



# Carbon and chlorine isotope fractionation during Fenton-like degradation of trichloroethene



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## HIGHLIGHTS

- Dual C–Cl isotope fractionation for Fenton-like degradation of TCE was determined.
- The  $\epsilon_C$  and  $\epsilon_{Cl}$  values were  $-2.9 \pm 0.3\%$  and  $-0.9 \pm 0.1\%$ , respectively.
- The  $\Delta = \Delta\delta^{13}C/\Delta\delta^{37}Cl$  and  $\epsilon_C/\epsilon_{Cl}$  values were  $3.1 \pm 0.2$  and  $\epsilon_C/\epsilon_{Cl} = 3.2$ , respectively.
- The  $\epsilon_C/\epsilon_{Cl}$  value is similar to those for microbial reduction of TCE.

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## ABSTRACT

Dual isotope approach has been proposed as a viable tool for characterizing and assessing in situ contaminant transformation, however, little data is currently available on its applicability to chlorinated ethenes. This study determined carbon and chlorine isotope fractionation during Fenton-like degradation of trichloroethene (TCE). Carbon and chlorine isotope enrichment factors were  $\epsilon_C = -2.9 \pm 0.3\%$  and  $\epsilon_{Cl} = -0.9 \pm 0.1\%$ , respectively. An observed small secondary chlorine isotope effect ( $AKIE_{Cl} = 1.001$ ) was consistent with an initial transformation by adding hydroxyl radicals ( $\cdot OH$ ) to C=C bonds without cleavage of C–Cl bonds. The relative change in carbon and chlorine isotope ratios ( $\Delta = \Delta\delta^{13}C/\Delta\delta^{37}Cl$ ) was calculated to be  $3.1 \pm 0.2$ , approximately equal to the ratio of chlorine and carbon isotope enrichment factors ( $\epsilon_C/\epsilon_{Cl} = 3.2$ ). The similarity of the  $\Delta$  (or  $\epsilon_C/\epsilon_{Cl}$ ) values between Fenton-like degradation and microbial reductive dechlorination of TCE was observed, indicating that application of solely dual isotope approach may be limited in distinguishing the two transformation pathways.

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## 1. Introduction

Contamination in soil and groundwater by chlorinated ethenes (e.g., trichloroethene (TCE)) has been a serious environmental concern due to carcinogenicity (Guha et al., 2012). Hence, significant effort has been devoted to investigate remediation of these contaminants (Sutton et al., 2011; Tobiszewski and Namieśnik, 2012). Of the pool of remediation strategies, in situ chemical oxidation (ISCO) has been demonstrated as an efficient and extensive technology for the degradation of various recalcitrant chlorinated organic compounds (ITRC, 2005; US EPA, 2006). Fenton reaction

and Fenton-like reaction, involving the generation of highly reactive hydroxyl radicals ( $\cdot OH$ ) from hydrogen peroxide ( $H_2O_2$ ) through reduction and oxidation (redox) cycles of iron (Fe) and a series of radical propagation and termination reactions, has gained popularity as ISCO techniques (Chen et al., 2001; Kang et al., 2006). Naturally-occurring iron-bearing minerals (i.e. goethite, magnetite and pyrite), which are widespread in the natural environment, can catalyze  $H_2O_2$  and initiate Fenton-like degradation of recalcitrant chlorinated organic contaminants (Teel et al., 2001; Garrido-Ramírez et al., 2010; Che et al., 2011; Che and Lee, 2011). Meanwhile, mineral-catalyzed  $H_2O_2$  decomposition may also provide sufficient molecular oxygen to promote microbial growth and enhance in situ aerobic degradation of chlorinated ethenes (Pardieck et al., 1992; Sutton et al., 2011).

To effectively design and evaluate in situ remediation strategies, a reliable means of identifying and quantifying the

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remediation process must be developed. Conventional monitoring and assessment strategies for in situ remediation rely on concentration or mass-based estimates, geochemical approaches, metabolite analysis, microbial and molecular methods (Bombach et al., 2010). However, it can often be difficult due to complex biogeochemical and hydrological conditions. The identification of enhancement of aerobic bioremediation utilizing  $H_2O_2$  might be compromised by the fact that mineral-catalyzed Fenton-like reaction and aerobic oxidation processes of chlorinated ethenes can take place simultaneously and sometimes lead to the same products (Sutton et al., 2011). Moreover, quantifying the contribution of mineral-catalyzed Fenton-like reaction and aerobic oxidation processes by chemical analysis of the samples obtained from a limited number of sampling points is very difficult, because nondegradative processes (e.g., dilution, adsorption) also contribute to the attenuation of chlorinated ethenes in soil and groundwater. Much interest is therefore directed at compound specific isotope analysis (CSIA) as a powerful tool for monitoring, assessing, and validating of in situ remediation within contaminated aquifers (Braeckvelt et al., 2012; Thullner et al., 2012). The application of CSIA relies on the phenomenon that changes in contaminant concentrations due to transformation are systematically associated with an isotopic fractionation effect according to the Rayleigh equation (Mariotti et al., 1981), following from the specific degradation mechanism.

