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Laboratory and Field Scale Evaluation of Geochemical Controls on Groundwater Transport of Nitroaromatic Ammunition Residues

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Sorption to soils and sediments of nitroaromatic explosives may be due to interactions with natural organic matter (NOM) or complex formation with clays, which strongly depends on the type of exchangeable cations, i.e., the base saturation of the clays. We examined the relative importance of these two processes for NAC sorption at aquifer material and evaluated the potential of decreasing or enhancing the mobility of NACs in contaminated aquifers by stimulated cation exchange. Generally, sorption on NOM of 2,4,6-trinitrotoluene (TNT) and related nitroaromatic compounds (NACs) was low compared to sorption at clays, and no evidence for specific interactions with NOM was found. Adsorbed NOM hardly affected the complex formation of NACs with clays. NAC sorption at pure clays and at aquifer material depended on the K^+-saturation of these materials. Typical aquifer material containing ≤1% NOM and 3–5% clays exhibited similar sorption features than pure clay minerals, suggesting that NAC sorption to the bulk aquifer matrix was dominated by complex formation at clays. We applied these laboratory findings to a two-step field test designed to control the groundwater transport of NACs by the injection of electrolytes. 4-Nitrotoluene (4-NT) and KCl were injected into a sandy aquifer, and their groundwater transport was monitored at an extraction well. Subsequent injection of $CaCl_2$ remobilized the previously adsorbed 4-NT due to ion exchange of Ca^{2+} for K^+ at clays present in the aquifer matrix. The susceptibility of NAC sorption to the composition of exchangeable cations at clays was confirmed for TNT and related NACs. Controlling the base saturation of the aquifer matrix by electrolyte injections thus opens new perspectives for gentle remediation of sites contaminated with nitroaromatic explosives.

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Introduction

The widespread use of nitroaromatic compounds (NACs) (*1*), in particular their use as explosives and ammunition (*2*), has led to subsurface contamination at sites where such compounds are applied, produced, or handled. One prominent example is the pollution of soils and aquifers by nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT) or 1,3-dinitrobenzene (1,3-DNB). At such contaminated sites, mixtures of various NACs are present resulting from impurities of technical grade explosives, disposal of intermediates or side products (e.g., various mono- and dinitrotoluene isomers such as 4-nitrotoluenes (4-NT)), or from reductive transformation processes of NACs (e.g., aminonitrobenzenes and toluenes (*3, 4*)). To assess and eventually to control the mobility and reactivity of such hazardous pollutants in the subsurface, the molecular interactions and environmental factors that determine their sorption behavior must be understood.

Several studies have dealt with sorption and transport of TNT and related NACs in natural (*5–10*) and model (*11–18*) subsurface systems. These investigations showed that sorption of NACs to subsurface materials, in contrast to many other neutral organic contaminants, may be dominated by strong and specific interactions with certain matrix components rather than by hydrophobic partitioning.

In earlier work we have shown that, among the minerals commonly found in soils and aquifers, only phyllosilicates such as clay minerals are strong and specific sorbents for NACs (*11*). The dominant sorption mechanism is electron donor–acceptor (EDA) complex formation between siloxane oxygens of the clays (σ-donors) and NACs (π-acceptors) (*19*). The type and surface density of exchangeable cations present at clays was found to be the most important environmental factor for EDA complex formation. High surface densities of strongly hydrated cations (e.g., Na^+, Ca^{2+}) reduce the accessibility of siloxane sites for NACs, whereas weakly hydrated and thus less bulky exchangeable cations (e.g., K^+, NH_4^+) allow better for inner sphere EDA complexes at siloxane sites. However, the specific sorption of NACs at clay minerals has been investigated only under homoionic conditions in model systems. In the work presented here, we evaluate the effects and the significance of cation exchange at clays on sorption and transport of NACs in the subsurface under *mixed ionic conditions* and in *complex natural matrices* such as aquifer sediments.

Recently, it was found that TNT and aminonitrotoluenes were removed from aqueous solution by colloidal NOM to a much higher extent than expected from the hydrophobicity of these NACs (*20, 21*). Although the nature of NAC–NOM interactions still is subject to current research, it is likely that in certain environmental settings such interactions may affect the sorption of NACs to the solid matrix. NOM may either be a sorbent for NACs in the aqueous or the solid phase and/or may interfere with EDA complexes of NACs at clays by its tendency to form surface coatings at these minerals (*22*).

Hence, the specific objectives of the present study were (i) to quantify the relative importance of exchangeable cations at clays and natural organic matter on sorption of NACs in aquifers and (ii) to evaluate the potential of induced changes of the subsurface geochemistry with respect to NOM and exchangeable cations as an option to mobilize or retard NACs at contaminated sites.

