Assessment of TCE Oxidation by $KMnO_4$ using Stable Carbon and Chlorine Isotopes at a Fractured Bedrock Site

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The oxidation of chlorinated ethenes by potassium permanganate ($KMnO_4$) is increasingly being used to remediate contaminated ground water. Typically the remediation of these sites is assessed by tracking changes in the concentrations of the chlorinated compounds and the chloride produced by the reaction. However, this method can be problematic in a fractured bedrock environment, due to the inherent complexity of the fracture network and the injection process that can displace contaminant mass and result in erroneous determinations. In this study, carbon and chlorine isotopes were tested to monitor the oxidation of trichloroethene (TCE) by potassium permanganate at a fractured limestone site. Laboratory experiments were performed to evaluate isotope enrichment factors, and the isotopic composition of a TCE plume was monitored under pre-injection and post-injection conditions.

Large fractionation of stable carbon isotopes was observed in laboratory experiments at various mass ratios of TCE to potassium permanganate with values for the enrichment factor around -28.0‰, which is in agreement with previous studies. The experimental data suggests that carbon isotope fractionation remained constant with time, and was independent of the permanganate to TCE ratio. In contrast, the fractionation of stable chlorine isotopes during oxidation of TCE by potassium permanganate was negligible, and implies that chlorine isotopes are not sensitive tracers to monitor oxidation of TCE in contaminated ground water.

Field remediation at a TCE site involved a single injection of 40,000 L (2.5% by wt) of $KMnO_4$ solution distributed in several wells. Pre-injection conditions showed TCE concentrations as high as 175 mg/L with $\delta^{13}C$ values around -25.5‰. No changes were observed in ^{37}Cl composition for pre and post injection conditions, which is in agreement with the laboratory data. Significant carbon isotope fractionation associated with a decrease in TCE concentration was observed in post-injection ground water samples taken at several locations within the contaminated plume, with a maximum $\delta^{13}C$ value of +5.1‰. Part of this isotope shift is due to TCE oxidation. The chloride and isotope data showed that continuous input of aqueous TCE by diffusion from the rock matrix occurred during the oxidation process. A rebound effect is documented by the isotope data as the potassium permanganate is consumed. Furthermore, the isotope data showed that a significant decrease in TCE concentrations observed in some wells located away from the injection points was due to ground water displacement that resulted from the injection process instead of oxidation. This study showed that carbon isotopes can be used to assess the dynamics between TCE oxidation in the fracture network and diffusion from the rock matrix in fractured rock aquifers.

Introduction

Chlorinated ethenes frequently form persistent plumes in fractured bedrock aquifers. Long term diffusion-controlled release of contaminant mass, especially from a porous rock matrix can result in extensive treatment periods using conventional methods (Mutch et al., 1991). In situ chemical oxidation via potassium permanganate injection is one possible treatment method currently being employed to destroy chlorinated ethenes in dense non-aqueous phase liquid (DNAPL) source zones and ground water plumes. Permanganate has been shown in laboratory and field studies to effectively destroy trichloroethene (TCE) DNAPL in sandy aquifers (Parker et al., 2002; Schnarr et al., 1998). The use of permanganate injection to oxidize chlorinated ethenes in aquifers is particularly attractive due to rapid reaction rates, a high aqueous solubility, simple oxidant preparation, and relatively low treatment costs (Yan and Schwartz, 1999; Schnarr et al., 1998).

The evaluation of DNAPL field site remediation normally involves monitoring concentration changes over time. Conventional methods rely on observing chlorinated ethene concentration decreases and chloride concentration increases to indicate contaminant mass destruction. However, the interpretation of observed concentration changes in a fractured rock aquifer can be complicated by different factors: a) complexity of the fracture network; b) permanganate injection can readily displace contaminated ground water within the aquifer, inducing concentration changes; c) chloride concentrations may accumulate in aquifers with repeated permanganate injection episodes, potentially causing chloride concentration changes as a result of the injection process and density driven movement; and d) diffusion of contaminant mass from the rock matrix and dissolution from DNAPL can cause rebounding chlorinated ethene concentrations. All of these factors can lead to incorrect determinations.

