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MONITORING IN SITU OXIDATION OF TCE BY PERMANGANATE USING CARBON ISOTOPES

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ABSTRACT: Injection of permanganate is increasingly used as a method for in situ destruction of chlorinated ethenes in sources zones and plumes. Application of the method requires reliable tools to verify that the permanganate has come in contact with the chlorinated ethenes and to demonstrate that oxidation of chlorinated ethenes occurs. The main aim of this study was to evaluate if stable carbon isotope ratios of TCE can be used to monitor TCE oxidation. The approach is based on the expectation that the reaction rate for TCE oxidation is slightly faster for molecules with ^{12}C than for molecules with ^{13}C and thus, TCE becomes increasingly enriched in ^{13}C as the reaction proceeds (shift to more positive $\delta^{13}C$ values). The occurrence of isotope fractionation during oxidation of TCE was investigated in laboratory experiments with TCE having an initial $\delta^{13}C$ value of –27.4%. A strong increase in the $\delta^{13}C$ to values >+50% was observed during oxidation with permanganate confirming that TCE oxidation is accompanied by significant carbon isotope fractionation.

Carbon isotope ratios were also measured at a field site where permanganate was injected during three episodes to treat a TCE source zone and a TCE plume. At that site, interpretation of Cl^- concentrations as an indicator for treatment progress was difficult. Cl^- concentrations initially increased but then remained constant, decreased again or increased in zones, where no significant amount of TCE was expected. In contrast, a strong increase of the $\delta^{13}C$ of TCE from –27.5 to +38.5% could be observed which made it possible to locate zones of TCE oxidation. After the last permanganate injection, a reverse trend of the $\delta^{13}C$ towards the initial $\delta^{13}C$ of TCE could be observed suggesting desorption or dissolution of small amounts of TCE remaining in the aquifer sediments.

INTRODUCTION

Laboratory and field studies have shown that oxidation of chlorinated ethenes by permanganate is potentially an effective method to destroy chlorinated ethenes present as dense non-aqueous liquid (DNAPL) in aquifers (Nelson et al., 2001; Schnarr et al., 1998). When implementing the permanganate method, monitoring tools are required to verify that the permanganate solution has come in contact with chlorinated ethenes and destruction of chlorinated ethenes occurs. Concentration decreases of chlorinated ethenes and increases of Cl^- have been used as indicators of chlorinated ethene mass destruction. However, concentrations of chlorinated ethenes can decrease due to displacement of contaminated water by the injected permanganate solution rather than oxidation or concentrations may remain elevated even though destruction occurs due to continuous dissolution of immiscible phase. While Cl^- concentrations may initially be a sensitive monitoring parameter, after a large amount of Cl^- has accumulated, interpretation of Cl^-

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data can become ambiguous because concentration changes may be due to the movement of fluids with different Cl^- levels induced by permanganate injection and density gradients.

The aim of the study was to assess the use of carbon isotopes as a complementary tool to identity in situ destruction of chlorinated ethenes. Stable isotopes have shown promise as a method to assess biodegradation of chlorinated hydrocarbons or petroleum hydrocarbons (Hunkeler et al., 1999; Hunkeler et al., 2001; Sherwood Lollar et al., 1999) and to evaluate transformation of chlorinated hydrocarbons by zero valent iron (Dayan et al., 1999). The method 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. Usually molecules with light isotopes are transformed faster than molecules with heavy isotopes. As a result, the reactant becomes increasingly enriched in heavy isotopes while the product is depleted in heavy isotopes relative to the reactant. This unequal distribution of isotopes between product and reactant is denoted as isotope fractionation. The trend towards a higher content of heavier isotopes in the reactant during transformation processes has been used to monitor biodegradation of chlorinated ethenes at field sites (Hunkeler et al, 2002). The aim of this study was to evaluate if isotope fractionation also occurs during oxidation of chlorinated ethenes by permanganate and to determine whether isotope analysis can be used to verify in situ oxidation of chlorinated ethenes at field sites.

