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Competitive sorption and multiple-species subsurface transport of nitro-aromatic explosives: implications for their mobility at contaminated sites

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Abstract Subsurface contamination with nitro-aromatic explosives and related compounds has become a problem at many ordnance and ammunition facilities. Results of our column experiments demonstrate that competition for sorption sites at phyllosilicates may substantially enhance the mobility of individual nitro-aromatic compounds (NACs) in porous media when present in mixtures. Competitive sorption of NACs in mixtures is controlled by two major factors: (a) the *relative* affinities of the NACs for phyllosilicate sorbents and (b) the degree of surface site saturation of these sorbents. A transport model that accounted for competitive sorption effects by a Langmuir approach successfully predicted the multiple-species transport of three model NACs that exhibited very different affinities for phyllosilicates. Generally, the differences in the mobilities of these compounds were substantially larger when present in mixtures compared to single solute conditions. Differences in NAC mobilities may be further accentuated by nitro-reduction, an important transformation pathway of NACs in the subsurface. The resulting (nitro)anilines exhibit low affinities for phyllosilicates and thus are weak competitors which enhances their mobility in anoxic subsurface environments.

INTRODUCTION

Soil and groundwater contamination by munitions related compounds has become an issue of increasing scientific and public perception during the last decade. Nitro-aromatic compounds (NACs) are one of the most important groups of contaminants at such sites due to their widespread use as explosives and their significant toxicity towards humans and biota. A predominant retention mechanism of most NACs in the subsurface is complex formation with phyllosilicate minerals of the solid matrix such as clays (Haderlein *et al.*, 1996; Weissmahr *et al.*, 1998). The extent of adsorption to such minerals strongly depends on the type and position of NAC substituents. Planar NACs with several electron withdrawing substituents, including several poly-nitrated explosives, exhibit the highest complex formation constants. Complex formation of NACs with phyllosilicates is a fast and reversible process and the resulting sorption isotherms are distinctly non-linear. Their general shape can be described by a Langmuir-type isotherm (Haderlein *et al.*, 1996). In previous work we have examined the effects of this nonlinear sorption process on the transport of NACs as *single solutes* in porous media (Fesch *et al.*, 1998). However, a

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characteristic of virtually any NAC contaminated site is the presence of mixtures of *several* nitroaromatic pollutants such as the explosives 2,4,6-trinitrotoluene (TNT) and 1,3-dinitrobenzene (1,3-DNB), various intermediates and by-products from their manufacturing, e.g. 4-nitrotoluene (4-NT), as well as metabolites of these compounds. Since all NACs adsorb by the same mechanisms at phyllosilicates, competition for sorption sites is expected among mixtures of NACs at many contaminated sites.

In this work, we investigated the transport of *mixtures* of nitroaromatic munitions residues in porous media by laboratory column experiments under water saturated conditions. The major goals were (a) to evaluate how the sorption and the mobilities of munitions related NACs are affected by the presence of sorbing nitroaromatic co-solutes, and (b) to quantitatively describe the transport of NACs in porous media under such conditions. To this end, we studied the transport behaviour of TNT, 1,3-DNB and 4-NT which exhibit very different affinities towards clay minerals. Single- and multiple solute miscible displacement experiments were conducted in combination with single-solute batch experiments. We analysed the solute breakthrough curves (BTCs) with the help of AQUASIM, a computer code for the analysis of one dimensional transport of reactive solutes in porous media (Reichert, 1994; Simon & Reichert, 1997).

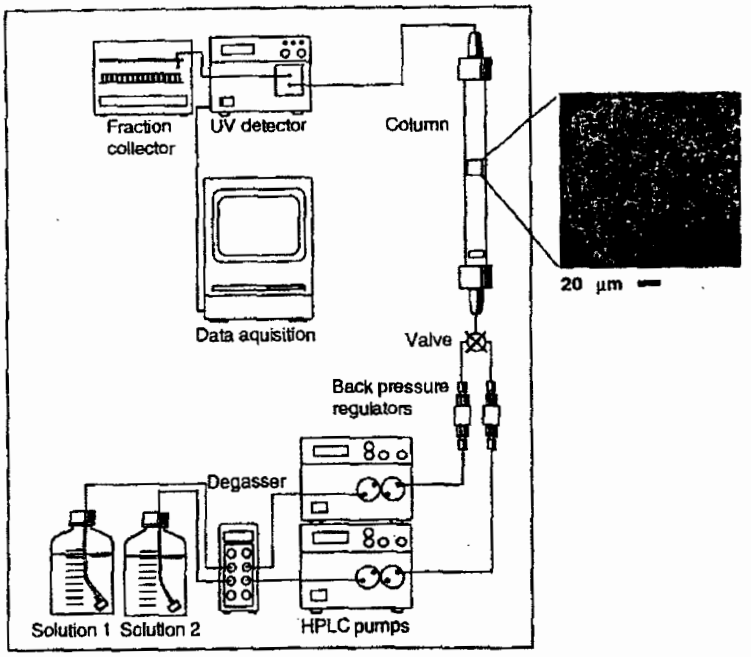

Fig. 1 Experimental set-up of the column experiments. The enlarged section is an REM micrograph of the column packing showing clay mineral sorbents attached to the surface of quartz grains.