A study in a sand aquifer has shown that carbon isotopes are an additional tool that can be used to evaluate the oxidation of chlorinated ethenes by potassium permanganate (Hunkeler et al., 2003). The objective of this study was to test the application of carbon and chlorine isotopes to monitor the oxidation of TCE by potassium permanganate in a fractured limestone aquifer. The study approach included conducting laboratory experiments to determine carbon and chlorine isotope fractionations during the oxidation of TCE under different TCE/$KMnO_4$ ratios, and monitoring the isotope composition and concentration of TCE during pre-injection and post-injection conditions at the field site.

Site Description and Background

The field site consists of an industrial facility located close to the St. Lawrence River in Eastern Ontario. Chlorinated solvent contamination was detected in ground water on the south end of the property in 1989. A TCE plume with concentrations several orders of magnitude larger than associated degradation products exists in the shallow bedrock aquifer.

Field site geology is comprised of a thin layer of sand and fill overburden, approximately one metre thick in many locations, overlying sedimentary rock. A dolomitic limestone of variable thickness overlies granite at depths ranging from 14 to 24 metres below ground surface (m bgs). Data obtained during a borehole drilling program conducted in 2004 and 2005 revealed that the limestone bedrock is relatively non-porous and moderately fractured. Fractures occur predominantly along horizontal and sub horizontal bedding planes.

The ground water table is encountered within the shallow bedrock. The highest TCE concentrations detected in ground water occur immediately south of the site building in the shallow bedrock at depths less than 15 m bgs (Figure 1). This area coincides with the location of a former TCE above ground storage tank (AST), and is believed to be the source zone. Plume TCE concentrations decrease towards the south in the direction of ground water flow. Monitoring and injection wells are either screened or open boreholes with well bottoms located at depths less than 10 m bgs.

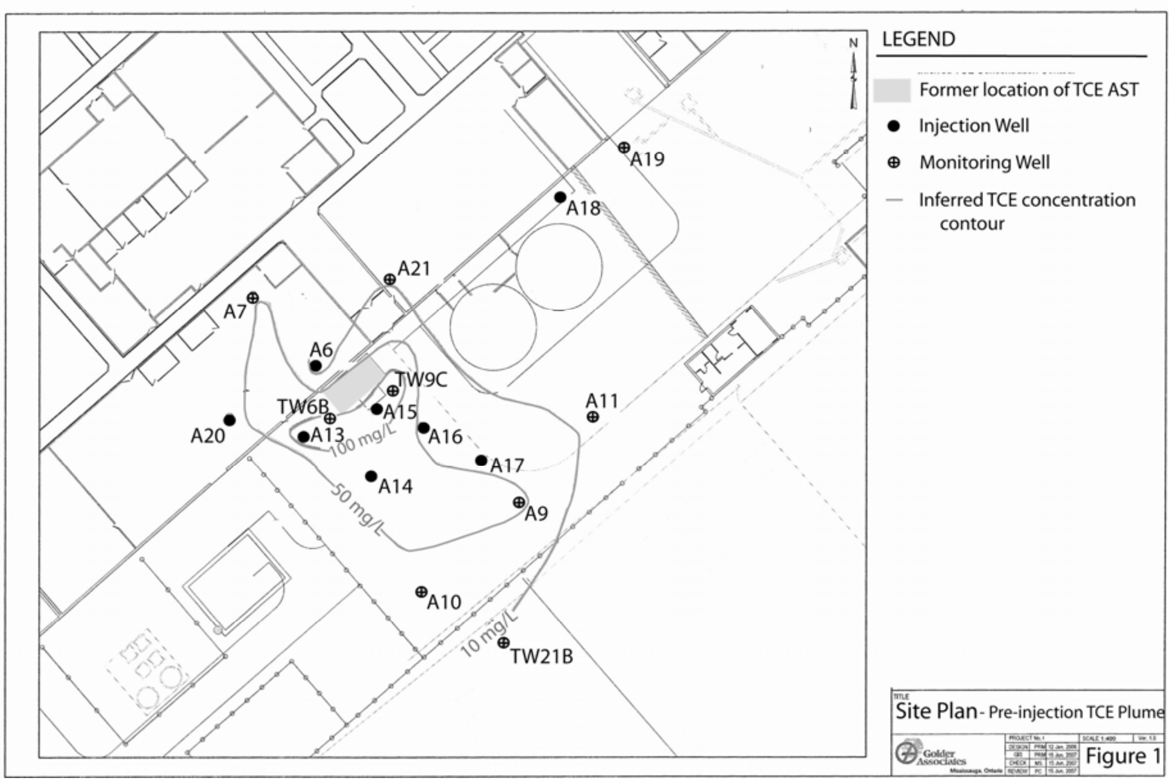

Figure 1. Field site plan shows the pre-injection TCE plume and the injection and monitoring well locations. Wells A6, A7, A20 and A21 are located inside the building. All other monitoring wells are located outside the building.