To this end, we conducted laboratory batch experiments with model sorbents (clays, NOM) and with an aquifer matrix

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TABLE 1. Names, Abbreviations, Octanol/Water Partitioning Constants (log K_{ow}), and Adsorption Coefficients (log K_d) for Homoionic K^+-Clays of the Nitroaromatic Compounds Studied

compound	abbrev	log K_{ow}	log K_d (L kg^{-1}) (K^+-kaolinite)	log K_d (L kg^{-1}) (K^+-montmorillonite)
2,4,6-trinitrotoluene	TNT	1.6[a]	3.3	4.3
2-amino-4,6-dinitrotoluene	2-ADNT	0.7[b]	2.4	3.5
1,3-dinitrobenzene	1,3-DNB	1.5[a]	2.3	3.7
4-methylnitrobenzene	4-NT	2.4[a]	1.0	1.7
4-*n*-butylnitrobenzene	*n*-butyl-NB	3.9[a,c]	1.3	n.d.[d]

[a] Reference *43*. [b] Estimated from K_{ow} (TNT) using π constants given in ref *43*. [c] Value for *tert*-butylnitrobenzene. [d] Not determined.

from an ammunition contaminated site. Furthermore, we conducted a field scale test to evaluate the potential of in-situ stimulation of cation exchange by electrolyte injections to control the mobility of NACs in contaminated aquifers. To distinguish between the contributions of different sorption mechanisms to the overall sorption of NACs, we applied the concept of molecular probing (*23, 24*) by using several reactive tracers with complementary sorption properties. Hydrophobic partitioning to the solid matrix was quantified based on the sorption of *p*-cresol, which exhibits a similar hydrophobicity as TNT, but is not capable of forming EDA complexes. We determined the significance of natural clays as sorbents for NACs by studying the sorption of three nitroaromatic probe compounds (TNT, 1,3-DNB, 4-NT) which differ in their tendency to form EDA complexes. We will discuss how the sorption of other NACs can be determined relative to these reactive tracers, which forms a basis for the general applicability of the results of this study.

Experimental Section

Nitroaromatic compounds used are listed in Table 1 together with their abbreviations used throughout the paper and some pertinent physicochemical properties. Aqueous NAC solutions were prepared from 0.1 M methanolic stock solutions (for laboratory batch experiments) or by dissolution of pure NACs (field injection test). The concentrations of methanol in the assays were ≤0.5% (v/v) and had no measurable effects on the sorption of NACs nor NOM.

Natural organic matter (NOM) used in our experiments was the humic acids fraction of a peat humic substance (Aldrich Na^+-humate), a well characterized and frequently used humic material (*25*). Na^+-humate was dissolved in water at pH 8 and filtered (Schott no. 3, 10−6 μm). The filtrate was acidified with HCl to pH 2, and the resulting precipitate was collected on a filter and stored after freeze-drying until use. Stock solutions of this material (100 mg·L^{-1}) in either 0.1 M KCl or NaCl were prepared and diluted with the respective background electrolyte to yield dissolved NOM concentrations of 0.05−100 mg·L^{-1}.

Sorption of NOM to clay minerals was investigated by equilibrating homoionic clay suspensions for 2 h with NOM spikes in a given background electrolyte (KCl or NaCl) and pH (pH 5 buffered with acetate; pH 8 buffered with borate). Control experiments showed that these buffers (20 mM) had no measurable effect on the adsorption of this NOM to the kaolinite and montmorillonite clays used. The aqueous concentrations of NOM were determined photometrically in 5 cm quartz cells at 250, 350, and 450 nm. The amount of adsorbed NOM was calculated from the difference between initial and equilibrium aqueous NOM concentrations. To investigate the effect of surface bound NOM on the sorption of NACs, we chose experimental conditions (ionic strength, *I*, pH, total NOM concentration) yielding a high fraction of adsorbed NOM in equilibrium with low aqueous NOM concentrations (see Results and Discussion). Ten milligrams of homoionic clays was spiked with 1.5 mL of a 25 mg·L^{-1} NOM solution at pH = 5 and I = 0.1 M (NaCl or KCl).

Sorption of NACs to clay, NOM, and aquifer matrix was studied in triplicates, using 1.8 mL screw cap glass vials, centrifugation for phase separation, and direct HPLC−UV analysis of the solutes in the aqueous supernatant (*13, 14*). Sorption of NACs in the presence of adsorbed NOM was determined by spiking a 1.5 mL solution containing 1−10 μM NACs and 25 mg·L^{-1} NOM (pH 5, I = 0.1 M) to 10 mg of clay. We chose relatively short equilibration periods (2 h) to focus on fast and reversible sorption processes. Prolonged exposure to humic substances in nonsterile systems may lead to conditions that result in reductive transformation and irreversible binding of certain NACs to NOM (*10, 20, 21*). We did not detect hydroxylamino or amino transformation products in our batch systems nor significant solute losses in blank samples and thus calculated the amount of sorbed NAC from the difference in initial and equilibrium aqueous solute concentrations. The RSD of the sorption coefficients (K_d-values) generally was ≤10%, typically 5 ± 2%.

Bi-ionic Ca/K and Na/K clays were obtained by mixing appropriate amounts of homoionic clays and suspending and equilibrating them in distilled water or electrolyte for 12 h. Homoionized clays were prepared by repeated washing of size fractionated (<2 μm) native clays with 0.1 M chloride electrolytes followed by dialysis and freeze-drying. The clays used were China Clay kaolinite (purchased from The English Clays Lovering Poching & Co. Ltd, Cornwall, U.K.) and SAz-1 montmorillonite (purchased from the Source Clay Minerals Repository, University of Missouri, Columbia), for a mineralogical characterization of the clays see ref *11*. The composition of exchangeable cations at the clays was determined by the NH_4Ac method (*26*). To study NAC adsorption to bi-ionic clays at low ionic strength (I < 0.1 mM), the mixtures of homoionic clays were equilibrated with NAC solutions in distilled water. Thus, the net composition of exchangeable cations at the clays remained constant. For the experiments at higher ionic strength (I = 10 or 100 mM), the bi-ionic clays were equilibrated with NACs dissolved in 10 or 100 mM KCl, respectively. Furthermore, at I = 100 mM, sorption experiments were performed by spiking the bi-ionic clays with NAC solutions containing different Ca/K and Na/K ratios of the background electrolyte. Since the initial composition of exchangeable cations at the clays changed in the presence of added background electrolytes, the equilibrium solutions were analyzed for K^+, Na^+, and Ca^{2+} by ICP-AES. From the difference in initial and equilibrium aqueous cation concentrations and from the known initial fractions of exchangeable cations at the clays, the equilibrium composition of exchangeable cations at the clays was calculated.

