

Molecular Dynamic Simulations of Carbon and Chlorine Isotopologue Fractionation of Chlorohydrocarbons during Diffusion in Liquid Water

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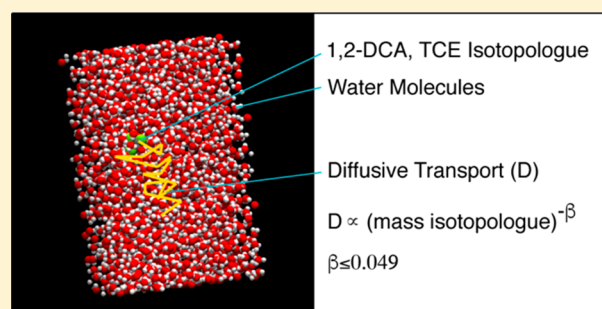
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S Supporting Information

ABSTRACT: Until now, the magnitude of isotopologue fractionation of organic compounds due to aqueous-phase diffusion has been quantified only experimentally. This study aims to determine the extent of aqueous-phase diffusion-induced isotopologue fractionation of organic compounds for the first time on a computational basis using molecular dynamic simulations (MDS). The MDS were conducted for different organic compounds including chlorinated ethenes (trichloroethene (TCE)) and ethanes (1,2-dichloroethane (1,2-DCA)) and for different isotopologues (carbon and chlorine). The MDS revealed a weak power law mass (m) dependency of the diffusion coefficient ($D \propto m^{-\beta}$ with $\beta \leq 0.049$) for carbon and chlorine isotopologues of TCE and 1,2-DCA, consistent with experimental results.

The MDS showed that the mass of the diffusing species is the key controlling factor for diffusion-induced isotopologue fractionation and not the molecular volume as suggested by previous studies. Furthermore, the MDS revealed that the weak power law mass dependency of the diffusive transport rate originates from an interplay between strongly mass-dependent short-term and mass-independent long-term solute–solvent interactions. Hence, the presented MDS results provide for the first a time a theoretical rationale for the experimentally observed magnitude of isotopologue fractionation of organic compounds caused by aqueous-phase diffusion.



1. INTRODUCTION

Organic compounds are ubiquitous subsurface contaminants at many industrial sites worldwide.¹ Caused by improper handling and disposal, organic contaminants such as chlorohydrocarbons are often released at the surface as dense nonaqueous-phase liquids (DNAPLs) and rapidly migrate into the subsurface due to their high density, low viscosity, and interfacial tension.² When large quantities are released, DNAPLs are able to migrate through the unsaturated zone into aquifer systems, where they are slowly dissolved forming a persistent groundwater contaminant plume. For the long-term fate of organic contaminants in aquifer systems, aqueous-phase diffusion is a key controlling process.^{3,4} During the transportation in aquifers, organic contaminants tend to accumulate on top of underlying aquitards and diffuse into them retarding their migration.^{5–8} After source depletion or remediation, organic contaminants back-diffuse from the aquitard due the reversal of the aquifer–aquitard concentration gradient and serve as a long-term contamination source for the adjacent aquifer. Despite the high relevance of aqueous-phase diffusion for organic contaminant migration in aquifer–aquitard systems, a mechanistic comprehension of its impact on the fractionation of isotopically distinct organic molecules (isotopologues) is lacking. Until now,

the magnitude of aqueous-phase diffusion-induced isotopologue fractionation of organic contaminants has been only recently investigated by a few experimental studies^{9–15} due to the difficulty of conducting experiments with a sufficient precision. The few conducted experimental studies determined beta values (β) for quantifying the magnitude of isotopologue fractionation due to aqueous-phase diffusion^{9–12,14,15} (eq 1)

$$\frac{D_H}{D_L} = \left(\frac{m_L}{m_H} \right)^\beta \quad (1)$$

where D_H and D_L (m^2/s) are the diffusion coefficients of the isotopically heavy and light species, respectively, and m_L and m_H are the molecular masses of the heavy and light species, respectively.

