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In Situ Anaerobic Transformation of Trichlorofluoroethene in Trichloroethene-Contaminated Groundwater

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Methods are needed to obtain in situ information on the transformation rates of trichloroethene (TCE), the most commonly detected organic groundwater contaminant. The objective of this research was to investigate the potential for determining TCE transformation rates in groundwater by measuring the transformation rate of its fluorinated surrogate, trichlorofluoroethene (TCFE). To explore this hypothesis, the in situ transport behavior, transformation pathway, and transformation rate of injected TCFE were determined in TCE-contaminated groundwater using single-well, push−pull tests. Although transport behavior varied between wells, TCFE, dichlorofluoroethene (DCFE), and TCE were transported similarly to each other. In the shallow water-bearing zone, TCFE was reductively dechlorinated to *cis*-DCFE, *trans*-DCFE, and (*E*)-1-chloro-2-fluoroethene (CFE), while co-injected TCE was concurrently transformed to *cis*-dichloroethene (DCE), *trans*-DCE, 1,1-DCE, and a trace amount of chloroethene (CE). With added formate and the injected TCFE concentration being a factor of 20 higher than that of TCE, the TCFE transformation rate ranged from 0.053 to 0.30 μmol/L-day, while that of TCE ranged from 0.009 to 0.012 μmol/L-day. Without added formate, the TCFE transformation rate decreased to 0.036 μmol/L-day. In the deeper water-bearing zone, TCFE transformation occurred only after a lag time of 55 days with added formate. No TCFE transformation occurred in groundwater that had not previously been exposed to TCE. The potential applicability for TCFE as an in situ transport and transformation surrogate for TCE was demonstrated.

Introduction

Trichloroethene (TCE), a nonflammable solvent used in large quantities by industry, is the most common organic groundwater contaminant (*1*) and is classified as a "probable human carcinogen" (*2*). Based on evidence that subsurface microorganisms are capable of degrading TCE under specific biogeochemical conditions, in situ bioremediation of TCE-contaminated groundwater is being investigated (*3*). TCE degradation under methanogenic and sulfate-reducing conditions in laboratory (*4*) and field studies (*5*−*10*) has been reported. Anaerobic TCE degradation occurs by reductive dechlorination, a reaction in which hydrogen atoms sequentially replace chlorine substituents. Thus, in the commonly observed TCE transformation pathway, TCE is sequentially reduced to the dichloroethene (DCE) isomers, chloroethene (CE), and ethene (Figure 1a).

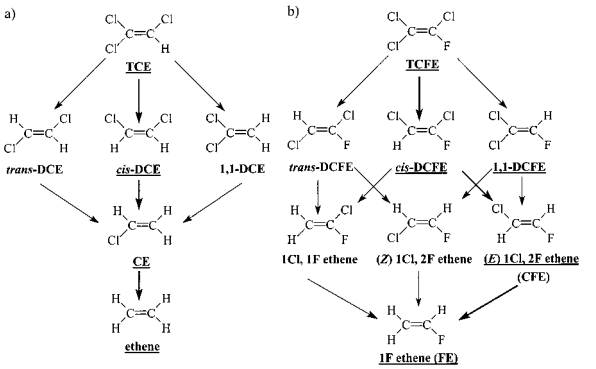

FIGURE 1. Reductive dechlorination pathways for (a) TCE (*5*) and (b) TCFE (*12*). The predominant isomers and pathways are indicated by underlines and heavy arrows.

In situ TCE transformation rates, which are needed to assess the potential for intrinsic bioremediation and to design and monitor engineered bioremediation projects, have been reported (*11*). However, the common method for estimating in situ rates, monitoring temporal and spatial changes in TCE and transformation product concentrations, is problematic. Vancheeswaran et al. (*12*) argued that transformation rates obtained in this way are often ambiguous because (a) small changes in TCE and transformation product concentrations are difficult to measure in the presence of high background concentrations, (b) microbially generated transformation products cannot be distinguished from those that are present in the background, and (c) concentration changes due to transformation are obscured by nonbiological processes such as advection, dispersion, sorption/desorption, and the dissolution of nonaqueous phase TCE. Furthermore, groundwater tracer tests that involve the addition of TCE to reinjected groundwater is problematic even if the endogenous TCE and its degradation products are removed first (e.g., by air sparging). In these types of tracer tests, dilution of the tracer test solution with background groundwater renders it impossible to distinguish between injected and background TCE and its degradation products.

An alternative approach, in which the specified problems are avoided, involves measuring the transformation rate of injected trichlorofluoroethene (TCFE) in TCE-contaminated groundwater and estimating the TCE transformation rate from that of TCFE (*12*). In groundwater microcosm experiments, trichlorofluoroethene (TCFE) was reductively dechlorinated to "fluorine-labeled" transformation products by a pathway analogous to that of TCE (*12*) (Figure 1b). Moreover, with comparable initial TCFE and TCE concentrations, zero-order TCFE and TCE transformation rates were similar in single-compound tests as well as in tests where TCFE and TCE were present together. In free enzyme, corrinoid-

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mediated experiments (*13*) with comparable initial TCFE and TCE concentrations, reductive dechlorination of TCFE and TCE followed second-order kinetics and TCFE transformation rates were 12 to 25 times higher than those of TCE.