Aquifer sediment samples were collected from core drillings in the vicinity of an ammunition waste site (Elsnig, Germany), where we also performed the field injection

TABLE 2. Mineralogical Composition[a] and Specific Surface Area[b] of the Elsnig Aquifer Sediments Used

sample	quartz (%)	plagioclase (%)	K^+-feldspar (%)	kaolinite (%)	illite (%)	other (%)	BET ($m^2 g^{-1}$)
B	74	9	12		5		1.91
C	55	12	11	3	17	1	2.48

[a] Determined by XRD for the size fraction <63 μm. [b] Determined by N_2 BET for the size fraction <250 μm; data from ref *44*.

experiment (see below). The aquifer material had a low organic matter content (f_{om} < 0.001), a CEC of about 0.3 mol·kg^{-1}, and a porosity of 0.31 (*27*). Particle size distribution was determined by dry-sieving and resulted in the following: 3.0% gravel (6300–2000 μm), 90% coarse sand (2000–200 μm), 5.5% fine sand (200–65 μm), and 1.5% silt and clays (<63 μm). We used the size fraction < 250 μm of two core subsamples, designated sample B and sample C, for sorption experiments with NACs. The mineralogical analysis of the d < 63 μm subfraction of these samples is shown in Table 2. Sorption of NACs was studied in the presence of 0.1 M KCl or 0.1 M $CaCl_2$ and both untreated sediment samples and samples which previously had been homoionized by repeated washings with the respective electrolyte.

The sorption kinetics of TNT to K^+-homoionic aquifer samples was investigated and found to be biphasic. A fast initial adsorption was followed by a slow decrease of the aqueous concentration of TNT with time after 30 min (data not shown). The contribution of the slow sorption step to the total adsorption of TNT was minor (<10%); sorption equilibrium, however, was not reached within the first 4 h. The adsorption of NACs in suspensions of pure clays reached equilibrium within a few minutes (*14*). The biphasic adsorption kinetics observed with soil suspensions is consistent with a fast initial adsorption to surface sites of easily accessible clays followed by retarded diffusion of TNT into micropores of the soil particles as observed for sorption of NACs to porous media containing aggregated clay minerals (*18, 28*). Alternatively, abrasion or disintegration of clay particles during continuous shaking of the soil suspensions may have increased available surface sites with time.

A forced gradient field injection experiment was conducted at a sandy Pleistocene aquifer in the vicinity of a former ammunition production site (Elsnig, Saxony, FRG). The field site is located next to a large groundwater reservoir in the Elbe river valley. During World War II, the Elsnig ammunition plant produced artillery ammunition, bombs, and pyrotechnics. As a result of these activities and the destruction of the plant after the war, contamination with NACs of a large fraction of the surrounding soil and groundwater occurred (*27*). Our test site, however, was not affected by the ammunition contaminated plume.

The hydrogeological situation at Elsnig is characteristic for a heterogeneous glacio-fluvial aquifer system, consisting of alternating layers of gravel and sand deposits with occasional occurrence of lenses of silt, clay, or lignite. In the vicinity of the ammunition site, the hydraulic conductivity ranged from $5 \cdot 10^{-6}$ to $6 \cdot 10^{-5}$ m/s. At our test site, the aquifer is approximately 10 m thick and confined by an impervious clay layer at its bottom 30 m below surface. The aquifer matrix at the test site primarily consists of loamy sand with sandy deposits and occasional inclusions of lignite lenses. The temperature of the groundwater was about 10 °C.

Two forced gradient injection experiments (at constant injection rates of $Q = 1.8$ m^3/h) were conducted after a steady state flow regime had been reached (see Figure 1). 4-Nitrotoluene (4-NT) was chosen as model NAC in this injection experiment for several reasons. 4-NT has a similar hydrophobicity to TNT and sorbs by the same EDA-mechanism to clays. However, 4-NT exhibits a much lower affinity for clays and thus is less strongly retarded in the aquifer than TNT (*11*). This allowed us to study the effects of induced cation exchange on the mobility of NACs at relatively short time scales. Further, 4-NT is relatively persistent with respect to biodegradation and chemical reduction processes (*4, 23*). Compared to other NACs (e.g., 2,6-DNT, 2,4,6-TNT, 2-NT), 4-NT exhibits a lower toxicity (*1*) and thus has been approved by the local authorities to be used in the injection experiment. Finally, 4-NT is one of the major contaminants present in soils and groundwaters at many TNT production sites.

