



Quantifying the impact of immobile water regions on the fate of nitroaromatic compounds in dual-porosity media



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ABSTRACT

Nitroaromatic compounds (NACs) are reduced by structural or surface bound Fe (II) species under anaerobic conditions in the subsurface. This reaction preferentially occurs on clay minerals which are mainly present in areas with low hydraulic conductivity containing nearly immobile water. Diffusion is the dominating transport process in these zones. Due to the complexity in such heterogeneous systems, the mathematical prediction of reactive solute transport taking into account diffusive mass exchange into immobile water regions still remains challenging. Therefore, the influence of immobile water regions on the fate of 4-Cl-Nitrobenzene (4-Cl-Nb) was quantified in dual-porosity column experiments at three different mean transit times under saturated anaerobic conditions in the presence of soluble Fe (II). A multi-tracer approach and a Single Fissure Dispersion Model (SFDM) were used to estimate input parameter to further model the transport of 4-Cl-Nb. Reactive solute transport of 4-Cl-Nb was quantified considering instantaneous sorption on to the clay matrix and a reduction within the immobile water region following first-order kinetics. The experimental results indicated that sorption onto the clay matrix enhanced the mass exchange of 4-Cl-Nb into immobile water region compared to nonreactive solutes. At the same time the abiotic reduction of 4-Cl-Nb limited the process of back diffusion to mobile water regions. Fitted retardation factors ($R_{im} = 4.62 \pm 0.68$) and decay rates ($k = 1.51 \pm 0.08 \text{ h}^{-1}$) were independent on tested flow velocities. Findings of this study can advance the understanding on the fate of NACs in the subsurface which is essential for prediction of reactive solute transport at field scale.

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1. Introduction

Nitroaromatic compounds (NACs) are important explosives and have been released to the environment by ammunition production sites since world war one. In some cases, waste water of the production accidentally reached the groundwater including about 30 NACs such as 2,4,6-trinitrotoluene (TNT) or byproducts like 4-Cl-nitrobenzene (4-Cl-Nb) (Rodgers and Bunce, 2001). Other contamination sources are explosive residues, open detonation and burning on military training

ranges, army depots and ordnance disposal sites (Crockett et al., 1996). There are about 3420 identified sites in Germany with possible contamination of explosive related compounds (Thieme, 1996).

The transport and mobility of NACs in saturated media depends on the sorption behavior onto the aquifers' matrix. NACs adsorb specifically and reversibly to clay minerals by forming electron donor-acceptor complexes (EDA) (Haderlein et al., 1996; Haderlein and Schwarzenbach, 1993). The adsorption is high to clay minerals with exchangeable cations (K^+ , NH_4^+) and small for homoionic clay minerals (Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+}). Sorption capacity increases from kaolinite to illite to montmorillonite and is negligibly small to aluminum and

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iron (hydr)oxides, carbonates and quartz (Haderlein et al., 1996). Weissmahr et al. (1999) demonstrated in a field experiment that 4-Nitrotoluene can be mobilized by injecting CaCl_2 to the contaminated groundwater. K^+ at clay minerals was exchanged by the injected Ca^{2+} . This resulted in a lower capacity to adsorb NACs. Furthermore, competition for sorption sites enhances the mobility of individual NACs. Highly sorbing NACs fill the available sorption sites in the first place. Less sorbing NACs can than only be sorbed in a smaller extent and thus, are more mobile (Fesch and Haderlein, 1998).

NACs can be degraded by microorganisms or due to abiotic reduction. The formed metabolites, however, are equal or even more toxic compared to the parent compound. Beside biotic degradation processes, it was found that NACs are abiotically reduced by surface bound Fe(II) species to aromatic anilines (Hofstetter et al., 1999). Hofstetter et al. (1999) investigated the reduction of TNT in both batch and column experiments with Fe(II) present at the surface of Fe(III)(hydr)oxides. Fe(II) species associated with nontronite and hectorite showed to have different reactivity to reduce NACs. Fe(II) bound by ion exchange did not contribute to the reduction while structural and Fe(II) complexed by surface hydroxyl groups were the important reducing Fe(II) species (Hofstetter et al., 2003). Elsner et al. (2004) determined pseudo-first-order rate constants for the reduction of 4-Cl-nitrobenzene in different Fe(II) mineral systems in batch experiments. Particularly iron rich clay minerals (smectite) with a high sorption capacity and availability of Fe(II) are of importance. Here, both structural and surface bound Fe(II) contribute to the reduction process (Hofstetter et al., 2006). This reduction can be partly limited by the availability of Fe(II). Heijman et al. (1995) conducted column experiments including a reduction of NACs coupled with microbial iron reduction. Different monosubstituted nitrobenzenes were reduced at a similar rate indicating that the regeneration of reactive sites was the rate-limiting process.

