

Specific Adsorption of Nitroaromatic Explosives and Pesticides to Clay Minerals

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It is demonstrated that nitroaromatic compounds (NACs) may adsorb specifically and reversibly to natural clay minerals in aqueous suspension. Adsorption of NACs to clays is high when the exchangeable cations at the clays include K^+ or NH_4^+ but is negligibly small for homoionic Na^+ , Ca^{2+} , Mg^{2+} , and Al^{3+} -clays. Highest adsorption coefficients (K_d values up to 60 000 L kg^{-1}) are found for polynitroaromatic compounds including some important contaminants such as explosives (e.g., trinitrotoluene, trinitrobenzene, dinitrotoluidines) and dinitrophenol herbicides (e.g., DNOC, DINOSEB). Nonaromatic nitro compounds (e.g., RDX) generally exhibit very low K_d values. The specific adsorption of NACs can be rationalized by electron donor-acceptor (EDA) complex formation with oxygens present at the external siloxane surface(s) of clay minerals. K_d values of a given NAC and clay mineral can be estimated from known K_d values of other NACs, even when measured at other clay minerals. The affinity and the adsorption capacity of the clays for NACs increase in the order kaolinite < illite < montmorillonite. Thus, clay minerals, depending on their abundance and degree of K^+ - (or NH_4^+) saturation, may control the phase distribution and thus the mobility and (bio)availability of NACs in soils and aquifers. Implications of the results with respect to remediation measures at contaminated sites are discussed.

Introduction

Nitroaromatic compounds are widely used as pesticides, explosives, solvents, and intermediates in the synthesis of dyes and other high volume chemicals (1, 2). Many of these compounds and their transformation products are of significant toxicological concern (3, 4). NACs are ubiquitous environmental pollutants, particularly in subsurface environments (5). Contamination of soils and groundwaters with nitroaromatic munitions residues such as 2,4,6-trinitrotoluene (TNT) and other nitro- and aminonitro-

toluenes has recently drawn considerable public attention due to the high number of contaminated sites and the substantial efforts necessary for ongoing and future remediation measures (6, 7).

In order to assess the fate of NACs in the subsurface and to control their mobility and reactivity during remediation processes, the sorption behavior of these compounds must be understood. Partitioning of organic pollutants into particulate organic matter is commonly assumed to be the major sorption mechanism for solid matrices exhibiting an appreciable fraction of organic matter (i.e., $f_{om} > 10^{-3} kg_{om}/kg_{solid}$), particularly when dealing with hydrophobic compounds (8-12). In such cases, predictive sorption and transport models have been applied with reasonable success (8, 13, 14). There are, however, situations where adsorption to other natural surfaces may also become important or may even dominate the overall sorption process. This is the case for environments where very little organic material is present, e.g., in many aquifers (15-19), and for compounds that may specifically adsorb to surface sites of natural minerals (20-22).

In previous work (23, 24), we have demonstrated that NACs, particularly those exhibiting several nitro groups or other electron-withdrawing substituents that are in resonance with the aromatic ring, may adsorb specifically and reversibly to the siloxane surface of the clay mineral kaolinite, but not to other natural minerals including aluminum and iron (hydr)oxides, carbonates, and quartz. It was found that the affinity of a given NAC strongly depends on the type of exchangeable cation(s) adsorbed to the siloxane surface of kaolinite. Significant adsorption of NACs was observed in the presence of weakly hydrated cations (i.e., Cs^+ , Rb^+ , K^+ , or NH_4^+), while strongly hydrated cations such as H^+ , Na^+ , Ca^{2+} , Mg^{2+} , or Al^{3+} prevented any specific interaction. The specific adsorption of NACs to kaolinite was interpreted in terms of coplanar electron donor-acceptor (EDA) formation (i.e., $\eta \rightarrow \pi$ -complex interactions) with oxygen ligands at the external siloxane surface of kaolinite as e^- -donors and the π -system of the NACs as e^- -acceptor. The strong impact of exchangeable cations on the adsorption of NACs indicates that these sites are only accessible for NACs in the presence of weakly hydrated cations that fit into the ditrigonal cavities of the siloxane surface. We have concluded that in the presence of adsorbed K^+ or NH_4^+ , such sites may represent important surfaces for the adsorption of NACs in soils and aquifers.