In 1992, a ground water pump and treat system was constructed at the south property boundary down gradient of the source zone to limit off-site migration. Persistent elevated TCE concentrations have remained in the source zone despite operation of the pump and treat system for 15 years. The persistence of the ground water plume and TCE in the source zone at concentrations of up to 20% of the pure phase solubility indicates significant diffusion of TCE from the bedrock matrix, or the possible presence of residual free-phase DNAPL in the shallow bedrock. A pilot-test permanganate injection in the source zone was conducted in 2005.

Materials and Methods

Laboratory Experiments

Carbon and chlorine isotope fractionations resulting from the oxidation of TCE by potassium permanganate were evaluated in a laboratory study. Three oxidation experiments reflecting different mass ratios of TCE to potassium permanganate were conducted to investigate the effect of excess and limited oxidant concentrations. One experiment with excess oxidant concentration and two experiments with limited oxidant concentrations were carried out. The stoichiometry of the oxidation of TCE by potassium permanganate requires a ratio of potassium permanganate to TCE of 2:1. The excess oxidant experiment was characterized by an initial molar ratio of potassium permanganate to TCE of 13:1, while the limited oxidant experiments were characterized by initial molar ratios of potassium permanganate to TCE of 1.5:1 and 0.5:1.

A TCE solution with a designed concentration of 70 ppm was prepared by diluting a reagent grade, saturated TCE stock solution. The prepared TCE solution was added to 65 mL glass vials containing potassium permanganate solution. The oxidation reaction was stopped at predetermined time intervals by quenching with a sodium thiosulfate and calcium nitrate solution.

Analytical Methods

Aqueous TCE concentrations in laboratory and field samples were determined on a gas chromatograph equipped with an electron capture detector (GC-ECD).

Chloride concentrations in ground water samples were determined using ion chromatography. Ground water samples were filtered with 0.45 μm glass syringe filters prior to chloride analysis.

A continuous flow gas chromatograph connected via a combustion interface to an isotope ratio mass spectrometer (GC-C-IRMS) system was used to determine the carbon isotope ratios of TCE as described in Hunkeler and Aravena (2000). Chlorine isotope ratios were analyzed by a continuous flow-isotope ratio mass spectrometer equipped with gas chromatograph and a CTC analytics CombiPAL SPME autosampler as described in Shouakar-Stash et al. (2006). Carbon and chlorine isotope ratios ($^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$) are expressed in delta notation ($\delta^{13}C$ and $\delta^{37}Cl$) measured relative to the Vienna Peedee Belemnite (VPDB) and standard mean ocean chloride (SMOC) standards, respectively. The $\delta^{13}C$ and $\delta^{37}Cl$ values are given by $\delta = (R_{sample}/R_{reference} - 1) \times 1000$, where R_{sample} and $R_{reference}$ are the carbon and chlorine isotope ratios of the aqueous sample and the respective standard. The precision for carbon isotope analysis is ± 0.5‰, while that for chlorine isotope analysis ± 0.1‰.

Field Study

Ground water monitoring and sampling was conducted at the field site once before potassium permanganate injection, and three times after injection. Pre-injection ground water sampling was conducted one week prior to permanganate injection, while post injection ground water sampling was conducted in weeks 1, 5, and 34 after the injection. Ground water was sampled after monitoring wells were purged by removing three well volumes of water or until dry. Sampling was completed with dedicated polyethylene bailers or inertial hand pumps. Water samples were collected in 40 ml glass vials without headspace and sealed with Teflon lined caps. All ground water samples were preserved with sodium azide. Ground water samples collected after permanganate injection were quenched in the field with a sodium thiosulfate and calcium nitrate solution to prevent further oxidation of TCE.

The field test involved a single injection episode of $KMnO_4$ solution over the course of two weeks in October 2006. A total volume of 40,000 L of 2.5% by weight $KMnO_4$ was injected, distributed in eight wells located in the source zone (A6, A13, A14, A15, A16, A17, A18 and A20, Figure 1).

