Science of the Total Environment 596–597 (2017) 169–177

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Contrasting dual (C, Cl) isotope fractionation offers potential to distinguish reductive chloroethene transformation from breakdown by permanganate

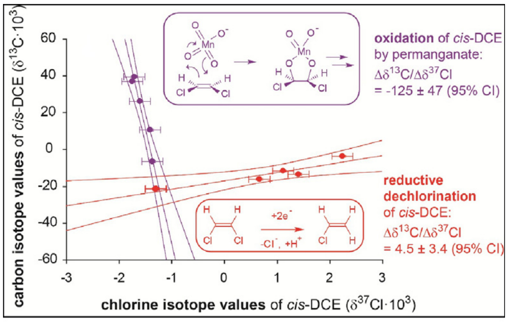
Eylem Doğan-Subaşı [a,b], Martin Elsner [c], Shiran Qiu [c], Stefan Cretnik [c], Siavash Atashgahi [a],
Orfan Shouakar-Stash [d], Nico Boon [b], Winnie Dejonghe [a], Leen Bastiaens [a,*]

[a] *Flemish Institute for Technological Research (VITO), Separation and Conversion Technology, Boeretang 200, 2400 Mol, Belgium*
[b] *Laboratory of Microbial Ecology and Technology (LabMET), Ghent University, Coupure Links 653, 9000 Gent, Belgium*
[c] *Institute of Groundwater Ecology, Helmholtz Zentrum München-National Research Center for Environmental Health, Ingolstädter Landstrasse 1, D-85764 Neuherberg, Germany*
[d] *Department of Earth Sciences, University of Waterloo, 200 University Avenue W., Waterloo, Ont. N2L 3G1, Canada*

HIGHLIGHTS

- An inverse isotope effect during chemical oxidation is achieved for chlorine isotope.
- Dual element isotope approach (C, Cl) differentiates removal mechanisms of *cis*-DCE (and TCE).
- After permanganate treatment, reductive dechlorination is not completely suppressed.
- Dual element isotope has potential to distinguish dilution, dechlorination and oxidation.

GRAPHICAL ABSTRACT



CI = confidence interval

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form 31 March 2017
Accepted 31 March 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
cis-DCE
TCE
Dual element isotope
Permanganate
Reductive dechlorination

ABSTRACT

cis-1,2-Dichloroethene (*cis*-DCE) and trichloroethene (TCE) are persistent, toxic and mobile pollutants in groundwater systems. They are both conducive to reductive dehalogenation and to oxidation by permanganate. In this study, the potential of dual element (C, Cl) compound specific isotope analyses (CSIA) for distinguishing between chemical oxidation and anaerobic reductive dechlorination of *cis*-DCE and TCE was investigated. Well-controlled *cis*-DCE degradation batch tests gave similar carbon isotope enrichment factors ε_C (‰), but starkly contrasting dual element isotope slopes $\Delta\delta^{13}C/\Delta\delta^{37}Cl$ for permanganate oxidation ($\varepsilon_C = -26‰ \pm 6‰$, $\Delta\delta^{13}C/\Delta\delta^{37}Cl \approx -125 \pm 47$) compared to reductive dechlorination ($\varepsilon_C = -18‰ \pm 4‰$, $\Delta\delta^{13}C/\Delta\delta^{37}Cl \approx 4.5 \pm 3.4$). The difference can be tracked down to distinctly different chlorine isotope fractionation: an inverse isotope effect during chemical oxidation ($\varepsilon_{Cl} = +0.2‰ \pm 0.1‰$) compared to a large normal isotope effect in reductive dechlorination ($\varepsilon_{Cl} = -3.3‰ \pm 0.9‰$) ($p \ll 0.05$). A similar trend was observed for TCE. The dual isotope approach was evaluated in the field before and up to 443 days after a pilot scale permanganate injection in the subsurface. Our study indicates, for the first time, the potential of the dual element isotope approach for distinguishing *cis*-DCE (and TCE) concentration drops caused by dilution, oxidation by permanganate and reductive dechlorination both at laboratory and field scale.

