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Mechanistic approach to multi-element isotope modeling of organic contaminant degradation

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HIGHLIGHTS

- New multi-element isotope modeling approach based on position-specific isotopologues.
- The method mechanistically tracks contaminant transformation via different pathways.
- 2D and 3D isotope modeling applications: toluene, MTBE and nitrobenzene degradation.

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ABSTRACT

We propose a multi-element isotope modeling approach to simultaneously predict the evolution of different isotopes during the transformation of organic contaminants. The isotopic trends of different elements are explicitly simulated by tracking position-specific isotopologues that contain the isotopes located at fractionating positions. Our approach is self-consistent and provides a mechanistic description of different degradation pathways that accounts for the influence of both primary and secondary isotope effects during contaminant degradation. The method is particularly suited to quantitatively describe the isotopic evolution of relatively large organic contaminant molecules. For such compounds, an integrated approach, simultaneously considering all possible isotopologues, would be impractical due to the large number of isotopologues. We apply the proposed modeling approach to the degradation of toluene, methyl tert-butyl ether (MTBE) and nitrobenzene observed in previous experimental studies. Our model successfully predicts the multi-element isotope data (both 2D and 3D), and accurately captures the distinct trends observed for different reaction pathways. The proposed approach provides an improved and mechanistic methodology to interpret multi-element isotope data and to predict the extent of multi-element isotope fractionation that goes beyond commonly applied modeling descriptions and simplified methods based on the ratio between bulk enrichment factors or on linear regression in dual-isotope plots.

1. Introduction

Compound specific isotope analysis (CSIA) is a valuable tool for assessing the transformation and fate of organic contaminants in environmental systems (Schmidt et al., 2004). To date, carbon has been the most commonly analyzed element for practical applications of CSIA to investigate the degradation of various organic contaminants in both laboratory and field studies (Bill et al., 2001; Sherwood Lollar et al., 2001; Hunkeler et al., 2002; Slater et al., 2002; Blessing et al., 2009; Liang et al., 2009; Amaral et al., 2011). In recent years, stable isotope techniques have been extended to other elements such as hydrogen, oxygen, nitrogen and chlorine. For instance, recent advances in analytical techniques promoted the development and implementation of chlorine CSIA (Sakaguchi-Soder et al., 2007; Aeppli et al., 2010; Bernstein et al., 2011; Hitzfeld et al., 2011; Jin et al., 2011). The possibility to analyze the isotopic evolution of different elements has led to an increasing number of applications of dual-element (2D) isotope approaches that have shown considerable advantages compared to single-element CSIA and a great potential to identify, elucidate and quantify environmental transformation processes (Morasch et al., 2001; Mancini et al., 2003; Zwank et al., 2005; Vogt et al., 2008; Abe et al., 2009; Fischer et al., 2010; Kumar et al., 2013). By combining CSIA of different isotope pairs, reaction pathways can be identified and effectively visualized in dual-isotope plots. Numerous experimental studies have applied 2D isotope approaches to investigate the transformation of common groundwater organic contaminants including toluene (Morasch et al., 2001;

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Fischer et al., 2008; Vogt et al., 2008), MTBE (Kuder et al., 2005; Elsner et al., 2007) and nitrobenzene (Hofstetter et al., 2008b).

The assessment of 2D isotope experimental data commonly relies on the interpretation of dual-isotope plots based on the ratio between bulk enrichment factors or on linear regression of measured dual-isotope data. As we discussed in a previous study focused on chlorinated ethenes degradation (Jin et al., 2013), the interpretation of dual-isotope data becomes more challenging when the bulk enrichment factors of the different fractionating elements differ significantly and in the presence of mass-transfer limitations which can occur in both batch (Thullner et al., 2008; Tobler et al., 2008; Aeppli et al., 2009; Thullner et al., 2012) and flow-through systems (Rolle et al., 2010; Eckert et al., 2012).

Despite the fact that modeling approaches are required to improve the interpretation of multi-element isotope data for environmentally-relevant transformation processes of organic contaminants, their development and application are still rather limited and have been mainly focused on carbon and chlorine isotopes to predict C and Cl isotope fractionation of chlorinated solvents during degradation reactions (Hunkeler et al., 2009; Van Breukelen and Rolle, 2012; Jin et al., 2013).

This study aims at contributing to fill the gap between the mechanistic understanding of contaminants transformation based on multi-element isotope analysis, which has considerably improved, facilitated by the advances in analytical techniques, and the current state of the art of modeling approaches to quantitatively describe and interpret multi-element isotope evolution. We study the degradation of important organic contaminants such as toluene, MTBE and nitrobenzene and we focus on the evolution of carbon–hydrogen (C, H) and carbon–nitrogen (C, N) isotope pairs as well as on 3D (C, H, N) isotope fractionation as in the case of nitrobenzene oxidative transformation. The organic contaminants selected for this study are relatively large molecules for which an integrated method, simultaneously tracking all isotopologues, such as the one we recently proposed for chlorinated solvents (Jin et al., 2013), would not be practical due to the large number of isotopologues. Therefore, we propose a new multi-element modeling approach based on position-specific isotopologues which only considers isotopically-sensitive atoms (i.e., atoms directly located at reactive positions or at positions adjacent to a reactive bond). To illustrate and validate the proposed methodology, we apply the model to predict the multi-element isotopic evolution for different degradation pathways observed in previous experimental studies.

