Compound-specific carbon isotopic fractionation during transport of phthalate esters in sandy aquifer

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HIGHLIGHTS

- Transport of 3 phthalate esters in sandy aquifer was studied using column experiment.
- Phthalate esters were mainly trapped into the pore space in the transport process in sandy aquifer.
- Carbon isotopic fractionation was observed at the initial transport process.

GRAPHICAL ABSTRACT
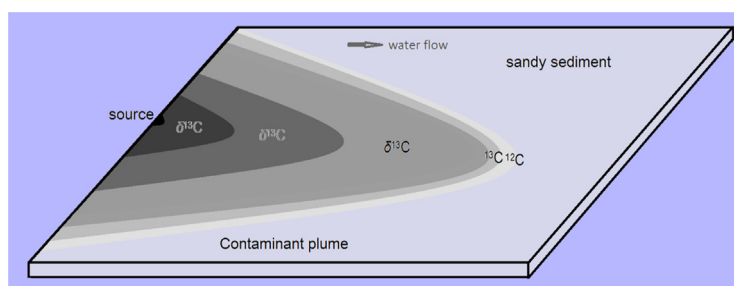
ABSTRACT

The present paper aims to evaluate the carbon isotopic fractionation of phthalate esters (PAEs) during transport in an sandy aquifer. Breakthrough curves of di-methyl phthalate (DMP), di-ethyl phthalate (DEP), and di-*n*-butyl phthalate (DBP) in mixed solution were determined by miscible displacement experiment, and simulated using HYDRUS-1D software. The stable carbon isotopes ($\delta^{13}C$) of 3 PAEs in effluent were analyzed at different times. Results showed that, in the transport process in sandy sediment, PAEs are mainly trapped into the pore space instead of being adsorbed on the surface of particles. At the initial stage of transport, PAEs with lighter carbon tend to run faster in the sandy sediment, and PAEs with heavier carbon run after. However, there is no priority for the transport of PAEs with different carbon isotopes at Stage II with mainly time-limited sorption. So the transport-based isotope fractionation occurs in the front area of contaminant plume. This effect may be relevant for interpreting carbon isotope signatures in the real contaminant site.

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1. Introduction

Groundwater is an important freshwater resource for drinking. Besides inorganic pollutants such as arsenic, fluoride, and nitrate, more and more toxic organic compounds have been reported to contaminate groundwater (Bozzo et al., 2013; Doherty and Oti-toloju, 2013; Han et al., 2013). Phthalate esters (PAEs) are a group of synthetic compounds widely used as additives in plastic products, as well as cosmetics, fragrances, lubricants, defoaming agents, and pesticides. PAEs have been increasingly detected in groundwater and aquifer sediment (Zhang et al., 2009; Liu et al., 2010a, 2010b). As some PAEs are suspected endocrine-disrupting compounds, the occurrence of PAEs in water supplies poses a serious threat to potable water supplies. It is meaningful to identify the source of PAEs and their transport and fate in subsurface environ-

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ment, so as to predict the expansion and design the remediation of PAEs in the environment.

Compound-specific isotope analysis (CSIA) is increasingly used to assess the fate of contaminants such as hydrocarbons, chlorinated solvents, and gasoline additives in soils, sediments and aquifers (Schmidt et al., 2004; Philp, 2007). The microbiological and abiotic transformation of aqueous-phase contaminants often favors isotopically-light, compared to isotopically-heavy, contaminant molecules (LaBolle et al., 2008). Relationships between isotopic fractionation and transformation ascertained from microcosm experiments, together with measurements of isotope analyses, are used as a basis to investigate and quantify possible contaminant degradation at field sites (Meckenstock et al., 2004; Philp, 2007). This application is based on the assumption that predominantly physical processes like dilution (mixing), volatilization, and sorption do not influence the ratios of stable isotopes in groundwater. It is generally accepted that the effects of volatilization and mixing on carbon isotope fractionation are small and can thus be neglected in most cases (Poulson and Drever, 1999; Abe and Hunkeler, 2006; Fischer et al., 2007; Bouchard et al., 2008; Hohener and Yu, 2012). However, there is ongoing discussion on whether sorption may result in carbon isotopic fractionation in aquifers.

There is evidence that isotopic shifts of some organic pollutants, such as chlorinated ethenes, aromatic hydrocarbons, and cyclohexane, during equilibrium sorption in single-step sorption experiments on graphite, activated carbon, lignite, lignite coke, and soil were below the uncertainty of the analytical techniques by mass spectrometry ($\pm 0.5\permil$) (Slater et al., 2000; Schuth et al., 2003; Hohener and Yu, 2012). In contrast, significant carbon isotope fractionation in benzene or toluene in multistep sorption experiments on humic acids, and also in benzene, 2,4-dimethylphenol and o-xylene during chromatography experiments in a humic-acid coated HPLC column were observed (Kopinke et al., 2005). However, the present database of fractionation factors for sorption of contaminants to geosorbents covers only several volatile compounds. More data are thus needed in order to reliably assess the influence of sorption on carbon isotope ratios in a wider class of groundwater contaminants (Hohener and Yu, 2012). Additionally, most above conclusions were drawn from equilibrium sorption experiments (Slater et al., 2000; Schuth et al., 2003; Hohener and Yu, 2012). The sorption behaviors of organic compounds in batch experiments and continuous flow conditions are very different (Liu et al., 2013), and the latter is generally non-equilibrium and closer to the field situation.