The objective of this research was to determine the transport behavior, transformation pathway, and transformation rate of TCFE under defined conditions in TCE-contaminated groundwater at a former chemical manufacturing plant in the San Francisco Bay area. To this end, single-well, push−pull tests with TCFE were conducted in two water-bearing zones with different contaminant and biogeochemical characteristics. In a "push−pull" test, a prepared test solution containing the compounds of interest and a conservative tracer is injected ("pushed") into the saturated zone of an aquifer and then extracted ("pulled") from the same location (*14*, *15*). Breakthrough curves, which are used to assess the transport or transformation behavior of the injected compounds, are constructed from samples collected during the extraction phase of the test.

Experimental Section

Chemicals. Trichloroethene (TCE) (99.5% purity), chloroethene (CE) (97%), sodium formate, and sodium bromide were obtained from Fisher Scientific (Fair Lawn, NJ). *cis*-Dichloroethene (*cis*-DCE) (97%), *trans*-dichloroethene (*trans*-DCE) (98%), and 1,1-dichloroethene (1,1-DCE) (99%) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Trichlorofluoroethene (TCFE) [97% pure, containing 0.1% *cis*-dichloroethene (DCFE) and 0.1% *trans*-DCFE] and DCFE (98% pure mixture consisting of 50% cis and 50% trans isomers) were obtained from ABCR Chemicals (Karlsruhe, Germany). 1,2-chlorofluoroethene [97% pure mixture consisting of 31% (*E*) and 69% (*Z*) isomers] was obtained from SynQuest Laboratories, Inc. (Alachua, FL). Fluoroethene (FE) (98%) was obtained from Lancaster Synthesis (Pelham, NH). Ethene (19.2 ppm in nitrogen) was obtained from Airco Special Gases (Vancouver, WA). 1-chloropropane and 1-chlorobutane, which were used as internal standards for gas chromatography (GC) quantitation, were obtained from Matheson Company (Cincinnati, OH) and Mallinckrodt, Inc. (St. Louis, MO), respectively.

Site Description. The tests in this study were conducted in TCE-contaminated groundwater at a former chemical manufacturing plant in the San Francisco Bay area where TCE reductive dechlorination has been monitored in recent years (*7*, *8*). Tests were conducted in two distinct water-bearing zones, the A-zone and the C-zone. The A-zone is an unconfined shallow layer composed mainly of placed fill over Bay Mud. The water table lies within 3 m of the ground surface. The groundwater velocity ranges from 1.5 to 6 m/year. The C-zone underlies the Bay Mud and is characterized by alluvial fan deposits, approximately 6 to 23 m below the ground surface. Groundwater velocities range from 6 to 31 m/year. The water table slopes to the west in both zones.

Monitoring well installations and subsurface investigations began at the site in the early 1980s. TCE and tetrachloroethene (PCE), pesticides, BTEX (benzene, toluene, ethylbenzene, and xylene), and metals were detected in the A-zone. TCE and PCE were detected in the C-zone. Neither DCE isomers nor CE were ever used or produced at the facility. Using a reductive dechlorination screening process that compares measured concentrations of contaminants and biogeochemical indicators to threshold values (*16*), Buscheck found that there was strong evidence for reductive dechlorination in the A-zone and weaker evidence for reductive dechlorination in the C-zone (*8*).

Push-Pull Tests. A series of push−pull tests was conducted to obtain information on aqueous TCFE and TCE transport and transformation in the selected A-zone well, RI-10A, and in selected C-zone wells, GW-15C and GW-21C. These wells contain a range of background contaminant and biogeochemical indicator concentrations (Table 1).

TABLE 1. Contaminants and Biogeochemical Indicators in Selected Wells

	conc (μmol/L)[a]		
	A-zone well	C-zone wells	
	RI-10A	GW-15C	GW-21C
trichloroethene (TCE)	ND[b]	240	ND
cis-1,2-dichloroethene (*cis*-DCE)	0.017	ND	ND
benzene	0.078	0.32	ND
toluene	0.0041	ND	ND
ethylbenzene	0.0029	ND	ND
total xylenes	0.005	ND	ND
ethene	ND	0.0043	ND
ethane	ND	ND	ND
methane	18	0.26	ND
total organic carbon	15000	ND	ND
dissolved oxygen	130	5.6	18
nitrate-N	ND	ND	ND
sulfate	960	490	170
total dissolved iron	95	ND	ND

[a] Samples collected in May−June, 1999. Chlorinated hydrocarbons and BTEX compounds by EPA method 8021B; ethene, ethane, and methane by RSK-175; total organic carbon by EPA 9060; dissolved oxygen by membrane electrode probe; nitrate-N and sulfate by EPA 9056; iron by EPA 6010B. [b] Not detected.

