



## Dual element (C–Cl) isotope approach to distinguish abiotic reactions of chlorinated methanes by Fe(0) and by Fe(II) on iron minerals at neutral and alkaline pH

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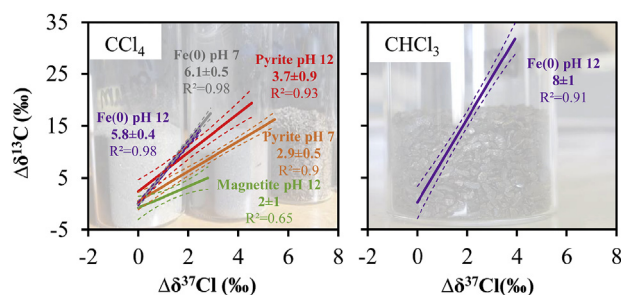
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### HIGHLIGHTS

- Carbon tetrachloride (CT) and chloroform (CF) C and Cl isotope fractionation study.
- CT and CF abiotic reactions with Fe(0), FeCl<sub>2</sub>, pyrite and magnetite were assessed.
- Unlike at pH 12, at pH 7 only CT degradation by Fe(0) and pyrite was detected.
- Different C–Cl plots for CT hydrogenolysis and CT hydrolytic or thiolytic reduction.
- Reactions with Fe(0) and pyrite showed similar  $\Delta$  for each compound regardless pH.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A dual element C–Cl isotopic study was performed for assessing chlorinated methanes (CMs) abiotic transformation reactions mediated by iron minerals and Fe(0) to further distinguish them in natural attenuation monitoring or when applying remediation strategies in polluted sites. Isotope fractionation was investigated during carbon tetrachloride (CT) and chloroform (CF) degradation in anoxic batch experiments with Fe(0), with FeCl<sub>2</sub>(aq), and with Fe-bearing minerals (magnetite, Mag and pyrite, Py) amended with FeCl<sub>2</sub>(aq), at two different pH values (7 and 12) representative of field and remediation conditions. At pH 7, only CT batches with Fe(0) and Py underwent degradation and CF accumulation evidenced hydrogenolysis. With Py, thiolytic reduction was revealed by CS<sub>2</sub> yield and is a likely reason for different  $\Delta$  value ( $\Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl}$ ) comparing with Fe(0) experiments at pH 7 ( $2.9 \pm 0.5$  and  $6.1 \pm 0.5$ , respectively). At pH 12, all CT experiments showed degradation to CF, again with significant differences in  $\Delta$  values between Fe(0) ( $5.8 \pm 0.4$ ) and Fe-bearing minerals (Mag,  $2 \pm 1$ , and Py,  $3.7 \pm 0.9$ ), probably evidencing other parallel pathways (hydrolytic and thiolytic reduction). Variation of pH did not significantly affect the  $\Delta$  values of CT degradation by Fe(0) nor Py.

CF degradation by Fe(0) at pH 12 showed a  $\Delta$  ( $8 \pm 1$ ) similar to that reported at pH 7 ( $8 \pm 2$ ), suggesting CF hydrogenolysis as the main reaction and that CF alkaline hydrolysis ( $13.0 \pm 0.8$ ) was negligible.

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Our data establish a base for discerning the predominant or combined pathways of CMs natural attenuation or for assessing the effectiveness of remediation strategies using recycled minerals or Fe(0).  
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## 1. Introduction

Chloroform (CF, CHCl<sub>3</sub>) and carbon tetrachloride (CT, CCl<sub>4</sub>) are chlorinated volatile organic compounds (VOCs) from the group of chlorinated methanes (CMs). Both are toxic and predicted to be carcinogenic substances (IARC, 1999). They are found in groundwater as a consequence of releases from chemical manufacturing processes or accidental spills (Zogorski et al., 2006), although CF can also be naturally formed (Cappelletti et al., 2012; Hunkeler et al., 2012; Breider et al., 2013).

Abiotic CMs degradation in groundwater mainly proceeds under anoxic conditions. The main CT degradation pathway is hydrolysis to CF, although CT reduction followed by hydrolytic or thiolitic substitution of dechlorinated intermediates to CO, CO<sub>2</sub> or CS<sub>2</sub> is also possible (He et al., 2015). Abiotic CF degradation processes under anoxic conditions include hydrolysis to DCM and reductive elimination to CH<sub>4</sub> (Song and Carraway, 2006; He et al., 2015). Bioremediation strategies for CMs are scarce (Penny et al., 2010; Cappelletti et al., 2012; Koenig et al., 2015). Thus, although both compounds can be biotically (Penny et al., 2010; Cappelletti et al., 2012) or abiotically degraded, they are considered recalcitrant compounds requiring targeted remediation strategies in groundwater.

