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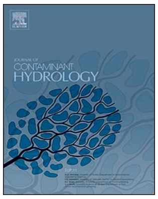

Modeling 3D-CSIA data: Carbon, chlorine, and hydrogen isotope fractionation during reductive dechlorination of TCE to ethene

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ABSTRACT

Reactive transport modeling of multi-element, compound-specific isotope analysis (CSIA) data has great potential to quantify sequential microbial reductive dechlorination (SRD) and alternative pathways such as oxidation, in support of remediation of chlorinated solvents in groundwater. As a key step towards this goal, a model was developed that simulates simultaneous carbon, chlorine, and hydrogen isotope fractionation during SRD of trichloroethene, via cis-1,2-dichloroethene (and *trans*-DCE as minor pathway), and vinyl chloride to ethene, following Monod kinetics. A simple correction term for individual isotope/isotopologue rates avoided multi-element isotopologue modeling. The model was successfully validated with data from a mixed culture *Dehalococcoides* microcosm. Simulation of Cl-CSIA required incorporation of secondary kinetic isotope effects (SKIEs). Assuming a limited degree of intramolecular heterogeneity of δ^{37}Cl in TCE decreased the magnitudes of SKIEs required at the non-reacting Cl positions, without compromising the goodness of model fit, whereas a good fit of a model involving intramolecular C—Cl bond competition required an unlikely degree of intramolecular heterogeneity. Simulation of H-CSIA required SKIEs in H atoms originally present in the reacting compounds, especially for TCE, together with imprints of strongly depleted δ^{2}H during protonation in the products. Scenario modeling illustrates the potential of H-CSIA for source apportionment.

1. Introduction

At many contaminated sites, monitored natural attenuation (MNA) of chlorinated ethenes is the preferred and cost-effective remediation approach (Meckenstock et al., 2015). Microbial sequential reductive dechlorination (SRD) of chlorinated ethenes is usually the main transformation process in MNA. The dechlorination proceeds from the primary contaminants tetrachloroethene (PCE) and/or trichloroethene (TCE), to daughter products cis- and trans-1,2-dichloroethene (cDCE and tDCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), and finally to nontoxic ethene (ETH). Degradation may, however, also occur via alternative transformation pathways such as (an)aerobic oxidation (Bradley, 2011; Bradley and Chapelle, 2011; Chu et al., 2004; Pooley et al., 2009) and chemical reduction (Damgaard et al., 2013; Darlington et al., 2013; Ferrey et al., 2004; Lee and Batchelor, 2002) of lower and higher chlorinated ethenes, respectively. At field sites, the efficacy of SRD can be verified by quantitation of the degradation products that are pathway-specific. However, assessment of the alternative pathways of chlorinated ethene destruction is more difficult, since the degradation products (Cl^{-}, CO_2) blend with the natural background levels. Moreover, degradation of SRD products can lead to an underestimation of the SRD performance as it seems that parent compounds are not well degraded because product concentrations are low. Consequently, less sustainable remedies, such as pump and treat, may be instituted or continued unnecessarily.

Compound-specific stable isotope analysis (CSIA) has been applied in contaminant studies, to detect and identify degradation processes (Hunkeler et al., 2008). One complication in interpretation of CSIA data is potential occurrence of sequential/parallel transformations, e.g., SRD followed by aerobic degradation of SRD products (Arp et al., 2001; Mundle et al., 2012). Multi-dimensional CSIA, i.e., CSIA of more than one element (C, Cl, H), as started with 2-D carbon and hydrogen CSIA of MTBE to discriminate anaerobic from aerobic transformation, holds particular promise also for detecting individual degradation pathways of chlorinated solvents. In addition to a growing number of reports on combined C and Cl isotope effects in various chlorinated solvent

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degradation systems (Abe et al., 2009; Audi-Miro et al., 2013; Cretnik et al., 2013; Wiegert et al., 2012) several CSIA applications focus specifically on discrimination of such alternative reaction mechanisms for chlorinated ethenes (Badin et al., 2016; Badin et al., 2014; Dogan-Subasi et al., 2017).

