Effect of Experimental Conditions on Carbon Isotopic Fractionation of Trichloroethene Reaction with Granular Iron

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Introduction

Permeable reactive barriers (PRBs) containing granular iron have proven to be effective for remediation of groundwater contaminated with chlorinated ethenes.[1,2] In recent studies, compound-specific carbon isotope analysis has been used to study chlorinated ethene reactions with iron.[3-8] Significant carbon isotopic fractionation has been measured during dechlorination of chlorinated ethenes by iron. More importantly, the shifts in the isotopic composition of the residual chlorinated ethenes are highly reproducible and can be described by a Rayleigh model defined as $R = R_0 f^{(\alpha-1)}$, where R is the ratio of $^{13}C/^{12}C$ at a given fraction remaining f; R_0 is the initial ratio of $^{13}C/^{12}C$; and a is the isotopic fractionation factor[6,7]. In practice, the enrichment factor (ε), $\varepsilon = 1000(\alpha-1)$, is used to represent the change in isotopic composition during the dechlorination processes.

Slater et al.[6] determined carbon isotopic enrichment factors for TCE reactions with both iron filings and electrolytic iron. The iron samples were acid-washed or autoclaved before used in the batch experiments. A consistent enrichment factor of -16.7‰ was observed in the reactions involving iron filings and autoclaved electrolytic iron. Similarly, Schüth et al.[7] observed a consistent enrichment factor for iron from two different manufacturers, and for iron retrieved from a PRB. However, the average enrichment factor of -9.9‰ measured by Schüth et al. [7] was substantially different from the value measured by Slater et al.[6]. Under the respective sets of experimental conditions, both studies suggest that the carbon enrichment factor is independent of iron origin, surface condition, and reaction rate. However, the difference in the enrichment factors measured in these two studies indicates that experimental conditions may be important in determining the magnitude of the enrichment factor.

If a reaction involving chlorinated ethene and iron can be represented by a characteristic enrichment factor, this parameter may be used to study the reaction mechanism, and to monitor progress in degradation reactions occurring in field sites. However, it is necessary to understand the factors influencing the measured enrichment factor, before this parameter can be applied to a chlorinated ethene – iron system. The objective of this study was to determine the effect of experimental conditions on the carbon enrichment factor during dechlorination of TCE by iron.

Materials and Methods

Reagent-grade trichloroethene and millipore water were used in the experiments. The granular iron used was obtained from Connelly-GPM Inc. This material was sieved through a 60-mesh screen to remove fine particles before use, and had a surface area of 0.95 m^2/g.

Batch experiments were carried out in this study. In the baseline experiment (with a duplicate), an initial TCE concentration of approximately 10 mg/L was used. In each sample, 10 g of iron were placed in a 60 mL serum bottle, which was then filled with the TCE solution. Sample bottles were loaded on a rotary shaker rotated at a speed of approximately 20 rpm. The solution was sampled after reaction times of 2h, 6h, 1d, 2d, 3d, 5d, 7d, and 10d. Sufficient replicate samples were prepared for each reaction series so that every bottle was opened and sampled only once. The effect of initial TCE concentration, headspace, iron/solution ratio and mixing status on enrichment factor were examined using a series of experiments. In each experiment, only one parameter was varied relative to the baseline, and the following parameters were studied: 1 mg/L TCE (low TCE), 60 mg/L (high TCE), 10 mL headspace, 2 g iron, no mixing, shaking once per day, and slow mixing rate. To evaluate the effect of continuous abrasion of the iron particles during the rotation of sample bottles, in one experiment a pair of magnets was used to hold the iron particles in place during mixing.

Samples for analysis of TCE concentration were prepared using a pentane extraction method and analyzed by a GC-ECD. A headspace method was used to analyze the concentrations of DCE isomers and vinyl chloride by a GC-PID. Samples for carbon isotopic analysis were prepared by a headspace SPME (Solid Phase Micro Extraction) method. Compound-specific carbon isotopic ratios were determined using a continuous flow GC-C-IRMS system, consisting of a HP gas chromatograph, a combustion interface, and a MicromassIsoprimeisotope ratio mass spectrometer.