However, β values are empirical coefficients which may also include other factors that potentially affect diffusive isotopologue fractionation such as volume, shape, molecular structure,

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polarity, temperature, or solute–solvent interactions.¹² Indeed, the obtained beta values for various organic compounds are conflicting, which reveals that different parameters might control the magnitude of aqueous-phase diffusion-induced isotopologue fractionation for different organic compounds.⁹ Supplementary to the experimental investigations, a small number of field modeling studies evaluated if aqueous-phase diffusion leads to measured shifts of isotope ratios under field conditions in aquifer systems.^{16,17} However, these studies used estimated beta values in their simulations and did not quantify them and, hence, provided no theoretical rationale for the experimentally determined beta values. Consequently, the obtained beta values (eq 1) by the experimental studies remain on a phenomenological level, and a mechanistic understanding of isotopologue fractionation of organic compounds during diffusion in liquid water is lacking.

Molecular dynamic simulations (MDS) have been increasingly used as a computational tool to gain molecular-scale insight into properties of water and solutes.^{18–22} MDS provide the advantage that the behavior of individual atoms and molecules can be investigated as opposed to experimental and field studies, which only assess their average behavior. Despite the widespread application of MDS, only a few studies investigate the mass dependency of the diffusive transport rate in the aqueous phase based on MDS.^{23–26} The main constraint was that determined diffusion coefficients for isotopes at natural abundance remained within the uncertainty of MDS results prohibiting the assessment of a relationship between the diffusive transport rate and the mass of the diffusing species. However, by using hypothetical isotopes having large mass differences and beta values (eq 1), recent MDS studies of diffusing ions and noble gas isotopes in liquid water showed that MDS can be used to assess the mass dependency of the diffusive transport rate.^{23–25} The beta value is nonsensitive to mass differences between isotope pairs, and hence, fractionation between hypothetical isotopes having large mass differences and isotopes at natural abundance can be related.^{23–25,27} The conducted MDS studies were consistent with experimental studies under natural isotope abundance conditions and provided for the first time a theoretical, molecular-scale-based rationale for the observed magnitude of isotope fractionation of ions and noble gases during aqueous-phase diffusion. In contrast to inorganic species, MDS addressing aqueous-phase diffusion-induced isotopologue fractionation of organic compounds are lacking. Hence, experimental studies, which investigated the magnitude of isotopologue fractionation due to aqueous-phase diffusion of organic compounds have neither a theoretical nor a computational basis.

To address this research gap, we conducted for the first time MDS of isotopically distinct organic contaminants that diffuse in liquid water to gain a molecular-scale-based, mechanistic understanding of aqueous-phase diffusion-induced isotope fractionation. The MDS were conducted for different organic contaminants including chlorinated ethenes (trichloroethene (TCE)) and chlorinated ethanes (1,2-dichloroethane (1,2-DCA)) and for different isotopologues (carbon and chlorine) and compared with experimental results using beta values. These novel MDS provide for the first time a computational rationale for the phenomenological experimental results of aqueous-phase diffusion-induced isotopologue fractionation of organic contaminants.

2. MATERIALS AND METHODS

A detailed description of the used MDS method for simulating diffusing carbon and chlorine isotopologues of TCE and 1,2-DCA in liquid water can be found in the [Supporting Information \(SI\)](#). Briefly, MDS of TCE and 1,2-DCA carbon and chlorine isotopologues in liquid water were carried out with the software Lammmps²¹ on the “Cori” Supercomputer at the U.S. National Energy Research Scientific Computing Center (NERSC). A simulation box with a volume of 58,368 Å³ ($x = 32$ Å, $y = 32$ Å, $z = 57$ Å) was created containing 1884 water molecules and one TCE or 1,2-DCA molecule, whereby the trajectories of the water, TCE, and 1,2-DCA molecules were simulated by integrating Newton’s differential equations of motions. While water molecules were treated as rigid and nonpolarizable as in previous MDS studies,^{23–25,28} the TCE and 1,2-DCA isotopologues were simulated as nonrigid molecules by imposing energy potentials for the bond length and the torsional and bond angles according to Plimpton²⁹ (Tables S1 and S2). Long-term and short-term interactions within the chlorohydrocarbon and water molecules as well as between them were simulated using Coulomb forces and Lennard-Jones potentials, respectively (Table S1). To simulate 1,2-DCA and TCE carbon and chlorine isotopologue fractionation caused by aqueous-phase diffusion, hypothetical 1,2-DCA and TCE carbon and chlorine isotopologues were generated by varying the chlorine and carbon atom masses in the 1,2-DCA and TCE molecules in a specific range (2–133 Da) according to previous MDS studies.^{23–25} For chlorine, the masses of all atoms in the 1,2-DCA and TCE isotopologues were varied equally as at natural abundance isotopic substitution occurs for all chlorine atoms caused by the high abundance of both stable chlorine isotopes (³⁵Cl = 75.76%; ³⁷Cl = 24.24%).³⁰ This resulted in a mass range of the simulated hypothetical 1,2-DCA and TCE chlorine isotopologues between 31 and 421 Da (Tables S3 and S4). In contrast, for carbon, the mass of only one atom in the 1,2-DCA and TCE isotopologues was varied as isotopologues with two heavy carbon isotopes (¹³C) are rare due to the low abundance of the heavy carbon compared to the light isotope (¹²C = 98.93%; ¹³C = 1.07%).³⁰ This yielded a mass range of the simulated hypothetical carbon isotopologues of 1,2-DCA and TCE between 90 and 421 Da (Tables S3 and S4). The MDS were conducted for 50 ns, whereby the diffusion coefficients for the different TCE and 1,2-DCA isotopologues were calculated from their mean square displacement ($\langle l^2 \rangle$) using the well-known Einstein relation⁹

