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Normal and Inverse Diffusive Isotope Fractionation of Deuterated Toluene and Benzene in Aqueous Systems

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1 Abstract

2 Diffusive isotope fractionation of organic contaminants in aqueous solution is difficult to quantify 3 and only a few experimental datasets are available for compounds of environmental interest. In this study, we investigate diffusive fractionation of perdeuterated and non-deuterated benzene and 4 toluene. Multitracer experiments were carried out in 1-D gel dissection tubes and in a quasi 2-D 5 6 flow-through porous medium. The experiments allowed us to simultaneously and directly compare 7 the diffusive and dispersive behavior of benzene and toluene. We observed an unexpected, opposite 8 behavior of the two monoaromatic hydrocarbons. Toluene showed a normal diffusive isotope effect (D_{C7D8}/D_{C7H8}=0.96) with enrichment of the non-deuterated isotopologue in the direction of the 9 diffusive and transverse dispersive fluxes. Conversely, the measured trends for benzene indicate 10 inverse diffusive fractionation ($D_{C6D6}/D_{C6H6}=1.02$), with a remarkably faster diffusion rate of the 11 perdeuterated isotopologue that was enriched in the downgradient portion of the diffusion tubes and 12 at the fringes of the contaminant plumes in the flow-through setup. These outcomes can neither be 13 interpreted as mass-dependent fractionation nor be described as purely hydrodynamic (i.e., mass 14 independent) effects. The results of this study are relevant for the use of labeled/non-labeled 15 16 mixtures of organic compounds as conservative and (bio)reactive tracers in environmental 17 applications.

19 Introduction

Aromatic hydrocarbons are widespread contaminants, frequently found in soils and aquatic 20 21 environments. Among these chemicals BTEX (i.e., benzene, toluene, ethylbenzene and xylene) compounds are of particular concern due to their relatively high solubility, mobility and toxicity.¹ 22 Mixtures of labeled and nonlabeled compounds have been often applied as a diagnostic tool to 23 understand and quantify contaminant transport and transformation mechanisms. For instance, in the 24 field of groundwater contamination, deuterium-labeled BTEX compounds have been used in tracer 25 26 tests, push-pull tests and in situ microcosms to evaluate contaminant retardation and in situ rates of transformation during groundwater bioremediation and natural attenuation.²⁻⁶ One important aspect 27 that has not (yet) been evaluated in detail is the extent of diffusive isotope fractionation of BTEX 28 29 compounds in aqueous solution and its implications in environmental systems. The evaluation of such effect is important since recent investigation of subsurface solute transport has highlighted the 30 key controlling role of aqueous diffusion for groundwater contaminant transport at different 31 scales.⁷⁻¹⁰ Despite the increased recognition of the quantitative importance and of the macroscopic 32 impact of small scale diffusive processes on large scale transport of organic contaminants, only a 33 34 few experimental and modeling studies have attempted to quantify diffusive isotope fractionation for organic compounds.¹¹⁻¹⁶ The lack of data and mechanistic understanding of organic chemicals' 35 diffusive isotope fractionation becomes apparent when compared with the advances in the related 36 37 field of inorganic isotope geochemistry, in which numerous studies have been carried out to investigate diffusive isotope effects of major cations, anions and dissolved gases in both aqueous 38 solutions¹⁷⁻²⁹ and non-aqueous systems.³⁰⁻³³ 39

In this work we focus on diffusive transport of perdeuterated and non-deuterated benzene and
toluene. The diffusive behavior of these chemicals (particularly of benzene) was investigated in
early studies,³⁴⁻³⁶ mostly as self-diffusion or as tracer diffusion in organic solvents. However, to the

43 best of our knowledge, no study has reported a comparison of diffusive isotope fractionation of these contaminants in aqueous solution. The purpose of this Letter is to report the unexpected, 44 45 contrasting fractionation behavior of toluene and benzene that we have observed in a series of experiments performed in different setups under purely diffusive conditions (1-D gel dissection 46 tubes), as well as in flow-through systems (2-D flow-through chamber). A key feature of the 47 experiments was the simultaneous presence of non-deuterated and perdeuterated mixtures of 48 toluene and benzene undergoing diffusion and lateral dispersion. In this way, in each experiment the 49 50 4 tracers (C_6H_6 , C_6D_6 , C_7H_8 , C_7D_8) were all transported under the same conditions, which facilitates a direct comparison of the effects of diffusion and transverse dispersion on the concentration of 51 non-deuterated and perdeuterated benzene and toluene and, more importantly, on their diffusive 52 53 isotope fractionation.