*In situ* chemical oxidation is not an effective treatment for CT and CF due to the highly oxidized state of carbon (Huang et al., 2005; Huling and Pivetz, 2006). Alkaline hydrolysis (AH) has been studied for CF at laboratory and field scale as a new and effective remediation strategy (Torrentó et al., 2014) but CT hydrolysis is pH independent and extremely slow (Jeffers et al., 1989). Fortunately, zero-valent metals and Fe-bearing minerals have proven to mediate the transformation of CF and CT at laboratory scale (e.g. Matheson and Tratnyek, 1994; Támara and Butler, 2004; Feng and Lim, 2005; Zwank et al., 2005; He et al., 2015; Lee et al., 2015). Fe(0) has been commonly used in permeable reactive barriers (PRBs) since it is a strong reducing agent, cheaper and less harmful than other zero-valent metals (Vodyanitskii, 2014). Micro-sized Fe(0) has been used in long-functioning PRBs, while nano-sized Fe(0) injections have been recently used to renew PRBs in highly polluted sites (Obiri-Nyarko et al., 2014). Some minerals such as magnetite (Fe<sub>3</sub>O<sub>4</sub>, Mag hereafter) can be formed in Fe(0) PRBs reducing their efficiency (Vodyanitskii, 2014), while others, such as FeS, can promote CT degradation (Obiri-Nyarko et al., 2014). Since long-term evolution of PRBs is still not fully understood (Obiri-Nyarko et al., 2014) and Fe-bearing minerals such as pyrite (FeS<sub>2</sub>, Py hereafter), green rusts or Mag are naturally ubiquitous in anoxic aquifers and/or in transition zones (Ferrey et al., 2004; Scheutz et al., 2011), it is interesting to assess their influence on CMs degradation.

Detection of CMs natural attenuation or monitoring of the above-mentioned remediation strategies can be challenging when relying on only by-products, since these daughter products can be further degraded, are difficult to quantify in the field (e.g. gases), could come from other parent compounds or stem from a secondary source (i.e. CF). In such cases, compound specific isotope analysis (CSIA) has been developed and matured into a widely applied method allowing the investigation of VOCs transformation reactions and the associated isotopic fractionation values ( $\epsilon$ )

(Renpenning and Nijenhuis, 2016). The occurrence of limiting steps prior to the reaction step that mask the real magnitude of the  $\epsilon$  has been shown when mineral phases are involved in abiotic degradation processes (Elsner et al., 2007). Controlled laboratory studies are thus required to confine the ranges of possible  $\epsilon$  values and determine conservative estimates of quantification of CMs degradation extent in the field. The concept of dual element (C–Cl) isotope plots featuring slopes ( $\Lambda = \Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl}$ ) that are characteristic of different reaction mechanism, holds promise to provide information on the manner and order of chemical bond cleavage for organohalides (Nijenhuis et al., 2016) and this, in turn, may help to distinguish potential competing processes and to assess their individual effectiveness as field remediation strategies (Van Breukelen, 2007). Although some abiotic  $\Lambda$  values for CF were recently published (Heckel et al., 2017a; Torrentó et al., 2017), neither  $\Lambda$  for CT abiotic reactions nor field demonstrations are available.

In a multiple-compound polluted site in Òdena (Catalonia) (Palau et al., 2014), shifts in carbon isotopic composition of CF were attributed to AH (Torrentó et al., 2014) since alkaline conditions (pH ~12) were generated in recharge water concrete-based interception trenches. In contrast, detected shifts in the carbon isotopic composition of CT could not be explained by AH but here, reduction by Fe-bearing materials from the construction wastes used in the trenches could have played an important role (Torrentó et al., 2014). The presence of surficial iron patinas growths and of variable iron amounts in concrete-based aggregates obtained from one of the boreholes was confirmed by Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS) and X-ray fluorescence (XRF) (data not published), but specific mineral phases are still under study.

In order to close this knowledge gap on isotopic data of abiotic CMs reactions and, therefore, to allow better field interpretations such as in the case of Òdena, this study aims at providing dual element isotope data on abiotic degradation of CT and CF by Fe(0) and Fe-bearing minerals with FeCl<sub>2</sub>(aq) under anoxic conditions at pH 7 and 12. Characterization is based on monitoring the carbon and chloride isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$ ) of CF and CT, as well as on detecting volatile dissolved by-products to identify the existence of parallel reaction pathways. Nano-sized Fe(0) was used for CT experiments because it is more reactive than micro-sized Fe(0) (Song and Carraway, 2006). CF experiments at pH 12 were performed with milli-sized Fe(0) to compare the pH effect with published pH 7 experiments (Torrentó et al., 2017). Py and Mag were chosen as Fe-bearing minerals because they involve different potential redox species for reaction with CMs (Fe(II), and S<sub>2</sub><sup>2-</sup> in Py, according to Kriegman-King and Reinhard (1994) and represent widespread oxidation products of Fe(0) in PRBs (He et al., 2015) and mining or industrial wastes, which are potential recyclable materials for remediation.

## 2. Materials and methods

### 2.1. Experimental setup

Experiments were prepared in an anaerobic chamber and performed in 42 mL VOA/EPA glass vials capped with PTFE-coated rubber stoppers and plastic screw caps. A summary of

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