$$D = \frac{1}{2n} \lim_{t \rightarrow \infty} \frac{d\langle l^2 \rangle}{dt} \quad (n = \text{order of dimension}) \quad (2)$$

To investigate the mass dependency of the obtained diffusion coefficients for the hypothetical TCE and 1,2-DCA carbon and chlorine isotopologues from eq 2, $\log(D)$ versus $\log(m)$ plots were used, in which the slope of the regression line corresponds to the beta value (eq 1) as illustrated with the following equation:

$$\log(D_i) = A - \beta \log(m_i) \quad (3)$$

The uncertainty of the beta value was determined based on the 95% confidence interval of the regression line in the $\log(D)$ – $\log(m)$ plots.

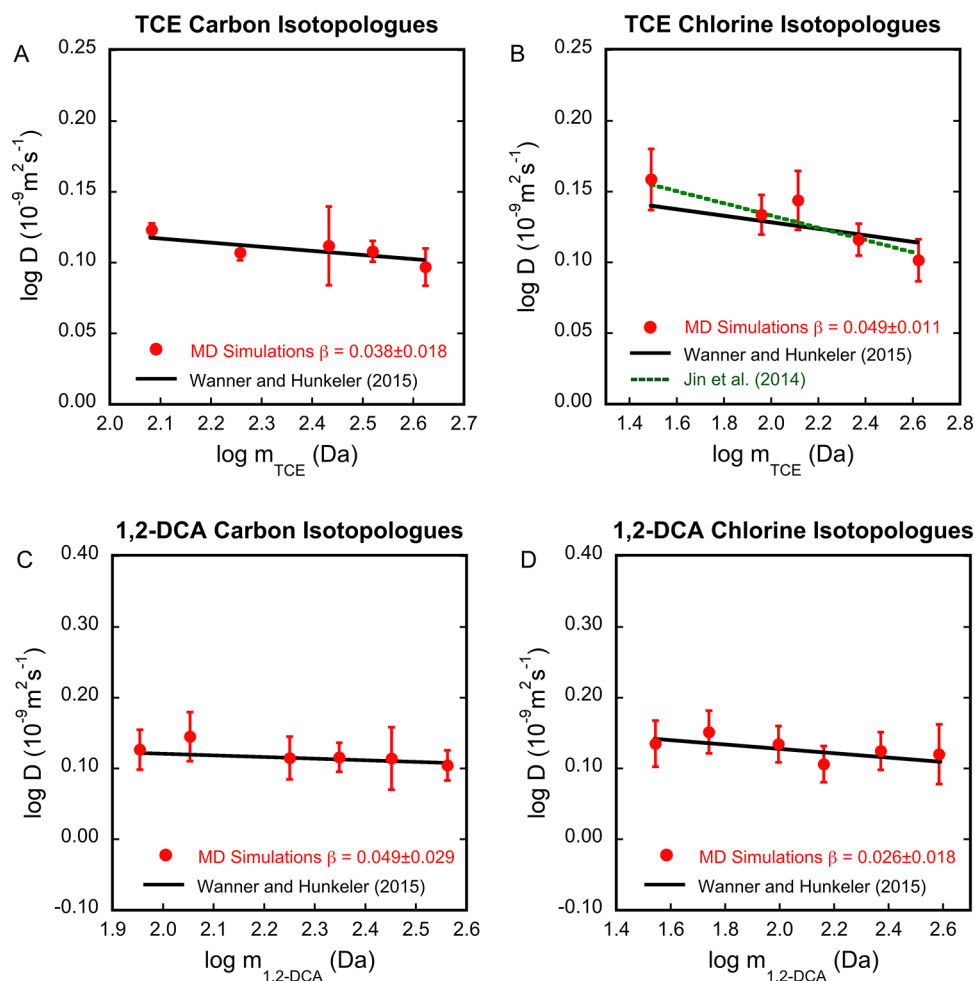


Figure 1. Log–log plots of diffusion coefficients ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) TCE carbon (A) and chlorine (B) and 1,2-DCA carbon (C) and chlorine (D) isotopologues in liquid water at 298 K obtained from MD simulations as a function of their hypothetical masses. The error bars indicate the uncertainty (standard error of the mean) of the determined diffusion coefficients. The beta values were determined from the slope of the regression line through the obtained data points, whereby the error of the beta values was estimated based on the 95% confidence interval of the regression line. The solid black and dashed green lines represent the experimentally determined β -values for the carbon and chlorine isotopologues of TCE and 1,2-DCA by Wanner and Hunkeler¹⁰ and Jin et al.,¹¹ respectively.

3. RESULTS AND DISCUSSION

For the naturally most abundant TCE and 1,2-DCA isotopologues (^{130}TCE and $^{99}\text{1,2-DCA}$; Tables S3 and S4), diffusion coefficients of $1.39 \times 10^{-9} \pm 0.07 \times 10^{-9} \text{ m}^2/\text{s}$ and $1.36 \times 10^{-9} \pm 0.08 \times 10^{-9} \text{ m}^2/\text{s}$, respectively were determined using the MDS. These values were in agreement with aqueous-phase diffusion coefficients available in the literature at 298 K for TCE ($1.14 \times 10^{-9} \pm 0.23 \times 10^{-9} \text{ m}^2/\text{s}$) and 1,2-DCA ($1.23 \times 10^{-9} \pm 0.25 \times 10^{-9} \text{ m}^2/\text{s}$).