Evaluation of Isotope Fractionation

Isotope fractionation during the oxidation of TCE under excess and limited permanganate supply conditions can be assessed using the Rayleigh equation. The Rayleigh equation is defined by

$$R = R_0 \cdot F^{(\alpha-1)} \tag{1}$$

where R is the carbon isotope ratio of the remaining TCE, R_0 is the initial carbon isotope ratio of the TCE, F is the fraction of TCE remaining, and α is the isotope fractionation factor. Isotope fractionation can be expressed in ‰, as an isotopic enrichment factor ε, given by $\varepsilon = 1000 \cdot (\alpha-1)$. The carbon isotopic composition of the TCE at a remaining fraction F and that of the initial TCE prior to oxidation is represented by $\delta^{13}C$ and $\delta^{13}C_0$, respectively. The isotopic enrichment factor was evaluated with the Rayleigh equation as expressed in terms of an isotopic enrichment factor and $\delta^{13}C$ values as given by

$$1000 \cdot \ln\left(\frac{\delta^{13}C + 1000}{\delta^{13}C_0 + 1000}\right) = \varepsilon \ln F \tag{2}$$

Results

Laboratory Experiments

Excess and limited permanganate supply experiments were characterized by an exponential decrease in TCE concentration with a coincident increase in carbon isotope ratios with time. TCE oxidation by excess permanganate was rapid, consuming approximately 99% of the TCE in 10 minutes. A pseudo-first-order rate constant with a value of 7.2×10^{-3} s^{-1} was determined. The oxidation of TCE by limited permanganate supply was much slower, following second-order kinetics with rate constants of 1.49 and 0.11 L mol^{-1} s^{-1} for the 1.5:1 and 0.5:1 experiments, respectively. Reaction half-lives calculated for the excess and limited 1.5:1 and 0.5:1 experiments were 1.6, 21, and 279 minutes, respectively.

Large carbon isotope fractionation was observed during the oxidation of TCE by permanganate. The isotopic composition of the TCE changed from an initial $\delta^{13}C$ value of -33.2‰ to final values of +94.0, +5.3 and -22.4‰ for the excess 13:1 ratio, and limited 1.5:1 and 0.5:1 ratio experiments, respectively. Negligible fractionation of stable chlorine isotopes was observed in the laboratory as a result of TCE oxidation by permanganate. Chlorine isotopic compositions changed insignificantly, with no evident $\delta^{37}Cl$ trend over the course of the experiments. The $\delta^{37}Cl$ values changed from an initial value of +3.4‰ to final values ranging from +3.3‰ to +3.5‰.

Carbon isotopic enrichment factors were determined using equation (2) and least-squares linear regression analysis. Experimental $\delta^{13}C$-concentration data for the three permanganate experiments plotted as straight lines and were characterized by good fit to the regression analysis, with r^2 values ranging from 0.9952 to 0.9995. Carbon isotopic enrichment factors with values of -28.6, -28.2, and -27.1‰ were determined for the excess and limited 1.5:1 and 0.5:1 experiments, respectively. These values are consistent with the range of values reported in previous experimental studies (-20.9 to -26.8 ± 1.1) (Hunkeler et al., 2003; Poulson and Naraoka, 2002).

Field Study

The carbon isotopic composition of TCE determined from 15 pre-injection ground water samples varied between $\delta^{13}C$ values of -24.7 and -26.7‰, with an average value of -25.8 ± 0.7‰. These $\delta^{13}C$ values are slightly more enriched than the characteristic range for TCE as determined in isotopic composition studies (Jendrzejewski et al., 1997, 2001; Beneteau et al., 1999; Holt et al., 1997; van Warmerdam et al., 1995). It is likely that biodegradation of TCE in the aquifer may have resulted in enriched $\delta^{13}C$ values, which is also supported by the detection of cis-1,2-dichloroethene (cis-DCE) in the ground water at concentrations one to two orders of magnitude smaller than that of TCE. However, because TCE $\delta^{13}C$ values do not vary significantly, the carbon isotopic composition of the TCE is well constrained and provides a good basis to monitor isotopic changes resulting from carbon isotope fractionation during chemical oxidation.