MATERIAL AND METHDOS

Laboratory studies. Carbon isotope fractionation during oxidation of trichloroethene by potassium permanganate was investigated in a laboratory study. Permanganate solution was added to triplicate 40 ml VOC vials containing 70 ppm TCE. The reaction was quenched at regular time intervals using a thiosulfate solution. The concentration of TCE was determined after pentane extraction of aqueous samples using a gas chromatograph with an ECD detector. The carbon isotope ratio of TCE was determined using a gas chromatograph connected via a combustion interface to an isotope-ratio mass spectrometer as described in Hunkeler et al. (1999). Carbon isotope ratios ($^{13}C/^{12}C$) are reported in the usual delta notation ($\delta^{13}C$) relative to the VPDB (Vienna Peedee Belemnite) standard. 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. The accuracy of the measurement is about 0.5%. More positive $\delta^{13}C$ numbers indicate a higher content of the heavy isotope ^{13}C.

Frequently, the shift of $\delta^{13}C$ as function of the reaction progress can be described by the Rayleigh equation, which is given by:

$$1000 \cdot \ln \frac{\delta^{13}C_S + 1000}{\delta^{13}C_{So} + 1000} = \varepsilon \cdot \ln f \qquad (1)$$

where $\delta^{13}C_S$ is the carbon isotope ratio of the substrate at a remaining fraction f (f=1 at beginning of reaction, f=0 when reaction completed) and $\delta^{13}C_{So}$ the initial carbon isotope ratio of the substrate. The parameter ε is denoted as isotopic enrichment factor and is a measure of the magnitude of isotope fractionation. Equation 1 can be used to evaluate if ε

remains constant during the reaction and to determine its value.

Field study. The field site consists of an industrial property in Florida, US where chlorinated solvents were spilled in the period between March 1995 and April 1997. The geology of the site is comprised of fine to medium grained sand, approximately 26 m thick, overlying a fossiliferous limestone. Limestone fragments appear at a depth of 15 m below ground surface (bgs) and increase in both size and frequency downward to the limestone layer. The water table at the site fluctuates from the surface to a depth of 1.5 m bgs. The groundwater system is close to being stagnant with very low horizontal and no vertical gradients. The DNAPL infiltrated below ground surface and moved downward to accumulate at a maximum depth of 16.8 to 18.3 m bgs, where downward migration was impeded by thin layers of coarse sand. The highest concentration of dissolved TCE, the main contaminant at the site, was 625.5 ppm and occurred at a depth of 18.5 m bgs. Cis-1,2-dichloroethene (cis-DCE), a by-product of biodegradation of TCE and 1,1,1-TCA are also present at the site. The DNAPL contaminated zone was treated using the passive, episodic permanganate method (Parker et al., 2002, Nelson et al. 2001), which involves injection of permanganate solution over a short period of time followed by a rest period to allow for diffusive and density driven transport of permanganate and reaction with the chlorinated ethenes. Three injection episodes were conducted: Episode 1 (March 31 to April 10, 2000), episode 2 (June 1 to 7, 2000), episode 3 (September 28 and October 4, 2000). The potassium permanganate solution was injected above and within the contaminated zone using a drive point that was driven to desired depth using a direct-push drill rig. The concentrations of TCE, $KMnO_4$ and Cl^- were monitored in detail before and after injections using a network of multi-level samplers. More information about the injections is provided by Parker et al. (2002; this volume).

