Carbon isotope fractionation of chlorinated ethenes during oxidation by Fe^{2+} activated persulfate

Massimo Marchesi [a,b,*], Ramon Aravena [b], Kanwartej S. Sra [c,d], Neil.R. Thomson [c], Neus Otero [a], Albert Soler [a], Silvia Mancini [d]

[a] Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Barcelona, Catalunya 08028, Spain
[b] Earth and Environmental Department, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
[c] Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
[d] Golder Associates Inc, Toronto, Ontario, Canada L5N 5Z7

ABSTRACT

The increased use of persulfate ($S_2O_8^{2-}$) for *in situ* chemical oxidation to treat groundwater and soils contaminated by chlorinated hydrocarbon compounds (CHCs) requires unbiased methods to assess treatment performance. Stable carbon isotope analysis offers a potential tool for assessing the *in situ* treatment performance of persulfate at sites contaminated with CHCs. This study investigated the extent of C isotope fractionation during oxidation of tetrachloroethene (PCE), trichloroethene (TCE) and cis-dichloroethene (cis-DCE) by persulfate activated by ferrous ion (Fe^{2+}). An average carbon isotope enrichment factor ε_{bulk} of −4.9‰ for PCE, −3.6‰ for TCE and −7.6‰ for cis-DCE were obtained in batch experiments. Variations in the initial $S_2O_8^{2-}/Fe^{2+}/CHC$ molar ratios did not result in any significant differences in carbon isotope fractionation. The occurrence of carbon isotope fractionation during oxidation and the lack of dependence of enrichment factors upon the $S_2O_8^{2-}/Fe^{2+}/CHC$ molar ratio demonstrate that carbon isotope analysis can potentially be used at contaminated sites as an additional technique to estimate treatment efficacy during oxidation of CHCs by Fe^{2+} activated persulfate.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

In situ chemical oxidation (ISCO) has emerged as an effective and efficient technology for the remediation of soil and groundwater contaminated with chlorinated hydrocarbon compounds (CHCs). Application of ISCO technology involves the injection or release of a chemical oxidant along with activators or other co-amendments, if required, directly into the treatment zone. The injected reagent solution has the capability to oxidize groundwater or soil contaminants into less harmful chemical compounds with the potential for complete mineralization in the case of CHCs, and other by-products depending on the reagent used (U.S. EPA, 2006).

Persulfate ($S_2O_8^{2-}$) has gained popularity as an ISCO oxidant due to its high stability in the subsurface and extensive reactivity with environmentally relevant contaminants particularly when an activation strategy is used to generate sulfate free-radicals. While its persistence appears to be orders of magnitude higher than that of peroxide (Sra et al., 2010), it has been shown that activated persulfate can treat contaminants that are known to be recalcitrant to permanganate oxidation (e.g., chlorinated alkanes, MTBE) (Block et al., 2004). Numerous persulfate activation strategies are available to catalyze the formation of sulfate free radicals ($SO_4^{-}\bullet$) such as transition metals, hydrogen peroxide, heat, or alkaline conditions. Among those, the addition of Fe^{2+} appears to be an inexpensive and practical way of achieving persulfate activation (Liang et al., 2004a, 2004b, 2008a and 2004a,b, 2008a, 2009), and has been employed at numerous contaminated sites (U.S. EPA, 2006).

Assessing ISCO treatment performance is prone to numerous uncertainties if only the decrease in the concentration of the target compound or the increase in chloride (Cl^-) concentration is considered (Thomson et al., 2007). Changes in the target compound concentration can also occur through non-chemical oxidation processes such as displacement or dilution of contaminated groundwater by the injected reagent solution, or by sorption, dispersion, or rebound processes (Thomson et al., 2008). Interpretation of Cl^- data may be ambiguous in the presence of high background Cl^- concentration levels, and is further complicated because Cl^- may be involved as a free radical scavenger (Liang et al., 2006). Thus, interpretation of concentration data alone may be insufficient to evaluate the effectiveness of a persulfate ISCO treatment (Hunkeler et al., 2003). Stable carbon isotope analysis has been increasingly applied as a technique to monitor the efficacy of abiotic remediation as well as microbial degradation processes (Poulson and Naraoka, 2002; Hunkeler et al., 2003; Poulson et al., 2003; Meckenstock et al., 2004). Due to mass-dependent differences in activation energies for the transformation of compounds with different isotopes (e.g., ^{13}C and ^{12}C), compounds with lighter isotopes (^{12}C) react on average faster

* Corresponding author at: Earth Sciences Department, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1. Tel.: +1 519 888 4567x35372.
E-mail address: m2marche@uwaterloo.ca (M. Marchesi).

than those with heavy isotopes (^{13}C), leading to isotope fractionation. The result is an enrichment of heavy isotopes in the residual contaminant as the reaction proceeds (Clark and Fritz, 1997).

