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Biodegradation of vapor-phase toluene in unsaturated porous media: Column experiments[☆]

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ABSTRACT

Biodegradation of organic chemicals in the vapor phase of soils and vertical flow filters has gained attention as promising approach to clean up volatile organic compounds (VOC). The drivers of VOC biodegradation in unsaturated systems however still remain poorly understood. Here, we analyzed the processes controlling aerobic VOC biodegradation in a laboratory setup mimicking the unsaturated zone above a shallow aquifer. The setup allowed for diffusive vapor-phase transport and biodegradation of three VOC: non-deuterated and deuterated toluene as two compounds of highly differing biodegradability but (nearly) identical physical and chemical properties, and MTBE as (at the applied experimental conditions) non-biodegradable tracer and internal control. Our results showed for toluene an effective microbial degradation within centimeter VOC transport distances despite high gas-phase diffusivity. Degradation rates were controlled by the reactivity of the compounds while oxic conditions were found everywhere in the system. This confirms hypotheses that vadose zone biodegradation rates can be extremely high and are able to prevent the outgassing of VOC to the atmosphere within a centimeter range if compound properties and site conditions allow for sufficiently high degradation rates.

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1. Introduction

Volatile organic compounds (VOC) significantly contribute to groundwater contamination. Due to their high vapor pressure and high air to liquid partition ratios, VOC are prone to enter the soil air and gas-phase transport of VOC in the vadose zone has been identified as an important mechanism contributing to the spreading of contaminants (Mendoza and Frind, 1990; Molins et al., 2010). Diffusion coefficients of VOC in the gas phase are up to 4 orders of magnitude greater than those in the aqueous phase. Hence the presence of a continuous air phase causes diffusive fluxes in the unsaturated zone to be significantly greater than those in the saturated zone (Rivett et al., 2011). In unsaturated subsurface environments diffusive migration hence may lead to above ground emissions or vapor intrusion into buildings, and may impose significant risks to environmental and human health (Luo et al., 2013). In turn, the capillary fringe, or more generally the interface between groundwater and the vadose zone, is seen as a hotspot of

microbial activity (Kurt and Spain, 2013). This holds especially true when diffusion of oxygen from the surface and of volatilized groundwater VOC coincide and support metabolic activity of microorganisms as described in Kurt and Spain (2013). The groundwater-vadose zone environment thus represents an interface characterized by steep redox gradients, high availability of electron donors and acceptors and concomitant high microbial activity (Winderl et al., 2008). Similar phenomena can be observed at the interface between contaminated and clean groundwater (Bauer et al., 2008) and in contaminated meromictic lakes (Wick et al., 2000). The groundwater-vadose zone therefore likely promotes the biodegradation of VOC and limits above ground emissions of VOC.

Up to now, biotechnological approaches to degrade vapor-phase VOC emerging from the subsurface are scarce. However, few existing field studies (e.g., van Afferden et al., 2011) indicate a high potential of microbial attenuation in the vadose zone as a cost-effective and energy-efficient method for the clean-up of VOC in the vadose zone and other unsaturated porous media. This is supported by laboratory studies showing that vapor-phase petroleum hydrocarbons are biodegraded across relatively short meter-scale distances (Abreu, 2006; Davis et al., 2009; Fisher et al., 1993, 94; Holden and Fierer, 2005; Kurt and Spain, 2013; Luo et al., 2013,

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2009; Patterson and Davis, 2009). More recent studies indicate that even lower, centimeter to decimeter-scale distances might be sufficient for the removal of vapor-phase hydrocarbons (De Biase et al., 2011; Hanzel et al., 2012). However, a rigorous experimental analysis of the processes controlling the diffusive transport and biodegradation of volatile organic contaminants in these systems is missing. In the existing studies such abiotic factors have varying potential to influence the observed VOC removal, or the studies emphasize the importance of gas-phase diffusive transport for the degradation of VOC in unsaturated porous media but lack a spatially resolved analysis of VOC reactive transport (e.g., Kristensen et al., 2012). For instance, the presence of organic phases can promote VOC removal by retarding the spreading of the sorbing compounds and by improving the gas-phase to water-phase mass transfer of hydrophobic compounds (e.g., Béchohra et al., 2015). Numerical model simulations of De Biase et al. (2013) indicate that biodegradation rates need to be very high to avoid undesired VOC emissions, but cannot provide a direct evidence if such high rates can be achieved in a highly unsaturated system with diffusion-driven transport in the vapor phase. These previous findings raise the questions if indeed such high rates can be achieved in unsaturated porous media and if conditions favoring high diffusive VOC fluxes allow for VOC removal due to biodegradation across centimeter to decimeter-scale distances also in absence of abiotic retardations.