54

55 Materials and Methods

56 Chemicals and Analytical Methods. High-purity organic compounds (99.5%, Sigma-Aldrich, 57 Germany) were used in the experiments. Measurements were carried out with a 7890A gas 58 chromatograph (GC) with a capillary column (30m×250 µm, 1.0 µm film thickness; Agilent, USA) 59 coupled to a 5975C tri-axis mass selective detector (MSD) (Agilent, USA). Headspace samples 60 were injected for analysis using a COMBIPAL multi-purpose autosampler system.

1-D Diffusion Experiment. Gel dissection experiments were performed in cylindrical glass tubes (1.1 cm diameter and 20 cm length) using agarose gel prepared with a minimum amount (1% w/w) of phyto agar (Duchefa, Netherlands). Agar solutions containing mixtures of dissolved toluene, perdeuterated toluene, benzene and perdeuterated benzene (1:1:1:1 volume proportion) were prepared and filled in the first 10 cm of the diffusion tubes. This zone acted as contaminant source during the experiments in which the compounds diffused towards the remaining portion of the tubes that was filled with pure gel medium. The tubes were kept horizontally at a constant temperature of
20 °C. After 9 and 15 days, the tubes were sampled by cutting the gel into 1 cm slices with a scalpel.
The slices were immediately sealed in 10 ml glass vials with screw caps and sent to GC analysis.

2-D Flow-through Experiment. Flow-through experiments were performed in a quasi two-70 dimensional flow-through chamber (inner dimensions: 80cm×18cm×1cm, L×H×W), equipped with 71 72 10 equally-spaced (1 cm spacing) ports both at the inlet and at the outlet. The flow-through system was filled with homogeneous quartz sand (Euroquarz, Germany) with grain diameter of 1.0-1.5 mm. 73 74 The sand was washed in an acidic solution and dried for 12 hours in an oven at 120 °C before filling the flow-through chamber. The sand was filled with a wet-packing procedure using ultra-pure Milli-75 Q water (EvoquaWater, USA) to avoid air entrapment in the porous medium.³⁷ The inlet and outlet 76 77 ports were connected to two high-precision multi-channel peristaltic pumps (IPC-N24, Ismatec, Switzerland). Sampling was performed with a 10-channel syringe pump (KD Scientific, USA). The 78 79 system was operated at a seepage velocity of 0.8 m/d. An aqueous solution containing the four isotopologues was continuously injected from the two lowermost ports at the inlet of the flow-80 through chamber. After establishing a steady-state plume (i.e., exchanging at least two pore 81 82 volumes), samples were taken at the outlet ports and analyzed for the concentrations of deuterated 83 and non-deuterated compounds.

Modeling Approach. The governing equations for contaminant transport in the two experimental setups are the 1-D Fick's second law of diffusion³⁸ in the gel dissection tubes, and the 2-D steady state advection dispersion equation in the 2-D flow-through setup.³⁹⁻⁴⁰ The models used to quantitatively interpret the experimental results are based, respectively, on a numerical and an analytical solution of these governing equations. The key parameters controlling transport of the different toluene and benzene isotopologues are their diffusion coefficients and, in the flow-through setup, their transverse hydrodynamic dispersion coefficients. The governing equations and their boundary conditions are summarized in the Supporting Information together with concentration
maps of the steady-state plumes in the 2-D flow-through setup.