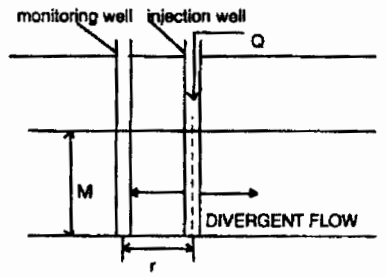

FIGURE 1. Setup of the forced gradient field injection experiment (aquifer thickness, M = 10 m; distance from injection to monitoring well, r = 3.8 m; infiltration rate, Q = 1.8 m^3/h).

The first part of the field test involved the injection of chloride (KCl) as nonreactive tracer and 4-NT as reactive tracer. Injection of KCl (9 g/L) lasted 10 h, followed by the injection of a 2 h 4-NT pulse at a concentration of 4.3 mg/L. After the injection of KCl and 4-NT, pristine water was infiltrated for 15 days to maintain the hydraulic gradient. The second experiment involved the injection of a 10 h $CaCl_2$ pulse (9 g/L), followed by injection of pristine water for additional 11 days.

Groundwater samples were taken from a monitoring well, that was located 3.8 m from the injection well (see Figure 1). Groundwater was sampled at a flow rate of 2 L/min and was reinfiltrated trough the monitoring well after sampling. To follow the breakthrough of 4-NT and of the electrolytes, groundwater samples were collected quasicontinuously during the entire experiment (26 days). Specific conductance and pH were measured on-line in a flow-through device. The chemical composition of the pristine groundwater was characterized with regard to pH (7.1), electrical conductivity (1.2 mS/cm), Ca^{2+} (54.7 mg/L), Mg^{2+} (6.7 mg/L), K^+ (1.6 mg/L), and Na^+ (10.4 mg/L). 4-NT data were collected approximately every 24 h. 4-NT was extracted from 1 L samples twice with dichloromethane. After phase separation, the CH_2Cl_2 extracts were dried over anhydrous sodium sulfate, diluted in methanol, and analyzed by reversed phase HPLC (RP18 column, methanol/water eluent, UV detection at 254 and 235 nm).

Results and Discussion

Role of Organic Matter Coatings on the Sorption of NACs at Clays. The presence of natural organic matter (NOM) may influence sorption of NACs at clay minerals in several ways. NOM adsorbed at clay minerals may compete with NACs for sorption sites, thus decreasing their adsorption. Conversely, adsorbed NOM may increase the adsorption of NACs by providing an additional sorbent phase at the mineral surfaces. We studied the adsorption of NACs to clays in the presence of adsorbed NOM to test these hypotheses. Four NACs were chosen as probes, covering a wide range with respect to EDA complex formation and hydrophobicity (Table 1). TNT, 1,3-DNB, and 2-ADNT are explosives related NACs frequently encountered at contaminated sites. 4-*n*-Butyl-NB was chosen

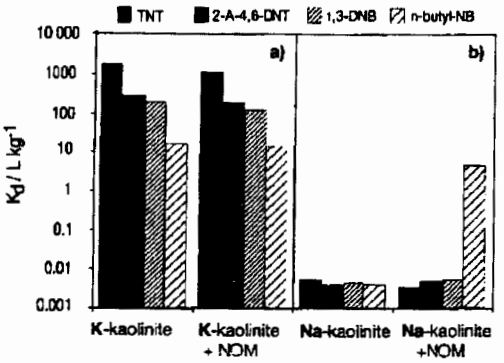

FIGURE 2. Effect of adsorbed natural organic matter (NOM) on sorption constants (K_d-values) of nitroaromatic compounds determined in aqueous suspensions of homoionic K^+-kaolinite (a) and Na^+-kaolinite (b) (I = 0.1 M, pH = 5.0, T = 21 °C).

to extend the range of hydrophobicity of the probe compounds.

Sorption isotherms of NOM at kaolinite and montmorillonite served to determine the experimental conditions resulting in high surface concentrations of NOM but low concentrations of dissolved NOM. The adsorption isotherms of NOM at homoionic K^+- and Na^+-kaolinite as well as K^+-montmorillonite at pH 5 and I = 0.1 M were of the Langmuir type, exhibiting a distinct saturation concentration (data not shown (*29*)). At low NOM surface coverage, sorption of NOM was 10 times higher, and the fraction of adsorbed NOM was 3 times higher at kaolinite than at montmorillonite (in terms of K_d given in L·kg^{-1}) although montmorillonite has a much higher specific surface area than kaolinite. In agreement with earlier studies (*30*) these results suggest that NOM adsorbs predominantly at aluminol groups of clays. At montmorillonite, ≡Al−OH groups are present only at edge sites, whereas at kaolinite, aluminol groups are also present at the basal gibbsite planes (*31*).

Sorption of NOM at clays was strongly pH dependent. At pH 8 the adsorption of NOM at K^+-kaolinite was much lower than at pH 5 (data not shown). This can be interpreted as increased electrostatic repulsion between deprotonated aluminol sites at the clays and deprotonated hydroxyl groups of the NOM (*32*).

Sorption of NOM at Na^+-kaolinite was slightly lower than at K^+-kaolinite, consistent with earlier findings (*33, 34*). For our further experiments, we chose experimental conditions (pH = 5 and I = 0.1 M) in the region of the NOM sorption isotherms where the concentration of adsorbed NOM was high and in large excess of the mass of dissolved NOM. The corresponding NOM concentrations sorbed at K^+- and Na^+-kaolinite were 3.5 g·kg^{-1} (f_{om} = 0.0035) in equilibrium with 5 mg·L^{-1} dissolved NOM. At K^+-montmorillonite NOM concentrations were 2 g·kg^{-1} (f_{om} = 0.002) and 10 mg·L^{-1}, respectively.