The sorption and abiotic reduction of NACs is reasonable to occur particularly in layers with high clay content (e.g. clay lenses). These regions have a low hydraulic conductivity and water is nearly immobile. Therefore, not advection or dispersion but diffusion is the dominating transport process in these zones. Although diffusion is a rather slow process, it was shown that the diffusive exchange from mobile to immobile water regions influences the fate of solutes in groundwater depending on the mean transit time (Knorr et al., 2016). Fesch et al. (1998) conducted column experiments with aggregated porous media and modelled transport of NACs with a multi-rate model considering sorption processes and retarded diffusion into the radial aggregates. They found that even very low fractions of immobile water can influence the transport of NACs when sorption sites are concentrated in such regions.

In mobile-immobile or dual-porosity systems transport is described by advection and dispersion in mobile water regions with a mass exchange into immobile water regions. Mathematically, this exchange can be described either by a first-order transfer coefficient (van Genuchten and Wierenga, 1976; Haggerty and Gorelick, 1995; Babey et al., 2015; Van Genuchten and Wagenet, 1989) or a parameter which is based on the molecular diffusion coefficient of the solute of interest (van Genuchten et al., 1984; Tang et al., 1981; Sudicky

and Frind, 1982; Neretnieks, 1980; Małozzewski and Zuber, 1985; Małozzewski and Zuber, 1990). The advantage of the second group of models is that a smaller number of fitting parameters is required. Furthermore, the parameter describing diffusive mass exchange has a physical meaning. This is not the case for empirical fitted parameters.

In theoretical calculations (Małozzewski, 1994) and in dual-porosity column experiments (Knorr et al., 2016) it was shown that breakthrough curves (BTCs) of tracers with a higher diffusion coefficient show lower maximum peak concentrations, more pronounced tailings and lower mass recoveries in comparison to tracers with a smaller diffusion coefficient. A multi-tracer experiment is useful to indirectly validate a model and to estimate flow and transport parameters of mobile and immobile water regions. Parameters estimated by tracer experiments are essential to further model the fate of contaminants in groundwater. Additional processes like sorption and decay need to be considered in that case. Reaction rates can be estimated with different methods such as batch, column and stirred flow chamber experiments (Bermúdez-Couso et al., 2012). However, sorption rates obtained from batch experiment are often not suitable for transport studies because they are generally overestimated in comparison to values estimated in column experiments (e.g. Dontsova et al., 2006; Fesch et al., 1998; Rahman et al., 2004).

In case of NACs, sorption and reduction rates are expected to be different in mobile and immobile water region depending on the physical and chemical conditions. The impact of immobile water regions in dual-porosity sediments on reactive transport remains unknown. Still, it is expected that the transport behavior is significantly influenced, because of diffusion, the high potential for abiotic reduction and sorption capacity. In addition, the influence of immobile water regions on the fate of NACs at different mean transit times has not been investigated so far. In this context, the mathematical description of transport processes is particularly challenging including sorption, abiotic reduction and the diffusive mass exchange between mobile and immobile water regions.

The objectives of this study were to i) investigate the influence of immobile water regions on the transport and abiotic reduction of 4-Cl-Nb at different water transit times in controlled dual-porosity column experiments, ii) characterize properties of mobile and immobile regions applying a multi-tracer approach, and to iii) quantify observed processes using an analytical model which describes the exchange between mobile and immobile regions based on the molecular diffusion coefficient. The experimental results and the quantification of observed processes advance the understanding of reactive transport in highly heterogeneous porous media and help to improve the prediction of contaminant fluxes.

2. Material and methods

2.1. Chemicals

4-chloronitrobenzene (4-Cl-Nb), 4-chloroaniline (4-Cl-An), 4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), Iron(II) chloride (FeCl_2) and potassium bromide (KBr) were purchased by Sigma Aldrich (St. Louis, USA). Deuterium ^2H laded water (92.0 atom%) was purchased by Chemotrade (Leipzig, Germany).

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