



## Kinetic and isotope analyses of tetrachloroethylene and trichloroethylene degradation by model Fe(II)-bearing minerals

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### ABSTRACT

The kinetics and in some cases stable carbon isotope fractionation associated with abiotic reductive dechlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE) by model Fe(II)-bearing minerals present in anaerobic soils were measured. The minerals studied were chloride green rust (GR-Cl), sulfate green rust (GR-SO<sub>4</sub>), pyrite, magnetite, and adsorbed Fe(II) or FeS formed at the surface of goethite by treatment with dissolved Fe(II) or S(-II). We observed some abiotic transformation of PCE and TCE in every system studied, as evidenced by the presence of abiotic reaction products. Bulk enrichment factors ( $\epsilon_{\text{bulk}}$  values) for TCE transformation by GR-Cl and pyrite were  $-23.0 \pm 1.8\text{‰}$  and  $-21.7 \pm 1.0\text{‰}$ , respectively, which are more negative than reported values for microbial TCE dechlorination and could provide one means for distinguishing microbial from abiotic dechlorination of TCE in the environment. Considering the time scale of subsurface remediation technologies, including natural attenuation, minerals such as green rusts, pyrite, and magnetite have the potential to contribute to the transformation of PCE and TCE at contaminated sites.

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### 1. Introduction

There is growing interest in remediation technologies that utilize abiotic minerals for reductive transformation of ground water contaminants such as tetrachloroethylene (PCE) and trichloroethylene (TCE) (Everett et al., 2006; Shen and Wilson, 2007). One advantage of mineral over microbially mediated transformation of PCE and TCE is generation of acetylene and/or ethylene as the primary reaction products (Brown et al., 2006), rather than lesser chlorinated ethenes that are typical of microbial transformation (Hagblom and Bossert, 2003). Many current remediation technologies involve reactive minerals; for example permeable reactive barriers that contain plant derived mulch generate FeS and FeS<sub>2</sub> in a process that begins with microbial sulfate reduction (Shen and Wilson, 2007; He et al., 2008). In addition, the surface of zero-valent iron used in permeable reactive barriers is oxidized to minerals such as green rusts (Refait et al., 1998) that contribute to contaminant dechlorination. Many reactive minerals also occur naturally and can contribute to the natural attenuation of ground water contaminants. For example, green rusts, pyrite, and magnetite have all been shown to degrade PCE and TCE (Sivavec and Horney, 1997; Weerasooriya and Dharmasena, 2001; Lee and

Batchelor, 2002a,b; Maithreepala and Doong, 2005). Goethite, the most common iron oxide in soil and sediments (Rickard, 1974), reacts with dissolved Fe(II) to form surface associated Fe(II) that has been shown to degrade carbon tetrachloride and hexachloroethane (Elsner et al., 2004; Shao and Butler, 2007). Reaction of goethite with S(-II) produced by sulfate reducing bacteria results in Fe(III) reductive dissolution followed by precipitation of FeS (Pyzik and Sommer, 1981) that is capable of degrading carbon tetrachloride (Shao and Butler, 2007). To effectively design and monitor remediation processes involving reactive minerals (i.e. to determine the residence time and/or required mass of reagents) we need accurate data on the reactivity of different minerals with contaminants such as PCE and TCE.

Compound specific isotope analysis (CSIA) for carbon is a new tool to monitor in situ remediation technologies, and is reviewed in detail elsewhere (Elsner et al., 2005). Because chemical bonds containing <sup>12</sup>C are broken more easily than those containing the stable isotope <sup>13</sup>C, reactions in which bond cleavage is the rate limiting step will tend to result in enrichment of the unreacted parent compound with <sup>13</sup>C. The magnitude of this isotope fractionation can be described by the bulk enrichment factor,  $\epsilon_{\text{bulk}}$  (Elsner et al., 2005). With isotope data, one can use the Rayleigh equation (Mariotti et al., 1981) to estimate the amount of parent compound (e.g. PCE or TCE) degraded (Elsner et al., 2005). Previous studies have shown that  $\epsilon_{\text{bulk}}$  values for PCE or TCE transformation by different abiotic reductants vary significantly (Slater et al., 2002;

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Zwank, 2004). In order to accurately use isotope analysis to estimate the extent of abiotic degradation, it is critical to know accurate  $\epsilon_{\text{bulk}}$  values for different mineral that can react with PCE or TCE.