Sorption of NACs at Clays with and without Adsorbed NOM. Figure 2a shows adsorption constants for the linear range of the adsorption isotherms (K_d-values) of the four NACs studied obtained in homoionic K^+-kaolinite suspensions. The relative affinity of the NACs for the clay was similar in clay systems with and without NOM. TNT (three electron withdrawing nitro substituents) exhibited the highest affinity, and *n*-butyl-NB exhibited the lowest affinity for clays. However, in the presence of adsorbed NOM, both the K_d as well as the maximum surface coverage of all NACs studied were lowered by about 30%. This effect of surface bound NOM on the adsorption of NACs is consistent with our picture of NOM sorption occurring primarily at edge aluminol groups of clays. Since NACs predominantly sorb to the siloxane surfaces of clays (*13*), little competition for sorption sites of NACs and NOM was found. The observed 30% decrease of NAC adsorption at K^+-kaolinite may be due to small amounts of NOM adsorbed at the siloxane plane of the clay, e.g., by complexation to exchangeable cations and/or by sorption at surface sites resulting from imperfections of the siloxane planes. Note that an eventual cosolvent effect of dissolved NOM is negligible since the concentration of dissolved NOM (≤5 mg·L^{-1}) and also the ratio of dissolved to total NOM (≤10%) was very low in our experiments.

These results show that adsorbed NOM may slightly decrease EDA complex formation of NACs at two layer clays such as kaolinite, which exhibit a relatively high fraction of Al−OH sites. At three-layer minerals such as montmorillonite, the impact of adsorbed NOM on EDA complex formation of NACs is negligible (data not shown) due to their low density of ≡Al−OH sites and partial intercalation of sorbed NACs in the interlamellar space of such minerals (*19*).

To investigate the properties of adsorbed NOM as additional sorbent phase for NACs at minerals, experiments with homoionic Na^+-kaolinite were performed (Figure 2b). Note that, at homoionic Na^+-clays, EDA complex formation of NACs is suppressed (*13, 14*). Generally, very low K_d-values were measured for NACs with moderate to low K_{ow}-values, regardless whether NOM was present or not. Compound specific factors such as type and position of substituents did not significantly affect the adsorption of NACs to adsorbed NOM. These findings suggest that specific interactions of NACs with adsorbed NOM, e.g., EDA complex formation (*16*), were not significant under the conditions studied. Consistent with the results shown in Figure 2b, hydrophobic partitioning into organic matter of solutes exhibiting log K_{ow}-values ≤2 (i.e., TNT, 2-ADNT, 1,3-DNB) can be estimated to result in K_d-values of less than 0.5 L·kg^{-1} for our sorbent matrix (f_{om} = 0.0035 (*35*). Sorption of the more hydrophobic 4-*n*-butylnitrobenzene (log K_{ow} = 3.89) significantly increased in the presence of adsorbed NOM. The measured K_d value of 5 L·kg^{-1} agrees well with estimates assuming hydrophobic partitioning into the organic matter as major sorption mechanism.

Significance of Organic Coatings at Soil Minerals for the Sorption of NACs. Adsorbed NOM generally had a minor effect on EDA complex formation of NACs to clay minerals. The slight decrease in K_d-values observed at K^+-kaolinite may be regarded as a "worst case" situation. Ionic strength and pH in typical soils and aquifers would lead to considerably lower concentrations of NOM adsorbed at clay minerals than under our experimental conditions. In the presence of strongly hydrated exchangeable cations, organic coatings at clays and other mineral phases may enhance the adsorption only for fairly hydrophobic NACs (log K_{ow} > 3). Much higher concentrations of particulate or surface bound organic matter than those present in our experiments (f_{om} = 2−4 g·kg^{-1}) are required to enhance significantly sorption of most NACs of environmental concern, including explosives and dinitrophenol pesticides (log K_{ow}-values range from 1.5 to 2.5). Apart from hydrophobic interactions, no evidence for specific interactions between NACs and NOM was found. Strong interactions of NACs such as TNT and 2-ADNT with NOM, as reported by other investigators (*21*), may be due to (partial) reductive transformation and subsequent binding of NACs mediated by NOM (*10, 36*). Our experimental conditions were designed to prevent such reactions. In a contaminated aquifer, we do not expect NOM to play a dominant role for sorption and transport of NACs when present in typical concentrations and in the absence of reductants as mimicked in our experiments.

Effect of K^+-Saturation of Clays on Their Affinity for NACs. Adsorption of NACs to clay minerals has primarily been studied at homoionic clays. In natural systems such as

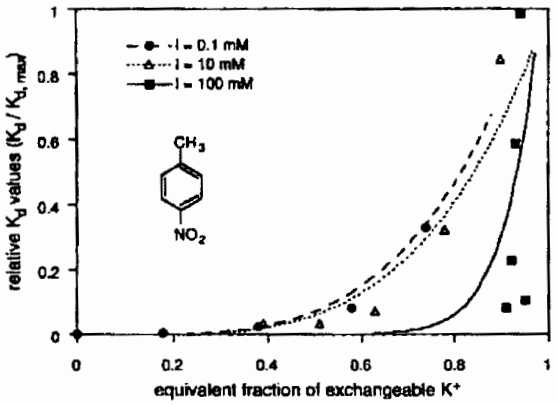

FIGURE 3. Adsorption of 4-nitrotoluene to bi-ionic K^+/Ca^{2+} montmorillonite. Normalized K_d-values as function of ionic strength, *I*, and the K^+-base saturation of the clay, f_{K^+}, (i.e., the equivalent fraction of exchangeable K^+). The lines are meant to guide the eye and represent power functions fitted to the data of each ionic strength (pH = 6.5, *T* = 21 °C).