TABLE 2. Push−Pull Test Descriptions

			test solution composition			
test	well	zone	bromide (mmol/L)	TCFE (μmol/L)	TCE (μmol/L)	formate (mmol/L)
			Transport Tests			
1	RI-10A	A	1.3	8.9	0.019	
2	GW-21C	C	1.2	15		
3	GW-15C	C	1.3	14		
			Transformation Tests			
4	RI-10A	A	1.2	16	0.78	2.0
5	RI-10A	A	1.3	13		
6	GW-15C	C	1.3	19		8.3
7	GW-21C	C	1.4	33		

Transport Tests. Test solutions consisted of tap water, bromide (to serve as a conservative tracer), TCFE, and in one case, TCE (Table 2). Although it would have been desirable to use site groundwater in these experiments, the use of tap water was required to obtain regulatory approval to conduct these tests at this site. Note that because the purchased TCFE standard contained 0.1% *cis*-DCFE and 0.1% *trans*-DCFE, ~0.015 μmol/L of these compounds were also injected in every test. The test solution was prepared by adding bromide to the tap water and then sparging the solution for at least 4 h with compressed air to mix and aerate the solution prior to injection. A concentrated aqueous solution of TCFE (and TCE, where applicable) was stored in a collapsible metallized-film gas-sampling bag (Chromatography Research Supplies, Addison, IL) to prevent volatilization losses during injection (Figure 2). TCFE and TCE were added to the tap water/bromide solution by metering the solution from the bag into the main injection line with a piston pump (Fluid Metering Inc., Oyster Bay, NY) (Figure 2). TCFE/TCE equilibration between the inner polyethylene layer of the bag and the TCFE/TCE solution was established by waiting at least 2 h between filling the bag and starting the injection. TCFE/TCE equilibration between the injection line tubing and the test solution was established by purging the injection lines with test

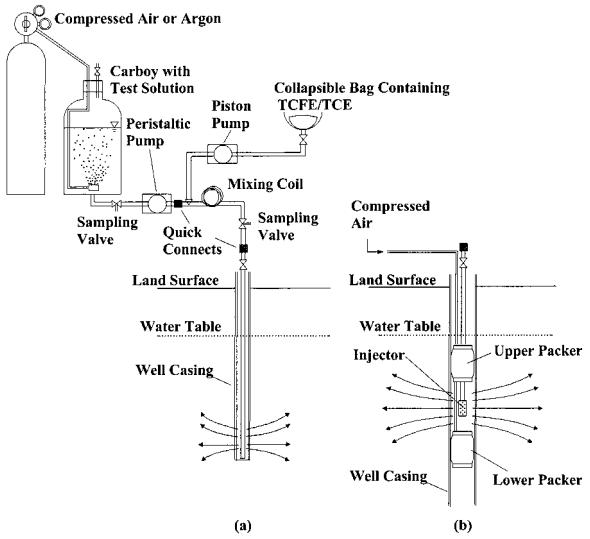

FIGURE 2. Experimental setup for test solution injection in (a) the A-zone well and (b) C-zone wells (not drawn to scale).

solution for 10 min prior to starting the injection phase. Equilibration times were determined in preliminary laboratory experiments.

The injection/extraction procedure for tests in the A- and C-zones were not identical since well diameters were 2.5 cm in the A-zone and 10 cm in the C-zone. In the A-zone test, 50 L of test solution was injected into the bottom of the well at a flow rate of ~0.2 L/min (Figure 2a). In C-zone tests, ~250 L of test solution was injected between a pair of inflatable packers at a rate of ~2 L/min (Figure 2b). The packers were used to isolate a meter-long section of the well screen. In all tests, the test solution was injected through 6-mm nylon-braided tubing (Kuryama Co., Santa Fe Springs, CA) into the well with a Masterflex peristaltic pump (Barnant Co., Barrington, IL). Five to 10 samples of the test solution, which were analyzed to determine injected concentrations, were collected from the sample valve during injection.

Immediately after completion of the injection phase, the carboy and the section of the injection line between the two quick connects were removed, and the flow direction of the peristaltic pump was reversed. In the A-zone test, 67 L of test solution/groundwater mixture were extracted at a rate of ~0.2 L/min; 20 samples were collected. In C-zone tests, ~500 L of test solution/groundwater mixture were extracted at a rate of ~2 L/min; ~50 samples were collected. All samples were collected in volatile organic analysis vials without headspace, shipped on ice, and stored at 4 °C until analysis. Samples for volatiles were collected in duplicate, and duplicate analyses were performed on approximately 10% of the samples. Samples for bromide were collected and analyzed in duplicate. All samples except those for bromide were preserved in 0.75% (v/v) concentrated HCl.

Transformation Tests. Two transformation tests were conducted in the A-zone well and one was conducted in each C-zone well. Test solutions consisted of tap water, bromide, TCFE, and in some cases, TCE and formate (Table 2). The test solution was prepared by adding bromide and formate to the tap water and then sparging the solution for at least 4 h with compressed argon to mix and remove dissolved oxygen prior to the start of the injection phase. TCFE and TCE were then added to the test solution using a piston pump as described for the transport tests. The injected test solution volumes and injection flow rates for the transformation tests were identical to those described for the transport tests. Samples of the test solution/groundwater mixture were collected approximately once per week for up to 82 days. Prior to sample collection, A- and C-zone wells were purged by extracting 0.3 and 12 L of groundwater, respectively. Samples were preserved and stored as described for the transport tests.