The first objective of this research was to measure  $\epsilon_{\text{bulk}}$  values for transformation of PCE and TCE by Fe(II) minerals that could be used in subsurface remediation technologies and that have been shown to transform chlorinated aliphatic pollutants. To do this, we needed to measure concentration of PCE or TCE versus time in the presence of these minerals. Our second objective was to use this kinetic data to identify mineral species with the greatest reactivity toward PCE and TCE to aid in choosing remediation technologies. To meet our objectives, a series of batch experiments were carried out with the following minerals: chloride green rust (GR-Cl), sulfate green rust (GR-SO<sub>4</sub>), pyrite, magnetite, and Fe(II) or S(-II) treated goethite.

## 2. Materials and methods

### 2.1. Chemicals

The following chemicals were from Sigma–Aldrich (St. Louis, MO): sodium sulfide nonahydrate, sodium acetate, FeCl<sub>2</sub> · 4H<sub>2</sub>O (99%), PCE (99%), TCE (99.5%), *cis* 1,2-dichloroethylene (*cis*-DCE), and N-(2-hydroxyethyl)-piperazine-N'-3-propanesulfonic acid (HEPES). Methanol, acetaldehyde, and sodium hydroxide were from Fisher Scientific (Pittsburgh, PA). Ethane (1018 ppm in N<sub>2</sub>), ethylene (1026 ppm in N<sub>2</sub>), acetylene (1001 ppm in N<sub>2</sub>), and vinyl chloride (VC) (1019 ppm in N<sub>2</sub>) were from Scott Specialty Gases (Houston, TX). Ethanol was from AAPER Alcohol and Chemical Co. (Shelbyville, KY). All aqueous solutions were prepared with Nanopure water (18.0 MΩ cm resistivity, Barnstead Ultrapure Water System, IA).

### 2.2. Preparation and characterization of minerals

Pyrite from Zacatecas, Mexico was purchased from Ward's (Rochester, NY) and processed for 30 min in a Shatterbox Laboratory Mill (Model 8500, Spex Industries Inc., Metuchen, NJ), then immediately transferred to an anaerobic chamber with an atmosphere of approximately 96% N<sub>2</sub>/4% H<sub>2</sub> and a catalytic O<sub>2</sub> removal system (Coy Products, Grass Lake, MI). Crushed pyrite was then washed with 1 M N<sub>2</sub>-sparged HCl and air-dried in the anaerobic chamber. GR-Cl was synthesized by partial oxidation of ferrous hydroxide according to Refait et al. (1998) except that 1 M NaOH and 0.7 M FeCl<sub>2</sub> were used for synthesis of the ferrous hydroxide. The resulting blue-green precipitate was freeze-dried with a custom vacuum valve to exclude oxygen. GR-SO<sub>4</sub> was synthesized by the method of O'Loughlin et al. (2003). Magnetite was prepared using the method of Kang et al. (1996). Goethite was prepared as described in Atkinson et al. (1967).

All iron minerals were characterized by X-ray diffraction (XRD) (Rigaku DMAX X-ray Diffractometer) after freeze-drying. To prevent oxidation during XRD analysis, GR-Cl and GR-SO<sub>4</sub> samples were prepared in the anaerobic chamber by mixing them with petroleum jelly. Pyrite and magnetite samples were stable with respect to oxidation during the period of XRD analysis. The peak patterns of mineral samples were consistent with those in the Powder Diffraction File (PDF) (Joint Committee on Powder Diffraction Standards (JCPDS, 1990)). All minerals were poorly crystalline. Fig. S1 in Supplementary material shows XRD patterns for GR-Cl and GR-SO<sub>4</sub>. The specific surface areas of GR-Cl, GR-SO<sub>4</sub>, pyrite, magnetite, and goethite were (in m<sup>2</sup> g<sup>-1</sup>) 21, 3.7, 7.5, 90, and 74, respectively, determined by BET surface analysis (Autosorb-1, Quantachrome Instruments, Boynton Beach, FL).