Reactive transport modeling (RTM) could become an essential tool in evaluation of such CSIA data. RTM can simulate sequential/parallel degradation reactions with chains of daughter products in SRD of halogenated hydrocarbons (Atteia et al., 2008; Höhener, 2016; Van Breukelen et al., 2005), and can account for potential relevance of the physical processes DNAPL dissolution (Aeppli et al., 2009; Hwang et al., 2013), sorption (Eckert et al., 2013; Höhener and Yu, 2012; Kopinke et al., 2005; Van Breukelen and Prommer, 2008), and transverse hydrodynamic dispersion (Eckert et al., 2013; Rolle et al., 2010; Van Breukelen and Rolle, 2012; Wanner and Hunkeler, 2015). Isotope effects modeling during SRD of chlorinated ethenes has been performed for lab (Van Breukelen et al., 2005) and field-generated C-CSIA data, but modeling of Cl fractionation has been relatively limited (Höhener, 2016; Palau et al., 2014b; Wiegert et al., 2012) while a model on H-CSIA does not yet exist.

Studies of Cl isotope fractionation in reactions of organochlorine compounds focus on the so-called primary isotope effects, i.e., isotope fractionation of the atoms positioned at the reacting molecular bonds (Paneth, 2006). In accordance with that consensus, the existing models of Cl isotope fractionation were developed for isotope fractionation involving only the primary effects (Hunkeler et al., 2009; Jin et al., 2013). However, it was also suggested that reactions of chlorinated hydrocarbons (Palau et al., 2014a) may result in fractionation of non-reactive Cl atoms (secondary isotope effects) or possibly combine both primary and secondary effects (Abe et al., 2009; Cretnik et al., 2014; Kuder et al., 2013; Palau et al., 2014a). Höhener (2016) recently extended the analytical BIOCHLOR model with calculation of carbon and chlorine stable isotope ratios in chloroethenes and accounting for secondary chlorine isotope effects in the TCE to cDCE step. Likewise, to address the potential contributions from Cl isotope effects occurring at non-reactive positions, the present numerical model considers isotope effects occurring at all Cl positions within the reacting molecules.

Recently, Kuder et al. (2013) presented a dataset on SRD of TCE to ETH by a *Dehalococcoides* culture, including 3D-CSIA (C, Cl, H) results, at high temporal resolution. This dataset allows for further validation and improvement of the chlorine isotopologue fractionation model developed by Hunkeler et al. (2009) and the development and validation of a hydrogen isotope fractionation model. The objectives of the current study were (i) to extend the current chlorine isotope fractionation model (Hunkeler et al., 2009) as adopted in subsequent studies (Höhener, 2016; Jin et al., 2013; Palau et al., 2014b; Wiegert et al., 2012) for isotope effects occurring at multiple Cl positions of TCE (Höhener, 2016) and of DCE, and for intramolecular heterogeneity in δ^{37}Cl of the source compound (TCE); (ii) to develop a completely novel model of hydrogen isotope fractionation during SRD; and (iii) to validate the models with the experimental data (Kuder et al., 2013). The validated models requiring Monod kinetics are expected to form a template for CSIA interpretation of SRD of halogenated hydrocarbons and contribute towards CSIA-based support of remediation of chlorinated solvent groundwater pollution at field sites.

2. Methodology

2.1. Experimental data for model validation

Model validation used data from a microcosm experiment on dechlorination of TCE by a *Dehalococcoides* (Dhc) culture. A detailed description of that experiment is available elsewhere (Kuder et al., 2013). In summary, microcosms were set up with Bio-Dechlor Inoculum (BDI) culture (Amos et al., 2008) a consortium of Dhc strains that is capable of complete dechlorination of PCE via TCE, DCE, and VC to ETH. The microcosms were amended with TCE and lactate electron donor. Concentrations and C, Cl, and H isotope ratios were determined for TCE and the aforementioned reaction products over the course of degradation.