If a significant isotope fractionation can be associated with the oxidation reaction, then carbon isotope composition in the field can potentially indicate areas where *in situ* treatment is not working as expected, or zones where the oxidant or the activator are not present. In these situations, changes in CHCs concentration and Cl$^-$ would not be accompanied by any variation in the carbon isotope composition, indicating that the changes in the CHCs content are due to processes such as displacement or dilution of contaminated groundwater. This isotopic tool can potentially be used to monitor the effect of CHCs rebound from aquifer sediments after the oxidant has been depleted, and to evaluate the dynamics between oxidation and dissolution of residual non-aqueous phase liquids (NAPLs), thereby providing information about locations where NAPL is still present. In such a case, the carbon isotope composition will show a shift towards enriched δ^{13}C values due to the oxidation process, and thereafter the δ^{13}C will approach initial δ^{13}C values. This pattern will clearly indicate a rebound process reflecting that NAPL is still present and a source of dissolved CHCs.

The isotopic ratio is expressed in the unit of per mil (‰) deviation from the international standard Vienna Pee Dee Belemnite (VPDB) in the usual δ^{13}C notation:

$$\delta^{13}C = [(R - R_{st})/R_{st}] \times 1000 (‰) \tag{1}$$

where R and R_{st} are the isotope ratio (^{13}C/^{12}C) of the sample and the standard respectively.

Quantification of the extent of contaminant transformation based on carbon isotopes requires experimental determination of the ^{13}C fractionation factor associated with the reaction under consideration. Fractionation of stable carbon isotopes has been determined for transformation of organic carbon compounds by different processes such as biodegradation (Meckenstock et al., 2004), reductive dechlorination by zero valent iron (Schüth et al., 2003; VanStone et al., 2005) or palladium catalysts with hydrogen (Bill et al., 2001), and, more recently, oxidation by permanganate (Poulson and Naraoka, 2002; Hunkeler et al., 2003) and peroxide (Poulson et al., 2003). To date, the isotopic fractionation factors associated with oxidation by persulfate have not been determined for any environmentally relevant organic contaminants. As for other chemical oxidation experiments (Poulson and Naraoka, 2002; Hunkeler et al., 2003; Poulson et al., 2003), the isotope fractionation can be evaluated assuming a Rayleigh fractionation trend. By using the δ^{13}C notation for the isotopic composition, F for fraction of compound remaining at time t (concentration at time t/initial concentration), δ^{13}C$_{co}$ for the initial isotope signature, and α for the fractionation factor, the Rayleigh equation can be expressed as:

$$\ln\left[\left(\delta^{13}C_{co} + \Delta\delta^{13}C + 1000\right)/\left(\delta^{13}C_{co} + 1000\right)\right] \times 1000 = \alpha \ln f \tag{2}$$

where $\Delta\delta^{13}$C represents the difference between the isotope signatures at time t and time zero. When the fractionation factor α is very small, a more practical way to describe the isotope fractionation is the enrichment factor ε, expressed by $\varepsilon = (\alpha - 1) \times 1000$. In this study, the results are presented as an enrichment factor ε determined from the slope of the best linear least-squares fit to Eq. (2). As suggested by Scott et al. (2004), ε was determined by not forcing the linear least-squares through the origin. To compare the isotope fractionation in different oxidation systems from literature, the bulk isotope fractionation data (ε_{bulk}) have been transformed into a position-specific enrichment factor (ε reactive position) using the approach described in Elsner et al. (2005). Additional details are provided in the Supplemental Information (SI).

A prerequisite for applying this isotopic technique at appropriate field sites is proof that the isotope fractionation pattern is not affected by changes in the ratio of persulfate to the target compound and

activator. These changes can occur due to mixing of persulfate and the activator solution with groundwater during injection. This is an important consideration because different persulfate doses are used at different sites and during various stages of treatment at the same site. The main objective of this study was to quantify the carbon isotope fractionation factor associated with ferrous (Fe^{2+}) activated persulfate treatment of tetrachloroethene (PCE), trichloroethene (TCE) and cis-dichloroethene (cis-DCE). Recent studies have focused on TCE reaction kinetics and persulfate treatment efficiency under various environmental conditions (Liang et al., 2004a, 2004b, 2006 and 2004a,b, 2006, 2007). For example, Liang et al. (2004b) studied TCE degradation using Fe^{2+} as a persulfate activator, and how different S$_2$O$_8^{2-}$/Fe^{2+} conditions affect CHC mineralization, S$_2$O$_8^{2-}$/Fe^{2+} consumption, and treatment efficiency. In contrast, in the present effort we were not interested in quantifying kinetics but rather we designed a study specifically to assess whether differences in ferrous ion, persulfate, and CHC molar ratios yield differences in the carbon isotopic fractionation factors. The data generated were used to assess the potential for stable carbon isotope analysis to be employed as a tool to estimate ISCO treatment performance.