Results and Discussion

Dechlorination of TCE by iron can be described by the first order decay model (Fig. 1). Compared to the initial TCE concentration, the first sampling point after 2h of reaction showed a decrease of 30% to 50% in the concentration of TCE, caused primarily by adsorption onto the iron particles. In this study, the initial TCE concentration was not included in calculations of the reaction rate constants.
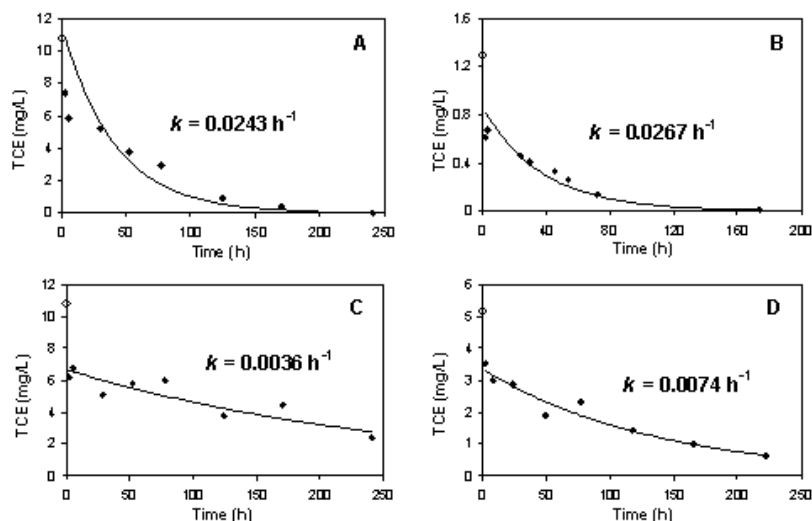

Fig. 1. Concentration of TCE versus reaction time under different experimental conditions. (A) Baseline experiment; (B) TCE concentration of 1 mg/L; (C) No mixing; (D) Mixing daily. Initial TCE concentration: open diamond; TCE concentration during reaction: solid diamond.

There is excellent agreement between the rate constants calculated for the baseline (Fig. 1A) and duplicate experiments (0.0243 h^{-1} vs. 0.0252 h^{-1}). Compared to the baseline experiment, the rate constant was slightly higher in the experiment with 1 mg/L TCE solution (Fig. 1B). In the experiment with 60 mg/L TCE solution, the rate constant was half that measured in the baseline. There was no difference in rate constant between samples with 10 mL headspace and those with no headspace. A rate constant similar to the baseline was also found in samples containing only 2 g iron, when the rate constant is normalized to the mass of iron. Rate constants varied with mixing conditions. The lowest reaction rate was measured in the experiment in which no mixing was applied (Fig. 1C). For the samples that were shaken daily, the rate constant was twice that measured in the experiment without shaking (Fig. 1D), whereas an intermediate rate constant was observed in the samples where a pair of magnets was used during mixing.