RESULTS AND DISCUSSION

In the laboratory experiment, the concentration of TCE exponentially decreased with time due to oxidation of TCE by permanganate (Figure 1). Within 10 minutes of reaction, 70 ppm of TCE was consumed. The TCE had an initial $\delta^{13}C$ of –27.3%. During the reaction, a steady increase of the $\delta^{13}C$ was observed and after 10 minutes a $\delta^{13}C$ value of +58.3 to +64.5% was reached in the residual TCE. This demonstrates that TCE molecules with ^{12}C are transformed faster than TCE molecules with ^{13}C, leading to an enrichment of ^{13}C in the remaining TCE (more positive $\delta^{13}C$ values). To evaluate if the shift in $\delta^{13}C$ follows a systematic trend, the data were plotted according to equation 1 (Figure 2). A linear relationship between **lnf and** $\ln((\delta^{13}C_S + 1000)/(\delta^{13}C_{So} + 1000))$ was found demonstrating that the magnitude isotope fractionation remains constant with time. Using least square linear regression, an isotopic enrichment factor of –25.1% was obtained. The enrichment factor is larger than those previously observed for TCE transformation by microbial reductive dechlorination (-2.5 to –13.8%, Bloom et al., 2000; Slater et al., 2001) and by reductive dechlorination by zero valent iron (-8.6%, Dayan et al., 1999).

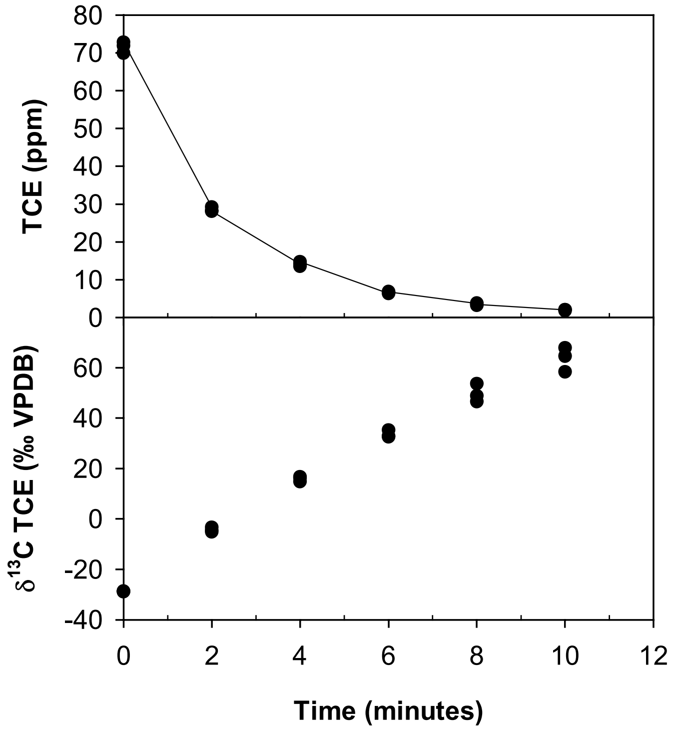

FIGURE 1. Decrease of TCE concentration and increase of δ^{13}C of TCE during oxidation by permanganate in laboratory experiment.

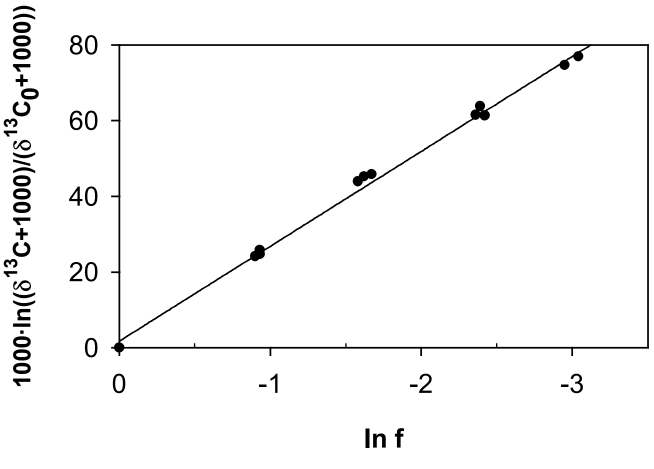

FIGURE 2. Results of TCE experiment plotted according to equation 1 (see text) to evaluate if isotope fractionation remains constant during experiment.