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94 **Results and Discussion**

Two examples of benzene and toluene spatial profiles measured in the 1-D setup after 9 and 15 days 95 of diffusion are illustrated in Figure 1. The plots show typical diffusion curves with small 96 differences between deuterated and non-deuterated compounds that are difficult to appreciate in the 97 98 concentration plots. The differences become apparent by plotting the ratios C₆D₆/C₆H₆ and C_7D_8/C_7H_8 . These ratios surprisingly show an opposite trend with a decreasing pattern for toluene, 99 and a reverse, increasing trend for benzene. To quantify these observations we used a simple 100 inverse power law model,^{21,41} which relates the diffusion coefficients of the deuterated and non-101 102 deuterated isotopologues to their molecular masses:

$$\frac{D_{C_n D_m}}{D_{C_n H_m}} = \left(\frac{m_{C_n H_m}}{m_{C_n D_m}}\right)^{\beta}$$
(1)



Figure 1. Spatial profiles of concentration and isotopologue ratio for benzene and toluene along the length of the diffusion tubes in the 9-day experiment A (panels a-c) and in the 15-day experiment C (panels d-f). The symbols (squares for the non-deuterated, triangles for the perdeuterated isotopologues, circles for the ratios) represent the measured data, whereas the lines are the outcomes of the simulations.

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Fitting the experimental data allowed estimating the values of the diffusion coefficients for the nondeuterated and D-labeled isotopologues and, thus, the value of the exponent β expressing the mass dependence of the isotopologues diffusion coefficients. The fitting procedure was carried out using the function *lsqnonlin* implemented in MATLAB. Table 1 summarizes the results obtained for the different tube experiments and reports the observed diffusive isotope fractionation. Both the graphical representation of the experimental data (Figure 1) and the parameters reported in Table 1

116 show a normal isotope effect for toluene and an inverse isotope effect for benzene. In the case of toluene, the deuterated isotopologue has a slightly lower diffusion coefficient and results in 117 118 decreasing isotope ratios as the toluene species diffuse towards the pure gel medium. For benzene, instead, the data show an inverse diffusive isotope effect: the molecules of the deuterated 119 isotopologue diffuse at a slightly faster rate and become enriched in the initially pure gel medium, 120 as benzene diffuses from the contamination source. This behavior was consistently observed in all 121 experiments. The β (0.444-0.490) values for toluene are consistent with those of previous 122 experiments,¹⁵ whereas the negative values for benzene clearly indicate an inverse isotope effect. 123 Average values characterizing normal and inverse isotope fractionation observed for toluene and 124 benzene in these diffusion experiments $D_{C7D8}/D_{C7H8} = 0.962 \pm 0.002$ 125 are: and $D_{C6D6}/D_{C6H6}=1.019\pm0.002.$ 126

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Experiment	Time	D _{CnHm}	D _{CnDm}	β	$\mathbf{D}_{CnDm} / \mathbf{D}_{CnHm}$
	[Days]	$[\times 10^{-9} \text{m}^2 \text{s}^{-1}]$	$[\times 10^{-9} \text{m}^2 \text{s}^{-1}]$	[-]	[-]
Benzene					
А	9	0.958 ± 0.040	0.976 ± 0.017	-0.251	1.019
В	9	0.958 ± 0.008	0.978 ± 0.007	-0.279	1.021
С	15	0.956±0.021	0.972 ± 0.020	-0.218	1.016
D	15	0.957 ± 0.025	0.974 ± 0.024	-0.238	1.018
Toluene					
А	9	0.800 ± 0.010	0.768 ± 0.009	0.490	0.960
В	9	0.811±0.015	0.780 ± 0.012	0.460	0.962
С	15	0.798±0.012	0.769±0.010	0.444	0.964
D	15	0.810±0.019	0.780 ± 0.016	0.453	0.963

128 Table 1. Summary of the results for the multitracer 1-D diffusion experiments.

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Figure 2 shows vertical profiles of concentration and isotope ratio observed for the simultaneous transport of deuterated and non-deuterated benzene and toluene in the flow-through chamber. The concentration trends show a typical transverse dispersion profile for plumes continuously injected in a homogeneous porous medium. The isotope ratio measured at the different ports confirms the 134 normal diffusive fractionation for toluene and the inverse fractionation for benzene. In fact, the ratio C_7D_8/C_7H_8 decreases from the core towards the outer fringe of the plume, whereas the ratio 135 C₆D₆/C₆H₆ increases towards the plume fringe. No fitting procedure was used to evaluate the data 136 from the flow-through experiment. Instead, the experimental results were evaluated with pure 137 forward modeling of solute transport based on the average diffusion coefficients of the 4 138 compounds determined in the tube diffusion setups. The key parameter in this setup is the 139 transverse hydrodynamic dispersion coefficients, which is compound (and isotopologue) specific 140 141 and was described with the following parameterization:

$$D_T = D_P + D_{aq} \left(\frac{Pe^2}{Pe + 2 + 4\delta^2} \right)^{0.5}$$
⁽²⁾

where $D_P [L^2/T]$ denotes the velocity-independent pore diffusion coefficient; $Pe = vd/D_{aa}$ [-] is the 142 grain Péclet number, in which d [L] is the average grain size diameter and v [L/T] is the seepage 143 velocity; δ [-] is the ratio between the length of a pore channel and its hydraulic radius; a value of 144 δ =5.37 was determined in previous tracer experiments performed in a range of porous media, grain 145 sizes and seepage velocities comprising the conditions of the current flow-through setup.⁴² This 146 147 parameterization of transverse dispersion has been tested for solute transport in similar quasi 2-D systems⁴³⁻⁴⁵ and verified in pore-scale studies⁴⁶⁻⁴⁷ and fully three-dimensional flow-through 148 experiments.³⁸ The essential feature of Eq. 2 is that it acknowledges the importance of aqueous 149 diffusion also in the non-linear, velocity-dependent mechanical dispersion term. The good 150 151 agreement of the predictive, purely forward simulations for both measured concentrations and ratios (Figure 2) shows the capability of the model to capture the diffusive fractionation effects in the 152 flow-through system and also the accuracy of the experimentally determined values of aqueous 153 diffusion for the deuterated and non-deuterated tracers obtained from the 1-D tube experiments. The 154 latter compare very well with the values of aqueous diffusion coefficients computed with classical 155

empirical correlations for organic compounds (see Table S2 in the Supporting Information); this also indicates that sorption of toluene and benzene was not important in our experiments. The values of the transverse dispersion coefficients, determined according to Eq. 2, and used in the profiles and isotope ratio maps shown in Figure 2 are: $D_{T,C7H8}=1.563\times10^{-9}$, $D_{T,C7D8}=1.547\times10^{-9}$, $D_{T,C6H6}=1.641\times10^{-9}$ and $D_{T,C6D6}=1.649\times10^{-9}$ m²/s.



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Figure 2. Observed and simulated vertical profiles of concentrations and ratios at the outlet of the flow-through setup (a-b, d-e) and spatial maps of the isotopologue ratio for benzene (c) and toluene (f). The concentration data at the outlet ports (squares for the non-deuterated, triangles for the perdeuterated isotopologues) are average of triplicate measurements of two sampling events of the steady-state plumes, carried out after flushing 2 and 4 pore volumes (i.e., 48 and 96 hours, respectively).

169 Diffusive isotope fractionation in condensed systems, such as aqueous solutions, is challenging to investigate and to conceptualize in a solid theoretical framework. Different factors that may affect 170 171 diffusive isotope fractionation include solute mass, volume, shape, molecular structure, polarity, temperature and solute-solvent interactions. Mass and volume dependencies have dominated the 172 discussion about diffusive fractionation in condensed systems and the interpretation of diffusion 173 experiments. Models that have been proposed to capture the effects of diffusive fractionation 174 include the so-called hydrodynamic description (e.g., Stokes-Einstein relation), as well as the 175 extension to the condensed phase of formulations derived from Chapman-Enskog kinetic theory of 176 gas diffusion.³⁸ The hydrodynamic model does not include mass dependence and the key parameter 177 is the radius and, thus, the molar volume of the solute, whereas the kinetic theory predicts an 178 inverse square root relation with the reduced mass.⁴¹ Most of the experimental studies for different 179 aqueous solutes have reported a mass dependence that is typically weaker than the inverse square 180 root relation from kinetic theory. A simple power law expression (Eq. 1), in which the exponent is 181 derived by fitting the experimental data, is the model that is most often used to relate the diffusive 182 isotope effects to the mass of the diffusing solutes in theoretical, computational and experimental 183 studies.^{21,24-26,41} It is worth pointing out that in this simple model the exponent β is an empirical 184 coefficient which also lumps other factors such as steric effects and solute-solvent interactions that 185 186 are likely to play an important role on diffusive isotope fractionation. Indeed, the data presented in this study show normal and inverse isotope effects that can neither be interpreted on the basis of 187 mass dependencies nor be ascribed as purely hydrodynamic (i.e., mass independent) effects. In fact, 188 based on the sole mass difference the deuterated benzene should have shown lower diffusion rates 189 than the non-labeled isotopologue. Instead, an inverse effect was observed both in the tube diffusion 190 experiments and in the flow-through setup. Our experiments also allow excluding a purely 191 hydrodynamic interpretation of the results. Molar volumes of deuterated benzene and toluene have 192

