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Carbon isotope fractionation of 1,1,1-trichloroethane during base-catalyzed persulfate treatment

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HIGHLIGHTS

- Treatability and C fractionation of 1,1,1-TCA by base-catalyzed $S_2O_8^{2-}$ was studied.
- The rate of degradation of 1,1,1-TCA increased with a higher OH^-:$S_2O_8^{2-}$ ratio.
- Base-catalyzed $S_2O_8^{2-}$ can potentially treat recalcitrant compound like 1,1,1-TCA.
- An enrichment factor of −7.0‰ independent of the OH^-:$S_2O_8^{2-}$ ratio was obtained.
- Carbon isotope can potentially be used to estimate the ISCO treatment efficacy.

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ABSTRACT

The extent of carbon isotope fractionation during degradation of 1,1,1-trichloroethane (1,1,1-TCA) by a base-catalyzed persulfate ($S_2O_8^{2-}$) treatment system was investigated. Significant destruction of 1,1,1-TCA was observed at a pH of ~12. An increase in the NaOH:$S_2O_8^{2-}$ molar ratio from 0.2:1 to 8:1 enhanced the reaction rate of 1,1,1-TCA by a factor of ~5 to yield complete (>99.9%) destruction. An average carbon isotope enrichment fractionation factor which was independent of the NaOH:$S_2O_8^{2-}$ molar ratio of -7.0 ± 0.2‰ was obtained. This significant carbon isotope fractionation and the lack of dependence on changes in the NaOH:$S_2O_8^{2-}$ molar ratio demonstrates that carbon isotope analysis can potentially be used *in situ* as a performance assessment tool to estimate the degradation effectiveness of 1,1,1-TCA by a base-catalyzed persulfate system.

1. Introduction

1,1,1-Trichloroethane (1,1,1-TCA, $C_2H_3Cl_3$) is a common chlorinated organic compound found in soil and groundwater, and has been identified at more than 50% of the hazardous waste sites identified on the EPA National Priorities List (NPL) [1]. It frequently co-exists at contaminated sites with chlorinated ethenes (*e.g.*, trichloroethene (TCE)) since its industrial use is similar [2]. However, 1,1,1-TCA is more recalcitrant than common chlorinated ethenes due to the presence a single C—C bond [3].

One potential remediation technology is *in situ* chemical oxidation (ISCO) which involves the injection or release of a chemical reagent into the subsurface with the capability to degrade the target organic compound(s). Among the numerous oxidants and activation systems available, the emergence of persulfate ($S_2O_8^{2-}$) and its novel activation strategies has created the potential for treatment of chlorinated methanes and ethanes (like 1,1,1-TCA) [4]. Gates-Anderson et al. [5] observed very little degradation of 1,1,1-TCA with either peroxide or permanganate while Huang et al. [4] and Liang et al. [6] found that thermally activated persulfate (>40 °C) completely degraded chlorinated solvent compounds like 1,1,1-TCA. Numerous methods are available to activate persulfate such the use transition metals, peroxide, and heat, or establishing alkaline conditions. The most frequently applied activation method is base-catalyzed persulfate (pH > 11) which has been used at ~60% of the sites where persulfate has been employed [7]. Base-catalyzed persulfate treatment consists of establishing high pH conditions

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by adding a strong base (*e.g.*, sodium hydroxide) to the subsurface along with persulfate. Block et al. [8] and Brown et al. [9] suggested that some chlorinated methanes and ethanes can be destroyed using base-catalyzed persulfate.

Furman et al. [10,11] investigated the base activation mechanism and the effect of alkalinity on persulfate reactivity and showed complete degradation of the probe compound hexachloroethane. Furman et al. [10] reported that the base activation mechanism for persulfate starts with the base-catalyzed hydrolysis of a persulfate molecule to generate the hydroperoxide anion, a reducing species (HO_2^-, $E_h = -0.9$ V). The hydroperoxide anion then reduces another persulfate molecule generating the sulfate radical ($SO_4^{\bullet -}$) and the hydroperoxide anion is oxidized to the superoxide radical ($O_2^{\bullet -}$, $E_h = -2.4$ V), another strong reducing species. The overall reaction is given by [10]:

$$2S_2O_8^{2-} + 2H_2O \xrightarrow{OH^-} SO_4^{\bullet -} + O_2^{\bullet -} + 3SO_4^{2-} + 4H^+ \quad (1)$$

The production of these reducing species is what enables the base-catalyzed persulfate system to degrade highly oxidized organic compounds [10,11]. Furman et al. [11] also demonstrated that the generation of these reducing species was highly dependent on the base to persulfate molar ratio employed, indicating that for base to persulfate molar ratios above 3:1 the production of reducing species increased considerably.

