



Carbon and hydrogen isotope fractionation of benzene and toluene during hydrophobic sorption in multistep batch experiments



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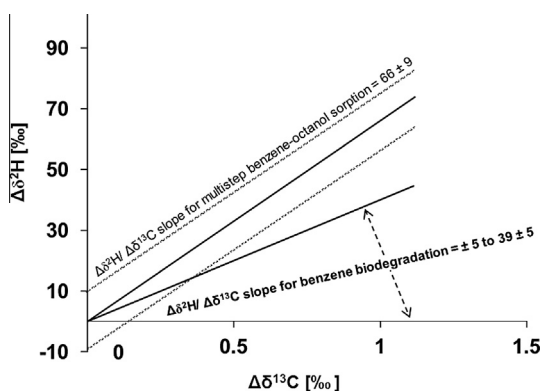
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HIGHLIGHTS

- Carbon and hydrogen isotope fractionation during multistep sorption was measured for benzene and toluene.
- Successive hydrophobic partitioning steps result in low isotope fractionation.
- We observed carbon and hydrogen isotope fractionation for the benzene–octanol pair.
- Functional groups of SOM may specifically interact with BTEX compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

The application of compound-specific stable isotope analysis (CSIA) for evaluating degradation of organic pollutants in the field implies that other processes affecting pollutant concentration are minor with respect to isotope fractionation. Sorption is associated with minor isotope fractionation and pollutants may undergo successive sorption-desorption steps during their migration in aquifers. However, little is known about isotope fractionation of BTEX compounds after consecutive sorption steps. Here, we show that partitioning of benzene and toluene between water and organic sorbents (i.e. 1-octanol, dichloromethane, cyclohexane, hexanoic acid and Amberlite XAD-2) generally exhibits very small carbon and hydrogen isotope effects in multistep batch experiments. However, carbon and hydrogen isotope fractionation was observed for the benzene–octanol pair after several sorption steps ($\Delta\delta^{13}\text{C} = 1.6 \pm 0.3\text{‰}$ and $\Delta\delta^2\text{H} = 88 \pm 3\text{‰}$), yielding isotope fractionation factors of $\alpha_{\text{C}} = 1.0030 \pm 0.0005$ and $\alpha_{\text{H}} = 1.195 \pm 0.026$. Our results indicate that the cumulative effect of successive hydrophobic partitioning steps in an aquifer generally results in insignificant isotope fractionation for benzene and toluene. However, significant carbon and hydrogen isotope fractionation cannot be excluded for specific sorbate–sorbent pairs, such as sorbates with π -electrons and sorbents with OH-groups. Consequently, functional groups of sedimentary organic matter (SOM) may specifically interact with BTEX compounds migrating in an aquifer, thereby resulting in potentially relevant isotope fractionation.

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1. Introduction

Monitored natural attenuation (MNA) is an approach gaining increased attention to manage aquifers contaminated with organic pollutants. Successful implementation of MNA requires a monitoring strategy relying on several lines of evidence to assess pollutant depletion (Bombach et al., 2010). Compound-specific stable isotope analysis (CSIA) is proposed to be a useful tool to assess pollutant biodegradation in aquifers (Elsner, 2010; Thullner et al., 2012). CSIA relies on the change in the stable isotope composition of a pollutant between its source and the plume as an indication of chemical or biochemical conversion. Since degradation can lead to stable isotope fractionation, an enrichment of heavier isotopes in the residual fraction of the degraded pollutant can be observed. Hence, stable isotope fractionation for carbon, hydrogen or other elements indicates *in situ* pollutant degradation, relying on the presumption that only degradation can significantly alter the isotope composition of a pollutant in aquifers. Physical attenuation processes, such as dilution, dispersion, volatilization and sorption, are generally considered not to result in significant isotope fractionation for groundwater pollutants (Dempster et al., 1997; Harrington et al., 1999; Schüth et al., 2003; Wang and Huang, 2003). However, little is known about isotope fractionation during sorption of hydrophobic pollutants in aquifers.

Partitioning of hydrophobic pollutants between groundwater and sedimentary organic matter (SOM) in aquifers can control the pollutant distribution and may lead to isotope fractionation. Hydrophobic sorption does not significantly alter the pollutant isotope composition in single step batch experiments, which suggests that sorption-based isotope effects are negligible or small in aquifers (Poulson et al., 1997; Harrington et al., 1999; Slater et al., 2000; Schüth et al., 2003; Höhener and Yu, 2012). However, hydrophobic pollutants undergo successive sorption-desorption steps between the mobile water phase and the stationary SOM phase, which may result in small but significant isotope fractionation (Kopinke et al., 2005; Thullner et al., 2012). Predictive calculations assumed that under certain conditions isotope fractionation is similar to that observed during biodegradation at an expanding front of a plume or in the case of a single contamination event (Kopinke et al., 2005; Van Breukelen and Prommer, 2008; Höhener and Atteia, 2010). Clearly, the cumulative effect of a large number of successive partitioning steps may lead to measurable isotope effects, as previously observed in chromatography-based studies (see for a review Filer, 1999).