soils or aquifers, however, clay minerals do not occur in homoionic forms but exhibit a mixture of various types of exchangeable cations such as Ca^{2+}, Na^+, or K^+. Under natural conditions, K^+ (and perhaps NH_4^+) are the only weakly hydrated exchangeable cations present in concentrations which are sufficient to promote sorption of NACs at clays. Hence, we studied the effect of partial K^+-saturation of clays on their affinity for NACs for binary mixtures of exchangeable cations (Ca/K and Na/K). The major objective was to assess the effect of partial K^+-saturation of clays on their ability to form EDA complexes with NACs in terms of a potential application of stimulated cation exchange to control the mobility of nitroaromatic pollutants at contaminated sites.

K_d-values of 4-nitrotoluene (4-NT) were determined for two- and three-layer clays at varying equivalent fractions of exchangeable K^+ and at various ionic strengths. Heterovalent (Ca/K) as well as homovalent (Na/K) bi-ionic clays (montmorillonite, smectite, and kaolinite) were investigated. Qualitatively, Ca/K and Na/K systems gave very similar results with respect to the effects of fractional K^+-saturation, f_{K^+}, and of varying ionic strength on the sorption properties of the clays (data for Na/K clays can be found in (*29*)). Sorption of 4-NT was very low at homoionic Na^+- or Ca^{2+}-clays and increased steadily with increasing K^+-saturation of the clays, as is illustrated for a Ca/K-montmorillonite system in Figure 3. However, the affinity of the clays for 4-NT did not increase linearly with f_{K^+} in most of the systems investigated (exceptions are Na/K-kaolinite at $I = 0.1$ M (*13, 29*)). At low f_{K^+}, the affinity of the clays for 4-NT was less sensitive to changes in K^+-saturation than at high K^+-saturation. At high ionic strength ($I = 100$ mM), this effect was more pronounced compared to low ($I = 0.1$ mM) or medium ionic strength ($I = 10$ mM). Note that, at homoionic clays, ionic strength did not affect EDA complex formation of NACs in the range of 0.1 mM < I < 100 mM (*14*).

These results are consistent with observations obtained with other clays (*12–14, 37, 38*), and we conclude that the extent of EDA complex formation of clays with NACs is controlled by the composition and distribution of hydrated cations at the Stern layer of siloxane surfaces at clays. Although a quantitative *prediction* of the accessibility of siloxane sites for NACs at clays as a function of the type and composition of exchangeable cations and of the ionic strength is still missing, changing the cation composition at clays is a promising option to manipulate specifically the sorption and thus the transport of NACs in the subsurface.

Groundwater Injection of Electrolytes To Evaluate Field Scale Retardation and Mobilization of 4-NT. We tested the applicability of electrolyte injections to control the groundwater transport of NACs in a dual well forced gradient field injection experiment (Figures 1 and 4). First, a 4-NT pulse was injected together with KCl, followed by the injection of pristine groundwater. The groundwater transport of 4-NT and electrolytes was monitored at a distance of 3.8 m through an extraction well.

The breakthrough of 4-NT occurred about 2 days after the breakthrough of the conductivity pulse (chloride) due to sorption of 4-NT to the aquifer matrix. The apparent average retardation factor of 4-NT relative to the chloride breakthrough was $R = 1.8$, corresponding to an average sorption coefficient of about 0.2 L/kg. The retardation factor of 4-NT was calculated as the ratio of the weighted travel times, t', of the observed chloride and 4-NT pulses in the extraction well (*39*)

$$R = \frac{t'(\text{4-NT})}{t'(\text{KCl})} \tag{1}$$

The travel times, t', were determined according to eq 2

$$t' = \frac{\sum_{i=0}^{J}(c_i \cdot \Delta t_i)}{\sum_{i=0}^{J}(c_i)} \tag{2}$$

where c_i is the aqueous solute concentration at the sampling time t_i.

The recovery, F, of 4-NT in the extraction well after the first part of the injection experiment ($t = 15$ days) was 28%. F was calculated from the observed breakthrough curves of 4-NT and chloride (measured as conductivity) at the monitoring well, as the ratio of the (calculated) solute mass centers of the pulses

$$F = \frac{\sum_{i=0}^{J}(c_i(\text{4-NT}) \cdot \Delta t_i \cdot Q_i)}{\sum_{i=0}^{J}(c_i(\text{Cl}^-) \cdot \Delta t_i \cdot Q_i)} \tag{3}$$

with Q_i being the average groundwater flow rate at the extraction well at time t_i.