The evaluation of ISCO performance for organic compounds following conventional concentration or mass-based estimates is generally difficult and prone to numerous uncertainties [12]. For chlorinated organic compounds, estimation of destruction effectiveness is usually based on the decrease in concentration (or mass load) of the target contaminant and/or an increase in chloride (Cl^-) concentration at a monitoring network downgradient of the source zone. However, changes in the organic compound concentrations between the target source zone and monitoring locations can also occur through non-chemical oxidation/reduction processes (*e.g.*, displacement of contaminated groundwater by the injected oxidant solution). Furthermore, even though oxidation/reduction of the target contaminant may have extensively occurred, the concentration may still remain elevated due to the continuous dissolution from residual non-aqueous phase liquids (*i.e.*, rebound [13]). Interpretation of Cl^- data may also be ambiguous in the presence of high background concentration levels, and, in the case of persulfate, Cl^- can react with the sulfate radical [14]. Hence, the use of concentration data alone may be insufficient to evaluate the effectiveness of an ISCO system [15].

Stable carbon isotope analysis has been increasingly applied as a complementary tool to monitor the *in situ* efficacy of abiotic and biotic treatment systems (*e.g.*, Refs. [15] and [16]). This technique is based on changes in the isotopic composition of the target contaminant and its degradation products. Due to mass-dependent differences in activation energies of the different isotopes ^{13}C and ^{12}C, the lighter isotope (^{12}C) reacts faster than the heavier isotope (^{13}C), leading to fractionation and an enrichment of heavy isotopes in the residual contaminant as the reaction proceeds [17]. Consequently the use of stable carbon isotope analysis to complement the concentration data can be very helpful in distinguishing between chemical oxidation and non-oxidation processes, and therefore in appropriately quantifying the effectiveness of chemical oxidation [15]. In order to test the carbon isotope approach as a potential tool to assess ISCO performance at the field scale, a series of bench-scale experiments were designed in this study. The experimental objectives were (a) to evaluate the carbon isotope fractionation factor, and (b) to assess whether the use of different initial hydroxide to persulfate molar ratios results in differences in the carbon isotopic fractionation and also in 1,1,1-TCA degradation rates.

2. Experimental methodology

2.1. Materials and experimental conditions

To determine the treatability and isotopic fractionation of 1,1,1-TCA, a series of aqueous batch experiments were conducted. Persulfate and 1,1,1-TCA concentrations, along with pH were monitored to evaluate the extent of degradation and to obtain kinetic information. The isotopic composition of 1,1,1-TCA was also quantified, and used to calculate the carbon isotope fractionation factor and to investigate its dependence upon treatment conditions.

All chemicals used were reagent grade: 1,1,1-TCA (99.9% purity, Fisher Scientific); sodium persulfate ($Na_2S_2O_8$, 98%, Alfa Aesar) and sodium hydroxide (NaOH, 99.5%, Alfa Aesar). A 1,1,1-TCA stock solution was prepared to a concentration of 25 mg/L (0.19 mM). This 1,1,1-TCA stock solution was mixed successively with a predetermined amount of persulfate to obtain a final persulfate concentration of 100 mM (~16 g/L), and in turn with different amounts of NaOH to obtain 0.2:1, 0.5:1, 2:1, and 8:1 NaOH:$S_2O_8^{2-}$ molar ratio solutions. Nominal 40 mL reactors capped with Teflon septa were used and were stored in the dark at ambient room temperature (*i.e.*, 20 °C). Reactors were completely filled (no headspace) to minimize volatilization. The initial concentration in the reactors was 20, 50, 200 and 800 mM for NaOH, and 0.15 mM (20 mg/L) for 1,1,1-TCA. Triplicate reactors were prepared for all experimental trials. The influence of the $S_2O_8^{2-}$:1,1,1-TCA molar ratio on treatment effectiveness was not investigated here since the persulfate concentration used was considered to be in excess (the approximate $S_2O_8^{2-}$:1,1,1-TCA initial molar ratio was >600:1).