2. Methods

2.1. Experimental set-up

A series of batch experiments were conducted at room temperature (20 °C) to evaluate the fractionation factor associated with the oxidation of PCE, TCE and cis-DCE (CHCs) by Fe^{2+} activated persulfate. Stabilizers (e.g., chelating reagents) are normally used to suppress the catalytic activity of transition metals and thus increase the longevity of dissolved ferrous iron *in situ*. To avoid using a chelating agent, we sequentially spiked the batch systems to maintain a supply of Fe^{2+}. The experiments were designed to simulate possible variations of S$_2$O$_8^{2-}$/Fe^{2+}/CHC molar ratios expected to occur during persulfate ISCO field applications, from a high excess S$_2$O$_8^{2-}$/Fe^{2+}/CHC molar ratios (100/5/1) to limited activator molar ratio (20/0.02/1). All the molar ratios investigated in this study are similar to those normally used in ISCO field applications.

Due to our experimental design, temporal variations were not considered and hence reaction rate coefficients were not estimated; however, changes in the initial S$_2$O$_8^{2-}$/Fe^{2+}/CHC molar ratios will result in different reaction rates as demonstrated in other studies (for MTBE (Chen et al., 2009) and BTEX (Liang et al., 2008b)). Since our interest was to investigate the isotope fractionation factor associated with the Fe^{2+} activated persulfate system, the influence of temperature was also not considered and we focused only on the potential effect of using different S$_2$O$_8^{2-}$/Fe^{2+}/CHC molar ratios. The potential for thermal activation at temperatures ranging from 5 to 25 °C can normally be excluded (Liang and Bruell, 2008c). Dahmani and Huang (2006) demonstrated that in a S$_2$O$_8^{2-}$/TCE system with a molar ratio of 10/1 almost no degradation of TCE was observed at a temperature of 20 °C over a 6 h reaction period, while Johnson et al. (2008) showed no significant activation of persulfate during the first 10 h at 30 °C. It was deemed important to exclude the presence of other activation systems since they likely induce different reaction mechanisms, and consequently potentially different isotopic fractionations would be produced.

2.2. Materials

All chemicals used were reagent grade: cis-DCE (95.5% purity), TCE (99.5% purity) and PCE (99.9% purity) were purchased from Fisher Scientific; sodium persulfate (Na$_2$S$_2$O$_8$, 98%) was purchased from Alfa Aesar; and ferrous sulfate (FeSO$_4$-7H$_2$O, 99.5%) was purchased from J.T. Barker, EM Science. Water was produced using a Barnstead RO-pure LP water purifier with NANO-pure II (Reverse Osmosis water, RO water).

2.3. Batch experiments design

Batch experiments were prepared following the method described by Liang et al. (2004b). The first experimental series explored the influence of persulfate content on the fractionation factor by increasing the $S_2O_8^{2-}$ content from a $S_2O_8^{2-}$/CHC molar ratio of 20/1 to 100/1 at a constant Fe^{2+}/CHC molar ratio of 5/1. The second experimental series was conducted by increasing the Fe^{2+} content from an initial Fe^{2+}/CHC molar ratio of 1/1 to 5/1 for PCE and cis-DCE, and from 0.2/1 to 5/1 for TCE at a constant $S_2O_8^{2-}$/CHC molar ratio of 20/1 to observe the influence of ferrous ion content on the fractionation factor.

The PCE, TCE and cis-DCE stock solutions were prepared at an initial concentration of 45–60 mg/l (approximately 0.35–0.45 mM) from saturated solutions prepared by stirring an excess of these compounds in RO water for ~24 h. All batch experiments were performed in triplicate using nominal 40 ml vials capped with Teflon septa with no headspace to prevent loss of CHCs due to volatilization. Each CHC solution was mixed with a predetermined amount of $S_2O_8^{2-}$ to obtain the required $S_2O_8^{2-}$/CHC molar ratio.