^{31,32} This indicates that the imposed force field in the MDS correctly reproduces the TCE- and 1,2-DCA-liquid water interactions. For the hypothetical carbon and chlorine TCE and 1,2-DCA isotopologues, the determined diffusion coefficients ranged between 1.25×10^{-9} and $1.40 \times 10^{-9} \text{ m}^2/\text{s}$ and between 1.26×10^{-9} and $1.44 \times 10^{-9} \text{ m}^2/\text{s}$, respectively (Tables S1 and S2). The calculated diffusion coefficients were higher for light compared to heavy carbon and chlorine isotopologues of TCE and 1,2-DCA (Figure 1). The calculated beta values (eq 2) revealed a weak power law mass dependency of the diffusion coefficient showing values of 0.038 ± 0.018 and 0.049 ± 0.029 for the carbon isotopologue and 0.049 ± 0.011 and 0.026 ± 0.018 for the chlorine isotopologue of the TCE and 1,2-DCA, respectively (Figure 1). The obtained

beta values from the MDS for carbon and chlorine isotopologues of TCE and 1,2-DCA were consistent with experimental results^{10,11} (Figure 1).

The revealed inverse proportionality between the mass of the hypothetical isotopologues and the diffusion coefficient by the MDS suggest that the mass of the diffusing species is the key parameter that controls aqueous-phase diffusion-induced isotopologue fractionation of chlorohydrocarbons. This finding contradicts the definitions of the well-known empirical diffusion coefficients by Wilke and Chang³¹ and Hayduk and Laudie³³ predicting an opposite isotope effect with a higher diffusive transport rate for isotopically heavy compared to light species^{31,33,34} due to the smaller molecular volume of heavy in comparison to light isotopologues.³⁵ Recent experimental investigations for deuterated versus nondeuterated benzene also observed a higher diffusive transport rate for heavy deuterated compared to light nondeuterated benzene, which was attributed to the differences in molecular volume being consistent with the definition of empirical diffusion coefficients.¹² However, the inconsistency of these investigations with experimental results for organic compounds showing natural isotope abundances^{10,11} and with the conducted MDS for

