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Monitoring Oxidation of Chlorinated Ethenes by Permanganate in Groundwater Using Stable Isotopes: Laboratory and Field Studies

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Permanganate injection is increasingly applied for in situ destruction of chlorinated ethenes in groundwater. This laboratory and field study demonstrates the roles that carbon isotope analysis can play in the assessment of oxidation of trichloroethene (TCE) by permanganate. In laboratory experiments a strong carbon isotope fractionation was observed during oxidation of TCE with similar isotopic enrichment factors (−25.1 to −26.8 ‰) for initial $KMnO_4$ concentrations between 67 and 1250 mg/L. At the field site, a single permanganate injection episode was conducted in a sandy aquifer contaminated with TCE as dense nonaqueous liquid (DNAPL). After injection, enriched $\delta^{13}C$ values of up to +204% and elevated Cl^- concentrations were observed at distances of up to 4 m from the injection point. Farther away, the Cl^- increased without any change in $\delta^{13}C$ of TCE suggesting that Cl^- was not produced locally but migrated to the sampling point. Except for the closest sampling location to the injection point, the $\delta^{13}C$ rebounded to the initial $\delta^{13}C$ again, likely due to dissolution of DNAPL. Isotope mass balance calculations made it possible to identify zones where TCE oxidation continued to occur during the rebound phase. The study indicates that $\delta^{13}C$ values can be used to assess the dynamics between TCE oxidation and dissolution and to locate zones of oxidation of chlorinated ethenes that cannot be identified from the Cl^- distribution alone.

Introduction

Chlorinated ethenes are among the most frequently detected organic contaminants in groundwater. They are usually present as a dense nonaqueous phase liquid (DNAPL), which serves as long-term source of dissolved compounds (*1*). To permanently restore an aquifer, the DNAPL has to be removed or destroyed. Several technologies have been proposed for source zone remediation. Chemical in situ oxidation with permanganate is a particularly attractive one, since the reaction of permanganate with chlorinated ethenes is fast, preparation of the treatment solution is simple, and the reagent is inexpensive. The effectiveness of permanganate to destroy chlorinated ethenes has been demonstrated in laboratory (*2, 3*) and controlled field studies (*4*−*6*). In field studies, permanganate treatment has been performed by continuously flushing the solution through the aquifer using injection and withdrawal wells (*4*) and by a passive, episodic permanganate method (*5, 6*). This last method involves injection of permanganate solution over a short period of time with no extraction wells, followed by a rest period to allow for diffusive and density driven transport of permanganate and reaction with the chlorinated ethenes. DNAPLs typically exhibit a complex spatial distribution as a result of geological heterogeneities of aquifers and multiple release points. Therefore, sensitive methods to verify that the permanganate solution has come into contact with the chlorinated ethenes and that destruction of chlorinated ethenes has occurred are crucial when implementing the permanganate approach.

In previous studies, decreasing concentrations of chlorinated ethenes and increasing concentrations of Cl^- have been used as indicators of contaminant destruction. However, under field conditions, concentrations of chlorinated ethenes can decrease due to displacement of contaminated water by the injected permanganate solution rather than oxidation of chlorinated ethenes or concentrations may remain elevated even though destruction occurs, due to continuous dissolution of chlorinated ethenes from DNAPL. While Cl^- concentrations may initially be a sensitive monitoring parameter, after a large amount of Cl^- has accumulated, interpretation of Cl^- data may become ambiguous because concentration changes can be due to the movement of fluids with different Cl^- levels induced by the permanganate injection and density gradients.

The aim of this study was to evaluate the potential of stable carbon isotope to be used as a complementary tool to assess in situ oxidation of chlorinated ethenes by potassium permanganate at the field scale. The isotope approach is based on the frequent occurrence of differences in reaction rates between molecules with light (^{12}C, H) and heavy (^{13}C, D) isotopes, respectively, which is denoted as kinetic isotope effect. The difference in reaction rates leads to an enrichment of heavy isotopes in the remaining portion of compound as the reaction proceeds. Isotope fractionation has been observed in laboratory studies during biodegradation of chlorinated hydrocarbons (*7*−*14*) or petroleum hydrocarbons (*11, 15*−*19*) and transformation of chlorinated hydrocarbons by zerovalent iron (*20, 21*). Recently, significant carbon isotope fractionation with average isotopic enrichment factors between −17 to −25.1 ‰ has also been observed for oxidation of different chlorinated ethenes by permanganate (*22, 23*). However, in contrast to biodegradation studies, the isotope method has not been tested yet at field sites where permanganate is injected for treatment of chlorinated ethenes.