The pre-injection chlorine isotopic composition of TCE determined at the same 15 wells was characterized by δ^{37}Cl values ranging between +0.8 and +2.6‰. Pre-injection δ^{37}Cl values fall within the experimental range determined for TCE in isotopic composition studies (Numata et al., 2002; Jendrzejewski et al., 1997, 2001; Beneteau et al., 1999; Holt et al., 1997; van Warmerdam et al., 1995; Tanaka and Rye, 1991;). The average TCE δ^{37}Cl value determined from 10 ground water samples one week after injection (1.7 ± 0.6) was equivalent to the initial pre-injection value (1.7 ± 0.5). The chlorine isotope ratios of TCE did not change as a result of oxidation by permanganate in the field, and is consistent with the laboratory results where chlorine isotope fractionation was deemed negligible. Consequently, the discussion will focus on the δ^{13}C data. Concentration and δ^{13}C values of TCE at selected wells that best represent the contaminated aquifer's response to permanganate injection are presented in Figure 2.

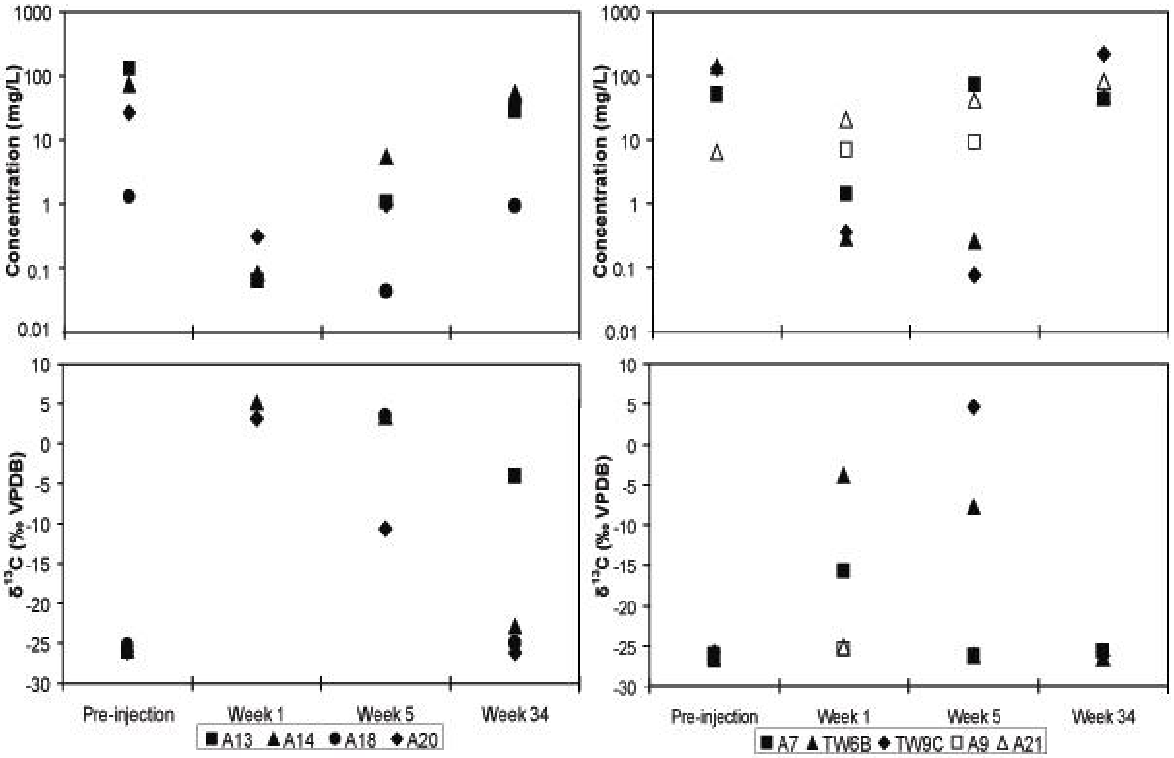

Figure 2. Concentration and δ^{13}C values of TCE in injection wells (A13, A14, A18, A20) and adjacent monitoring wells (A7, TW6B, TW9C, A9, A21) before permanganate injection, 1week, 5 weeks, and 34 weeks after permanganate injection. The TCE concentration in A18 in week 1 was below the MDL (1 µg/L) and consequently does not show up on the graph.

Pre-injection TCE concentrations ranged from 0.3 to 175 mg/L. The highest TCE concentrations were encountered in the source area at wells A13, A15, TW6B, and TW9C (Figure 1). Chloride concentrations prior to permanganate injection ranged from 36 to 614 mg/L.