Preliminary experiments indicated that a three-week long reaction period was necessary to obtain ~90% destruction of 1,1,1-TCA. Sampling was performed at Day 1, 3, 8, 15, and 22. The reactors were sacrificed and quenched in an ice bath, and then aliquots were taken for: persulfate analysis (1 mL), $\delta^{13}C$ determination (22 mL), quantification of 1,1,1-TCA concentration and potential degradation products (2 mL), and to measure pH. Preliminary experiments showed that the use of the ice bath was adequate to essentially stop the reaction over a 1–2 day period, since no significant variation in 1,1,1-TCA concentration was observed over this time frame (data not shown). All analyses were conducted within 24 h of sampling.

Based on previous studies [8], minimal degradation of 1,1,1-TCA was expected for the NaOH:$S_2O_8^{2-}$ molar ratio of 0.2:1 trial and hence isotopic analyses were not performed. The purpose of this trial was to investigate the effectiveness of the base-catalyzed persulfate system at a lower NaOH:$S_2O_8^{2-}$ molar ratio than the recommended ratio of 0.4:1 [8].

Aside from chemical degradation by the reducing species generated in the base-catalyzed persulfate system, destruction of 1,1,1-TCA may occur by hydrolysis [18]. For example, 1,1,1-TCA may react with OH^- to partially degrade into chloroethene which can then be completely mineralized in the presence of activated persulfate [8,14]. Myamoto and Urano [19] observed significant degradation of 1,1,1-TCA at neutral pH at 80 °C; however, the half-life at 15 and 20 °C estimated by using the Arrhenius equation is between 2 and 5 years [19]. To investigate the role of hydrolysis over the 22-day reaction period, another series of experiments (controls) were run at an initial pH of 7, 9, 11, and 13 without any persulfate added.

2.2. Analytical methods

The concentration of 1,1,1-TCA and potential chlorinated degradation products (*e.g.*, 1,1-dichloroethane and chloroethane) was determined by pentane extraction (2 mL sample to 2 mL pentane) and subsequent analysis on a Hewlett-Packard 6890 Plus gas chromatograph (GC) equipped with an HP-624 column

(30 m × 0.32 mm, 1.8 μm film thickness) and a micro-ECD detector. Carbon isotope analysis of 1,1,1-TCA was performed on a GC (Hewlett-Packard 6890; Agilent) coupled through a combustion interface to an isotope ratio mass spectrometer (Micromass Isochrom) as described by Hunkeler and Aravena [16]. Residual persulfate analysis was conducted following the procedure described by Huang et al. [20], and the solution pH was determined using a pH meter (WTW pH 3300i).

2.3. Quantification of isotope fractionation

Carbon isotope enrichment factors have been determined for many chlorinated organic carbon compounds under different abiotic processes, such as: oxidation by permanganate [15,21], hydrogen peroxide [22], and iron-activated persulfate [23]; and transformation by reductive dechlorination by zero valent iron [24,25] and reduction by palladium catalysts with hydrogen [26]. To apply this technique *in situ*, the enrichment factor must be sufficiently high and the fractionation signature must not be affected by reactant concentration variations in the subsurface (*e.g.*, $NaOH:S_2O_8^{2-}$:1,1,1-TCA ratio). These variations can arise due to mixing of the injection volume of persulfate (and activator when used) with groundwater, and due to the usual heterogeneous contaminant distribution in the subsurface.

The carbon isotopic ratio is usually expressed using the $\delta^{13}C$ notation in units of permil (‰) deviation from the international standard Vienna Pee Dee Belemnite (VPDB) as expressed by

$$\delta^{13}C = \frac{{}^{13}C/{}^{12}C_c - {}^{13}C/{}^{12}C_s}{{}^{13}C/{}^{12}C_s} \times 1000 \quad (2)$$

where ${}^{13}C/{}^{12}C_c$ and ${}^{13}C/{}^{12}C_s$ are the ratios for the sample and the standard, respectively. By using the $\delta^{13}C$ notation for the isotopic composition, F for the fraction of the compound remaining (defined as the ratio of the concentration at time t to the initial concentration), and $\Delta\delta^{13}C$ for the difference between the isotope composition at time t and initial concentration, the fractionation factor (α) can be expressed by the Rayleigh equation