In this study, the isotope method was tested at a field site consisting of a shallow sandy aquifer overlaying a clay aquitard. At the site, trichloroethene (TCE) had accumulated as residual and free phase DNAPL on top of the aquitard and was also present in the aqueous phase at concentrations up to solubility. The field site was equipped with a network of high-resolution multilevel bundle wells (15 cm spacing in vertical distance), which made it possible to gain detailed insight into shifts of isotope ratios after injection of permanganate and to assess their relationship to spatial and temporal variations of other parameters such as TCE and

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Cl^- concentrations. In addition, batch experiments were performed to evaluate carbon isotope fractionation during oxidation of TCE. The isotope study at the field site was part of a pilot scale test carried out to evaluate the performance of the passive permanganate method (*24*).

Material and Methods

Laboratory Experiments. Batch experiments were performed to determine the magnitude of carbon isotope fractionation associated with chemical oxidation of TCE by permanganate. VOC vials of 42 mL volume were used as reaction vessels and filled with aqueous solution containing dissolved chlorinated ethenes at initial concentration of 70 ppm. To determine whether the ratio between concentration of permanganate and TCE affects the magnitude of isotope fractionation, two sets of experiments were performed, one with less permanganate than required for complete oxidation of TCE and the other with permanganate in excess.

In the experiment with excess permanganate, the reaction was started by adding 5 mL of a solution containing 10.5 g/L of $KMnO_4$, which corresponds to a final $KMnO_4$ concentration of 1250 mg/L. The vessels were completely filled without any headspace to avoid partitioning of chlorinated ethenes between the aqueous phase and gas phase where no reaction takes place. The initial permanganate concentration was selected such that no more than 15% of the permanganate was consumed during the reaction. The samples were placed on a reciprocating shaker. Every two minutes, three reaction vessels were quenched by injecting 0.1 mL of a solution containing 0.5 M sodium thiosulfate and 0.06 M calcium nitrate. Calcium was added to the quenching solution to facilitate precipitation of the manganese oxide.

In the experiment with limited permanganate supply, the reaction was started by adding 4 mL of diluted $KMnO_4$ solution at concentrations smaller than necessary for complete consumption of TCE. The initial $KMnO_4$ concentrations (67 to 157 mg/L $KMnO_4$) were chosen such that residual TCE concentrations after reaction would be equally spaced on a logarithmic scale. Triplicates were prepared for each permanganate concentration level and for controls with no permanganate. The vials were placed on a reciprocating shaker for 48 h.

Field Study. The field site consists of an industrial property in North Haven, CT where TCE was released decades ago. The site lithology in the release area consists of 8.8 to 9.4 m of medium to fine grain sand underlain by an approximately 21.4 m thick clayey silt aquitard. The water table is located 3 to 4.5 m below ground surface (bgs). To characterize the contaminant distribution in detail and to monitor the remediation progress, bundle wells were installed consisting of $^1/_2$-inch polyethylene tubes centered around a single $^3/_4$-inch diameter PVC center stock (*25*). The sampling points of each bundle are numbered from the top to the bottom starting with 1. In addition, continuous soil cores were taken at each bundle location and tested for DNAPL presence using the Sudan IV dye method at one inch spacing (*6*). Residual-phase and free-phase DNAPL were detected at several locations close to the aquitard indicating that a thin patchy DNAPL pool was present above the aquitard (*24*). In November 1994, the majority of the DNAPL pool was enclosed by steel sheet-piles to isolate the TCE DNAPL zone from the moving groundwater.

The remediation trial was conducted using a particular passive $KMnO_4$ approach, whereby targeted injections of high concentration solutions of $KMnO_4$ are made in depth-specific zones using a short-screen drive point. After injection under pressure, which occurs for short periods of time, the dense permanganate solution continues to flow and sink by density-driven advection during a much longer time while mixing by fingering and diffusion (*5, 6, 26*). The pilot test at the site involved two injections at a single location. For a complete remediation of the aquifer, a few injection episodes at several locations would be required. A total of 4000 L of $KMnO_4$ solution with an average concentration of 43 g/L was injected into the sand aquifer in two 8-h events 4 days apart at a point 0.76 m above the aquitard. The purpose of the injection was to test the passive permanganate method using a high-resolution monitoring installation. Concentrations of Cl^-, concentrations of TCE, and $\delta^{13}C$ of TCE were determined before and at several intervals after the permanganate injection. The preinjection $\delta^{13}C$ was determined at 32 sampling points covering the entire study area to map variations in $\delta^{13}C$ that could occur due to multiple sources or events of TCE contamination or due to biodegradation of TCE. The hydraulic isolation of the TCE source, the fact that permanganate was injected only in one episode and at one location and depth, the use of a high resolution monitoring network, and the possibility to sample not only dissolved TCE but also actual TCE DNAPL causing the aqueous contamination made the site ideal for evaluation of the isotope method and to compare changes of the isotope ratios to changes of other monitoring parameters, particularly TCE and Cl^-.