---

* Corresponding author.
E-mail address: leen.bastiaens@vito.be (L. Bastiaens).

http://dx.doi.org/10.1016/j.scitotenv.2017.03.292
0048-9697/

1. Introduction

Chlorinated ethenes (CEs) like trichloroethene (TCE) and *cis*-1,2-dichloroethene (*cis*-DCE) are widespread groundwater contaminants often present as dense non-aqueous phase liquids (DNAPLs). During years, these DNAPLs slowly release the pollutant creating groundwater contamination plumes, leading to a common environmental problem (Stroo et al., 2012). As DNAPLs are hard to localize in the subsurface, remediation of CE-contaminated sites is challenging, *in situ* bioremediation and chemical oxidation (ISCO) are effective, well-established techniques for remediation of CEs contaminated sites. Anaerobic *in situ* bioremediation is based on microbial processes that replace chlorine with hydrogen, which requires the activity of a dehalogenase enzyme, an electron donor, a carbon source, while the CEs serve as electron acceptor. Several groups of bacteria such as *Desulfomonile*, *Dehalobacter*, *Desulfitobacterium* and *Desulfuromonas* are known for their dechlorination capacity, but only *Dehalococcoides mccartyi* is capable of performing the complete dechlorination from perchloroethene (PCE) to ethene (Tiehm and Schmidt, 2011) and has reductive dehalogenase (RDase) genes encoding the proteins responsible for the respiration of CEs. In respect to *in situ* studies, for instance, Atashgahi et al. (2016) performed an *in situ* glycerol injection to stimulate reductive dechlorination of *cis*-DCE and vinyl chloride (VC). The results indicated that in addition to monitoring dechlorinating guilds, supportive non-dechlorination community members and geochemical factors should be controlled to ensure robust dechlorination activity. ISCO, on the other hand, is based on complete oxidation of CEs by an oxidant (e.g. Fenton's reagent, persulfate) to generate chloride ion (Cl^-) and carbon dioxide. Among the different chemical oxidant agents, permanganate (MnO_4^-, PM) has been widely applied for *in situ* and *ex situ* remediation since it is less reactive, more persistent and relatively safe to handle in the field since large quantities of heat and gases are not produced (Tsail et al., 2008). Implementation of ISCO as a single treatment strategy may also not be a sustainable remediation solution for soils with a mixed pollution and/or residual free phase (Lee et al., 2007) or a high soil heterogeneity (Hrapovic et al., 2005). Therefore, an approach of ISCO followed by bioremediation might be a cost-effective alternative in the subsurface and reduce CEs concentrations to below regulatory limits by achieving desired removal efficiencies (Richardson et al., 2011). The study of Sutton et al. (2015) showed that mild permanganate treatments led to decreases in CEs concentrations and had a stimulatory effect on dechlorination, while stronger oxidant loads can completely and irreversibly disrupt microorganisms.