$$\ln\left(\frac{\delta^{13}C_{co} + \Delta\delta^{13}C + 1000}{\delta^{13}C_{co} + 1000}\right) = (\alpha - 1)\ln F \quad (3)$$

where $\delta^{13}C_{co}$ is the carbon isotopic ratio at the initial concentration. The Rayleigh equation can be used by assuming that the abundance of the heavier isotope is small compared to the lighter isotope, and that α remains constant during treatment [27]. A more practical way to describe isotope fractionation when α is very small is to use the enrichment factor ε defined as ε (‰) = $(\alpha - 1) \times 1000$.

3. Results and discussion

3.1. Destruction of 1,1,1-TCA

Fig. 1(a) shows the 1,1,1-TCA temporal concentration profiles as a result of treatment by base-catalyzed persulfate (each data point represents the average from triplicate reactors). The experimental controls (without persulfate) under all initial pH conditions yielded a relatively stable 1,1,1-TCA concentration over the 22-day reaction period. These data indicate that at 20 °C the degradation of 1,1,1-TCA by alkaline hydrolysis is insignificant, confirming the observations of Jeffers et al. [18] and Miyamoto and Urano [19] who estimated a half-life between 1.1 and 2 years for the hydrolysis of 1,1,1-TCA.

For all the $NaOH:S_2O_8^{2-}$ molar ratios explored a significant decrease in the concentration of 1,1,1-TCA was observed and is consistent with other studies [8,10,11]. An increase in the hydroxide concentration produced a higher rate of 1,1,1-TCA degradation and

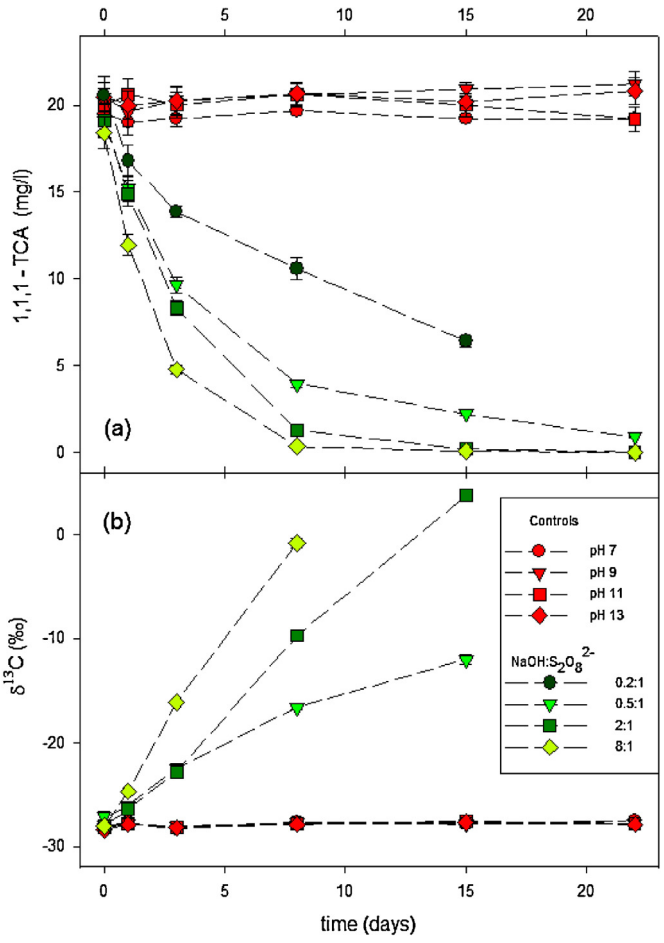

Fig. 1. (a) Variation of 1,1,1-TCA concentrations, and (b) $\delta^{13}C$ values for different $NaOH:S_2O_8^{2-}$ molar ratios and the control experiments.