Analytical Methods. To determine concentrations of TCE in aqueous samples from laboratory experiments and field experiments, aqueous samples were extracted using capillary GC grade pentane containing 500 μg/L of 1,2-dibromoethane as an internal standard. The pentane was transferred to a GC vial and analyzed on a Hewlett-Packard 6890 Plus gas chromatograph equipped with an HP-624 column (30 m × 0.32 mm, 1.8 μm film thickness) and a micro-ECD detector. Concentrations were calculated based on peak areas of samples and external standards, which were prepared from methanolic stock solutions and were extracted analogous to the samples. The detection limit of the method is 1 μg/L. Concentrations of TCE in core samples were determined as described in ref *5*. Concentrations of chloride were analyzed using ion chromatography.

Carbon isotope ratios of chlorinated ethenes were determined in the Environmental Isotope Laboratory, University of Waterloo using a gas chromatograph (Hewlett-Packard 6890; Agilent, Palo Alto, USA) coupled via a combustion interface to an isotope-ratio mass spectrometer (Micromass Isochrom; Micromass, Manchester, UK) as described in ref *7*. The chlorinated ethenes from aqueous samples were extracted using a solid-phase microextraction (SPME) method similar to that described by Hunkeler and Aravena (*27*). The $\delta^{13}C$ of TCE DNAPL from the site was determined after complete evaporation of a small amount of TCE in a 500 mL glass bottle that had been flushed by helium. Gaseous TCE was injected into a split-splitless injector (split ratio 10:1) of the analytical system described above using a gastight syringe. The analytical system was verified daily using external standards of chlorinated ethenes with known carbon isotope ratios. Carbon isotope ratios ($^{13}C/^{12}C$) are reported in the usual delta notation ($\delta^{13}C$) referenced to VPDB (Vienna Peedee Belemnite). The $\delta^{13}C$ value is defined as $\delta^{13}C = (R_s/R_r - 1) \times 1000$, where R_s and R_r are the $^{13}C/^{12}C$ ratios of the sample and the VPDB standard, respectively. All samples were measured in duplicate and the average value is reported. Deviation between the repeat measurements was generally smaller than 1‰ for values smaller than 50‰ and smaller than 2‰ for values larger than 50‰, which is sufficiently precise given the large shifts in $\delta^{13}C$. The detection limit for isotope analysis was 20 μg/L.

Quantification of Isotope Fractionation. Isotope fractionation during chemical or biological transformation of a compound can be evaluated using the Rayleigh equation for experiments with isotopes present at natural abundance levels. The Rayleigh equation makes it possible to determine

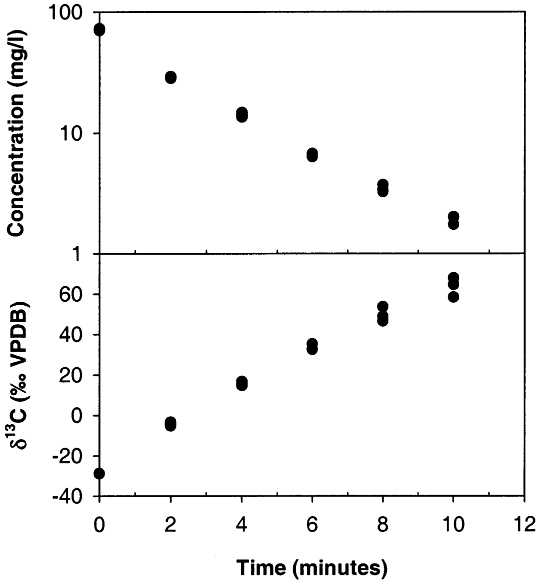

FIGURE 1. Concentration and δ^{13}C of TCE as a function of time in laboratory experiment. The uncertainty of the δ^{13}C values is smaller than the size of the marker.

if the fractionation factor remains constant over the course of the experiment and to quantify its value. According to the Rayleigh equation (*28*), the isotopic composition of the reactant is given by

$$R_S = R_{S_0} \cdot f^{(\alpha-1)} \tag{1}$$

where *f* is the fraction of reactant remaining, R_S is the isotope ratio of reactant at a remaining fraction *f*, R_{S_0} is the initial isotope ratio of the reactant, and α is the fractionation factor. The fractionation factor is defined by (*28*)

$$\alpha = \frac{dP_{13}/dP_{12}}{S_{13}/S_{12}} \tag{2}$$

where dP_{13}, dP_{12} are increments of product containing ^{13}C and ^{12}C, respectively, which appear at an infinitely short time (instantaneous product) and S_{13}, S_{12} are the concentration of reactant with ^{13}C and ^{12}C, respectively.