Analytical Methods. Concentrations of TCFE, DCFE, CFE, TCE, DCE, and CE were determined by headspace analysis with gas chromatography/mass spectrometry (GC/MS). Qualitative analysis of FE and ethene were performed by solid-phase microextraction with GC/MS. The GC/MS system was composed of a Hewlett-Packard (Palo Alto, CA) model 5890 GC and 5972 series MS detector. Chromatographic separations were performed on a Supelco (Bellefonte, PA) 30 m × 0.32 mm × 4 μm SPD-1 column. The identities of the TCFE degradation products were confirmed by comparing their spectra, which were obtained by operating the MS in scan mode, to published spectra (*12*). The MS was operated in selected ion monitoring mode for quantitation. 1-chloropropane and 1-chlorobutane were used as internal standards. The quantitation limits (signal/noise = 10) were ~0.005 μmol/L for analysis by headspace and ~0.2 μmol/L for analysis by solid-phase microextraction.

Bromide concentrations were determined by external calibration using a Dionex (Sunnyvale, CA) model DX-120 ion chromatograph equipped with an electrical conductivity detector and a Dionex AS14 column. Formate concentrations, as well as those of its potential degradation product, acetate, were determined by external calibration using a Waters Alliance (Milford, MA) high-pressure liquid chromatograph (HPLC). The HPLC was equipped with a model 2690 separations module, a model 996 photodiode array detector, and a Phenomenex (Torrance, CA) 150 mm × 4.60 mm × 5 μm Luna C18 column.

Results and Discussion

Transport Tests. Transport tests were conducted to determine the relative transport behavior of injected TCFE, DCFE, and TCE in A- and C-zones prior to initiation of the transformation tests. The potential for anaerobic transformation of injected TCFE and TCE during transport tests was minimized by (a) air-saturating the test solution prior to injection and (b) completing each test in less than 10 h. Transport test data were interpreted using breakthrough curves that display relative concentration against the cumulative volume extracted at the time the sample was collected divided by the volume of injected test solution. Relative concentration is defined as the measured concentration of a compound in a sample divided by the average concentration of the same compound in the injected test solution.

In the transport test conducted in RI-10A (test 1), the extraction phase breakthrough curves for TCFE and TCE were nearly identical (Figure 3a), indicating that TCFE and TCE were transported similarly. However, deviation of the TCFE/TCE breakthrough curve from that of bromide indicates that TCFE and TCE were not transported conservatively during the test. Since the test was conducted in less than 10 h, we assume that the observed mass loss was not due to transformation but was instead caused by TCFE/TCE sorption to sediment organic matter and/or TCFE/TCE partitioning to nonaqueous phase liquids that may be present in the A-zone. However, no NAPLs were detected during construction of RI-10A. Mass balance calculations indicated that 58, 41, and 38% of injected bromide, TCFE, and TCE were extracted during the test, respectively. The similarity in TCFE and TCE transport behavior supports the hypothesis that TCFE can be used as a surrogate for TCE in TCE-contaminated groundwater. The transport behavior of *cis*- and *trans*-DCFE could not be determined in this test due to interference with residual *cis*- and *trans*-DCFE from a prior test conducted in this well.

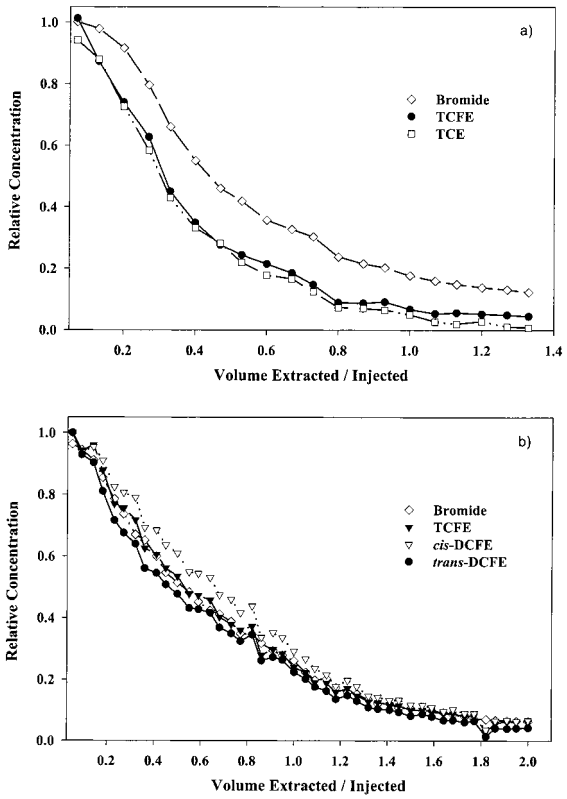

FIGURE 3. Breakthrough curves indicating (a) nonconservative transport of TCFE and TCE in A-zone well RI-10A (test 1) and (b) conservative transport of TCFE and DCFE isomers in C-zone well GW-21C (test 2).