almost complete destruction (>99.9%) was achieved at the higher molar ratios of 2:1 and 8:1. Partial degradation of 1,1,1-TCA was observed for the molar ratios 0.2:1 (~70% by Day 15) and 0.5:1 (>95% by Day 22). Furman et al. [11] observed similar behavior for their probe compound (hexachloroethane). A higher concentration of OH^- promotes the formation of a higher concentration of reductive species ($O_2^{\bullet -}$), resulting in an increased rate of degradation. No chlorinated degradation products were detected in the treatment and control reactors. Over the reaction period persulfate concentration decreased by ~44% in the 8:1 molar ratio system and by ~5% in the 0.2:1 molar ratio system. The overall treatment performance efficiency (ratio of fractional change in 1,1,1-TCA concentration to the fractional change in persulfate concentration) was highest (~15) for the lower molar ratio of 0.2:1 and decreased as the molar ratio increased (Table 1). The lower performance efficiency at higher $NaOH:S_2O_8^{2-}$ molar ratios indicates that a greater mass of persulfate is needed to degrade a given mass of 1,1,1-TCA when higher $NaOH:S_2O_8^{2-}$ molar ratios are used.

A small (<0.19 unit) decrease in pH was observed over the reaction period and this reduction was largest for the lowest molar ratio employed. Overall, the pH in all trials explored was suitable for alkaline activation (pH > 10.5) throughout the experimental period (Table 1). It was expected that the solution pH would decrease over time as the degradation of persulfate produces protons under alkaline conditions (see Eq. (1)). However, the presence of a high initial concentration of OH^- (from 20 to 800 mM) prevented a significant decrease in pH.

Table 1
Initial and final pH, $S_2O_8^{2-}$ consumed, treatment efficiency, and reaction rate coefficient (k) for the different NaOH:$S_2O_8^{2-}$ molar ratios and the control experiments.

NaOH:$S_2O_8^{2-}$	Initial pH	Final pH	$S_2O_8^{2-}$ consumed (%)	Efficiency[a]	k (day^{-1} M^{-1})[b]
0.2:1	12.06	11.87	4.6	15.0	1.11
0.5:1	12.28	11.81	20.5	7.5	1.93
2:1	12.68	12.52	35.9	4.2	4.87
8:1	12.94	12.90	44.1	3.1	5.31
pH 7	7.12	7.13	–	–	–
pH 9	9.22	9.19	–	–	–
pH 11	10.98	10.96	–	–	–
pH 13	13.07	13.06	–	–	–

[a] Defined as ratio of the fractional change in the 1,1,1-TCA concentration to the fractional change in persulfate concentration.
[b] See Eq. (4).

Assuming that the pH was constant for each experimental trial, the following kinetic model was deemed most appropriate to represent the data

$$r_{1,1,1\text{-TCA}} = -k[1,1,1-\text{TCA}]^n \left[S_2O_8^{2-}\right]^m \quad (4)$$

where k (day^{-1} M^{-1}) is the reaction rate coefficient, and n and m are the reaction orders with respect to 1,1,1-TCA and persulfate, respectively. Eq. (4) was linearized and a least-squares method was used to determine the rate law parameters. The best-fit reaction orders for both 1,1,1-TCA and persulfate were unity, and k varied from 1.11 to 5.31 day^{-1} M^{-1} as the molar ratio increased (Table 1). This 5 fold increase in k is directly related to the increase in OH^-; however, it appears that k may be stabilizing as the molar ratio approaches higher values. This suggests that an increase in the concentration of OH^- causes the generated reactive species to be involved in competing reactions which results in a relatively constant 1,1,1-TCA degradation rate. Additional research is required to elucidate the competing reactions and how they impact the treatment efficiency.

3.2. Extent of carbon fractionation

The experimental controls (without persulfate) for the range of initial pH trials investigated showed no loss in 1,1,1-TCA mass (<5%), and no variation in the $\delta^{13}C$ 1,1,1-TCA value (<0.5‰) throughout the experimental period (Fig. 1(b)). The isotopic data from the controls (n = 12) where used to establish a baseline $\delta^{13}C$ value for 1,1,1-TCA of −28.0 ± 0.4‰ (95% confidence interval).