By using the δ^{13}C notation for carbon isotope ratios and the relationship that links the fractionation factor α to the isotopic enrichment factor ϵ, $\epsilon = (\alpha - 1)\cdot 1000$, eq 1 transforms to

$$1000\cdot\ln\frac{\delta^{13}C_S + 1000}{\delta^{13}C_{S_0} + 1000} = \epsilon\cdot\ln f \tag{3}$$

where $\delta^{13}C_S$ is the carbon isotope ratio of the reactant at a remaining fraction *f* and $\delta^{13}C_{S_0}$ is the initial carbon isotope ratio of the reactant. In this study, isotope fractionation is expressed as isotopic enrichment factors.

Results and Discussion

Laboratory Experiments. Figure 1 shows the concentration and δ^{13}C of TCE during the laboratory experiment with excess TCE. The concentration decreased exponentially with time, as indicated by a linear trend in the logarithm of the concentration versus time plot and after about 10 min, most of the TCE was consumed. Previous studies showed that oxidation of TCE by permanganate is a second-order reaction (*2*). The linear trend observed in the semilogarithmic plot is attributed to the fact that less than 15% of the permanganate is consumed during the experiment and thus the reaction progresses approximately according to pseudo-first-order kinetics (*2*). To compare the reaction kinetics observed in this study to that of previous studies, the second-order rate constant was calculated by dividing the pseudo-first-order rate contant, which was obtained from linear regression, by the initial permanganate concentration. The calculated second-order rate constant (46 M^{-1} min^{-1}) is similar to the second-order rate constant (40 M^{-1} min^{-1}) determined by Yan and Schwartz (*2*).

TABLE 1. Isotopic Enrichment Factors (‰) for Chemical Oxidation of TCE by Permanganate and R^2 of Linear Regression[c]

method	TCE	reference
permanganate	−25.1 ± 0.4 (0.9957)[a]	this study
	−26.8 ± 1.1 (0.9819)[b]	this study
	−21.4	22
microbial reductive dechlorination	−2.5 to −6.6	9
	−7.1	11
	−13.8	12
microbial oxidation of TCE	−18.2 to −20.7	13
zerovalent iron	−8.6	20

[a] Excess permanganate supply [b] Limited permanganate supply [c] Comparison with isotopic enrichment factors for reductive dechlorination or oxidation of TCE by microorganisms and reductive transformation by zero-valent iron. The reported uncertainty corresponds to the confidence interval obtained from the linear regression.

The δ^{13}C of TCE steadily increased with time following an almost linear trend (Figure 1). Larger variations in the δ^{13}C of replicates can be observed for later points in time. These differences may be due to slight variations in the reaction rate between replicates due to slight variations in the initial permanganate and TCE concentrations. The nearly linear trend of the δ^{13}C data indicates that the isotopic enrichment factor remains constant during the experiment. For a first-order reaction with a constant isotopic enrichment factor, an approximately linear increase of the δ^{13}C with time is expected (*14*). The δ^{13}C of the control without permanganate (−29.2 ± 0.08 ‰, $n = 3$) corresponded well to the δ^{13}C of the added TCE (−29.4 ± 0.2, $n = 4$). In the experiment with limited permanganate supply, between 4 and 44% of the initially added TCE was found in solution after a reaction period of 48 h confirming that the amount of $KMnO_4$ was limiting the extent of reaction. In this experiment, the of TCE increased to values of +67‰.

To evaluate in more detail whether the isotopic enrichment factor remains constant with time, the isotopic enrichment factor values were quantified according to eq 3 using least-squares linear regression (Table 1). Similar isotopic enrichment factors were obtained for TCE experiments with excess and limited permanganate supply, with values of −25.1 ± 0.4‰ and −26.8 ± 1.1‰, respectively. This suggests that the permanganate to TCE ratio does not affect the magnitude of isotope fractionation. The isotopic enrichment factors were slightly larger than the average value of −21.4‰ reported by Poulson and Naraoka (*22*). The difference could be due to the difference in experimental design. Poulson and Naraoka (*22*) created a headspace in their bottles and thus part of the TCE was in the gaseous phase where no oxidation occurs, while in this study completely filled bottles were used. This could lead to more negative δ^{13}C values in the gaseous phase compared to the aqueous phase and thus to smaller calculated isotopic enrichment factors.

The magnitude of isotope fractionation during oxidation of chlorinated ethenes by permanganate is in the range typical for primary carbon isotope effects (*29*). For a chemical reaction, a primary kinetic isotope effect with respect to an element is expected if during the rate-limiting step, a bond involving the respective element is formed or broken (*29*).