The addition of Fe^{+2} was performed sequentially in 6 to 8 equally spaced episodes by removing 1 ml from a reactor using a high precision syringe and replacing this volume with 1 ml of Fe^{2+} solution. The stock Fe^{2+} solution was prepared using $FeSO_4 \cdot 7H_2O$ and the concentrations were selected so that the required initial molar ratios were obtained in each experimental series. As demonstrated by Liang et al. (2004b), after the first addition of Fe^{2+} the pH decreased to ~2.5, and Fe^{2+} remained available in the dissolved phase for activation. Liang et al. (2004b) demonstrated that using the same $S_2O_8^{2-}$/Fe^{2+}/CHC molar ratio range that targets contaminant (only TCE in their experiments) degradation appeared to occur almost instantaneously and then stall, hence little or no further degradation was observed after 5 min, with no variation in concentration was observed for the next 3 h. Consequently, after a reaction time of 5 min the reactors were quenched in an ice bath, and aliquots were extracted for chemical analyses as soon as possible (<1 h).

All reactors were shaken continuously on an OVAN shaker between injections and the entire period for one experimental run did not exceed 6–8 h. Experimental controls were prepared with the CHC and persulfate only and were handled in an identical manner as the activated persulfate reactors with sequential addition of RO water instead of the Fe^{2+} solution.

2.4. Analytical methods

TCE and PCE concentrations were analyzed on a Hewlett Packard 5890 Series II gas chromatograph (GC) equipped with a DB-624 column (30 m × 0.32 mm, 1.8 μm film thickness)) and a micro Ni^{63}-ECD detector (method detection limit of 3 μg/L). 2 ml sample was extracted using a 2 ml pentane solution containing an internal standard 500 μg/L of 1,2-dibromoethane. The extraction was done on an orbital shaker for 15 min at 300 revolutions per minute (RPM). The supernatant was then removed, placed in a 2 ml glass crimp-top GC vial and injected into the capillary column (1 μL) using a HP-7673 liquid auto sampler. The injector was in split mode (split ratio of 10:1), He was used as a carrier gas at a flow rate of 2.4 ml/min, and the inlet was kept at a temperature of 220 °C. The oven temperature program was at 30 °C for the first 2 min, heated to 220 °C at a rate of 8 °C/min and finally held at 220 °C for 2 min. Cis-DCE concentration was analyzed by headspace technique. The headspace was created in the aqueous samples using a ratio of 6.0 ml headspace to 4.0 ml aqueous sample. The samples were placed on a rotary shaker for 15 min to allow equilibration between the water and the gas phase, and then 1 ml sample was injected into a GC (same model as described above) using a Hewlett Packard 7694 headspace sampler 1 ml sample. Same column, carrier gas, and column condition as described above have been used, with the inlet kept at a temperature of 100 °C. The detector was a Hnu Photo ionization detector (PID), the lamp potential was 10.2 eV and the detector was set at a temperature

of 150 °C (method detection limit of 2 μg/L). The accuracy of the methods was verified daily using external standards prepared and extracted analogous to the samples. Concentrations were adjusted considering the dilution resulting from the Fe^{2+} solution (or RO water for the control experiment) injected during the experimental period.

For carbon isotope analysis, CHCs were extracted from the aqueous sample using the headspace solid-phase micro-extraction (HS-SPME) method with a 75 μm CAR-PDMS fiber (Supelco, Bellefonte, PA, USA) during a 15 min extraction time. The analysis was performed using the same GC model as described above coupled, by a combustion interface (kept at 850 °C), to an isotope ratio mass spectrometer (IRMS, Micromass Isochrom; Micromass, Manchester, UK). A manual injection method was implemented, and same capillary column, GC conditions, carrier gas and inlet condition as for TCE and PCE concentration analyses have been used.

3. Results and discussion

3.1. Oxidation results

During PCE, TCE and cis-DCE treatment, no transient chlorinated degradation products appearing as other volatile organic compounds were observed. After the sequential additions of the Fe^{2+} solution the concentration of PCE and TCE decreased in a range from 93 to 99% depending on $S_2O_8^{2-}$/Fe^{2+}/CHC molar ratios, while concentration for cis-DCE decreased in a range only from 74 to 89% (considering only $S_2O_8^{2-}$/Fe^{2+}/CHC molar ratios of 20/1/1, 20/5/1 and 100/5/1 (see Table 1). For the TCE experiments with a persulfate/CHC molar ratio of 20/1, concentration decreased (after 6 sequential additions of Fe^{2+}) by 77%, 94%, and 96% for an initial Fe^{2+}/TCE molar ratio of 0.2/1, 1/1 and 5/1. Each run in the TCE experiments used an initial Fe^{2+}/TCE molar ratio that was 5 times higher with respect to the prior experimental run (for example experiment with Fe^{2+}/TCE molar ratio 1/1 and 5/1), resulting in TCE oxidation that only increased by 17% and 2% between successive runs. This suggests that at higher Fe^{2+}/TCE molar ratios, the oxidation efficiency is reduced as the abundance of ferrous ions leads to an increased competition for the sulfate free radicals as suggested by Liang et al. (2004b).