The isotope composition of the residual 1,1,1-TCA became more enriched in the heavier isotope (^{13}C) over time for all the NaOH:$S_2O_8^{2-}$ molar ratios explored (Fig. 1(b)). For example, the $\delta^{13}C$ 1,1,1-TCA value increased from −28.0‰ at the beginning of the experiment to +3.7‰ after 15 days (99% degradation of 1,1,1-TCA) for the 2:1 NaOH:$S_2O_8^{2-}$ molar ratio. For the 8:1 and 0.5:1 NaOH:$S_2O_8^{2-}$ molar ratios, the $\delta^{13}C$ value increased to −0.9 and −12.1‰ after 98 and 88% degradation of 1,1,1-TCA, respectively. The isotopic enrichment pattern confirmed the normal isotope effect associated with degradation [17,28]. This increase in the $\delta^{13}C$ value in the remaining 1,1,1-TCA allows for the potential to estimate the degradation progress during base-catalyzed persulfate treatment.

While the 1,1,1-TCA concentration decreased exponentially with time, the $\delta^{13}C$ profiles were essentially linear (Fig. 1(b)). To estimate the isotopic enrichment factor, Eq. (3) was fit to the data by linear regression using $1000\ln[(\delta^{13}C_{co} + \Delta\delta^{13}C + 1000)/(\delta^{13}C_{co} + 1000)]$ *versus* ln F, and forcing the intercept through the origin (Fig. 2). The resulting enrichment factors for the different NaOH:$S_2O_8^{2-}$ ratios are presented in Table 2. The pattern of $\delta^{13}C$ for 1,1,1-TCA (Fig. 2) together with the excellent fits (r^2 varied from 0.98 to 1.00), is consistent with the Rayleigh isotopic evolution model. This clearly indicates that the observed enrichment fractionation factor was constant throughout the reaction process or at least until 99% degradation of the 1,1,1-TCA mass occurred. The isotopic enrichment factors for 1,1,1-TCA ranged from −6.9 ± 0.4‰ to −7.1 ± 0.2‰ and were consistent across all trials with an average enrichment factor of −7.0 ± 0.2‰.

The trend shown on Fig. 2 using an average enrichment factor of −7.0 ± 0.2‰ can hypothetically be used to estimate the degree of degradation for the base-catalyzed persulfate treatment of 1,1,1 TCA. For example, a $\delta^{13}C$ enrichment of 1.4‰ is associated with 20% degradation whereas a 19.7‰ enrichment is associated with 95% degradation. Both of these $\delta^{13}C$ variations are significantly larger than the uncertainty in the $\delta^{13}C$ determination (±0.5‰ is the typical error in carbon isotope ratio measurement by compound-specific isotope analysis (CSIA) for chlorinated solvents [27]). This indicates that the magnitude of the enrichment fractionation factor is significantly large enough to minimize errors in the interpretation of isotopic field data.

It is important to note that a variation in the NaOH:$S_2O_8^{2-}$ molar ratios from 0.5:1 to 8:1 resulted in a very slight difference in the enrichment factor (0.2‰), confirming that the investigated molar ratios did not have any influence on the isotopic fractionation in our experimental design. This finding is essential to use isotopic composition to monitor the effectiveness of base catalyzed persulfate *in situ*. Isotopic composition changes can also be used to help understand the dynamics associated with contaminant rebound during and after treatment [15], and to differentiate between dilution (no isotopic changes) and degradation (enrichment pattern) at locations away from the injection zone where a decrease in concentration can occur due to displacement or dilution.

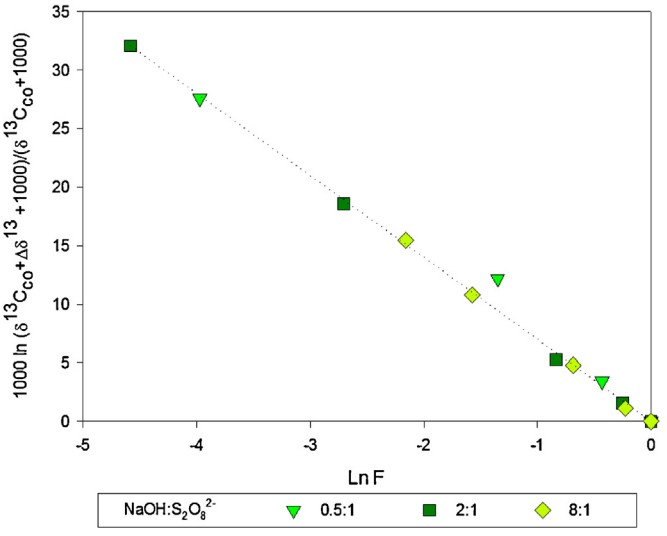

Fig. 2. Linearized ^{13}C enrichment of 1,1,1-TCA according to Eq. (3), for different NaOH:$S_2O_8^{2-}$ molar ratios. The best fit Rayleigh trend line (dashed) is shown.