2. Modeling approach

During the transformation of organic contaminants the cleavage of chemical bonds results in primary or secondary isotope effects for the atoms located at the reacting bond positions or in adjacent positions, respectively. As mentioned above, for relatively large organic contaminant molecules an integrated approach, based on the simultaneous tracking of all multi-element isotopologues, is impractical due to the large number of isotopologues (i.e., 72, 78 and 84 molecular isotopologues for the organic compounds considered in this study: toluene, MTBE and nitrobenzene, respectively). Therefore, we define a limited number of position-specific isotopologues which are exclusively based on the isotopically-sensitive atoms. We start to illustrate the proposed methodology for dual-element (2D) isotope modeling.

The relative abundances of position-specific isotopologues containing two elements, X and Y, can be computed with a binomial distribution combining the occurrence of both X and Y isotopes:

$$A_j = \binom{u}{v} \cdot X_H^{v} \cdot X_L^{u-v} \cdot \binom{h}{i} \cdot Y_H^{i} \cdot Y_L^{h-i} \tag{1}$$

where A_j is the relative abundance of the jth position-specific isotopologue containing v heavy X- isotopes out of total u X-atoms and i heavy Y-isotopes out of total h Y-atoms and X and Y are the abundances of X and Y isotopes.

When a reaction occurs, each isotope of a position-specific isotopologue is fractionating and the corresponding apparent kinetic isotope effects (AKIEs) are given as (Elsner et al., 2005):

$$\mathrm{AKIE} \approx \frac{1}{1 + n/x \cdot \varepsilon_{bulk}} \tag{2}$$

$$\alpha = \frac{1}{\mathrm{AKIE}} \tag{3}$$

where n is the number of atoms of the element considered, x is the number of the atoms of the element located at fractionating position, $\varepsilon_{\mathrm{bulk}}$ is the bulk enrichment factor, α is the fractionation factor at fractionating position.

Assuming first-order kinetics, the reaction rate of the jth position-specific isotopologue, X_uY_h, reads as:

$${}^{j}r_{X_uY_h} = -k \cdot (\alpha_X)^{v} \cdot (\alpha_Y)^{i} \cdot C_j \tag{4}$$

where ${}^{j}r_{X_uY_h}$ is the reaction rate for the jth position-specific isotopologue, X_uY_h, which contains v heavy X-isotopes out of total u X-atoms and i heavy Y-isotopes out of h Y-atoms, C_j is the concentration of the jth position-specific isotopologue, and α_X and α_Y are the fractionation factors on the isotopically-sensitive positions for X and Y, respectively (see Eq. (3)). The product of the fractionation factors takes into account that both X and Y can fractionate during the considered reaction. The exponents v and i of α_X and α_Y indicate that several atoms of the same element can simultaneously fractionate. This occurs, for instance, when several atoms of the same element are located adjacent to a reactive position and undergo secondary isotope effects.

The concentration change of a certain organic compound can be described by tracking each position-specific isotopologue. Therefore, the governing mass balance equation for a given organic compound consists of a system of ordinary differential equations based on the degradation rates of the position-specific isotopologues:

$$\frac{dC}{dt} = -\sum_{j=1}^{m} {}^{j}r_{X_uY_h} \tag{5}$$

where C is the total concentration of the organic compound, t is the time, m is the number of all possible position-specific isotopologues, and ${}^{j}r_{X_uY_h}$ is the reaction rate of a position-specific isotopologue that, in case of first order reaction kinetics, reads as Eq. (4).

We solve the differential equations using Matlab and we run the models for a simulation time corresponding to 90% reduction of the initial contaminant concentrations. The computed concentrations of each position-specific isotopologue are used to determine the isotope ratios. The position-specific isotope ratios of element X and Y for the isotopologues X_uY_h are calculated by considering the total number of heavy and light isotopes, and are described by the equations proposed in Jin et al. (2011):

$$R'_X = \frac{\mathrm{Tot}(\mathrm{X_H})}{\mathrm{Tot}(\mathrm{X_L})} = \frac{\sum_{j=1}^{m} v\ {}^{j}C_{X_uY_h}}{\sum_{j=1}^{m} (u-v)\ {}^{j}C_{X_uY_h}} \tag{6}$$

$$R'_Y = \frac{\mathrm{Tot}(\mathrm{Y_H})}{\mathrm{Tot}(\mathrm{Y_L})} = \frac{\sum_{j=1}^{m} i\ {}^{j}C_{X_uY_h}}{\sum_{j=1}^{m} (h-i)\ {}^{j}C_{X_uY_h}} \tag{7}$$

in which R'_X and R'_Y are the isotope ratios of all the X and Y atoms on isotopically-sensitive positions, C is the concentration of the jth position-specific isotopologue, and u, v, h and i are the same as defined in Eq. (4).