193 been shown to be smaller than those of the corresponding non-labeled isotopologues; for instance, Bartell and Roskos⁴⁸ report the following values at 20 °C: V_{C6D6}=88.62 mL/mol, V_{C6H6}=88.86 194 195 mL/mol, V_{C7D8}=105.98 mL/mol, and V_{C7H8}=106.28 mL/mol. These differences are commonly attributed to the smaller effective radius of the C-D bonds compared to the C-H bonds.⁴⁸⁻⁴⁹ However, 196 a pure hydrodynamic interpretation, based on a simple Stokes-Einstein relation and considering the 197 molar volumes reported above, would predict very weak inverse isotope effects 198 $(D_{CnDm}/D_{CnHm}=1.0009)$ for both compounds. This was not observed in this study, in which stronger 199 200 inverse and normal diffusive isotope fractionation effects were observed for benzene and toluene, respectively. We hypothesize that the geometry of the hydration shells surrounding the aromatic 201 molecules and the solvation dynamics play a major role for diffusive isotope fractionation of 202 203 deuterated and non-deuterated benzene and toluene in aqueous solutions. For instance, a recent computational study of benzene hydration⁵⁰ reports that the hydration shell of a benzene molecule 204 has an average number of 31 water molecules and this number can change and diminish 205 substantially upon increase of temperature and decrease of density. To explain the unexpected 206 inverse fractionation observed for benzene, one could hypothesize a similar effect on benzene 207 208 hydration due to the deuterium substitutions. Processes connected to the hydrophobic effect of aromatic molecules in solution and associated changes of density and orientation of water 209 molecules surrounding the solute,⁵¹ as well as the structure and patterns of solute hydration⁵² appear 210 to be more important than the effects due to mass and molar volume differences. This hypothesis 211 will require future substantiation that might be provided by molecular dynamic simulations of 212 aqueous diffusion of deuterated and non-deuterated species. Such simulations have been performed 213 for instance for charged species^{22,53-54} and have contributed to elucidate the importance of the 214 hydration shell and of the interaction between solute and water molecules for the observed isotope 215 fractionation of different ions in aqueous solution. The different interaction of deuterated and non-216

deuterated benzene and toluene molecules with water molecules appears to be an important factor to explain the experimental observations of this study. This can be deduced also by comparing the results of this study with earlier experiments. For instance, benzene self-diffusion⁵⁵ and tracer diffusion in chlorobenzene⁵⁶ showed only very minor or no isotope effects during diffusion of C_6H_6 and C_6D_6 in these organic liquids, which contrasts with the rather large fractionation consistently observed in the different aqueous systems considered in our study.

We think that the normal and inverse diffusive fractionation effects observed for deuterated and 223 224 non-deuterated BTEX will stimulate further research to develop a mechanistic understanding of transport and transformation of these contaminants and their labeled mixtures in different 225 environments. Despite fractionation of D/H substituted aromatic compounds due to biodegradation 226 can be large and may be dominant for many transformation pathways,⁵⁷ our study shows that 227 diffusive fractionation is also significant and should be considered when these chemicals are used as 228 tracers and diagnostic tools in environmental systems in which transport and transformation 229 processes are typically coupled. On a broader perspective, the results of this study, showing 230 different diffusive isotope fractionation of very similar compounds, also have implications for the 231 fast developing field of compound specific stable isotope analysis (CSIA) techniques⁵⁸⁻⁵⁹, which 232 will greatly benefit from data for different environmental contaminants. The path towards 233 developing a comprehensive database of organic pollutant diffusive isotope fractionation and a 234 235 sound theory capturing the key mechanisms causing diffusive fractionation is inherently complex but rich of intriguing future challenges. 236

237

238 **Supporting Information**

239 Description of the flow-through system and of the modeling approach used to quantitatively240 interpret the results in the different experimental setups.

- 241 The authors declare no competing financial interests.
- 242

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