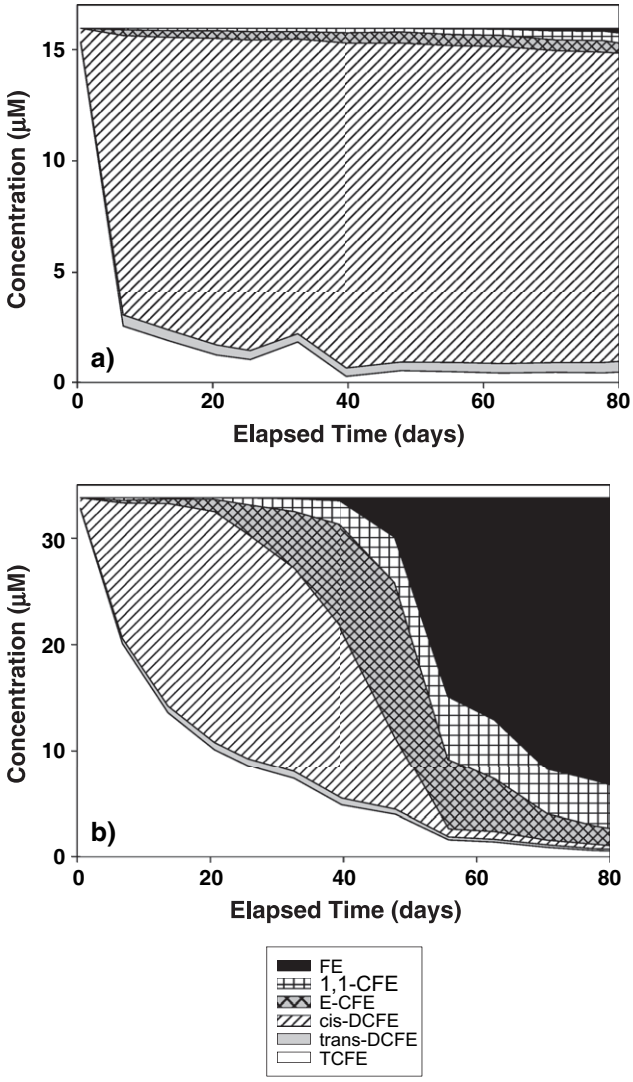

Figure 5. In situ transformation of the injected TCFE in upper (a) and lower (b) silty-sand layers in LDPC3 (hydrogen addition).

The TCFE tests in the hydrogen pretreated LDPC3 layers yielded rates (0.20/d and 0.10/d in the shallow and deep layers, respectively) that were higher than the background rate (0.02/d) obtained for well 15C (Hageman et al. 2001). The rates for TCFE in LDPC3 were comparable to the rates for C-zone wells (0.05/d to 0.15/d) after the addition of fumarate (Hageman et al. 2004). The TCFE test conducted in the shallow layer of LPDC3, which previously received only hydrogen, gave primarily *cis*-DCFE, with only very minor amounts of CFE and FE (Figure 5a), which was very similar to the product distribution for C-zone wells after the fumarate additions (Hageman et al. 2004). In contrast, the TCFE test conducted in the lower layer, which received both hydrogen and lactate during the pilot study, indicated extensive transformation of TCFE with a high conversion to FE (Figure 5b).

For the pilot study, Bennett et al. (2003a) reported no transformation of TCE to VC or ethene for either treatment layer in LDPC3. However, the 2 weeks between the addition of lactate and the cessation of the pilot test may have been too brief for measurable reductive dechlorination of

cis-DCE to occur. For example, Hageman et al. (2004) found small but measurable FE production from injected TCFE only after repeated additions of the substrate fumarate to C-zone wells over a period of months.

Conclusions

Push-pull tests conducted in remedial test cells containing lactate, zero-valent iron, or hydrogen installed at a TCE-contaminated field site indicated that TCFE is a good surrogate for monitoring TCE remediation technologies. TCFE and TCE have similar chemical properties, and both are transformed by analogous pathways. The rates and transformation product profiles obtained for TCFE, which was injected into each test cell, provided unequivocal evidence as well as quantitative rate estimates for reductive dechlorination within each treatment layer. Based on the laboratory and field tests, TCFE is a good surrogate for estimating the behavior of TCE in remedial systems. Moreover, TCFE can be used to estimate TCE transformation rates even in the presence of high and variable concentrations of TCE and its transformation products in background ground water.

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