The second part of the injection experiment was started at day 15 with the injection of a $CaCl_2$ pulse (right-hand panels in Figure 4), after 4-NT concentrations in the extraction well dropped below the quantification limit of 1 μg/L. The goal of this second part of the field test was to evaluate if and to what extent sorbed 4-NT could be remobilized by exchanging weakly hydrated cations (K^+) at clays by strongly hydrated cations (Ca^{2+}). Two days after the injection of the $CaCl_2$ pulse, simultaneous breakthrough of conductivity and 4-NT occurred at the extraction well. Thus, the stimulated Ca/K ion exchange at clays of the aquifer matrix resulted in desorption and quasiconservative transport of 4-NT. This result suggests that sorption of 4-NT at the aquifer matrix was primarily due to EDA complex formation with clays, since other potential sorption mechanisms of 4-NT are not affected by Ca/K ion exchange. The plateau of the remobilized 4-NT pulse lasted for about 8 days. Eleven days after the $CaCl_2$ injection, an additional 17% of the total mass of injected 4-NT was recovered. Thereafter, the concentration of 4-NT in the injection well dropped to values close to the quan-

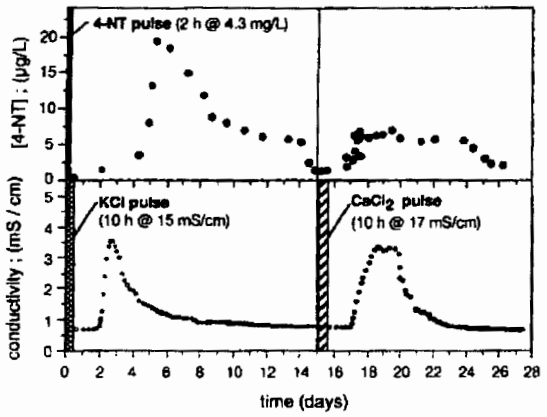

FIGURE 4. Field test conducted at the Elsnig aquifer to evaluate the effects of induced cation exchange by electrolyte injection to retard (KCl) and mobilize ($CaCl_2$) NACs at contaminated sites. The solute breakthrough curves were measured at a distance of 3.8 m downstream of the injection well (pH = 7.1, T = 10 °C).

tification limit of about 1 µg/L. The overall recovery of 4-NT 26 days after the compound's injection was 45%. Note that, toward the end of our field measurements, desorption of 4-NT was not supported any longer by elevated Ca^{2+} concentrations, and EDA complex formation at clays increased due to the higher K/Ca ratio of the pristine groundwater. The tailing of the 4-NT pulse suggests that the desorption of 4-NT continued after day 26. This slowly eluting fraction of 4-NT, which could not be quantified by the analytical technique used, is expected to contribute significantly to the missing fraction of the 4-NT mass balance. It should further be noted that, for practical reasons, we have chosen 4-NT as a relatively weakly sorbing NAC to be used in this field study. Polynitroaromatic compounds such as TNT or 1,3-DNB exhibit a much higher affinity for clay minerals and thus are more susceptible than 4-NT to mobilization due to induced cation exchange (see below and Table 1).

Effect of Induced Cation Exchange on Sorption of TNT and 1,3-DNB. To evaluate the applicability of induced cation exchange to control the mobility of strongly sorbing NACs such as the explosives TNT and 1,3-DNB, we complemented the results of the field injection experiment with laboratory batch sorption studies using samples of the Elsnig aquifer matrix as sorbents. To distinguish between the different potential adsorption mechanisms of NACs we used solute probes with complementary sorption properties. In addition to TNT and 1,3-DNB, which both exhibit a high tendency to form EDA complexes, *p*-cresol was used to quantify hydrophobic partitioning to the sediments. The two NACs used exhibit quite similar hydrophobicities as *p*-cresol (log K_{ow} =1.92), which does not form EDA complexes. Since (only) EDA adsorption of NACs is affected by the types of exchangeable cations present at clays (*13, 19*), a comparison of sorption at native sediments with sorption in the presence of KCl or $CaCl_2$ background electrolytes is indicative to what extent EDA complexes contribute to the overall sorption of NACs at the aquifer matrix.

Adsorption isotherms of TNT and 1,3-DNB were nonlinear and of saturation type, similar to isotherms obtained in suspensions of pure clays minerals. The general shape of the isotherms could be described satisfactorily by a Langmuir equation, but the adsorption affinity at low surface concentrations was underestimated by this approach. At very low surface concentrations of NACs, the isotherms were quasilinear. For this concentration range, we calculated adsorption constants, K_d, from the slope of the isotherms.

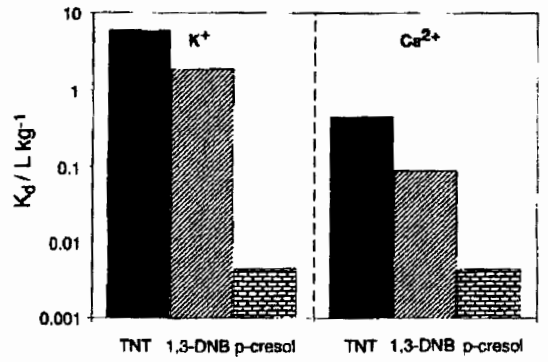

FIGURE 5. Effects of background electrolyte (KCl or $CaCl_2$) on the adsorption to Elsnig aquifer sediment in aqueous suspension of the explosives 1,3,5-trinitrotoluene and 1,3-dinitrobenzene and of a reference compound of similar hydrophobicity (*p*-cresol) (I = 0.1 M, pH = 6.5, T = 21 °C).