3.2. Extent of carbon isotope fractionation

Based on the control experiments ($n = 21$), the initial $\delta^{13}C$ of PCE, TCE and cis-DCE was −30.5‰, −31.1‰ and −25.5‰, respectively. Standard deviations for all compounds based on the replicate carbon isotope measurements for the control experiments were between 0.3‰ and 0.4‰. These results (Fig. 1, and Fig. A1 and Fig. A2 in SI) indicate that the control reactors showed no variations in $\delta^{13}C$ values of CHCs throughout the duration of these experiments, considering the range of analytical uncertainty of ±0.5‰ reported elsewhere for carbon isotope analysis of CHCs.

Table 1
Enrichment factors, $\Delta \delta^{13}C$ (‰), and % of degradation for CHCs at different $S_2O_8^{2-}$/Fe^{2+}/CHC molar ratios.

Compound	$S_2O_8^{2-}$/Fe^{2+}/CHC	% degradation	$\varepsilon_{c\ bulk}$ ‰	r^2	$\Delta \delta^{13}C$ (‰)
PCE	100/5/1	0–99	−4.9±0.2	0.997	25.2
PCE	20/5/1	0–98	−5.0±0.3	0.992	18.8
PCE	20/1/1	0–93	−4.6±0.4	0.987	10.9
TCE	100/5/1	0–99	−3.6±0.2	0.996	15.5
TCE	20/5/1	0–96	−3.5±0.3	0.992	11.2
TCE	20/1/1	0–94	−3.5±0.2	0.994	9.4
TCE	20/0.2/1	0–77	−3.9±0.4	0.987	7.0
cis-DCE	100/5/1	0–89	−7.4±0.3	0.995	16.6
cis-DCE	20/5/1	0–76	−7.7±0.4	0.986	11.2
cis-DCE	20/1/1	0–74[a]	−7.9±0.3	0.994	10.6

[a] Value after 8 mL of the Fe^{2+} solution added, all other values are after 6 mL of Fe^{2+} added.

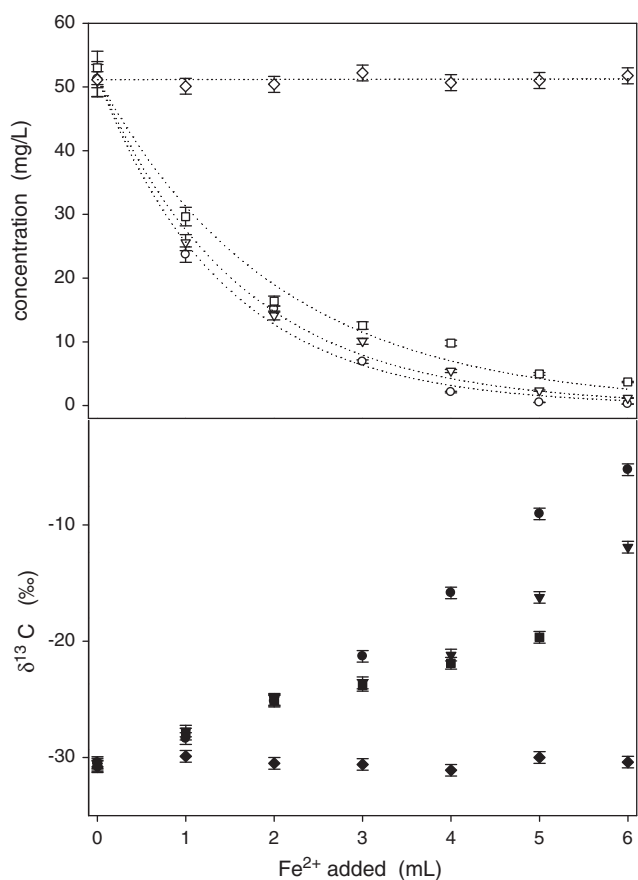**Fig. 1.** Variation of concentration of PCE (white symbols) and δ^{13}C values (black symbols) for different $S_2O_8^{2-}$/Fe^{2+}/PCE molar ratios of 20/1/1 (square), 20/5/1 (triangle) and 100/5/1 (circle) at sequential addition of Fe^{2+} and control experiments (rhombus). Dashed lines represent the best fit first-order expression.