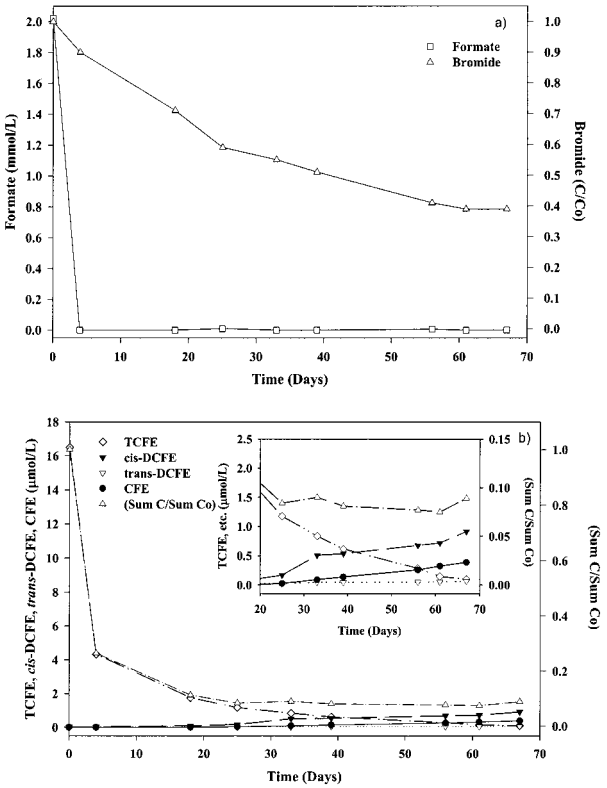

FIGURE 4. Test 4 data indicating (a) changes in concentration for formate and relative concentration for bromide and (b) reductive dechlorination of injected TCFE to *cis*-DCFE, *trans*-DCFE, and CFE in A-zone well RI-10A. Measured concentrations are not adjusted for dilution.

The effects of injected solute sorption on push−pull test extraction phase breakthrough curves were studied in numerical simulations (*17*, *18*). On the basis of those simulations, the TCFE and TCE transport behavior observed in test 1 cannot be attributed to equilibrium sorption with either linear or Langmuir isotherms. Thus, a more complicated sorption process, possibly influenced by diffusion-limited (nonequilibrium) mass transfer may be occurring.

In the transport test conducted in well GW-21C (test 2), TCFE, *cis*-DCFE, and *trans*-DCFE breakthrough curves were nearly identical to that of bromide (Figure 3b), indicating that all three compounds were conservatively transported. Mass balance calculations indicated that 69, 77, 64, and 70% of injected bromide, *cis*-DCFE, *trans*-DCFE, and TCFE were extracted during the test, respectively. TCFE was also conservatively transported in well GW-15C (test 3) (data not shown). The variation in transport behavior between wells may be due to varying soil organic carbon content or to the potential presence of NAPLs within the zone of influence of injected test solutions in some wells. However, when the complete series of transport tests, which included two tests in the A-zone and four in the C-zone, is considered, no correlations between transport behavior and zone, background chlorinated ethene concentrations, or total organic carbon could be identified (data not shown).

Transformation Tests. Transformation tests were conducted (a) to determine if injected TCFE could undergo reductive dechlorination in the selected water-bearing zones, (b) to compare the in situ transformation pathways and rates for TCFE and TCE, and (c) to determine TCFE transformation rates under different conditions and in wells with different background and biogeochemical characteristics.

A-Zone Tests. Test 4 was designed to compare the transformation pathways and rates of co-injected TCFE and TCE in the presence of injected formate (Table 2), which could serve directly as an electron donor or by stimulating microbial activity that produces electron donors. Relative concentrations for the bromide tracer (the measured bromide concentration C divided by the bromide concentration in the injected test solution, C_o) decreased with time as the test solution was gradually diluted with site groundwater (Figure 4a). By the end of the test, the bromide relative concentration was $C/C_o = 0.39$, indicating that this sample was a mixture of test solution (39%) and groundwater (61%). The effects of dilution on the concentration of a conservatively transported compound can be removed by dividing the compound's measured concentration by the relative concentration of the co-injected tracer (*19*). Conservative transport of formate was assumed for this study because of the high water solubility and negative charge of formate. Measured formate concentrations were divided by the bromide C/C_o to produce "dilution-adjusted" formate concentrations (Figure 5a,b). The rapid decrease in formate concentration suggests that an active anaerobic microbial community capable of utilizing formate was present. However, acetate, a potential fermentation product of formate resulting from acetogenesis, was not detected.

Measured TCFE concentration also decreased during test 4 (Figure 4b). The observed production of *cis*-DCFE, *trans*-DCFE, and (*E*)-1-chloro-2-fluoroethene (CFE) indicates that reductive dechlorination of injected TCFE occurred during this test. Fluoroethene (FE) was not detected. To increase the interpretability of the results and to compute transformation rates, it was necessary to adjust measured concentrations for dilution. However, the method used to adjust measured formate concentrations for dilution could not be employed since the transport test conducted in this well indicated nonconservative transport of TCFE, which means that relative concentrations of the bromide tracer cannot be used to correct for dilution of TCFE and its transformation

