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Position-specific isotope modeling of organic micropollutants transformation through different reaction pathways

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ABSTRACT

The degradation of organic micropollutants occurs via different reaction pathways. Compound specific isotope analysis is a valuable tool to identify such degradation pathways in different environmental systems. We propose a mechanism-based modeling approach that provides a quantitative framework to simultaneously evaluate concentration as well as bulk and position-specific multi-element isotope evolution during the transformation of organic micropollutants. The model explicitly simulates position-specific isotopologues for those atoms that experience isotope effects and, thereby, provides a mechanistic description of isotope fractionation occurring at different molecular positions. To demonstrate specific features of the modeling approach, we simulated the degradation of three selected organic micropollutants: dichlorobenzamide (BAM), isoproturon (IPU) and diclofenac (DCF). The model accurately reproduces the multi-element isotope data observed in previous experimental studies. Furthermore, it precisely captures the dual element isotope trends characteristic of different reaction pathways as well as their range of variation consistent with observed bulk isotope fractionation. It was also possible to directly validate the model capability to predict the evolution of position-specific isotope ratios with available experimental data. Therefore, the approach is useful both for a mechanism-based evaluation of experimental results and as a tool to explore transformation pathways in scenarios for which position-specific isotope data are not yet available.

1. Introduction

Numerous synthetic organic compounds are produced annually in vast quantities for industrial manufacturing processes, agricultural use, as well as for human and animal healthcare (Fenner et al., 2013; Schwarzenbach et al., 2010, 2006). These organic compounds and their metabolites are frequently detected at trace levels in fresh water environments and are therefore referred to as organic micropollutants. Organic micropollutants include a wide array of different compounds such as pesticides, herbicides, pharmaceuticals, food additives, and personal care products (Bao et al., 2012; Lapworth et al., 2012; Murray et al., 2010; Pal et al., 2010). With rapid advances in analytical techniques, new micropollutants have been discovered in the environment at a fast pace, causing increasing environmental concern (Carlson et al., 2013; Imfeld and Vuilleumier, 2012; Murray et al., 2010; Pal et al., 2010; Vorkamp et al., 2014). The assessment of the fate of these chemicals in the environment requires knowledge and information on their degradation pathways. However, the conventional approach based on concentration measurements of parent compounds and transformation products is often not conclusive, since a decrease of concentration might also be caused by dilution, sorption and further transformation of metabolites (Durst et al., 2013; Imfeld et al., 2013; Pal et al., 2010). Compound specific isotope analysis (CSIA) measures changes in stable isotope ratios of different elements, and represents a valuable tool to study the transformation of various organic contaminants (Elsner, 2010; Elsner et al., 2005). Recent studies have applied CSIA to investigate the transformation of different organic micropollutants (Bashir et al., 2015; Elsayed et al., 2014; Zhang et al., 2014). Different reaction pathways have been characterized by analyzing dual-element stable isotope ratios of the parent compounds in an increasing number of experimental studies (Hartenbach et al., 2008; Maier et al., 2014; Meyer and Elsner, 2013; Penning et al., 2010; Reinnicke et al., 2011) Multi-element isotope data obtained from this experimental work provide valuable insights into the degradation mechanisms of organic micropollutants. Isotope models are useful tools to predict and

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quantitatively evaluate the isotopic evolution during degradation reactions, to link observed isotopic data to specific reaction mechanisms (Hofstetter et al., 2007; Hunkeler et al., 2009; Jin and Rolle, 2014) and to describe isotope fractionation in complex environmental systems where both physical and transformation processes may cause isotope fractionation and affect the observed isotopic signals (Eckert et al., 2012; Jin et al., 2014, 2013; Thullner et al., 2012; Van Breukelen and Rolle, 2012). To date, multi-element isotope modeling studies have focused on widespread groundwater organic contaminants such as chlorinated ethenes, MTBE and BTEX (Centler et al., 2013; Jin and Rolle, 2014). Although multi-element isotope modeling would be beneficial to evaluate isotope data also for different organic micropollutants, such an approach is still lacking for these contaminants. In particular, micropollutants are typically large molecules for which bulk isotope fractionation observed in environmental samples is often significantly diluted. For this reason, position-specific information, which goes beyond bulk isotope ratios typically addressed in CSIA applications, greatly helps to gain insights on the occurrence and on the mechanisms of specific degradation reactions. In this study we aim at presenting and validating a multi-element isotope modeling approach that represents a valuable tool for the simultaneous quantitative interpretation of concentration as well as bulk and position-specific isotope data during the degradation of organic micropollutants. The approach builds on the foundations laid in a recent contribution (Jin and Rolle, 2014) that first proposed to incorporate mechanistic and position-specific understanding of contaminant degradation on model-based interpretation of isotope data. Model formulations are proposed in this study to simulate isotope fractionation during degradation of organic micropollutants. Such formulations are independent of commonly adopted linear regressions of dual-element isotope data. They are based on a mass conservation description of degradation reactions that allows incorporating mechanistic knowledge of isotopic evolution for different reaction pathways. The outcomes of the simulations highlight interesting and specific features characterizing micropollutants transformation and constitute a relevant improvement compared to commonly applied modeling approaches that rarely attempt to incorporate mechanistic information.