All the oxidation experiments showed an increase of δ^{13}C values during the course of oxidation, with ranges of -30.4‰ to -5.2‰, -31.4‰ to -15.9‰ and -25.8‰ to -9.2‰, for PCE, TCE and cis-DCE, respectively. These results confirm a normal isotope effect with molecules containing heavier isotopes (^{13}C) being more stable than those containing light isotopes which can be readily oxidized (Clark and Fritz, 1997; Elsner at al., 2005). Fig. 1 shows the δ^{13}C values and the concentrations of PCE following each sequential addition of Fe^{2+} (these trends are the same for TCE and cis-DCE, see Fig. A1 and A2 respectively in SI for different $S_2O_8^{2-}$/Fe^{2+}/PCE molar ratios (all experiments). PCE, TCE and cis-DCE concentrations decreased exponentially with increased addition of Fe^{2+}, whereas the δ^{13}C values increased following an almost linear trend. This suggests that the relationship of δ^{13}C to the fraction of remaining CHCs can be described using the Rayleigh model.

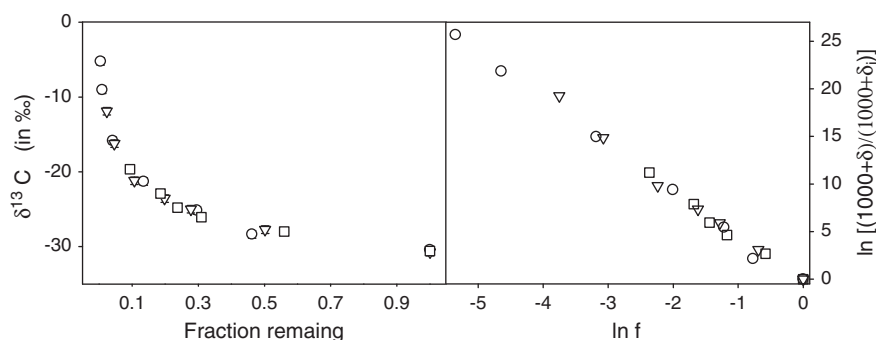Enrichment factors calculated for TCE ranged from -3.5 ± 0.3‰ to $-3.9.0\pm0.4$‰ (Table 1, using a 95% confidence interval), showing a good consistency for all four experimental runs (Fig. A3 in SI). An average enrichment factor for all TCE experiments of -3.6 ± 0.2‰ was calculated. The similarity of the ε obtained in the experiments offers further confirmation that the enrichment fractionation factor does not change during the oxidation process. It is important to note that enrichment factors obtained for TCE experiments with very different $S_2O_8^{2-}$/Fe^{2+}/TCE molar ratios were nearly identical. These results illustrate that the enrichment factor is independent of the $S_2O_8^{2-}$/Fe^{2+}/TCE molar ratios. For example, a variation in the $S_2O_8^{2-}$/Fe^{2+}/TCE molar ratios from 20/0.2/1 to 100/5/1 resulted in a very slight difference in the enrichment factor (0.4‰) which is statistically insignificant. This result is essential for the utility of using isotopic composition for monitoring ISCO treatment when an activator is required since following injection the oxidant and activator will interact with the target contaminant over a range of $S_2O_8^{2-}$/Fe^{2+}/CHC molar ratios.

Experimental results for cis-DCE show a narrow range of enrichment factor values, varying from -7.4‰ ±0.3‰ to -7.9‰ ±0.3‰. Similar to TCE, the enrichment factor appears to be independent of the $S_2O_8^{2-}$/Fe^{2+}/cis-DCE molar ratio, and the average enrichment factor for all cis-DCE experiments was -7.6‰ ±0.3‰ (Fig. A4 in SI). The enrichment factor for PCE oxidation also shows a narrow range of values for all the experimental runs which is in agreement with the results for TCE and cis-DCE. The ε values varied between -4.6 ± 0.4‰ and -5.0 ± 0.3‰. As with the other investigated compounds, the fractionation does not appear to be influenced by the $S_2O_8^{2-}$/Fe^{2+}/PCE molar ratio (Fig. 2). The average enrichment factor for all PCE experiments was -4.9‰ ±0.2‰.

The magnitude of the enrichment factors obtained here allows the Rayleigh equation to be used to potentially quantify the oxidation process *in situ*. For example, in the case of PCE (ε_{bulk} of -4.9‰ $\pm$ 0.2‰), a 40% oxidation will result in a δ^{13}C enrichment of 2.2‰, whereas a 90% oxidation will result in a δ^{13}C variation of 19.9‰. Both of these δ^{13}C enrichment values are significantly larger than the typical uncertainty of ±0.5‰. For oxidation of cis-DCE (ε_{bulk} of -7.6‰), the change in carbon isotope composition will be even much larger than the changes expected for PCE or TCE.