In the study presented in this paper, the work on NAC adsorption to kaolinite has been extended to other clay minerals and to environmentally more relevant nitroaromatic compounds. The major goals were to evaluate to what extent the postulated EDA complex formation is a general phenomenon and to assess the significance of this sorption mechanism for a variety of important NACs. To this end, the sorption of a series of nitroaromatic explosives and pesticides from aqueous solution to various natural clay minerals has been investigated in batch experiments in the presence of K^+ , Na^+ , or Ca^{2+} -electrolytes. The clay minerals used were kaolinite, illite, and montmorillonite. The compounds investigated included neutral and ionizable NACs, e.g., TNT and related compounds (i.e., dinitrotoluenes and various aminonitrotoluenes), alkylated dinitro-

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TABLE 1

Names, Abbreviations, Suppliers, UV/vis Absorption Maxima, Extinction Coefficients, Acidity Constants, n-Octanol/Water Partition Constants, and Adsorption Constants (K_d Values) for Monoionic K^+ -Montmorillonite of the Compounds Investigated

compd	abbrevn	supplier	λ_{max} (nm)	ϵ_{max} ($M^{-1} cm^{-1}$)	pK_a	log K_{ow}	K_d (K^+ -mont.) (L kg^{-1})
1,3,5-trinitrobenzene	TNB	d	227	25 000	—	1.18 ^k	>60000
2,4,6-trinitrotoluene	TNT	d	225	18 000	—	1.86 ^m	21500
N,2,4,6-tetranitro-N-methylaniline	TETRYL	d	227	23 000	nd	1.65 ^o	5.8
1,3,5-trinitro-hexahydro-1,3,5-triazine	RDX	d	236	11 000	—	0.87 ^m	1.2
2,4-dinitrotoluene	2,4-DNT	e	252	14 000	—	1.98 ^k	7400
2,6-dinitrotoluene	2,6-DNT	e	241	10 000	—	2.02 ^k	125
2-nitrotoluene	2-NT	e	265	5800	—	2.30 ^k	4.6
3-nitrotoluene	3-NT	e	273	7200	—	2.42 ^k	21
4-nitrotoluene	4-NT	e	285	9700	—	2.40 ^k	45
2-amino-4,6-dinitrotoluene	2-A-4,6-DNT	f	211	20 000	0.36 ⁿ	0.9 ^r	2900
4-amino-2,6-dinitrotoluene	4-A-2,6-DNT	f	215	17 000	0.95 ⁿ	0.9 ^r	125
2,6-diamino-4-nitrotoluene	2,6-DA-4-NT	f	210	28 000	2.54 ⁿ	-1.1 ^r	11
2,4-diamino-6-nitrotoluene	2,4-DA-6-NT	f	211	32 000	3.13 ⁿ	-1.1 ^r	3.5
2-nitroaniline	2-NA	e	224	11 000	1.02 ^p	1.82 ^k	8.4
3-nitroaniline	3-NA	e	225	14 000	2.47 ^p	1.37 ^k	3.5
4-nitroaniline	4-NA	e	369	13 000	-0.34 ^p	1.39 ^k	13.5
2,4-dinitro-6-methylphenol	DNOC	e	269	14 000	4.31 ⁱ	2.12 ^j	37000
2,6-dinitro-4-methylphenol	2,6-DNOC	a	253	8600	4.06 ⁱ	1.78 ^j	19000
2,4-dinitro-6-tert-butylphenol	DINOTERB	g	271	5600	5.32 ⁱ	3.54 ^k	28
2,4-dinitro-6-sec-butylphenol	DINOSEB	g	271	11 000	4.62 ⁱ	3.59 ^k	64
2,4-dinitro-6-sec-butylphenylmethyl ether	DINOSEB-ME	c	256	14 000	—	4.24 ⁱ	17
2,4-dinitro-6-sec-butylphenyl acetate	DINOSEB-AC	c	248	13 000	—	3.62 ⁱ	2.9
2-nitrophenol	2-NP	e	278	6300	7.23 ^{ij}	1.89 ^j	45
O,O-diethyl-O-(4-nitrophenyl) monothiophosphate	parathion	f	272	1100	—	3.81 ^k	9.6
O,O-dimethyl-O-(4-nitrophenyl) monothiophosphate	Me-parathion	h	271	8500	—	2.99 ^k	6.2
(trifluoromethyl)-2,6-dinitro-N,N'-dipropylaniline	trifluraline	b	272	7600	nd	3.06 ^k	8.1
(methylsulfonyl)-2,6-dinitro-N,N'-dipropylaniline	nitraline	c	285	9900	nd	2.65 ^k	3.0
nitrobenzene	NB	a	267	7600	—	1.84 ^k	7.2
1,2-dinitrobenzene	1,2-DNB	e	256	>10 000	—	1.58 ^k	4.2
1,3-dinitrobenzene	1,3-DNB	e	242	>10 000	—	1.49 ^k	4500
1,4-dinitrobenzene	1,4-DNB	a	264	>10 000	—	1.48 ^k	3100