Specifically, the goals of this work are to: (i) present and illustrate multi-element isotope modeling approaches for degradation of organic micropollutants based on position-specific isotopologues which track atoms in positions experiencing isotope effects; (ii) apply the model to predict multi-element isotope changes during degradation of selected important organic micropollutants such as dichlorobenzamide (BAM), isoproturon (IPU) and diclofenac (DCF); (iii) illustrate the capability of the model to describe position-specific isotope fractionation occurring at and close to reacting bonds, to capture both primary and secondary isotope effects and to explore their possible extent of variation consistently with observed bulk isotope data; (iv) directly validate the outcomes of the proposed position-specific isotope modeling with available position-specific isotope data; (v) show the potential of the model as predictive tool to explore the applicability of CSIA for different elements and degradation scenarios for which an experimental investigation is not (yet) available.

2. Modeling approach and reaction pathways

Biodegradation of organic micropollutants in the environment can follow different reaction pathways. Since micropollutants often have large and complex molecular structures and their biodegradation involves the cleavage of specific bonds, an efficient way to simulate multi-element isotope fractionation for these compounds is to track position-specific isotopologues, considering atoms at isotopically-sensitive positions. This method represents a convenient balance between a fully-integrated approach (i.e., considering all possible isotopologues) that has been proposed for small molecules such as chlorinated compounds (Jin et al., 2013) and common, simplified, formulations exclusively considering two virtual heavy and light species (e.g., Eckert et al., 2012) and preventing to capture specific characteristics of different degradation pathways. The proposed modeling framework allows incorporating mechanism-specific information in the simultaneous description of concentration and stable isotope evolution during micropollutants transformation.

The key steps of the model formulation are to:

- hypothesize the degradation reaction mechanisms and identify the fractionating atoms. Important elements for this initial conceptualization step are the insights of experimental investigation, ab-initio calculations and expert judgment;
- define position-specific isotopologues, which are a small subset of all possible isotopologues, exclusively containing atoms located at positions experiencing isotope effects. To identify the position-specific isotopologues we introduce a “string notation”, which, for a dual-isotope system involving two elements A and B, reads as: $[A_{p,s}{-}B_{p,s}]$, where the subscripts p and s indicate primary and secondary isotopic positions and the dash represents a chemical bond that may connect the fractionating atoms A and B;
- derive the fractionation factors for primary and secondary isotope effects based on corresponding apparent kinetic isotope effects (AKIEs). The latter can be calculated by reported enrichment factors or by directly fitting the model to measured position-specific isotope data;
- track the concentration evolution of each position-specific isotopologue undergoing degradation according to a specified kinetic rate law;
- compute the changes of position-specific and bulk isotope ratios.

2.1. Degradation mechanisms and position-specific isotopologues

To illustrate the proposed modeling approach three examples of micropollutants degradation have been selected. These examples include aerobic degradation of dichlorobenzamide (BAM), biotic hydrolysis of isoproturon (IPU) and aerobic degradation and reductive dechlorination of diclofenac (DCF). The degradation pathways for these compounds are schematically illustrated in Fig. 1.

Dichlorobenzamide is an important organic micropollutant. It is the main metabolite of the herbicide 2,6-dichlobenil and, due to its mobility, it is often found in groundwater at concentration levels higher than its parent compound (Holtze et al., 2008). Dual carbon and nitrogen isotope ratios were measured to monitor microbial degradation of BAM (Reinnicke et al., 2011). Significant carbon and nitrogen isotope fractionation were observed during BAM degradation through microbial hydrolysis by two bacterial stains, *Aminobacter* sp. MSH1 and *Aminobacter* sp. ASI1. A nucleophilic substitution results in carbon and nitrogen isotope fractionation at the carbonyl carbon as well as at the amide nitrogen. To model this reaction pathway we consider the position-specific isotopologues, [C—N], to track the C and N atoms in the reactive bond.

Isoproturon is used as systemic herbicide in cereal crops and it can be degraded by different reaction pathways such as hydroxylation, N-demethylation and biotic hydrolysis. Among these degradation pathways microbial hydrolysis of IPU is of special interest