To date, CSIA has mainly focused on carbon isotope fractionation effects during abiotic reduction (Dayan et al., 1999; Slater et al., 2002; Schüth et al., 2003; Liang et al., 2007, 2009), and biodegradation of chlorinated ethenes (Bloom et al., 2000; Slater et al., 2001; Barth et al., 2002; Lee et al., 2007; Liang et al., 2007; Abe et al., 2009). Furthermore, significant carbon isotope fractionation has also been observed for oxidation of chlorinated ethenes by permanganate (Poulson and Naraoka, 2002; Hunkeler et al., 2003) and Fenton-like reaction (Liu et al., 2013), although no significant isotopic fractionation has been observed during Fenton-like degradation of toluene (Ahad and Slater, 2008). Due to the variability of isotope fractionation factors for the same reaction mechanism caused by commitment to catalysis and the mixed effect of individual isotope fractionations caused by different transformation pathways simultaneously (Nijenhuis et al., 2005; Hofstetter et al., 2007), it is usually difficult to identify reaction mechanism and/or quantify the relative contribution of different pathways based on isotope data for a single element only (Elsner et al., 2005). The correlation between the isotope fractionation of two elements within the same molecule (dual isotope approach) which is independent of contaminant concentrations and commitment to catalysis has been proposed as a method to characterize and identify degradation pathway and/or to quantify the relative contribution of different pathways (Zwank et al., 2005; Hofstetter et al., 2008; Vogt et al., 2008; Abe et al., 2009). With recent technical advances in compound-specific isotope analysis (CSIA) for chlorine isotopes (Elsner et al., 2012), dual C–Cl isotope fractionation during abiotic reduction and biodegradation of chlorinated ethenes have been evaluated in both laboratory and field scales (Abe et al., 2009; Hunkeler et al., 2011; Lojkasek-Lima et al., 2012; Wiegert et al., 2012, 2013; Audí-Miro et al., 2013; Cretnik et al., 2013). However, dual C–Cl isotope fractionation for degradation of chlorinated ethenes by Fenton or Fenton-like reaction has not been investigated so far.

The main objectives of this study were: (1) to determine not only carbon, but for the first time also chlorine isotope enrichment factors for Fenton-like degradation of TCE, (2) to construct a dual carbon-chlorine isotope plot during Fenton-like degradation of TCE, and (3) to investigate the potential of two-dimensional carbon and chlorine isotope analysis as a technique to evaluate in situ remediation of the Fenton-like application.

## 2. Materials and methods

### 2.1. TCE degradation experiment

To investigate the carbon and chlorine isotope fractionation during trichloroethene (TCE) degradation in the magnetite-catalyzed Fenton-like reaction, batch experiments were performed in approximately 520 mL glass bottles. Bottles were filled with 15 g of magnetite and with 495 mL deionized water adjusted to pH 2.5 value by sulfuric acid ( $H_2SO_4$ , 98%; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Neat trichloroethene (TCE, 99.0%; Tianjin Hengxing Chemical Reagent Co., Ltd., Tianjin, China) was spiked by gastight micro-syringe into each bottle, yielding initial concentrations with  $50 \text{ mg L}^{-1}$ . The reaction was then initiated by adding 5 mL of hydrogen peroxide ( $H_2O_2$ , 30%; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) to each bottle resulting in 98 mM. Each bottle leaving approximately 20 mL of headspace was rapidly sealed with PTFE/silicone septum cap and completely mixed. All experiments were conducted with static at a room temperature ( $25^\circ\text{C}$ ). Each bottle was sacrificed by adding 5 mL of NaOH (10 M) and subsequently analyzed for the concentration and isotope of TCE at appropriate time intervals. Sodium hydroxide served as two purposes in this experiment: (1) to terminate the degradation reaction and (2) to remove excess carbon dioxide in the bottle. The batch experiment was carried out in triplicate. A control experiment was prepared similarly, but without addition of  $H_2O_2$ , indicated that other degradation mechanisms or losses were not significantly affecting the TCE concentration.

### 2.2. Concentration analysis

Aqueous TCE concentrations were determined using a headspace solid-phase microextraction (HS-SPME) method coupled with an Agilent 6890N gas chromatograph (GC). The GC was equipped with a  $^{63}\text{Ni}$  electron capture detector ( $\mu\text{ECD}$ ) and a DB-624 capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 1.40 \text{ }\mu\text{m}$ ). The temperatures of injector and detector were at  $230$  and  $250^\circ\text{C}$ , respectively. The oven temperature was programmed as follows:  $50^\circ\text{C}$  (1.0 min),  $15^\circ\text{C min}^{-1}$  to  $130^\circ\text{C}$  (2.0 min). The carrier gas was nitrogen at a flow rate of  $1.0 \text{ mL min}^{-1}$ . Extraction was conducted by the headspace solid-phase microextraction (HS-SPME) method as follows: aqueous samples ( $100 \text{ }\mu\text{L}$ ) were withdrawn by gastight micro-syringe and introduced to 8 mL vials containing 4 mL organic free distilled water. The vials were immediately sealed with open screw caps and PTFE/silicone septums and vigorously shaken by hand. Subsequently, the SPME fiber (coated with  $100 \text{ }\mu\text{m}$  polydimethylsiloxane, PDMS; Supelco, Bellefonte, PA, USA) was exposed to the headspace (4 mL) for 5 min at  $25^\circ\text{C}$ . After the extraction, the fiber was thermally desorbed for 2 min in the split/splitless injector ( $230^\circ\text{C}$ ). Reproducibility of concentration measurements was  $\pm 7.0\%$ .

### 2.3. Carbon and chlorine isotope analysis

After TCE quantification was performed, bottle was sacrificed to extract sufficient TCE for carbon and chlorine isotope analysis. This follows the procedures described in detail previously (Holt et al., 2001; Gan et al., 2013). Briefly, the water to be analyzed was aspirated into an evacuated sparging flask. The evacuated sparging flask was attached to a vacuum line where the TCE was vacuum-extracted while sparging the water with an atmospheric pressure stream of helium (He) carrier gas. The TCE was cryogenically separated from water vapor and transferred into a combustion tube (containing 1.0 g of CuO). Subsequently, the TCE was heated with the CuO for 1 h at  $720^\circ\text{C}$  to form  $\text{CO}_2$  and chloride. The  $\text{CO}_2$  formed

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