Pre-injection TCE concentrations in the injection wells generally decreased to levels near or below the method detection limit (MDL) by week 1 and started to rebound by week

5. Injection wells located along the periphery of the source zone rebounded completely, with TCE concentrations reaching or exceeding pre-injection levels by week 34. In contrast, injection wells located within the source zone experienced a slower rebound, with significantly lower TCE concentrations by week 34. Potassium permanganate was still present in these wells by week 34.

Chloride concentrations increased by less than a factor of 4 in wells where permanganate had been observed after injection. By week 34, chloride concentrations remained elevated in several wells while decreasing to pre-injection levels in other wells. Chloride levels generally remained elevated until permanganate was no longer observed in the wells.

Injection wells A18 and A20 were characterized initially by large decreases in TCE concentration and strong carbon isotope fractionation with $\delta^{13}C$ values reaching +3.5 and +3.1‰, respectively. Subsequently, TCE concentrations and $\delta^{13}C$ values rebounded to pre-injection levels by week 34. Low concentration or no potassium permanganate was detected in these wells by week 34. It is important to note that this parallel response observed in both wells occurred even though TCE concentrations differ by two orders of magnitude in these wells. A similar $\delta^{13}C$ trend was observed in injection well A6, however the TCE concentration at week 34 was much higher (20.6 mg/L) than the pre-injection condition (9.2 mg/L).

Injection wells A14 and A13 were characterized by a large increase in $\delta^{13}C$ values, reaching +5.1 and -4.1‰ in weeks 1 and 34, respectively. The $\delta^{13}C$ value at injection well A14 peaked in week 1, decreasing to -22.9‰ in week 34. Both A13 and A14 were characterized by rebounding TCE concentrations and $\delta^{13}C$ values that did not fully reach pre-injection levels by week 34. Potassium permanganate was still present in well A13 by week 34.

Several adjacent monitoring wells experienced a similar response to permanganate injection. At monitoring wells TW6B and TW9C, the TCE concentration decreased until week 5, and then rebounded by week 34. The TCE concentration at TW9C rebounded above pre-injection levels. At A7, the TCE concentration decreased and started to rebound after week 1, returning to higher concentration than pre-injection levels by week 5.

Significant carbon isotope fractionation followed by a rebound in $\delta^{13}C$ values to pre-injection levels was observed in monitoring wells A7, TW6B and TW9C. The $\delta^{13}C$ values at A7 and TW6B increased to -15.8 and -3.8‰ in week 1, respectively, while that at TW9C increased to +4.7‰ in week 5. A full rebound in $\delta^{13}C$ values back to pre-injection levels was observed in A7 by week 5 and in TW6B and TW9C by week 34. No traces of potassium permanganate were detected in these wells by week 34.

The presence of permanganate was never observed at any time during the field experiment in down gradient monitoring wells A9 and A11, or in A21 located slightly up and cross gradient (Figure 1). The TCE concentration and $\delta^{13}C$ trends observed in these wells differed from that in wells where permanganate presence was observed. Carbon isotope ratios at A9, A11, and A21 did not vary significantly and remained close to pre-injection values throughout the 34 weeks of the study. However, significant changes in TCE concentration were observed at A11 and A21 over the course of the field experiment, increasing by factors of approximately 5 and 13, respectively. At A9, the TCE concentration decreased by week 1 and remained lower than pre-injection levels.

Chloride concentration changes were also observed in monitoring wells A9, A11, and A21. Chloride concentrations in A9 and A21 increased over the course of the field experiment, while those in A11 decreased in weeks 1 and 5, rebounding back to pre-injection values in week 34.

Discussion

Laboratory Experiments

Kinetic and isotopic data collected in the laboratory experiments suggest that carbon isotope fractionation during TCE oxidation by permanganate is independent of the oxidation rate. Oxidation rates determined for the excess and limited oxidant experiments differed significantly, while the ^{13}C enrichment factors were reasonably well constrained. This finding is consistent with experimental results obtained by Poulson and Naraoka (2002).

Experimental data obtained during TCE oxidation experiments followed a Rayleigh fractionation trend, and suggest that the carbon isotopic enrichment factors remained constant with time. Furthermore, the carbon isotopic enrichment factors determined for the excess and limited permanganate experiments are similar, and suggest that the magnitude of carbon isotopic fractionation is independent of the permanganate to TCE ratio. In contrast, the fractionation of stable chlorine isotopes during oxidation of TCE by potassium permanganate was negligible, and implies that chlorine isotopes are not sensitive tracers to monitor oxidation of TCE in contaminated ground water.