The objective of this study is the experimental investigation of the main processes and parameters controlling the fate of VOC in unsaturated porous media. Particular focus is on the removal capacity of such an unsaturated system for VOC emerging from contaminated groundwater and on the ability of the system to act as a barrier for diffusion-driven VOC emissions to the atmosphere. For this purpose a controlled laboratory reactor set-up was selected which facilitates high diffusive transport rates with only minimal restriction by a residual water phase and no organic phase retarding the spreading of the VOC. The set-up allows monitoring VOC concentration profiles at the centimeter-scale and thus enables to assess also VOC degradation at high spatial resolution. To distinguish between biodegradation and potentially remaining abiotic removal processes the fate of three different VOC was investigated: two isotopomers of a reactive model compound (toluene (h-toluene) and per-deuterated toluene (d-toluene)) which exhibit nearly identical physical properties but highly different biodegradability, and a non-reactive VOC (MTBE). Furthermore, we have adopted a novel approach to analyze VOC in gas-phase and liquid phase at the same time, which allows checking the assumption of instantaneous equilibrium with respect to Henry's law. The results are relevant for bioremediation of areas of high VOC concentrations which could lead to atmospheric emissions or vapor intrusion to buildings through the basement and ultimately to human health impacts.

2. Experimental procedures

2.1. Reactor design and operation

2.1.1. Reactor design

Vertical chromoflax glass columns ($l = 35$ cm, $i.d. = 4.1$ cm; cf. Fig. 1) packed with agar-covered (approximate agar layer thickness of $60 \mu\text{m}$) glass beads ($d = 2.9\text{--}3.5$ mm) were used to study the spatiotemporal concentration of the VOC in a water-unsaturated fixed-bed reactor (tortuosity, $\tau = 0.5$, derived from measured drainage curves using standard soil physical procedures; porosity, $\phi = 0.39$). Sampling ports allowed the sampling of VOC from the vapor phase and from the liquid reservoir (liquid volume 2.375 L). The reactor was separated from the headspace of the liquid

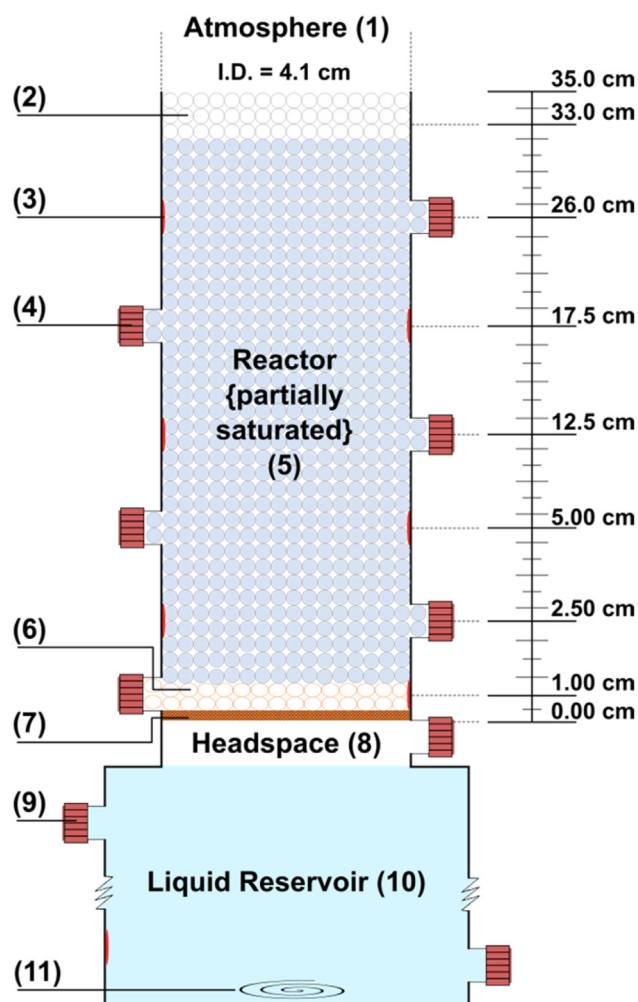


Fig. 1. Schematic view of the experimental setup to mimic a shallow aquifer. It consists of a stirred (11) liquid reservoir (10) containing the dissolved VOC and a vertical reactor column (5) filled with partially saturated glass beads. The reactor is filled with dry glass beads (2) at the top, is open to the atmosphere at its top (1) and separated from the headspace (8) of the liquid reservoir by a steel mesh (7) covered by a thin layer of PTFE beads (6). Dissolved and gas-phase VOC can be sampled by gas sampling points (6) and liquid sampling points (9), and oxygen by sensing spots (3). The scale represents the distance in cm from the steel mesh above the headspace of the reservoir.

reservoir (initial head space volume approximately 45 mL) by a stainless steel mesh ($d = 4.1$ cm, pore size = 1 mm) that was covered with a double layer of PTFE beads ($n = 66$, $d = 6$ mm) to avoid the formation of a liquid barrier at the base of the reactors. All reactors were open to the atmosphere on their top to allow vertical diffusion of the VOC emanating from the liquid reservoir. The upper 5 cm of the reactors were filled with dry glass beads to prevent microbial contamination from the atmosphere.

2.1.2. Reagents and analytical procedures

Toluene (h-toluene), methyl tertiary butyl ether MTBE (99%) and HgCl_2 (99.5%) were obtained from Merck KGaA. Per-deuterated toluene (99.6 atom % D, d-toluene) was purchased from Sigma–Aldrich Chemie Germany. Liquid and gasphase VOC samples were analysed with a Hewlett–Packard Agilent 6890N gas chromatograph equipped with a flame ionization detector (FID). The automated injection using the headspace auto-sampler (Hewlett–Packard 7694) with 1 mL injection volume and oven temperature of 95°C for liquid samples and 70°C for gas samples. To separate the liquid phase d- and h-toluene, fused silica capillary

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