### 2.3. Experimental procedures

Batch kinetic experiments were conducted in 5 mL flame sealed glass ampules using procedures described in Liang et al. (2007). The pH was buffered at 8 using HEPES buffer (50 mM). The ionic strength in all experiments was adjusted to 0.06 M by adding NaCl. Mineral mass loadings were (in g L<sup>-1</sup>): GR-Cl: 10; GR-SO<sub>4</sub>: 25; pyrite: 77; magnetite: 20; and goethite: 4. Surface area loadings are reported in Tables 1 and 2. High surface area loadings for pyrite and magnetite (Tables 1 and 2) were chosen based on previous studies that reported slow transformation of PCE and TCE by these minerals (Lee and Batchelor, 2002a). Experiments with Fe(II)- or S(-II)-treated goethite used 4 mM FeCl<sub>2</sub> or 1 mM Na<sub>2</sub>S, which were concentrations similar to previous experiments (Shao and Butler, 2007) in which rapid transformation of carbon tetrachloride was observed. Assuming a site density of 2.3 sites per nm<sup>2</sup> (Davis and Kent, 1990), we estimated that the surface site concentration of a 4 g L<sup>-1</sup> goethite slurry was approximately 1 mM. Thus, the added concentrations of FeCl<sub>2</sub> and Na<sub>2</sub>S were in theory sufficient to react with available surface Fe(III) atoms in experiments with Fe(II)- and S(-II)-treated goethite.

Samples were spiked with a PCE or TCE stock solution prepared in N<sub>2</sub>-sparged methanol to obtain an initial concentration of approximately 30 μM PCE or TCE, except for experiments with magnetite, where the initial concentration was approximately 15 μM in order to increase the molar ratio of reactive surface sites to PCE and TCE. Samples were analyzed by gas chromatography (GC) and GC/isotope ratio mass spectrometry (GC/IRMS) using previously reported methods (Liang et al., 2007). Briefly, isotope fractionation was determined by purge and trap concentration of aqueous samples using a Vocarb 3000 or Tenax-silica gel-charcoal trap interfaced with a Varian 3400 GC with a J&W DB-MTBE column (60 m × 0.32 mm × 1.8 μm). The GC program was 4 min isothermal at 40 °C, followed by a 6 °C min<sup>-1</sup> ramp up to the elution of TCE (the only compound analyzed by GC/IRMS; see below). The GC oven was kept at 220 °C after each analytical run. Following chromatographic separation, TCE was combusted in an alumina tube at 980 °C followed by isotope separation and quantification using a Finnigan MAT 252 mass spectrometer in the <sup>13</sup>C/<sup>12</sup>C configuration. Isotope ratios were measured against a CO<sub>2</sub> standard. The maximum standard deviations of the lowest and the highest δ<sup>13</sup>C of any standard run for a specific sample set did not exceed 0.5‰, with most values not exceeding 0.2‰. Select samples were analyzed in duplicate with the typical standard deviation less than 0.3‰.

For TCE transformation by pyrite, we conducted a separate batch experiment at a significantly higher initial concentration of TCE (approximately 7.5 mM) in order to quantify additional reaction products. For this experiment, the mass loading of pyrite was 400 g/L and the surface area loading was 3000 m<sup>2</sup> L<sup>-1</sup> (Table 2). Acetate was quantified by ion chromatography using the same instrumental setup as in Zhu et al. (2005). Ethanol and acetaldehyde were analyzed by a HP 6890 GC with an Agilent J&W DB-624 capillary column (30 m × 0.53 mm × 3 μm) and flame ionization detector (FID). The GC injector temperature was 250 °C and the detector temperature was 280 °C. The oven temperature was isothermal at 60 °C for 6.5 min.

### 2.4. Treatment of kinetic and isotope data

As discussed below, only certain experimental conditions showed significant transformation of PCE or TCE in the time scale of our experiments. In these cases, we fit data for aqueous concentration of PCE or TCE versus time to a pseudo-first-order rate model, adjusted the resulting rate constants to those that would be measured in a headspace-free system (Burriss et al., 1996), then

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