The present paper aims to investigate whether isotope fractionation occur during transport of PAEs within a contaminated aquifer. The breakthrough curves and transport of PAEs in sandy sediment column are simulated using HYDRUS-1D software (version 4.14, USA), and transport and carbon isotopic fractionation mechanisms are discussed according to the simulated parameters and CSIA results.

2. Materials and methods

2.1. Chemicals and materials

Three standard phthalate esters containing separate di-methyl phthalate (DMP), di-ethyl phthalate (DEP), and di-n-buthyl phthalate (DBP), all of 99.5% purity, were purchased from Chem Service, Inc (West Chester, PA, USA). The internal standard benzyl benzoate was purchased from Dr. Ehrenstorfer GmbH (Germany). Separate DMP and DEP agents for experiments, each with a purity of 99.5%, were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), and DBP (99.5%), from Tian-Jin Hengxing Chemical Preparation Co., Ltd (Tianjin, China). HPLC-grade methanol and n-alkane were purchased from TEDIA Com-

pany (Ohio, USA). All other reagents were of analytical grade. The PAEs stock solutions were prepared using methanol as solvent. To minimize any co-solvent effect, the volume percentage of methanol in each experiment solution was kept below 0.1% (v/v) (Yao et al., 2010).

To avoid contamination, no plastic equipment was used during the experiment. All glass was soaked in K_2CrO_4 sulfuric acid solution for at least 12 h, and rinsed with organic-free reagent water and finally baked at 180 °C for 4 h.

The sandy sediment used in this experiment is collected from the Baishazhou section of Yangzi River, and representative of sandy aquifer sediments of the alluvial JiangHan Plain, HuBei, China. The sample was air-dried and homogenized by sieving through a stainless steel 1-mm sieve. The physical–chemical properties of the sandy sediment are given in Table 1. Mineral composition was analyzed using a D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. Cu Kα radiation ($\lambda = 0.15418$ nm), with a step size of 0.02° in the 2θ range from 5° to 65°, was used in all samples. The data were processed with the Jade 5.0 software. The peaks were identified using the Powder Diffraction File (PDF) database created by International Centre for Diffraction Data (ICDD). Cation-exchange capacity (CEC) was measured by the $MgCl_2$-EDTA fast method (Lao, 1988). Particle composition was determined by weighing the samples passed through relative sieves.

2.2. Miscible displacement experiment

Miscible displacement experiments were conducted using the equipment illustrated in Fig. 1. Breakthrough curves were obtained by simultaneous miscible displacement of multicomponent PAE solutions, under conditions of constant flow and constant influent concentration, through a glass column packed with experimental sediment. The column of sediment was 1.6 cm in diameter and 4.8 cm in length; the bulk density of the sediment was 1.50, while volumetric pore water content was 0.37. Miscible displacement was affected by drawing the solution upward through the column with a constant flow bump. The reservoir system was designed to minimize loss through volatilization by a cap and a syringe needle was injected through the cap to adjust the air pressure equilibrium between inside and outside of the reservoir. A newly filled column was conditioned by pumping deionized water in order to obtain steady-state flow conditions and to remove any suspended colloids and soluble compounds, until the electrical conductivity (EC) of the effluent was near to that of deionized water. To determine the average pore-water velocity and dispersion coefficient of the column experiment, after the conditioning, a 0.05 M NaCl solution was pumped through the column at a flow rate of 2 mL min^{-1} and the electrical conductivity (EC) of the effluent was recorded until $EC_{effluent}/EC_{influent} \approx 1$. The 0.05 M NaCl solution was then changed to deionized water until $EC_{effluent}$ was near to that of deionized water. Then the influent was changed to a PAEs solution containing 20.0 mg L^{-1} each of DMP, DEP, and DBP. In order to maintain a uniform concentration of PAEs, the influent was always stirred by a magnetic stirrer. Column effluents were collected in glass tubes on a semi-automatic collector (Huxi, Shanghai, China) and PAE concentrations were analyzed immediately. The experiment was continued for 1200 min (about 185 pore volumes). The PAE concentrations in the influent were determined and showed stable (Supplementary material Fig. S1).

2.3. Analytical methods

Quantification with HPLC. The PAE concentrations were determined using a high performance liquid chromatography (HPLC) (Shimadzu LC-10AT, Japan) equipped with a variable wavelength