The K_d-value for the K^+-homoionized aquifer matrix of TNT was five times higher than that of 1,3-DNB, reflecting the differences in electron acceptor properties of these compounds (*14*). A similar ratio of K_d-values of TNT and 1,3-DNB was found for different types of K^+-homoionized clay minerals (Figure 2 and ref *11*). These results confirm that in the presence of weakly hydrated cations the overall adsorption of NACs to the Elsnig aquifer matrix was governed by EDA complex formation with clays rather than by other sorption mechanisms. K_d-values of *p*-cresol for these samples were very low, confirming that hydrophobic partitioning to this matrix was negligible.

Effect of Exchangeable Cations and Background Electrolytes. Figure 5 shows K_d-values of TNT and 1,3-DNB for untreated (i.e., not previously homoionized) aquifer matrix in the presence of 0.1 M KCl and $CaCl_2$ electrolytes, respectively. For both NACs, K_d-values in the presence of KCl were 1 order of magnitude greater than in the presence of $CaCl_2$. This is consistent with the effects of exchangeable cations found at pure clays (*11*) and in the field injection experiment (see above) and adds further evidence to our interpretation that sorption of NACs at the Elsnig aquifer matrix is dominated by EDA interactions with clays. Note that K_d-values of NACs at K^+-homoionized sediments were significantly higher than K_d-values for untreated sediments in the presence of 0.1 M KCl background electrolyte (*29*). Apparently, at untreated samples strongly hydrated cations such as Na^+, Ca^{2+}, or Mg^{2+} that were not completely exchanged by K^+ decreased the adsorption of NACs.

The sorption of TNT was very low when the native aquifer matrix was suspended in 0.1 M $CaCl_2$ (right panel in Figure 5). The K_d-values of TNT for untreated aquifer matrix suspended in KCl and $CaCl_2$ electrolytes were 4−5 times higher than the respective K_d of 1,3-DNB, as observed for K^+-homoionized material (data not shown) as well as for pure clays. This suggests that at native aquifer material samples and even after equilibration in 0.1 M $CaCl_2$ electrolyte, a small fraction of the sorption sites at clays remain available for EDA complex formation, consistent with the tailing of the 4-NT pulse observed at the end of the field experiment.

At Ca^{2+}-homoionized aquifer samples the K_d-values of TNT and 1,3-DNB were lowest, only half of those obtained with native aquifer matrix suspended in 0.1 M $CaCl_2$. Apparently, the small number of available sorption sites for EDA interactions present in native sediments which were suspended in $CaCl_2$ could be decreased further by Ca^{2+} homoionization of the aquifer matrix. The K_d-value for TNT at Ca^{2+}-homoionic soil matrix was similar to the K_d of *p*-cresol,

thus EDA complex formation at clays was *completely* suppressed only under such drastic conditions.

Practical Applications

Our study demonstrates that the cation composition at clay minerals is crucial for assessing the sorption and mobility of NACs at typical groundwater conditions. The observed effects of NAC substituents and the influence of exchangeable cations on the adsorption of NACs to the Elsnig aquifer matrix are fully consistent with the adsorption features of NACs in suspensions of pure clay minerals. Thus, mechanistic information obtained in clay mineral suspensions proved to be useful to interpret the sorption behavior and also to control the mobility of NACs in natural porous media. In practice, the presented results have implications for the development and application of new technologies in several areas of environmental engineering. Here, we will briefly address two fields of application which are currently under development or are being applied.

First, the effect of background electrolytes on the sorption of NACs in porous media gives rise to novel approaches for the treatment of sites contaminated with nitroaromatic contaminants such as explosives and their by- and degradation products. Enhanced release of adsorbed NACs from contaminated sediments may be desirable in the case of ex-situ treatment of the sediments or for in-situ pump and treat or funnel and gate remediation schemes (see, e.g., ref *40*). In such situations, the fraction of NACs in the mobile phase and thus their groundwater transport as well as their availability for microbial and chemical transformations (*41*) may be enhanced by the exchange of (naturally adsorbed) K^+ cations by strongly hydrated cations such as Na^+ or Ca^{2+}. Conversely, immobilization of NACs due to enhanced adsorption may be considered to secure groundwater wells and to gain time for further evaluation of the contaminated sites. In those situations injection of, e.g., KCl electrolytes into an aquifer may significantly enhance the adsorption of NACs. Our results further suggest that the efficiency of electrolyte injections to mobilize or retard NACs depends on the ionic strength of the groundwater. Since changes in the K^+-saturation affect the sorption properties of clays to a higher degree at low and medium ionic strength, enhanced retardation of NACs by KCl injections would be favorable under such conditions. Conversely, NACs should be mobilized most efficiently at higher ionic strength by injection and/or in the presence of strongly hydrated cations. Due to the peculiar subsurface chemistry of NACs, common practices used to mobilize organic groundwater contaminants, e.g., by the injection of surfactants, may be ineffective for such compounds.

Second, the effect of exchangeable cations on the sorption of NACs at clays can be exploited in environmental analytical chemistry. A novel solid phase material for highly selective extraction and enrichment of NACs and other organic π-acceptors from natural waters has recently been developed, consisting of spherical aggregates of clay minerals (*42*). Enrichment of analytes occurs in the presence of weakly hydrated cations; desorption is performed in a mixture of $CaCl_2$ and acetonitrile. Spherical clay aggregates also have a potential to be used as stationary phase in HPLC (*42*). Retention of π-acceptor solutes by EDA interactions at such materials can serve as an orthogonal separation mechanism to be used for compound identification.

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