Reversed-phase liquid chromatography (RP-LC) exhibits some analogies to the migration of a pollutant in an aquifer. Significant carbon and hydrogen isotope fractionation has been observed in RP-LC experiments (Caimi and Brenna, 1993, 1997; Poulson et al., 1997; Turowski et al., 2003; Kopinke et al., 2005; Valleix et al., 2006). It has been suggested that sorption can also cause significant shifts in pollutant isotope ratios in aquifers (Kopinke et al., 2005). However, the 'chromatographic efficiency' of an aquifer appeared to be smaller than that of RP-LC columns, thus leading to small or negligible isotope fractionation in aquifers (Schüth et al., 2003). Besides RP-LC-based studies, carbon isotope fractionation was also observed for benzene and toluene in multistep batch sorption experiments with dissolved humic acids (Kopinke et al., 2005). Although, the use of humic substances allows studying the environmental fate of organic compounds, variability in their structure and functional groups may limit the interpretation of the partitioning phenomenon resulting in isotope effects. Therefore, structurally well-defined sorbents or partitioning media, such as 1-octanol, can be more useful for studying sorption of organic pollutants with respect to isotope fractionation.

In the present study, carbon and hydrogen isotope effects during partitioning of benzene and toluene between water and sorbents with different chemical properties were evaluated in multistep batch experiments. Benzene and toluene were selected as model sorbate compounds due to their environmental significance and simple chemical structure. The sorbents were chosen to represent typical structural components of natural organic matter (NOM), such as aliphatic and aromatic moieties, carboxylic groups, hydroxyl groups, and various types of interaction between sorbents and sorbates including (i) non-specific van der Waals interactions (i.e. cyclohexane, amberlite XAD2) and (ii) specific hydrogen-bridging interactions (i.e. octanol, hexanoic acid). Dichloromethane was added as representative of the important class of dipolar aprotic solvents, which are able to polar interactions except hydrogen bonding. Multistep batch experiments were performed in order to generate a maximum isotope shift ($\Delta\delta^{13}\text{C}$ or $\Delta\delta^2\text{H}$) upon consecutive partitioning steps, while depletion of benzene and toluene during partitioning still enables measuring the isotope composition in the final solution.

2. Materials and methods

2.1. Chemicals

All chemicals were obtained in reagent quality from Merck (Germany). The physico-chemical properties and chemical structures of tested sorbates and sorbents are provided in Table 1. Amberlite XAD-2 is a nonionic styrene-divinylbenzene copolymer in the form of 20 mesh beads.

2.2. GC/FID and GC/C/IRMS measurements

For the analysis of concentrations as well as carbon and hydrogen isotope signatures of benzene and toluene, 10 mL aqueous samples were extracted with 500 μL of *n*-pentane at 80 rpm during 4 h.

The concentrations of benzene and toluene were measured on a gas chromatograph equipped with a flame ionization detector (GC-FID) (CP-3800 GC, Varian Inc., USA).

Solvent extraction using *n*-pentane is considered not to affect the isotope signature of BTEX (Dempster et al., 1997). The carbon and hydrogen isotope signatures of analytes were measured using two independent gas chromatography/isotope ratio mass spectrometry (GC/IRMS) systems as described elsewhere (Fischer et al., 2009).

The GC/IRMS systems were calibrated using gases (CO_2 and H_2) with known isotope composition (Coplen et al., 2006; Coplen, 2011). The carbon and hydrogen isotope ratios were expressed in the delta notation ($\delta^{13}\text{C}$ and $\delta^2\text{H}$) in per mil units (‰) relative to the international standards according to the following equation (Coplen, 2011):

$$\delta^{13}\text{C} \text{ or } \delta^2\text{H} = \frac{X_{\text{dissolved}}}{X_{\text{dissolved}}} \cdot \frac{1}{C_{\text{Oe}}} \quad (1)$$

where R_{sample} and R_{standard} are the $^{13}\text{C}/^{12}\text{C}$ ratios or $^2\text{H}/^1\text{H}$ ratios of the sample and an international standard, respectively. All samples were measured in at least three replicates. The total analytical uncertainty that incorporates both accuracy and reproducibility for the mean $\delta^{13}\text{C}$ -values was always better than $\pm 0.5\text{‰}$ and for the $\delta^2\text{H}$ -values better than $\pm 10\text{‰}$.

2.3. Batch experiments

Deionized water (1250 mL) was spiked separately with stock solutions of benzene and toluene yielding a final concentration of

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