Field Study

The post-injection field data showed significant carbon isotope enrichment associated with a decrease in TCE concentration. This is in agreement with the large carbon isotope fractionation measured in the laboratory experiments during the oxidation of TCE by potassium permanganate. The most enriched $\delta^{13}C$ value measured in this study was +5.1‰, which is much lower than the value of +204‰ reported by Hunkeler et al. (2003) in a sand aquifer, even though TCE concentration changes observed in both studies were within the same range. This implies that TCE input by diffusion from the rock matrix plays a major role during the oxidation process in a fractured rock environment. A recent study has shown that most of the contaminant mass present in a fractured rock aquifer impacted with volatile organic compounds (VOC), exists in the rock matrix (Hurley, 2003).

No changes were observed in the chlorine isotope composition during post-injection, which is in agreement with results from the laboratory experiments. Several wells showed a trend toward the $\delta^{13}C$ value of TCE under pre-injection conditions, which can be explained by a combination of input of TCE by diffusion from the rock matrix and a decreasing rate of TCE oxidation as the permanganate is consumed. This interpretation agreed with the potassium permanganate pattern observed in these wells.

Chloride concentration patterns show the role that diffusion of TCE from the rock matrix plays during the oxidation process. Based on the stoichiometry of the oxidation reaction, one mole of TCE produces 3 moles of chloride. Consequently, chloride concentrations were expected to increase where concentration and $\delta^{13}C$ data indicated the occurrence of TCE oxidation. Chloride concentration increases in A6, A18, A20, and TW9C in weeks 1 and 5 after permanganate injection were substantially greater than expected, based on the observed decreases in TCE concentration. This suggests that not only dissolved TCE present during pre-injection monitoring was oxidized, but that additional TCE underwent oxidation, consistent with the $\delta^{13}C$ data. As permanganate oxidizes and destroys aqueous TCE, a concentration gradient is created that in turn promotes TCE diffusion from the rock matrix. Fresh TCE diffusing from the rock matrix likely has a carbon isotopic composition comparable to that of the pre-injection aqueous TCE. Consequently, when low $\delta^{13}C$ TCE diffuses from the rock, it mixes with the remaining aqueous TCE that has been enriched in ^{13}C due to carbon isotope fractionation.

Concentration changes in some wells seem to be associated with ground water displacement that results from the injection process. The displacement of un-oxidized ground water with varying TCE concentrations could have resulted in the trends observed at A9, A11, and A21. The TCE concentration and $\delta^{13}C$ trends observed at A11 and A21 were likely caused by the displacement of high TCE concentration ground water present in the source zone prior to injection.

Chloride concentrations were not expected to increase in wells where permanganate was not observed. The absence of permanganate and low $\delta^{13}C$ values that remained within pre-injection levels throughout the field experiment in wells A9 and A21 indicates that TCE was not oxidized. Chloride concentration changes in these wells were likely due to ground water displacement during permanganate injection and possibly due to density driven movements after injection. The chloride concentration at monitoring well A21 steadily increased from 36 to 172 mg/L after injection, while the TCE concentration increased from 6.4 to 82.2 mg/L. This is consistent with the displacement of contaminated water away from the source area.

Conclusions

The laboratory study confirms the occurrence of a large carbon isotope fractionation during oxidation of TCE by potassium permanganate. Furthermore, the experimental data suggests that carbon isotope fractionation remained constant with time, and was independent of the permanganate to TCE ratio. Chlorine isotope fractionation observed during TCE oxidation by permanganate was negligible.

Strong enrichment of carbon isotope ratios coincident with TCE concentration decreases to low levels, frequently below MDL observed in injection and adjacent monitoring wells after permanganate injection into a fractured limestone aquifer is in agreement with the laboratory study. Carbon isotope ratios and TCE concentrations rebounded back to pre-injection levels in all wells, with the exception of locations where permanganate was still present at the end of the field experiment. The greater than expected chloride concentrations observed in several wells indicates a continuous input of TCE released by diffusion from the rock matrix during the oxidation process. Carbon isotope data and chloride concentration patterns in wells not affected by oxidation indicated that ground water displacement due to the injection process was responsible for changes in TCE concentration in these wells.

This study has shown that $\delta^{13}C$ values can be used to assess the dynamics between oxidation in the fracture network and diffusion of TCE from the rock matrix, and the role that ground water displacement resulting from the injection process plays in TCE concentration changes in fractured bedrock aquifers.

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