chlorohydrocarbons (Figure 1) questions the volume dependency of the diffusive transport rate for organic isotopologues. Hence, based on our MDS and the experimental results at natural isotope abundance, it can be likely assumed that heavy isotopologues of chlorohydrocarbons show generally a smaller diffusion coefficient compared to light isotopologues despite their smaller volume. This is further substantiated by all experimental data that is available for inorganic species such as ions and noble gases with isotope ratios at natural abundance showing thoroughly a faster diffusive transport rate for isotopically light compared to heavy species.^{9,14,15,23–25,27,36–43} Consequently, for species with isotope ratios at natural abundance, the molecular mass and not the molecular volume is likely controlling aqueous-phase diffusion-induced isotope fractionation.

Despite the consistency with experimental results at natural isotope abundance, the magnitude of TCE and 1,2-DCA carbon and chlorine isotopologue fractionation obtained from the MDS ($0.026 \leq \beta \leq 0.049$) is 1 order of magnitude lower than in the previously postulated kinetic theory predicting a beta value of 0.5.^{44,45} A similar mismatch between the kinetic theory and experimental results was observed for the vast inorganic species showing beta values ranging between 0 and 0.2.^{9,14,15,23–25,27,36–43} For inorganic species, some studies attributed the failure of the kinetic theory to the formation of solvation shells around the diffusing solutes.^{46,47} These studies argued that the magnitude of isotope fractionation due to aqueous-phase diffusion is consistent with the kinetic theory when replacing the solute mass by an assembly composed of solute and several solvent molecules ($m_i + n \times m_0$), where m_i is the solute and m_0 is the solvent mass and n can be treated as fitting parameter to obtain a beta value of 0.5.^{46,47} However, an impossible large amount of solvent molecules ($n = 110–274$) is necessary for the carbon and chlorine isotopologues of TCE and 1,2-DCA to obtain a beta value 0.5. This shows that the simple consideration of a diffusing assembly is also not valid to explain the weak power law mass dependency of the diffusive transport rate for carbon and chlorine isotopologues of TCE and 1,2-DCA. For inorganic species, it has been revealed that the mode coupling theory is more adequate to explain the weak power law mass dependency of the diffusion coefficient.^{24,48} According to this theory, the diffusing species frequently collides with neighboring water molecules, whereby these binary collisions modes of motion occur on short time scales and are strongly mass dependent showing a beta value of 0.5 following the kinetic theory. In contrast, on long time scales, the diffusing species is coupled to the hydrodynamic motion of the solvent exhibiting no mass dependency. Thus, the overall mass dependency of the diffusive transport rate results from a competition between the mass independent long-term hydrodynamic and mass dependent short-term binary collision modes of motion explaining the weak power law mass dependency of the diffusion coefficient with $\beta < 0.5$ and the failure of the kinetic theory. The agreement of the conducted MDS for carbon and chlorine isotopologues of 1,2-DCA and TCE with inorganic experimental studies under natural isotopic abundance conditions suggests that the mode coupling theory is also valid for chlorohydrocarbons. Furthermore, the consistency of our MDS results with all available experimental results for organic compounds with isotopes at natural abundance⁹ indicates that the underlying mechanisms and forces governing aqueous-phase diffusion-induced isotopologue fractionation are not fundamentally different for organic compounds other than TCE and 1,2-

DCA. Thus, the mode coupling theory likely applies for a large group of organic compounds.

Overall, the MDS results presented in this Letter provide for the first time a computational rationale for the observed weak power law mass dependency of the aqueous-phase diffusion coefficient of chlorohydrocarbons by experimental studies. The MDS open up the possibility to predict the magnitude of aqueous-phase diffusion-induced isotopologue fractionation for a wide spectrum of organic compounds. This will provide a basis for a superior comprehension of spatiotemporal isotope ratio trends of organic compounds in systems where the transport is diffusion-controlled such as aquitards. In contrast, in groundwater systems, where the transport is advection dominated, the weak power law mass dependency of the diffusion coefficient is likely of minor importance and can be likely neglected for the interpretation of stable isotope trends.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.9b00640](https://doi.org/10.1021/acs.estlett.9b00640).

Detailed description of molecular dynamic simulations methods. (PDF)

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Notes

The authors declare no competing financial interest.

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