Concentrations of TCE and Cl^- at the field site are shown for the multilevel bundle at which the highest TCE concentrations were detected (Figure 3). Permanganate solution was injected during all three episodes within a distance of 1.5 m of this multilevel bundle. The first diagram illustrates pre-injection concentrations, the second concentrations 7 weeks after the second injection, the third concentrations 9 weeks after the third and last injection, and the fourth concentrations 21 weeks after the last injection. Between February and July 2000, the concentration of TCE decreased at some of the monitoring points while it increased at others, between July and December 2000 it decreased to relatively low concentrations at all monitoring points. The Cl^- concentration increased at depths >17m bgs between February and July 2000, but no further increase was observed between July 2000 and December 2000 except for the deepest monitoring point despite a strong decrease in TCE concentrations. This makes it difficult to demonstrate TCE oxidation between July and December 2000 using Cl^- concentrations. Carbon isotope ratios were measured at the two sampling points with the highest initial TCE concentration. While the $\delta^{13}C$ of TCE remained the same at the upper sampling point between February and July 2000, a strong increase of the $\delta^{13}C$ can be observed at the lower sampling point clearly indicating TCE destruction by oxidation with permanganate. Between July 2000 and December 2000, when a decrease in TCE concentration was observed without an increase of Cl^-, again $\delta^{13}C$ values provide clear evidence for TCE oxidation. At the upper sampling point, the $\delta^{13}C$ increased from –27.5 to –4.4% indicating TCE oxidation, at the lower an increase from +32.9 to +38.5% could be observed. The Cl^- produced by TCE oxidation has migrated to greater depths explaining the elevated Cl^- concentration at >20 m. Parker et al. (2002) conclude that this site has only small dispersed gobules of DNAPL causing chloride tracking to be less sensitive for remediation assessment. Twenty one weeks after the last permanganate injection, the $\delta^{13}C$ values of TCE were close to the initial $\delta^{13}C$ values representative of the TCE source. The reverse trend towards the initial $\delta^{13}C$ value of TCE can be explained by desorption or dissolution of small amounts of TCE still present in the aquifer.

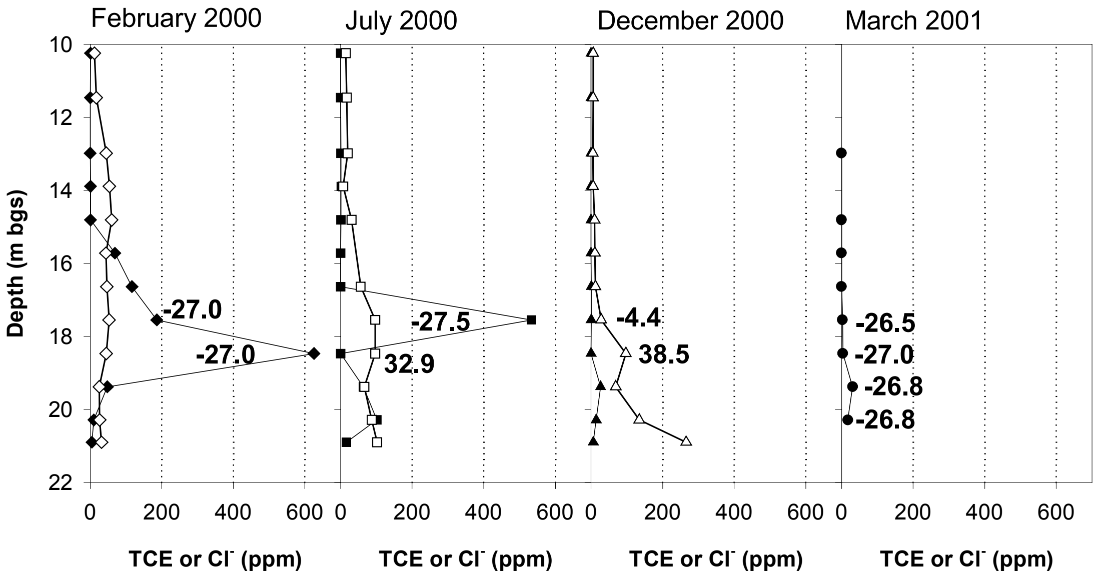

FIGURE 3. TCE concentration (filled marker), chloride concentrations (open markers) and $\delta^{13}C$ of TCE at selected points in multilevel bundle well in center of contaminated zone.