3.3. Estimation of AKIEc values

AKIEc values were calculated (see SI) to compare the isotope fractionations estimated in this study with those fractionation estimates appearing in the literature for other abiotic degradation processes. Calculated AKIEc values associated with Fe^{2+} activated persulfate oxidation of PCE, TCE and cis-DCE were 1.005, between 1.004 and 1.008, and between 1.008 and 1.015 respectively (Table 2). The oxidation of CHCs by permanganate produced higher AKIEc values between 1.018 and 1.019 for PCE, between 1.019 to 1.028 for TCE, and 1.022 for cis-DCE (Elsner et al., 2005). During oxidation by Fenton's reagent

Fig. 2. Remaining fraction of PCE versus measured δ^{13}C values (left) and linearized ^{13}C enrichment of PCE according to the Eq. (5) (right), for different $S_2O_8^{2-}$/Fe^{2+}/PCE molar ratios of 20/5/1 (triangle), 100/5/1 (circle), 20/1/1 (square) at sequential addition of Fe^{2+}.

Table 2
Approximate evaluation of $\varepsilon_{c\ reactive\ position}$ and $AKIE_c$.

Compound	$\varepsilon_{c\ bulk}$ ‰	n - x - z	$\varepsilon_{c\ reactive\ position}$	$AKIE_c$	Mechanism rate-limiting step	Reference
cis-DCE	−7.6	2 - 2- 2	−15.2	1.015	Hydrogen abstraction	This study
cis-DCE	−7.6	2 - concerted	−7.6	1.008	Electron transfer and addition to the double bond	This study
TCE	−3.6	2 - 1 - 1	−7.2	1.008	Hydrogen abstraction	This study
TCE	−3.6	2 - concerted	−3.6	1.004	Electron transfer and addition to the double bond	This study
PCE	−4.9	2 - concerted	−4.9	1.005	Electron transfer and addition to the double bond	This study
TCE	−2.5	2 - 1 - 1	−5.0	1.005	Hydrogen abstraction	Poulson et al. (2003)
TCE	−2.5	2 - concerted	−2.5	1.003	Electron transfer and addition to the double bond	Poulson et al. (2003)
PCE	−3.7	2 - concerted	−3.7	1.004	Electron transfer and addition to the double bond	Poulson et al. (2003)
cis-DCE	−21.1	2 - concerted	−21.1	1.022	Formation of a cyclic hypomanganate ester[a]	Elsner et al. (2005)
TCE	−18.5 to −26.8	2 - concerted	−18.5 to −26.8	1.019 to 1.028	Formation of a cyclic hypomanganate ester[a]	Elsner et al. (2005)
PCE	−15.7 to −17.7	2 - concerted	−15.7 to −17.7	1.016 to 1.018	Formation of a cyclic hypomanganate ester[a]	Elsner et al. (2005)

[a] Yan and Schwartz, 1999.

in contrast, AKIEc values of 1.004 for PCE, and between 1.003 and 1.005 (Table 2) for TCE were calculated from enrichment factors reported by Poulson et al. (2003). This similarity with AKIEc values obtained in this study is likely the result of the free radical oxidation which occurs during both activated peroxide and activated persulfate treatment. This similarity may indicate that both oxidants act by the same dominant pathway, or could confirm the relative presence of the hydroxyl radical, formed via the activation of persulfate as proposed by Anipsitakis and Dyonysiou (2004). However, this supposition contradicts studies suggesting that sulfate free radicals are the only radicals formed when persulfate is activated by the ferrous ion (Furholz and Haim, 1987). Our conclusion does not exclude either of these possibilities.

4. Conclusions

This study has shown the occurrence of a significant carbon isotope fractionation during the oxidation of PCE, TCE and cis-DCE by persulfate activated by ferrous ion. The enrichment factor varies between −4.9‰ for PCE, −3.6‰ for TCE and −7.6‰ for cis-DCE. This study also shows that the enrichment factors are constant during the oxidation reaction and their values are independent of the $S_2O_8^{2-}$/Fe^{2+}/CHC molar ratios. This investigation has shown the potential applicability of the isotope approach to monitor the performance of oxidation of chlorinated ethenes by persulfate activated by Fe^{2+}. This additional tool can be used to obtain relevant information to support treatment decisions at contaminated sites. We acknowledge that further research may be required to determine potential limitations for the use of the carbon isotopes method at the field scale.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.06.051.