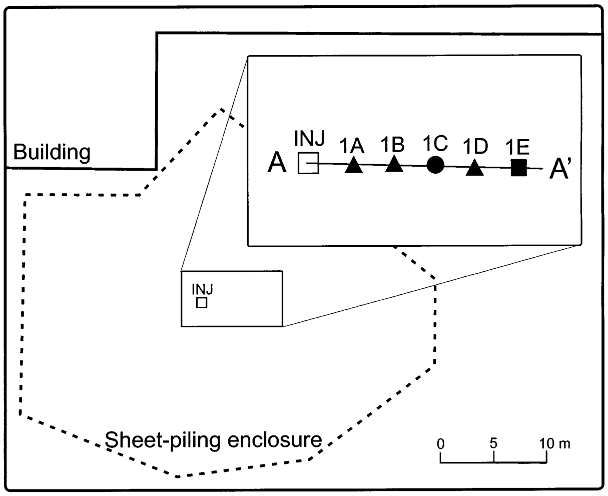

FIGURE 2. Map of field site with location of sheet-piling enclosure, bundle wells, and location of permanganate injection point (INJ). Circles: no DNAPL detected, triangle: DNAPL at residual saturation, square: free-phase DNAPL.

For oxidation of chlorinated ethenes by permanganate, the rate-limiting step consists of the production of a cyclic hypomanganate ester, which involves transformation of a double to a single carbon bond and formation of carbon−oxygen bonds (*30*). Thus, the observed substantial carbon isotope fractionation is consistent with the postulated reaction mechanism.

The isotopic enrichment factors are larger than those observed for microbial reductive dechlorination of TCE and for transformation of TCE by zerovalent iron (Table 1). However, the isotopic enrichment factors are relatively close to those found for biological oxidation of TCE by *Burkholderia cepacia G4* (*13*). This similarity could be due to a similar reaction mechanism for biological oxidation of TCE involving transformation of a double to a single carbon bond and formation of carbon−oxygen bonds during the initial transformation of TCE to an epoxide (*31*).

Field Study. The isotope study focused on the bundle wells located along cross-section A−A′ between the permanganate injection point and bundle well 1E (Figure 2). These bundles are 1 m apart and have sampling points at 15 cm intervals in vertical direction with the lowest sampling point immediately above the aquitard. Results from the 5 lowest sampling points of each bundle are discussed. Many other bundle wells were used to track TCE and Cl^- changes (*24*).

Preinjection TCE concentrations generally increased with depth (Figure 3), which is consistent with the presence of TCE DNAPL on top of the aquitard. A maximum concentration of 1408 mg/L was found in the deepest sampling point of 1D, which corresponds to the solubility of TCE reported by Broholm and Feenstra (*32*). The preinjection Cl^- concentration varied between 67 and 193 mg/L for the 20 sampling points. After permanganate injection, the TCE concentration at 1B, close to the injection point, decreased and remained near or below the method detection limit in the deepest three points during the entire experiment (Figure 3). At 1C, the TCE concentrations decreased in the three deepest points, remained low until week 7, and then rebounded again (Figure 3). At 1D, the TCE decreased in the deepest two points and started to rebound after week 7 in the deepest point and after week 11 in the second deepest point. At 1E, the farthest location with respect to the injection point, the TCE concentration decreased at the second deepest sampling point between injection and week 2 and then increased again to preinjection levels. At the deepest sampling point of 1E, the TCE concentration increased (Figure 3). At all four bundle wells, the concentration of Cl^- increased markedly, mainly in the deepest two sampling points with the largest increase observed at 1E (Figure 3). As illustrated for selected sampling points in Figure 4, the production of Cl^- was larger than expected based on the decrease of the TCE concentration indicating that not only the initially dissolved TCE was oxidized but further dissolution and oxidation of TCE occurred. Dissolution of TCE was probably enhanced by the increased concentration gradients created by removal of dissolved TCE due to oxidation with permanganate.

In the 32 preinjection samples, the $\delta^{13}C$ value of TCE was between −21.4‰ and −22.5‰ with an average value of −22.0 ± 0.23‰. The $\delta^{13}C$ value of dissolved TCE corresponded well to that of DNAPL TCE, which was −21.8 ± 0.12‰ (n = 4). Thus, variations in $\delta^{13}C$ values due to different sources or biodegradation of TCE at the site can be excluded. Based on the laboratory results, the $\delta^{13}C$ value of TCE at the field site should change toward enriched values as $KMnO_4$ oxidizes the TCE. While the aqueous TCE is being destroyed by the oxidation reaction, at locations where DNAPL still exists, concurrent or subsequent dissolution of TCE DNAPL is expected to produce a rebound effect in which the isotope composition shifts back toward its original value. Thus, the $\delta^{13}C$ of TCE should reflect dynamics of the interaction between TCE oxidation and dissolution.