CONCLUSIONS

The laboratory studies demonstrate that a very strong carbon isotope fractionation occurs during oxidation of TCE by potassium permanganate. A simple mathematical relation based on the Rayleigh equation describes the evolution of the $\delta^{13}C$ during TCE oxidation. The isotopic enrichment factor for TCE oxidation by potassium permanganate is much larger than values reported for biodegradation and reductive dechlorination by zero valent iron of TCE. At the field site, a strong trend towards enrichment of heavy isotopes could be observed, similar as in the laboratory experiment, followed by a reverse trend towards the initial $\delta^{13}C$ of TCE. Isotope analysis made it possible to demonstrate TCE oxidation at locations where Cl^- concentration did not yield unequivocal evidence for TCE oxidation, possibly due to migration of Cl^-. Furthermore, the observation that the $\delta^{13}C$ of TCE approached the initial $\delta^{13}C$ again after the last permanganate injection indicates that the isotope methods can be used repeatedly in situations where remediation occurs in several phases. Thus, this study suggests that $\delta^{13}C$ measurement in chlorinated ethenes can serve as a complementary tool to locate zones of oxidation of chlorinated ethenes and to follow the progress of the reaction.

ACKNOWLEDGMENTS

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REFERENCES

Bloom, Y., Aravena, R., Hunkeler, D., Edwards, E. and Frape, S.K., 2000. Carbon isotope fractionation during microbial dechlorination of trichloroethene, cis-1,2-dichloroethene and vinyl chloride: implication for assessment of natural attenuation. *Environ. Sci. Technol.*, *34*: 2768-2772.

Dayan, H., Abrajano, T., Sturchio, N.C. and Winsor, L., 1999. Carbon isotopic fractionation during reductive dehalogenation of chlorinated ethenes by metallic iron. *Org. Geochem.*, *30*: 755-763.

Hunkeler, D., Aravena, R. and Butler, B.J., 1999. Monitoring microbial dechlorination of tetrachloroethene (PCE) using compound-specific carbon isotope ratios: Microcosms and field experiments. *Environ. Sci. Technol.*, *33*(16): 2733-2738.

Hunkeler, D., Butler, B.J., Aravena, R. and Barker, J.F., 2001. Monitoring biodegradation of methyl tert-butyl ether (MTBE) using compound-specific carbon isotope analysis. *Environ. Sci. Technol.*, *35*: 676-681.

Hunkeler, D., Aravena, R. and Cox, E., 2002. Assessment of degradation pathways at sites with complex contaminant mixtures using isotopes. Proceedings: Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA May 20-23.

Parker, B.L., Cherry, J.A. and Al, T.A., 2002. Full-Scale permanganate remediation of a solvent DNAPL source zone in a sandy aquifer. Proceedings: Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA May 20-23.

Nelson, M.D., Parker, B.L., Al, T.A., Cherry, J.A. and Loomer, D., 2001. Geochemical reactions resulting from in situ oxidation of PCE-DNAPL by $KMnO_4$ in a sandy aquifer. *Environ. Sci. Technol.*, *35*: 1266-1275.

Schnarr, M. et al., 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichoroethylene and perchloroethylene DNAPLs in porous media. *J. Contam. Hydrol.*, *29*: 205-224.

Sherwood Lollar, B. et al., 1999. Contrasting carbon isotope fractionation during biodegradation of trichloroethylene and toluene: implications for intrinsic bioremediation. *Org. Geochem.*, *30*: 813-820.

Slater, G.F., Sherwood Lollar, B., Sleep, B. and Edwards, E., 2001. Variability in carbon isotopic fractionation during biodegradation of chlorinated ethenes: implications for field applications. *Environ. Sci. Technol.*, *35*: 901-907.