EXPERIMENTAL

Batch sorption experiments were carried out according to Fesch *et al.*, (1998). The solid matrix used in the batch sorption and miscible displacement experiments was quartz sand coated with aggregated montmorillonite clay minerals (see Fig. 1). This model sorbent mimics the typical distribution pattern of clays in natural matrices. Table 1 lists sorption data of the NACs studied for this material. The general set-up of the column experiments is shown in Fig. 1. A more detailed description of the experimental procedures can be found in Fesch *et al.* (1998). All experiments were conducted under the following conditions: $T = 22°C$, $I = 10$ mM KCl. In miscible displacement experiments the pore water velocity v was 3.0 cm min^{-1} and the aqueous concentration of each NAC during the solute input pulse, C_o, was 10 $\mu mol\ l^{-1}$.

Table 1 Affinity (K_L) and capacity (S_{max}) parameters for sorption of the nitroaromatic solutes to the matrix of the porous medium. The parameter values were obtained by fitting the Langmuir model (equation (1)) to experimental single-solute batch adsorption data.

Compound	Abbreviation	K_L (l μmol^{-1})	S_{max} ($\mu mol\ kg^{-1}$)
4-nitrotoluene	4-NT	0.0108	980
1,3-dinitrobenzene	1,3-DNB	0.118	980
2,4,6-trinitrotoluene	TNT	0.496	980

RESULTS AND DISCUSSION

Sorption and transport of NACs in single solute systems

Figure 2(a) illustrates some characteristic features of the transport of sorbing NACs in aggregated porous media. Shown are overlays of single solute BTCs of the NACs studied in the same column system. Consistent with the batch sorption data (see Table 1) the retardation of the solutes in the columns spanned a wide range and increased in the order 4-NT < 1,3-DNB < TNT. The BTCs of all NACs were non-symmetric, exhibiting quite sharp adsorption fronts but strongly tailing desorption fronts. The tailing of the BTCs also increased in the order 4-NT < 1,3-DNB < TNT, consistent with the degree of non-linearity of the batch sorption isotherms of the NACs. Furthermore, the retardation of these compounds decreased with increasing solute concentrations, C_o (not shown). Such features of BTCs are characteristic for solutes exhibiting convexly shaped, non-linear isotherms (Bürgisser *et al.*, 1993; Schweich *et al.*, 1983; Schweich *et al.*, 1980). The otherwise sharp adsorption fronts of the BTCs exhibited some tailing in their upper parts, suggesting the presence of non-equilibrium processes. This frontal tailing was more pronounced for strongly sorbing solutes and at low flow velocities (not shown). Non-equilibrium mass exchange with the clay mineral aggregates caused these effects as demonstrated by results of flow interruption experiments and by increased retardation of the BTCs with decreasing pore water velocities. The BTCs could be modelled precisely considering advective transport, retarded diffusion of NACs into clay aggregates of the matrix and their non-linear sorption behaviour (Fesch *et al.*, 1998).

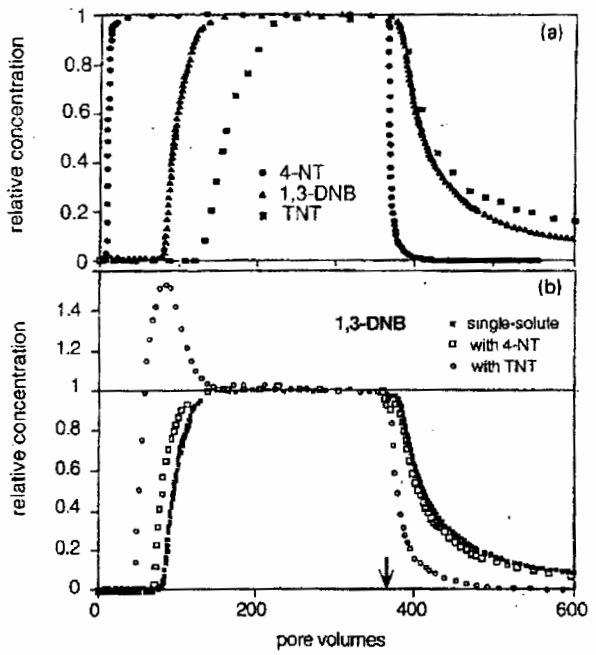

Fig. 2 (a) Comparison of single solute BTCs of 4-nitrotoluene (4-NT), 1,3-dinitrobenzene (1,3-DNB) and 2,4,6-trinitrotoluene (TNT) obtained in miscible displacement experiments. (b) BTC of 1,3-DNB as single solute and in binary mixtures with 4-NT and TNT, respectively. The arrow indicates the duration of the solute pulse(s).

