

# Diffusive Isotope Fractionation of Deuterated Benzene and Toluene in Aqueous Systems

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## Introduction

BTEX compounds (i.e., benzene, toluene, ethylbenzene and xylene) are widespread groundwater organic contaminants [1]. Despite the key controlling role of aqueous diffusion for groundwater contaminants transport [2,3], only a few studies have explored the extent and impact of diffusive deuterium isotope fractionation of organic compounds in aqueous solution [4,5]. In this work we experimentally investigate diffusive and dispersive displacement and fractionation of nondeuterated and perdeuterated benzene and toluene [6].

## Experimental Setups

Experiments were performed in two distinct setups (Fig. 1), focusing on (i) pure diffusion of the organic compounds under no-flow conditions, and (ii) hydrodynamic dispersion of the different contaminants under flow-through conditions.

**1-D Diffusion Experiments.** Gel dissection experiments were performed in cylindrical glass tubes using agarose gel (1% w/w). The tubes were sampled by cutting the gel into 1 cm slices with a scalpel. Each slice was sealed in glass vial with screw caps for GC-MS analyses.

**2-D Flow-Through Experiments.** The flow-through experiments were conducted in a quasi-2-D flow-through chamber filled with homogeneous quartz sand. High-resolution sampling was performed via 10 equally spaced ports at the outlets (1 cm spacing).

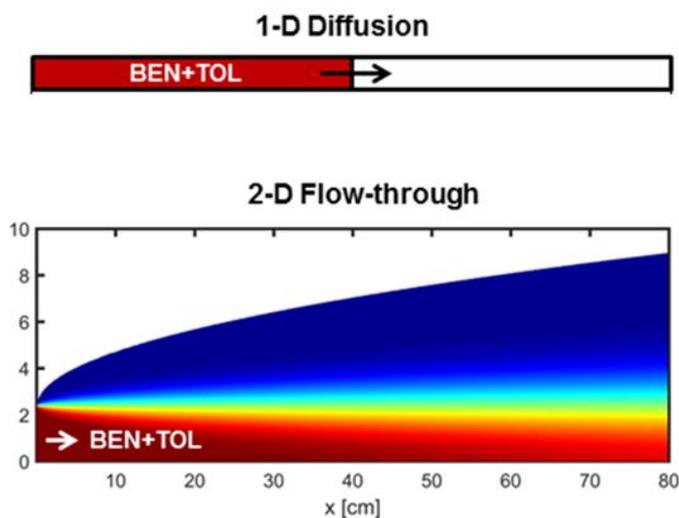


Figure 1. Sketch of the setups for the 1-D tube experiments and the 2-D flow-through experiments.

## Results

A normal diffusive isotope effect ( $D_{C_7D_8}/D_{C_7H_8} = 0.96$ ) was observed for toluene, resulting in enrichment of the nondeuterated isotopologue in the direction of the diffusive and transverse dispersive fluxes. Conversely, the measured trends for benzene indicated inverse diffusive fractionation ( $D_{C_6D_6}/D_{C_6H_6} = 1.02$ ). Remarkably faster diffusive/dispersive rates were observed for the perdeuterated isotopologue. These outcomes were consistently observed both for the diffusive fronts in the 1-D tubes and at the fringes of the contaminant plumes in the flow-through setup. The unexpected results of this study suggest that diffusive isotope fractionation of organic contaminants cannot be exclusively ascribed to mass and molar volume differences, but the interactions of the compounds with the surrounding water molecules, as well as the structures and patterns of solute hydration play a key role.

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