2.2. Nomenclature of the chlorine and hydrogen isotope effects

Parameters describing the magnitude of isotope effects use the rate constants (k) for heavy vs. light isotope species, where: $^{light}k/^{heavy}k = 1/\alpha$; $\varepsilon = \alpha - 1$. The fractionation factor (α) and enrichment factor (ε) can describe position-specific or "bulk" effects. The latter, indicated by the "bulk" subscript (e.g., ε_{bulk}) are averaged for all reactive and non-reactive positions of a molecule. KIE (kinetic isotope effect) is the ratio of $^{light}k$ and $^{heavy}k$ for a specific molecular position and a specific transformation process. In a primary KIE, the isotope substituted-position is at the reaction center. A secondary KIE (SKIE) is the effect of isotope substitution at a position remote from the reaction center (Elsner et al., 2005).

In the discussion, we refer to position-specific isotope effects, to reflect the different fates of individual atoms of the reacting compounds. We refer to ε_{RP} (at "reactive position", *i.e.*, the Cl position undergoing dechlorination) or as ε_{NRP} (at "non-reactive position", i.e., the Cl position not undergoing dechlorination). Isotope effects for the Cl atoms remote from the dechlorination site (e.g., α and βt for TCE in Fig. 1a) are by definition secondary KIEs (SKIEs). Observable isotope effects for the Cl atom undergoing dechlorination may be in fact primary or secondary, depending on the dechlorination process involved. The latter may occur if the initial transformation step does not involve C—Cl cleavage. It was previously proposed that the initial step in abiotic dechlorination of VC and cDCE by cobalamin is nucleophilic addition of cobalamin and the chloroethene species (Glod et al., 1997). A similar process was postulated for biodegradation of the same species by Dhc (Abe et al., 2009; Kuder et al., 2013). It is also possible that the

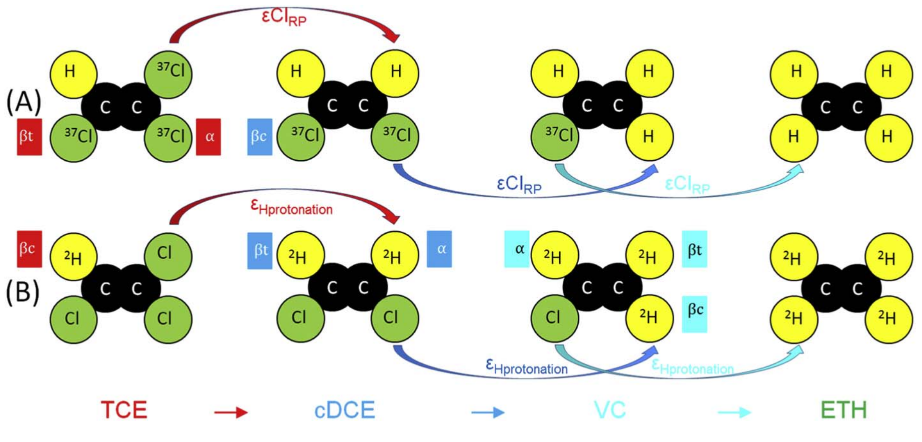

Fig. 1. (a) A scheme illustrating chlorine isotope effects that occur during SRD of TCE to ETH. Note that the isotope effects at the non-reacting positions (NRP) are defined with respect to the location of the reacting position (RP): α is the germinal position, β is/are the vicinal position(s); c (cis) and t (trans) represent the stereochemical position relative to the reacting position. In TCE transformation, SKIEs (ε_{NRP}) occur of type α and βt, while a KIE or SKIE (ε_{RP}) occurs at the dechlorination site (see text for additional explanations). (b) A scheme of hydrogen isotope fractionation in SRD of TCE to ETH, combining SKIEs (in TCE transformation, type βc) and the effects of inserting H atoms by protonation, $\varepsilon_{Hprotonation}$ (see below and also Eqs. 5 and 6). For simplicity, the reactions involving tDCE are omitted.