The retardation of the NACs within the columns (Fig. 2(a)) was consistent with their relative tendency to form complexes with phyllosilicate minerals such as clays (Weissmahr *et al.*, 1998). Thus, knowledge of the *relative* affinities of NACs for phyllosilicates can be used to infer the type of sorption processes of such compounds in dynamic systems, and also in the presence of non-equilibrium mass transfer due to poorly accessible sorption sites. For instance, Hildenbrand & Luckner (1995) studied the transport of nitro-aromatic explosives and related compounds in column experiments using a matrix originating from a munitions contaminated aquifer. They found a sequence of NAC mobilities very similar to the results presented in Fig. 2(a), suggesting that complex formation with phyllosilicates was the major mechanism for retardation of NACs under such quasi natural conditions.

Competitive sorption and transport of solute mixtures

Figures 2(b) and 3 illustrate the significance of competition effects for the transport of mixtures of NACs in porous media. Shown are BTCs of 1,3-DNB as a single solute, in binary mixtures with either 4-NT or TNT (Fig. 2(b)), and of both competing NACs (Figs 3(a),(b)). Compared to single solute conditions, the mobility of the solutes generally was enhanced when present in mixtures with other sorbing

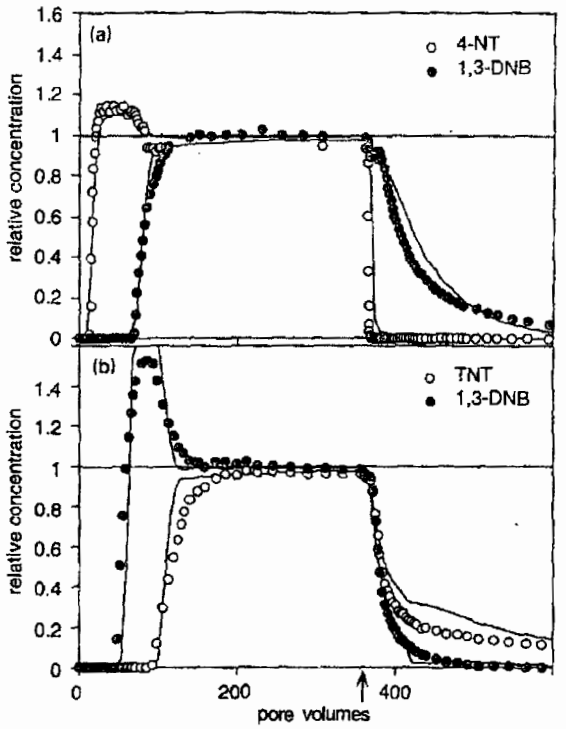

Fig. 3 Comparison of measured data (markers) and model simulations (lines) of NAC BTCs. Binary mixtures of the following NACs were injected (a) 1,3-DNB and 4-NT; (b) 1,3-DNB and TNT. The arrow indicates the duration of the NAC input pulse(s).

NACs. This is reflected by earlier solute breakthrough as well as by less tailing of the BTCs. However, the degree of mobilization of a given compound strongly depended on the *relative* affinities of this NAC and its competitor to the sorption sites. The data in Fig. 2(b) illustrate the effects on the BTCs of 1,3-DNB in the presence of a competing co-solute with either a higher (TNT) or a lower (4-NT) affinity than 1,3-DNB, respectively.

Besides the general trend of increased mobility, the BTCs of mixtures of NACs exhibit other remarkable features. The BTCs of weaker competitors show a distinct "overshooting" effect, i.e. the eluting concentrations partially exceeded the input concentrations of the solutes. This feature is seen in BTCs of 1,3-DNB when present in a binary mixture with TNT (Figs 2(b), 3(b)) or of 4-NT in a mixture with 1,3-DNB (Fig. 3(a)). The areas under the "overshooting" peaks represent the amount of solute replaced from the surface by the stronger sorbing NAC. Competitive sorption also accounts for the decreased tailing of the desorption fronts of the weaker sorbing solutes. Since competition of NACs for sorption sites is strongly concentration dependent, it is important to note that in the experiments shown all NACs were fed in equal concentrations and simultaneously to the columns.