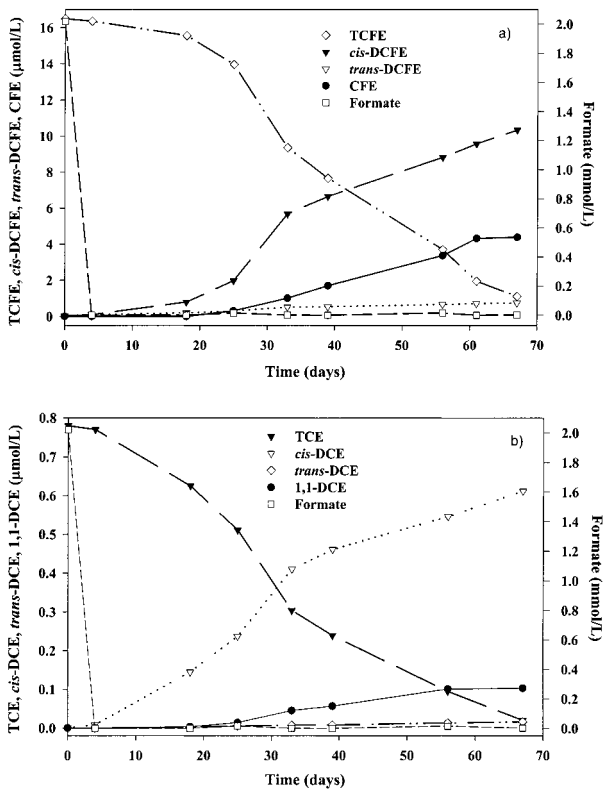

FIGURE 5. Reductive dechlorination of (a) injected TCFE to *cis*-DCFE, *trans*-DCFE, and CFE and (b) TCE to *cis*-DCE, *trans*-DCE, and 1,1-DCE in A-zone well RI-10A with added formate as an exogenous electron donor (test 4). Measured concentrations are adjusted for dilution.

products. Instead, an alternate dilution-adjustment method, which uses concentration ratio comparisons (*19*), was devised.

The method assumes that (a) the transport behaviors of TCFE and its transformation products are identical, and (b) all potential TCFE transformation products are identified and quantified in each sample. The first assumption is supported by the observed identical transport behavior for TCFE and DCFE isomers in test 1 (Figure 3) and by computed organic matter-water partition constants (K_{om}) for TCFE, *cis*-DCFE, *trans*-DCFE, CFE, and FE (log K_{om} = 2.7, 1.9, 1.9, 2.1, and 1.3, respectively). Values of K_{om} were computed from octanol−water partition constants (K_{ow}) (*20*), which were estimated from structural group contributions (*21*). For example, assuming equilibrium linear sorption and estimated values for aquifer organic matter content in the A- and C-zones (f_{om} = 0.0006−0.03), bulk density (2.12 g/cm^3), and porosity (0.2), estimated retardation factors for TCFE and its transformation products ranged from 1 to 26.

The second assumption is considered valid because all currently known transformation products of TCFE and TCE (Figure 1) were analyzed by GC/MS. Although CO_2 and CH_4 production during reductive dechlorination of TCE in microcosm experiments has been observed by others, their production is thought to be the result of a combination of anaerobic chloroethene oxidation to acetate and acetotrophic methanogenesis (*22*−*24*). Since chlorofluoroethene was not produced until day 25 of the test, production of CO_2 and CH_4 from chlorofluoroethene is likely not responsible for the observed reduction in TCFE concentrations in test 4.

Measured concentrations of TCFE and its transformation products were corrected for dilution by dividing the measured concentration by the dilution factor (Sum$C$/SumC_o) (Figure 4b) defined as

$$\frac{\mathrm{Sum}C}{\mathrm{Sum}C_o} = \frac{[TCFE] + [cis-DCFE] + [trans-DCFE] + [CFE]}{[TCFE]_o + [cis-DCFE]_o + [trans-DCFE]_o + [CFE]_o} \quad (1)$$

where, for example, [TCFE] and [TCFE]$_o$ are the measured TCFE concentrations in a sample and in the injected test solution, respectively.

The dilution corrected concentrations for TCFE and its transformation products during test 4 are plotted in Figure 5a and for co-injected TCE and its transformation products during the same test in Figure 5b. Dilution adjustments for TCE and its transformation products were performed using an analogous equation to eq 1. Note that dilution-adjusted concentrations are displayed in Figure 5 and subsequent figures. The dilution-adjusted concentrations show the overall similarities in transformation pathways and rates for TCFE and TCE. TCFE transformation to *cis*-DCFE, *trans*-DCFE, and CFE occurred concomitantly with the transformation of TCE to *cis*-DCE, *trans*-DCE, 1,1-DCE, and a trace amount of chloroethene (CE) (data not shown) (Figure 5). The observed similarity in the in situ TCFE and TCE transformation pathways, including isomer predominance (Figure 1), indicates that it may be possible to use TCFE to determine the extent of TCE transformation, an important parameter in bioremediation design. Slower dechlorination between 0 and 18 days and faster transformation between 18 and 67 days, were similar for TCFE and TCE, which suggests that TCFE and TCE transformations were affected by similar rate-controlling factors. The TCFE concentration decreased at a nearly linear rate, which was determined by linear regression

TABLE 3. Reductive Dechlorination Rates for TCFE, TCE, and Their Transformation Products in Push−Pull Transformation Tests

	transformation rates (µmol/L-day)[a]					
	A-zone tests			C-zone tests		
	test 4: with formate		test 5: without formate	test 6: with formate		test 7: without formate
days	0−18	18−67	0−80	0−55	55−82	0−80
TCFE	−0.053	−0.30	−0.036	0	−0.21	0
cis-DCFE	+0.044	+0.19	+0.029	0	+0.20	0
trans-DCFE	+0.009	+0.011	+0.0049	0	+0.011	0
CFE	0	+0.098	+0.0025	0	0	0
TCE	−0.009	−0.012				
cis-DCE	+0.009	+0.009				
trans-DCE	+0.00039	+0.00072				
1,1-DCE	+0.00015	+0.0022				

[a] "+" indicates increasing concentrations; "−" indicates decreasing concentrations.