By 2 weeks after permanganate injection, the $\delta^{13}C$ of TCE had strongly increased at some of the sampling points in bundles 1B, 1C, and 1D, producing maximum values of up to +204‰. In contrast, no changes were observed at 1E during the entire experiment (Figure 3). Abundant DNAPL exists at this location. The strong increase in $\delta^{13}C$ has to be associated with TCE consumption by oxidation. In 1B, an enriched $\delta^{13}C$ value compared to the initial $\delta^{13}C$ was observed even 19 weeks after permanganate injection. In contrast, in 1C and 1D, the $\delta^{13}C$ of TCE reached the $\delta^{13}C$ of DNAPL TCE again at week 19 (Figure 3). The trend toward the original $\delta^{13}C$ value can be explained by dissolution of TCE from DNAPL still present close to sampling points and by a decreasing TCE oxidation rate as $KMnO_4$ is consumed. The persistence of enriched $\delta^{13}C$ values at 1B suggests that complete oxidation of the small amount of TCE DNAPL initially present had occurred and therefore no complete rebound of the $\delta^{13}C$ values occurred. At the lowest two sampling points of 1B, TCE concentrations were below the detection limit for isotope analysis. Thus, the fast rebound of $\delta^{13}C$ value may aid in identifying zones where substantial amount of DNAPL are still present. At 1E, the $\delta^{13}C$ value of the TCE did not change despite increasing Cl^- concentrations. This suggests that the Cl^- was not produced locally at 1E but migrated toward 1E from zones closer to the injection point where oxidation of TCE occurred (e.g. around 1D). The migration of Cl^- was likely due to advection caused by the high density of solutions containing $KMnO_4$ and/or elevated concentration of chloride. The conclusion that Cl^- was not produced locally is also supported by the distribution of $KMnO_4$ concentration, which showed that $KMnO_4$ never reached 1E during the entire experiment (*24*). This demonstrates that increasing Cl^- concentrations do not necessarily indicate oxidation of chlorinated ethenes in the vicinity of the sampling point. Therefore, this translocated Cl^- indicates TCE destruction but not at the location where the Cl^- is found.

Quantitative Evaluation of Isotope Data. While the laboratory data demonstrate that isotope fractionation during oxidation of TCE can be described using equations based on the Rayleigh model, these equations cannot be directly applied to field data to evaluate the amount of TCE destroyed by oxidation. The Rayleigh equation relies on the assumption of a finite, well-mixed reactant reservoir, which is not valid