Modelling of BTCs

The general features of NAC sorption isotherms at clay minerals can be described by the Langmuir equation:

$$S = S_{max} \frac{K_L C}{1 + K_L C} \tag{1}$$

where S and C are the sorbed- and aqueous-phase solute concentrations, respectively, K_L denotes the Langmuir affinity constant and S_{max} is the maximum sorbed-phase solute concentration. We determined the isotherm parameters, K_L and S_{max}, in single-solute batch experiments (see Table 1). Since all competing NACs adsorb by the same mechanism to phyllosilicates (Weissmahr *et al.*, 1998; Weissmahr *et al.*, 1997), the sorbed-phase solute concentration of a component i in a mixture of j components may be estimated using a competitive Langmuir sorption isotherm (Fritz & Schlünder, 1981):

$$S_i = S_{max} \frac{K_{L,i} C_i}{1 + \sum_j K_{L,j} C_j} \tag{2}$$

where $K_{L,i}$ and $K_{L,j}$ are the respective single-solute isotherm parameter values. The maximum sorbed-phase solute concentration, S_{max}, is exclusively determined by the properties of the sorbent and, thus, is equal for all competing solutes. Note that this model used for describing competitive sorption of NACs does not account for surface site heterogeneity potentially present at natural phyllosilicates, nor for possible interactions of sorbed NACs among each other.

The solid lines in Figs 3(a) and (b) represent *simulated* BTCs of binary mixtures of NACs using a transport model which was validated using single solute miscible displacement experiments (Fesch *et al.*, 1998) but was extended to account for competition effects based on the competitive Langmuir model (equation (2)). The simulated BTCs nicely reflect the characteristic features of the measured data such as the overshooting fronts as well as the decreased retardation and tailing of the fronts in the presence of a competing co-solute. Estimates of the heights of the overshooting peaks were somewhat off the measured BTCs and the shapes of the calculated fronts slightly differed from the measured data. These deviations of predicted from measured data may result from a mismatch in the low concentration range of measured batch isotherms and the one-site Langmuir sorption isotherms used, especially for the solutes with high affinities towards the clay minerals (Haderlein & Schwarzenbach, 1993). More accurate results are expected for two-site Langmuir- or for Langmuir-Freundlich isotherm models (Fesch *et al.*, 1998) which were not considered here for the sake of simplicity and ease of parameter estimation. However, since the general features of the simulated and measured BTCs matched quite well, we are confident that the major processes influencing the mobility of NAC mixtures in the porous medium are competitive saturation-type sorption and retarded diffusion into and within clay aggregates. Preliminary experiments with three- and four-compound mixtures of NACs indicate that the proposed model is also capable of predicting the competition effects of NACs in more complex systems.

CONCLUSIONS

Our results demonstrate that competition for sorption sites at phyllosilicate minerals may substantially affect the mobility of individual NACs in porous media when present in mixtures. Generally, the transport of all sorbing NACs is enhanced due to competitive sorption compared to single solute situations. Two major factors determined the extent of mobilization of NACs in mixtures: (a) the *relative* affinities of the competing solutes to phyllosilicate sorbents and (b) the degree of surface site saturation which is determined by the aqueous concentrations of the competing NACs. Depending on the scenario considered, mobilization due to the presence of competing solutes can either be minimal or lead to an almost conservative transport behaviour of individual components of the NAC mixture.

The multiple-species transport of NACs in porous media could be predicted from single solute sorption experiments with the help of a transport model that accounted for competitive sorption effects by a competitive Langmuir approach. This simple model predicted reasonably well the various elution patterns observed for the BTCs of mixtures of NACs. For instance, the displacement of weaker NAC competitors by strongly sorbing NACs (e.g. TNT) resulted in aqueous phase concentrations of the weaker competitor that largely exceeded their concentrations in the feeding solutions. Such an elution behaviour may lead to misinterpretations of cleanup efficiencies when competitive sorption is not taken into account in evaluating groundwater remediation measures of NAC contamination.

It is important to note that some of the most toxic NACs commonly found at munitions contaminated sites are weak competitors compared to major components of the NAC mixture such as TNT. For instance, sorption and thus retardation of the very toxic 2,6-dinitrotoluene may strongly be diminished when present in mixtures with TNT, even at very low aqueous TNT concentrations. Furthermore, nitro-reduction, an important transformation pathway of NACs in the subsurface, gives rise to contaminants with lower affinities and lower competition efficiencies for clays than their (poly)nitrated precursors. Such compounds, e.g. (nitro)anilines, are potentially very mobile in anoxic groundwaters. Thus, competitive sorption must be considered as a crucial process in evaluating the mobility, the bioavailability and the exposure of nitroaromatic explosive residues in the subsurface.

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