^a Aldrich Chemical Co. (Steinheim, D). ^b Chemicals Service, (West Chester, PA). ^c Dr. Ehrendorfer (Augsburg, D). ^d Ems Chemie (Dottikon, CH). ^e Fluka AG (Buchs, CH). ^f Promochem (Wesel, D). ^g Riedel de Haen (Seelze, D). ^h Supelco Inc. (Bellefonte, PA). ⁱ Reference 39. ^j Reference 40. ^k Reference 41. ^l Reference 42. ^m Reference 2. ⁿ Reference 43. ^o Reference 44. ^p Estimated using the Hammett relationship (see, e.g., ref 21). ^r Estimated from K_{ow} (TNT) using π -constants given in ref 41.

TABLE 2

Properties of the Clay Minerals Investigated

clay mineral	origin	f_{oc} ($g g^{-1}$)	CEC ($mol kg^{-1}$)	surface area total ^a /external ^b ($m^2 g^{-1}$)	external siloxane surface area ($m^2 g^{-1}$)	NAC isotherms: linear range/adsorption capacity ($\mu mol kg^{-1}$)
kaolinite	Cornwall, U.K.	0.6×10^{-3}	0.3	12/12	4.8 ^c	120/6 $\times 10^3$
illite	Tokay, H	1.2×10^{-3}	1.6	70/35	26 ^d	800/25 $\times 10^3$
montmorillonite	Arizona	1.1×10^{-3}	12	820/95	71 ^d	1500/180 $\times 10^3$

^a Total surface area accessible for H₂O or glycol. ^b Surface area accessible for N₂. ^c Reference 45. ^d Assuming that the basal planes account for 75% of the external surface area.

phenol herbicides (e.g., DNOC, DINOSEB, and DINOT-ERB), and thiophosphate nitrophenyl esters (i.e., parathion and methylparathion). The results presented are novel from a basic scientific point of view and of direct practical use since they provide a basis for understanding and quantifying the sorption and thus the mobility and bioavailability (25) of many relevant NACs in the environment.

Experimental Section

Chemicals. The nitroaromatic compounds used in this study are listed in Table 1 together with abbreviations, suppliers, and important physical-chemical properties. The

NACs were used as received. No significant impurities were found by HPLC-UV analysis (see below). Inorganic chemicals were purchased from E. Merck AG (Dietikon, CH). All chemicals had the highest purity available ($\geq 97\%$) and were used without further purification.

Clay Mineral Sorbents. Some pertinent properties of the clay minerals used as sorbents are given in Table 2. A more comprehensive characterization of these sorbents can be found in ref 26. Kaolinite was chosen to represent nonexpandable two-layer clay minerals. Illite and montmorillonite were chosen to represent weakly and strongly expandable three-layer clay minerals, respectively. In

contrast to kaolinite, the interlamellar siloxane surfaces of these clays are (partly) accessible for cation exchange. The other surface functional groups of illite and montmorillonite minerals are comparable to those of kaolinite except for the lack of basal aluminol groups.