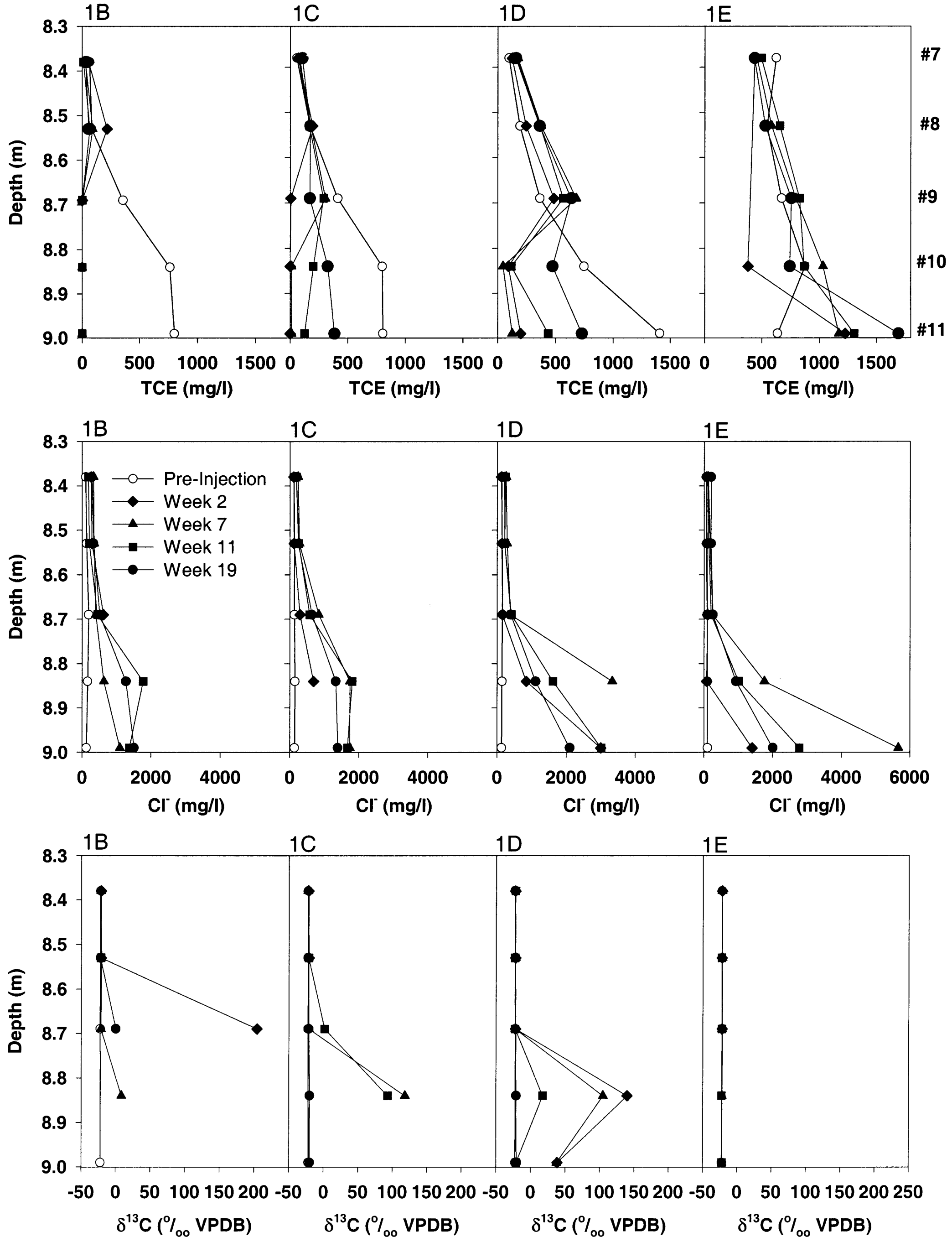

FIGURE 3. Concentration of TCE, concentration of Cl^- and $\delta^{13}C$ of TCE in the five deepest points (#7 to #11) of multilevel bundles 1B, 1C, 1D, and 1E before permanganate injection (open circles), 2 weeks after permanganate injection (diamond), 7 weeks after permanganate injection (triangle), 11 weeks after permanganate injection (square), and 19 weeks after permanganate injection (circle). The aquitard is located at 9 m below ground surface, and the permanganate was injected 0.76 m above the aquitard at the location shown in Figure 2.

in this case, for two reasons: (I) migration of fluids occurs due to $KMnO_4$ injection and later due to fluid density effects and (II) TCE DNAPL continuously dissolves due to the concentration gradient created by TCE oxidation. This newly formed aqueous TCE mixes with any aqueous TCE remaining. However, with appropriate spatial and temporal monitoring, isotope mass balance calculations can give insight into the relationship between TCE oxidation and dissolution during the phase of rebound of $\delta^{13}C$ values. During this phase, TCE concentrations could be controlled only by dissolution of DNAPL or by simultaneous dissolution and oxidation of TCE. To distinguish between these two scenarios, the expected $\delta^{13}C$ of TCE was calculated for the case where only dissolution occurs and compared to the measured $\delta^{13}C$ of TCE (Figure 5). These calculations used values from selected sampling points from the bundles 1C and 1D showing rebound of $\delta^{13}C$ values. The TCE concentration and $\delta^{13}C$ value at week 7 for the selected points were taken as a starting point because the lowest TCE concentrations were observed at week 7 and because the migration rate of fluids had likely become small by this time. For sampling point 1D-#10 and 1D-#11, the measured and expected $\delta^{13}C$ of TCE agree reasonably well. However for 1C-#10, a much more positive $\delta^{13}C$ value was measured than calculated (Figure 5). This suggests that for 1D-#10 and 1D-#11, the $\delta^{13}C$ rebound can be explained by dissolution of TCE DNAPL after an intense initial phase of

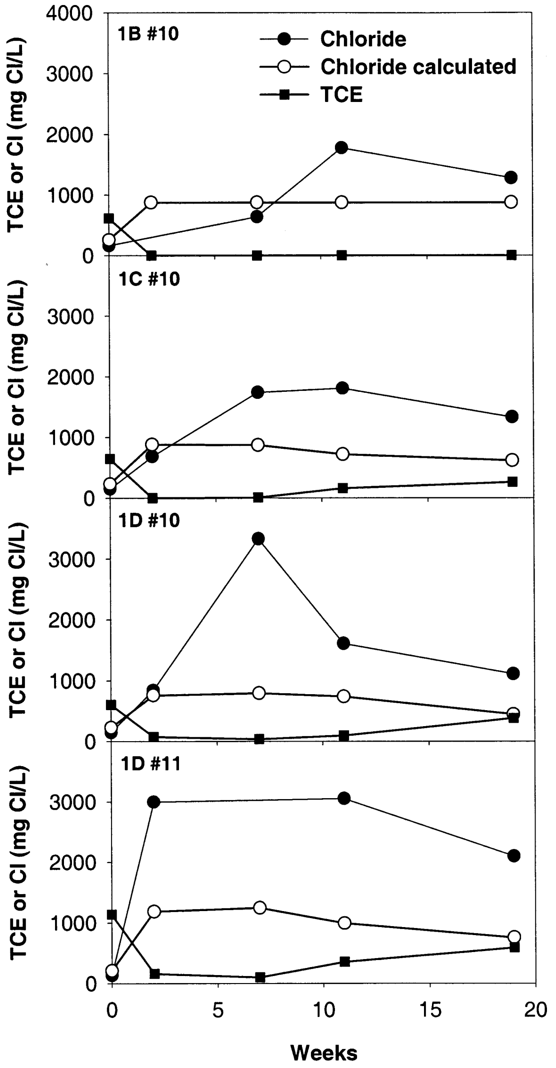

FIGURE 4. TCE concentration, chloride concentration and calculated chloride concentration assuming that only dissolved TCE was oxidized for selected sampling points. #10 is the second deepest and #11 the deepest sampling point.