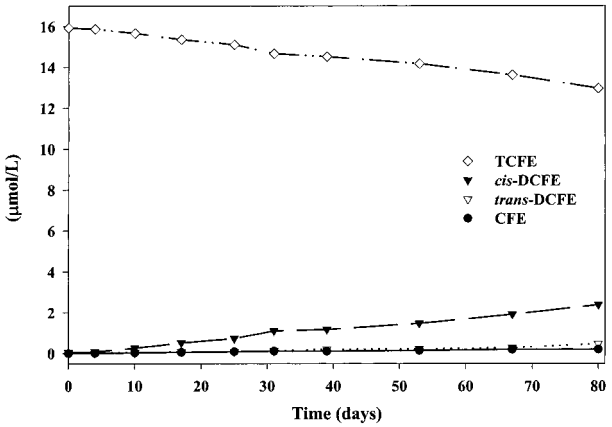

FIGURE 6. Reductive dechlorination of injected TCFE to *cis*-DCFE, *trans*-DCFE, and CFE in A-zone well RI-10A without added formate as an exogenous electron donor (test 5). Measured concentrations are adjusted for dilution.

analysis to be 0.053 μmol-L between 0 and 18 days and 0.30 μmol/L-day between 18 and 67 days (Table 3). Ninety-three percent of the injected TCFE was transformed during the 67-day test. The TCE concentration decreased in a nearly linear manner at a rate of 0.009 μmol/L-day between 0 and 18 days and 0.012 μmol/L-day between 18 and 67 days (Table 3). Ninety-seven percent of the injected TCE was transformed to identified products during the test.

Although the overall percentages of TCFE and TCE transformation were similar, TCFE was transformed at a rate 5.8 times larger than TCE between 0 and 18 days and 25 times larger than TCE between 18 and 67 days. This rate difference is likely due to the higher injected TCFE concentration (20 times higher than TCE). TCE was injected at a lower concentration to meet regulatory requirements.

Test 5 was designed to determine if TCFE transformation rates were limited by electron donor availability by conducting a second test in well RI-10A but without the addition of formate (Table 2). TCFE was again transformed to *cis*-DCFE, *trans*-DCFE, and CFE; FE was not detected (Figure 6). TCFE concentrations decreased and *cis*-DCFE, *trans*-DCFE, and CFE concentrations increased linearly. The TCFE transformation rate was 0.036 μmol/L-day and 19% of the injected TCFE was transformed during the 80-day test. These results indicate that TCFE transformation rates in well RI-10A were limited by the availability of electron donors since the transformation rate in test 5 without formate (Figure 6) was 1.5 to 8.3 times smaller than that in test 4 with formate (Figure 5). This observation is significant because it suggests that TCE transformation rates may be increased at this site by supplying exogenous electron donors.

C-Zone Tests. Test 6, conducted in well GW-15C, was designed to determine the rate of TCFE transformation in the C-zone with formate added as an electron donor (Table 2). Formate was utilized at a slower rate in this test as compared to test 4 conducted in the A-zone and was not completely degraded until day 27 (Figure 7). Acetate was not detected. No reductive dechlorination of TCFE was observed before day 55 (Figure 7). TCFE concentrations decreased at a rate of 0.21 μmol/L-day between 55 and 82 days (Table 3). Thirty-two percent of the injected TCFE was transformed to *cis*-DCFE and *trans*-DCFE during the 80-day test; CFE and FE were not detected. It was not possible within the scope of this project to conduct a second test in well GW-15C without formate.

Test 7, conducted in well GW-21C, was designed to determine if reductive dechlorination would occur in groundwater that had not previously been exposed to TCE or other co-contaminants (Tables 1 and 2). Transformation of TCFE

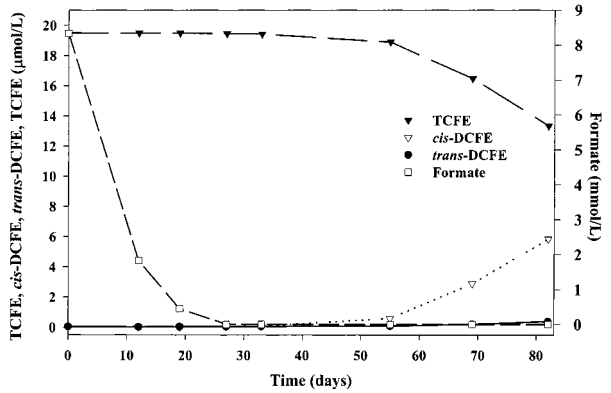

FIGURE 7. Reductive dechlorination of injected TCFE to *cis*- and *trans*-DCFE occurring after 55 days in C-zone well GW-15C with added formate as an exogenous electron donor (test 6). Measured concentrations are adjusted for dilution.