References

Anipsitakis GP, Dyonysiou DD. Radical generation by the interaction of transition metals with common oxidants. Environ Sci Technol 2004;38:3705–12.
Bill M, Schüth C, Barth JAC, Kalin RM. Carbon isotope fractionation during abiotic reductive dehalogenation of trichloroethene (TCE). Chemosphere 2001;44:1281–6.
Block PA, Brown RA, Robinson D. Novel activation technologies for sodium persulfate in situ chemical oxidation. Proceedings of the fourth international conference on the remediation of chlorinated and recalcitrant compounds, Monterey, CA, May 24–27; 2004.
Chen KF, Kao CM, Wu LC, Surampalli RY, Liang SH. Methyl tert-butyl ether (MTBE) degradation by ferrous ion-activated persulfate oxidation: feasibility and kinetics studies. Water Environ Res 2009;81(7):687–94.
Clark I, Fritz P. Environmental isotope in hydrogeology. New York: Lewis Publishers; 1997.
Dahmani AM, Huang K. Sodium persulfate oxidation for the remediation of chlorinated solvents (USEPA superfund innovative technology evaluation program). Water Air Soil Pollut Focus 2006;6:127–41.
Elsner M, Zwank L, Hunkeler D, Schwarzenbach RP. A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. Environ Sci Technol 2005;39:6896–916.
Furholz U, Haim A. Kinetics and mechanisms of the reactions of mononuclear and binuclear ruthenium (II) ammine complexes with peroxydisulfate. Inorg Chem 1987;26:3243–8.
Hunkeler D, Aravena R, Parker B, Cherry J. A monitoring oxidation of chlorinated ethenes by permanganate in groundwater using stable isotopes: laboratory and field studies. Environ Sci Technol 2003;37:798–804.
Johnson RL, Tratnyek PG, Johnson RO. Persulfate persistence under thermal activation conditions. Environ Sci Technol 2008;42:9350–6.
Liang C, Bruell CJ, Marley MC, Sperry KL. Persulfate oxidation for in situ remediation of TCE II. Activated by chelated ferrous ion. Chemosphere 2004a;55:1225–33.
Liang C, Bruell CJ, Marley MC, Sperry KL. Persulfate oxidation for in situ remediation of TCE I. Activated by ferrous ion with and without a persulfate–thiosulfate redox couple. Chemosphere 2004b;55:1213–23.
Liang C, Wang Z, Mohanty N. Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20°C. Sci Total Environ 2006;370:271–7.
Liang C, Wang Z, Bruell CJ. Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere 2007;66:116–23.
Liang C, Lee IL, Hsu IY, Liang CP, Lin YL. Persulfate oxidation of trichloroethylene with and without iron activation in porous media. Chemosphere 2008a;70:426–35.
Liang C, Huang C-F, Chen Y-J. Potential for activated persulfate degradation of BTEX contamination. Water Res 2008b;42:4091–100.
Liang C, Bruell CJ. Thermally activated persulfate oxidation of trichloroethylene: experimental investigation of reaction orders. Ind Eng Chem Res 2008;47:2912–8.
Liang C, Liang CP, Chen CC. pH dependence of persulfate activation by EDTA/Fe(III) for degradation of trichloroethylene. J Contam Hydrol 2009;106:173–82.
Meckenstock RU, Morash B, Griebler C, Richnow HH. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated aquifers. J Contam Hydrol 2004;75:215–55.
Poulson SR, Naraoka H. Carbon isotope fractionation during permanganate oxidation of chlorinated ethylenes (cDCE, TCE, PCE). Environ Sci Technol 2002;36:3270–4.
Poulson SR, Chikaraishi Y, Naraoka H. Carbon isotope fractionation of monoaromatic hydrocarbons and chlorinated ethylenes during oxidation by Fenton's reagent. Geochim Cosmochim Acta 2003(Suppl. 67). [Supplement, 382.].
Schüth C, Bill M, Barth JAC, Slater GF, Kalin RM. Carbon isotope fractionation during reductive dechlorination of TCE in batch experiments with iron samples from reactive barriers. J Contam Hydrol 2003;66:25–37.
Scott KM, Lu X, Cavanaugh CM, Liu JS. Optimal methods for estimating kinetic isotope effects from different forms of the Rayleigh distillation equation. Geochim Cosmochim Acta 2004;68:433–42.
VanStone N, Przepiora A, Vogan J, Lacrampe-Couloume G, Powers B, Perez E, et al. Monitoring trichloroethene remediation at an iron permeable reactive barrier using stable carbon isotopic analysis. J Contam Hydrol 2005;78:313–25.
Sra K, Thomson NR, Barker JF. Persistence of persulfate in uncontaminated aquifer materials. Environ Sci Technol 2010;44:3098–104.
Thomson NR, Hood ED, Farquhar GJ. Permanganate treatment of an emplaced DNAPL source. Ground Water Monit Rem 2007;27(4):74–85.
Thomson NR, Fraser M, Lamarche C, Barker J, Forsey S. Rebound of a creosote plume following partial source zone treatment with permanganate. J Contam Hydrol 2008;102:154–71.
U.S. EPA. In-situ Chemical Oxidation; EPA/600/R-06/072. Engineering Issue; 2006.
Yan YE, Schwartz FW. Oxidative degradation and kinetics of chlorinated ethylenes by potassium permanganate. J Contam Hydrol 1999;37:343–65.