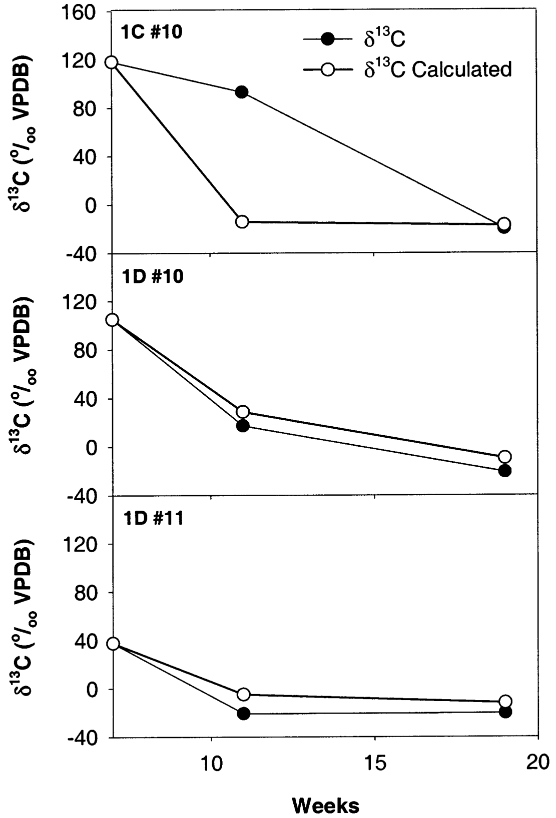

FIGURE 5. Measured δ^{13}C and calculated δ^{13}C of TCE assuming that after week 7 only dissolution of TCE and no further oxidation had occurred.

TCE oxidation, while at 1C-#10, TCE oxidation continued beyond week 7. The longer period of TCE oxidation in the vicinity of 1C is consistent with the presence of high concentrations of MnO_4^- between bundles B and C even at week 11 (*24*). In contrast around bundle 1D, only minimal MnO_4^- was observed at week 11 (*24*).

Implications for Application at Field Sites. At the study site, strong shifts in the δ^{13}C of TCE were observed, which are consistent with the large isotopic enrichment factor for TCE oxidation found in the laboratory experiment. However, the shifts were transient and the original δ^{13}C of TCE was reestablished in zones where TCE was still present as DNAPL. While the rebound of δ^{13}C values prevents a simple calculation of the amount of TCE that has been oxidized, it makes it possible to assess the dynamics between oxidation of the chlorinated ethenes and dissolution of the remaining DNAPL and indicates zones where DNAPL is still present. Furthermore, since original δ^{13}C values are reached again, it should be possible to use isotope data to monitor TCE oxidation in situations where $KMnO_4$ is injected in repeated episodes, which is common practice. With repeated injections, Cl^- is expected to accumulate limiting the usefulness of Cl^- as an indicator of continued oxidation of chlorinated ethenes. For example, in the deepest two sampling points of 1C and 1D, Cl^- concentrations remained elevated at 1100 to 2100 mg/L at the end of the experiment (Figure 3). The field data show that even during a single injection episode, the Cl^- concentrations do not always provide information about locations of TCE oxidation as exemplified by the large increase in Cl^- concentration at 1E where neither δ^{13}C shifts were observed nor was permanganate detected. At sites with natural groundwater flow, Cl^- is even more subject to continuing displacement than at the study site, which was hydraulically isolated by sheet-pilings. Similarly as Cl^-, partially oxidized TCE with enriched δ^{13}C values could migrate to areas outside the zone of TCE destruction, too. However, if migration occurs across zones where TCE DNAPL is still present, the δ^{13}C of dissolved TCE will likely approach that of TCE DNAPL again. In contrast to isotope data, Cl^- data can potentially be used to determine the total mass of TCE that has been oxidized. However for this to be feasible a sufficiently dense monitoring network is necessary and also Cl^- must not migrate outside the zone of monitoring. Both conditions are often not achieved at typical field sites. In addition to providing information on zones of chlorinated ethene destruction and on interactions of oxidation and dissolution at DNAPL sites, isotope data are likely also useful to assess oxidation of chlorinated ethenes at sites where permanganate is injected to treat plumes of dissolved compounds, particularly when high Cl^- background concentrations are present.

Acknowledgments

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