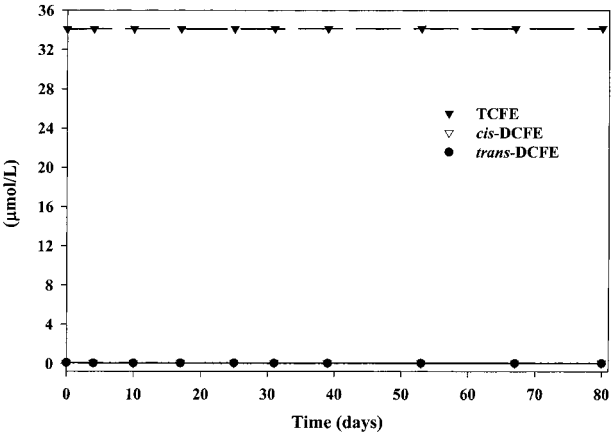

FIGURE 8. Absence of reductive dechlorination of injected TCFE in C-zone well GW-21C without added formate as an exogenous electron donor in groundwater that had not previously been exposed to TCE or other co-contaminants (test 7). Measured concentrations are adjusted for dilution.

was not observed in well GW-21C (Figure 8), which is consistent with the hypothesis that dechlorinating microorganisms, if present at this location, would not be active in an uncontaminated portion of the aquifer. The observed slower rate of TCFE transformation in tests conducted in the C-zone as compared to tests conducted in the A-zone is consistent with the conclusions drawn from the reductive dechlorination screening process conducted at this site by Buscheck (*8*). Although transformation was not observed in test 7, TCFE was recovered during the 3-month long field experiment, which indicates that the push−pull test format is appropriate for this type of field application.

In summary, the potential applicability of TCFE as an in situ surrogate for TCE transport and transformation was demonstrated by the similarity in TCFE and TCE transport behavior, the composition of reductive dechlorination transformation products that formed in situ, and in the general agreement between the rates of transformation for TCFE and TCE.

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Literature Cited

(1) Domenico, P. A.; Schwartz, F. W. *Physical and Chemical Hydrogeology*; John Wiley and Sons: New York, 1990.

(2) "Public Health Goal Document for Trichloroethylene"; California EPA Office of Environmental Health Hazard Assessment, 2000.

(3) National Research Council. *In Situ Bioremediation: When Does It Work?*; National Academy Press: Washington, D. C., 1993.

(4) Vogel, T. M.; Criddle, C. S.; McCarty, P. L. *Environ. Sci. Technol.* **1987**, *21*, 722.

(5) Semprini, L.; Kitandis, P. K.; Kampbell, D. H.; Wilson, J. T. *Water Resour. Res.* **1995**, *31*, 1051.

(6) Major, D. W.; Hodgins, E. W.; Butler, B. J. In *On-Site Bioreclamation: Processes for Xenobiotic and Hydrocarbon Treatment*; Hinchee, R. E., Olfenbuttel, R. F., Eds.; Butterworth-Heinemann: Boston, 1991.

(7) Buscheck, T. E.; O'Reilly, K. T.; Hickman, G. In *In Situ and On-Site Bioremediation (3)*; Battelle Press: Columbus, OH, 1997; Vol. 3, p 149.

(8) Buscheck, T. E. Chevron Research and Technology Company, unpublished report, 1998.

(9) Kaster, M. *Appl. Environ. Microbiol.* **1991**, *57*, 2039.

(10) McCarty, P. L.; Wilson, J. T. In *Bioremediation of Hazardous Wastes*; US EPA Office of Research and Development, EPA., Washington, D. C., 1992; pp 68; EPA/600/R-92/126.

(11) Suarez, M. P.; Rifai, H. S. *Biorem. J.* **1999**, *3*, 337.

(12) Vancheeswaran, S.; Hyman, M. R.; Semprini, L. *Environ. Sci. Technol.* **1999**, *33*, 2040.

(13) Glod, G.; Angst, W.; Hollinger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 253.

(14) Istok, J. D.; Humphrey, M. D.; Schroth, M. H.; Hyman, M. R.; O'Reilly, K. T. *Ground Water* **1997**, *35*, 619.

(15) Schroth, M. H.; Istok, J. D.; Conner, G. T.; Hyman, M. R.; Haggerty, R.; O'Reilly, K. T. *Ground Water* **1998**, *36*, 924.

(16) Wiedemeier, T. H.; Swanson, M. A.; Moutoux, D. E.; Wilson, J. T.; Kampbell, D. H.; Hansen, J. E.; Haas, P. In *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*; U.S. EPA Office of Research and Development: Washington, D.C., 1997. EPA/540/R-97/504.

(17) Schroth, M. H.; Istok, J. D.; Haggerty, R. *Adv. Water Res.* **2000**, *24*, 105.

(18) Istok, J. D.; Field, J. A.; Schroth, M. H.; Sawyer, T. E.; Humphrey, M. D. *Ground Water* **1999**, *37*, 589.

(19) Madsen, E. L. *Environ. Sci. Technol.* **1991**, *25*, 1662

(20) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley and Sons: New York, 1993.

(21) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; John Wiley and Sons: New York, 1979.

(22) Bradley, P. M.; Chapelle, F. H. *Environ. Sci. Technol.* **1999**, *33*, 3473.

(23) Bradley, P. M.; Chapelle, F. H. *Environ. Sci. Technol.* **1999**, *33*, 653.

(24) Bradley, P. M.; Chapelle, F. H. *Environ. Sci. Technol.* **2000**, *34*, 2761.

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