The baseline experiment (Fig. 2A), the duplicate, the headspace test, and the 60 mg/L TCE test all gave similar enrichment factor with an average value of -15.14±0.43‰. However, at the low TCE concentration (1 mg/L), the enrichment factor was considerably lower at -8.90‰ (Fig. 2B). Under conditions similar to the baseline, the enrichment factor decreased to -6.73‰ when no mixing was applied (Fig. 2C), and to -8.39‰ when the samples were shaken daily (Fig. 2D).
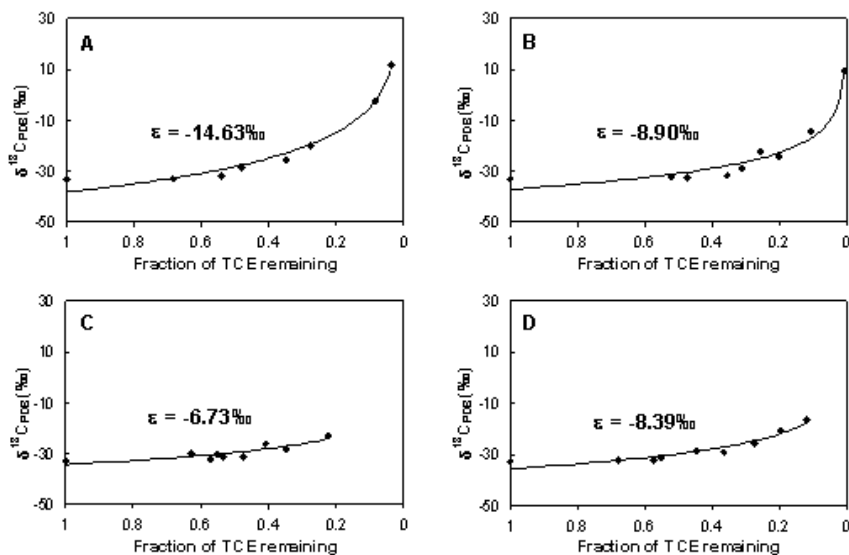
Fig. 2. Carbon isotopic composition of TCE versus fraction of TCE remaining. (A) Baseline experiment; (B) TCE concentration of 1 mg/L; (C) No mixing; (D) Mixing daily.

A linear relationship was observed between the enrichment factor and the rate constant for samples subjected to various degrees of mixing (Fig. 3), with high enrichment factors measured in the well-mixed samples. Deviation from the regression line was observed when a pair of magnets was used to hold the iron particles in place during mixing. When the iron particles are not secured with magnets, fresh iron is continuously exposed on the surface of the particles due to abrasion. Compositional variations have been previously identified from the surface to the core of Connelly iron particles,[9] and the observed deviation from the regression line may indicate that a different reaction process is involved on the freshly-exposed surfaces. At the TCE concentration of 60 mg/L, the reaction rate constant was half of that measured for 10 mg/L TCE, however, the enrichment factor was similar. On the other hand, at the TCE concentration of 1 mg/L, the enrichment factor was significantly lower than that measured for 10 mg/L TCE although the rate constant was only slightly higher.
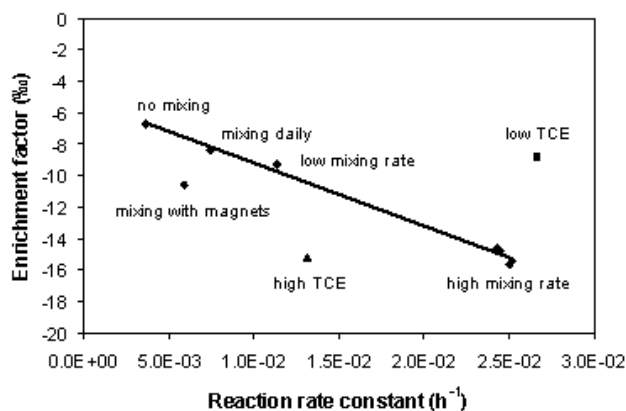

Fig. 3. Carbon isotopic enrichment factor versus reaction rate constant. The regression line was constructed with the exclusion of three data points: low TCE (1mg/L), high TCE (60 mg/L), and mixing with magnets, $R^2 = 0.9933$.

The iron/solution ratio had no observable effect on carbon isotopic enrichment factor within the range examined in this study. A consistent enrichment factor was observed in the experiments with TCE concentrations between 10 and 60 mg/L, whereas a much lower enrichment factor was measured with 1 mg/L TCE. Little change in enrichment factor was observed between samples with or without headspace. Mixing had a profound effect on the enrichment factor, and may explain the different enrichment factors measured by Slater et al.[6] and Schüth et al.[7] This study demonstrates that the magnitude of enrichment factor is dependent on experimental conditions. Therefore, caution

must be taken when applying a laboratory determined enrichment factor to evaluate the degradation process of the remediation technique at field sites.

Acknowledgements

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