When applying such a combined degradation strategy in the field, however, a decrease in the concentrations of CEs could potentially be due to three reasons: (i) chemical oxidation, (ii) biological processes or (iii) dilution through displacement of contaminated groundwater by the injected solution (Hunkeler et al., 2003). Compound specific isotope analysis (CSIA) of carbon isotopes has been used as a promising tool to detect the occurrence of chemical and biological degradation as opposed to dilution (Mancini et al., 2002; Hunkeler et al., 2003; Meckenstock et al., 2004). Gas chromatography-isotope ratio mass spectrometry is used to measure isotope ratios ($^{13}C/^{12}C$) at natural abundance inside organic molecules at low concentrations (Elsner et al., 2012). While biological or chemical degradation can profoundly change such carbon isotope ratios (Slater et al., 2001; Hunkeler et al., 2003; Elsner et al., 2005) physicochemical processes such as dispersion, sorption, dilution or volatilization have a minor impact on a pollutant's isotope signature (Schmidt et al., 2004; Hunkeler et al., 2008; Thullner et al., 2012). The reason is that stronger and less reactive molecular bonds are formed by heavy isotopes in comparison to light isotopes so that the heavy isotopes are degraded more slowly and become enriched among the remaining contaminant molecules. These characteristic changes in isotope values, in turn, can be measured by CSIA and provide direct evidence for the occurrence of a degradation process (Elsner et al., 2012; Meckenstock et al., 2004; Thullner et al., 2012). The ability to distinguish between chemical oxidation (Poulson and Naraoka, 2002; Hunkeler et al., 2003) and reductive dechlorination (Hunkeler et al., 1999; Slater et al., 2001; Lee et al., 2007; Fletcher et al., 2011) during and after the combined approach is however much more difficult since both processes were found to result in similar changes in carbon isotope values. Dual-element isotope analysis based on the isotope analysis of the C as well as Cl elements offers a new opportunity to solve this problem (Abe et al., 2009; Wiegert et al., 2013; Cretnik et al., 2013; Kuder et al., 2013). Several studies have indicated that a dual element isotope approach has the potential to distinguish different transformation pathways (Zwank et al., 2005; Elsner et al., 2005; Fischer et al., 2008; Elsner, 2010). However, analytical methods for dual element isotope analysis of $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ of chlorinated ethenes have only relatively recently become available and are still being improved (Shouakar-Stash et al., 2005; Sakaguchi-Söder et al., 2007; Bernstein et al., 2011; Aeppli et al., 2010; Jin et al., 2011). Abe et al. (2009) were the first to apply dual element (C, Cl) isotope fractionation to distinguish between microbial aerobic oxidation and microbial anaerobic reductive dechlorination of *cis*-DCE and VC. In a handful of other studies, dual element (C, Cl) isotope analysis was used to differentiate different CE removal mechanisms such as (1) abiotic transformation of *cis*-DCE by zero-valent iron (ZVI) and TCE by ZVI (Lojkasek-Lima et al., 2012; Audí-Miró et al., 2013) (2) reductive dechlorination of TCE by different microbial cultures (*Geobacter lovleyi* strain SZ and *Desulfitobacterium hafniense* Y51) (Cretnik et al., 2013), (3) transformation by the enzymatic cofactor cobalamin and by the simplified chemical model system cobaloxime (Cretnik et al., 2013), and (4) reductive dechlorination of PCE and TCE by reductive dehalogenases and enzymatic co-factors (Wiegert et al., 2013; Kuder et al., 2013; Cretnik et al., 2014; Badin et al., 2014; Renpenning et al., 2014). However, up to now, there are no studies on dual element (C, Cl) isotope analysis to discriminate anaerobic reductive dechlorination and chemical oxidation by PM of *cis*-DCE or TCE.

In this study, we therefore evaluated the possibility of using stable isotope analyses of two elements ($^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$) to distinguish between different scenarios of *cis*-DCE and TCE concentration reduction i.e. (1) degradation by chemical oxidation, (2) reductive dechlorination, and (3) dilution. To lay the basis for field data, *cis*-DCE isotope enrichment factors (ε_C, ε_{Cl}) during chemical oxidation and reductive dechlorination were first determined in lab scale microcosm tests. In addition, a TCE oxidation batch test with PM was conducted to identify C, Cl isotope fractionation patterns. Next, groundwater samples from a field site were collected before and after PM injection and subjected to C and Cl isotope analyses of *cis*-DCE which was the main pollutant in groundwater. Specifically, the aim of the field test was to evaluate the potential of the dual element isotope approach (1) for revealing whether *cis*-DCE degradation processes occurred in the test area, (2) for differentiating between chemical oxidation by PM and reductive dechlorination, and (3) for evaluating the occurrence of (bio)degradation after a PM injection. Calculated dual element isotope slopes based on the lab scale tests were used as reference to identify the concurrent modes of *cis*-DCE degradation (chemical oxidation vs. reductive dehalogenation) and dilution in the field. In this sense, this study is the first to test the potential of dual element (C, Cl) isotope analysis for distinguishing between *cis*-DCE removal by chemical oxidation vs. anaerobic reductive dechlorination in a laboratory as well as field application.

2. Material and methods

2.1. Laboratory experiments

2.1.1. Oxidation experiments of cis-DCE by permanganate

Duplicate batch experiments were set up in 250 mL bottles equipped with Mininert valves (Supelco, Bellefonte, Pennsylvania, USA). Each bottle contained 150 mL of an aqueous *cis*-DCE solution, prepared with MilliQ water, at a concentration of 60 mg/L (99%, Acros Organics).