Table 2
Enrichment factors, $\Delta\delta^{13}C$ (‰), 1,1,1-TCA degradation, and final $\delta^{13}C$ for 1,1,1-TCA for the different $NaOH:S_2O_8^{2-}$ molar ratio trials.

$NaOH:S_2O_8^{2-}$	Degradation	Final $\delta^{13}C$ (‰)	$\Delta\delta^{13}C$ (‰)	$\varepsilon_{c\ bulk}$ ‰	r^2
0.5:1	88%	−12.1	15.1	−7.2 ± 0.3	0.998
2:1	99‰	+3.7	31.7	−6.9 ± 0.4	0.999
8:1	98%	−0.9	27.2	−7.2 ± 0.3	0.984
Average	–	–	–	−7.0 ± 0.3	0.990

Unlike biotic systems where the complexity of different degradation pathways is derived from different microorganisms and results in a large variability in isotope fractionation factors [28] (*e.g.*, the enrichment fractionation factor for microbial reduction of TCE can vary from −2.5 to −13.8‰ [27]), the enrichment fractionation factors for abiotic degradation pathways should vary over a much smaller range for a specific compound under a fixed chemical reaction (*e.g.*, reductive dehalogenation of 1,1,1-TCA by Cr, Fe and Cu/Fe [29]). We note that Hunkeler et al. [15] obtained an enrichment fractionation factor slightly different than that reported by Poulson and Naraoka [21] (−21.4‰ compared to −26.8‰) for the oxidation of TCE by permanganate; however, this discrepancy is likely attributed to differences in the experimental system (the presence of headspace and thus volatilization processes). In the experiments performed in this study, no 1,1,1-TCA volatilization occurred and thus the generated enrichment fractionation factor represents a reference value for the treatment of 1,1,1-TCA by a base-catalyzed persulfate system.

In contrast to chlorinated ethenes, the body of literature related to the enrichment fractionation factor for 1,1,1-TCA degradation under biotic and abiotic treatment processes is limited. Elsner et al. [29] obtained a carbon isotope fractionation factor of −13.6 to −15.8‰ for reductive dehalogenation of 1,1,1-TCA by Cr, Fe and Cu/Fe, suggesting a consistency with a potential mechanism that involves the CCl_3 carbon center. The value of −7.0‰ obtained in this study is also consistent with a reduction mechanism which likely involves the CCl_3 carbon center through an electron transfer mechanism. However, no degradation products or intermediates were observed and further systematic research is needed.

Finally, a carbon isotope fractionation factor of −1.8‰ was reported for biodegradation of 1,1,1-TCA by Sherwood Lollar et al. [30], which is much smaller than the isotope fractionation factor of −7.0‰ obtained for abiotic degradation of 1,1,1-TCA in this study. This creates the possibility of using compound-specific isotope analysis to distinguish between these two degradation pathways.

4. Conclusions

This investigation demonstrated that 1,1,1-TCA can be degraded by employing base-catalyzed persulfate and that a significant carbon isotope fractionation occurs. Higher $NaOH:S_2O_8^{2-}$ molar ratios increased the rate of degradation of 1,1,1-TCA. Although the data are not conclusive, it appears that the 1,1,1-TCA reaction rate stabilizes as the $NaOH:S_2O_8^{2-}$ molar ratio increased. While a higher $NaOH:S_2O_8^{2-}$ molar ratio was able to increase the 1,1,1-TCA degradation rate, it reduced the treatment performance efficiency. An average enrichment fractionation factor of -7.0 ± 0.2‰ was determined, and this enrichment fractionation factor was independent of the $NaOH:S_2O_8^{2-}$ molar ratios employed.

Although additional research is required to determine the impact of other environmental parameters (*e.g.*, temperature, buffering capacity) on the fractionation factor, the results obtained from the present investigation show that the carbon isotope is potentially a useful tracer that can be used to assess the effectiveness of 1,1,1-TCA degradation *in situ* when a base-catalyzed persulfate system is employed.

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