Due to isomorphous substitution of structural Si^{4+} and/or Al^{3+} cations by lower valent cations, clay minerals bear a permanent (i.e., pH invariant) excess of negative charge and, therefore, are cation exchangers. In order to obtain homoionic clays, the naturally adsorbed cations were exchanged by the desired cation(s) by two alternative methods: The clays were repeatedly washed (i.e., suspended and centrifuged) with 0.1 M aqueous solutions of Cl^- -salts of the desired cation(s). Excess electrolyte was removed by dialysis or repeated washes with distilled water. Alternatively, the clay minerals in their native forms were equilibrated with an excess of homoionic cation exchange resin in aqueous suspension at pH 6. The exchange resin was separated from the clay minerals by sieving. The resulting homoionic clays were air-dried at 50 °C, and their cation exchange capacity (CEC) was determined (exchange with 0.2 M BaCl_2 at pH 4 and/or with 0.1 M HNO_3).

Both methods gave similar results with respect to cation exchange and adsorption of NACs. K_d values of NACs (see eq 2) for various preparations of a given clay were reproducible within 10%.

Sorption Experiments. Sorption experiments were performed according to ref 23. Borosilicate glass vials (1.8 mL, Supelco SA, Gland, Switzerland) with aluminum foil liners and septum screw caps (Supelco) were used in batch experiments. Stock solutions of the solutes (0.1 M) in methanol or acetonitrile (if poorly soluble in methanol) were kept refrigerated for further dilution in double-distilled water. Initial aqueous concentrations of NACs ranged from 0.1 μM up to 50% of aqueous solubility. NACs were diluted from stock solutions prepared in organic solvents; aqueous concentrations of these organic cosolvents never exceeded 0.5% (v/v) in the sorption experiments. Methanol or acetonitrile cosolvents up to 1% (v/v) had no measurable effect on the adsorption of NACs in clay mineral suspensions. Aqueous solutions of NACs in background electrolyte were spiked to known quantities of air-dried homoionic clay minerals. These suspensions were shaken in the dark on a rotary shaker at 30 rpm until thermal and sorption equilibrium were attained. Unless indicated otherwise, the equilibration time was 30–60 min, the background electrolyte was KCl, NaCl, or CaCl_2 , respectively, and the temperature was maintained at 21 ± 1.5 °C. Phase separation was achieved by centrifugation at 12 000 rpm for 1 min. Particle concentrations in the clay suspensions ranged from 5 to 200 g of solids L^{-1} depending on the extent of adsorption of the various NACs investigated. The effect of varying particle concentrations on the adsorption isotherms of NACs was found to be insignificant. The pH of the suspensions was 6.0 ± 0.5 unless indicated otherwise. If necessary, the pH was adjusted without buffers only by addition of diluted acid or base. The pH in suspension agreed well (± 0.1 pH) with the pH measured in the supernatant. Blank samples containing spike solutions of NACs but no sorbents were processed in the same way as the suspension samples and were used as external standards in the HPLC analysis. This accounted for the minor losses of NACs (<2%) during the experimental procedure.

Mass balances on the clay suspensions were determined for selected NACs by either extracting the solid phase with acetonitrile and/or desorbing the NACs by exchanging adsorbed K^+ by Ca^{2+} (see Results and Discussion). Since mass balance measurements showed very good recoveries (85–100%, see below), sorbed concentrations of the NACs were routinely calculated from the difference in aqueous initial and equilibrium concentrations. Individual points of the sorption isotherms were determined from two or three replicates (sample and blanks). Standard deviations for the sorbed concentrations as well as for the distribution coefficients, K_d (see eq 2), were calculated with the linear error propagation method. Standard deviations of K_d values within individual adsorption experiments and from day to day were typically in the order of 3–8%.

HPLC Analysis. Aqueous NAC concentrations were determined by direct injection of aqueous samples on a reversed phase HPLC system equipped with UV/vis detection at the wavelength of maximum absorption for each NAC (columns: RP-8 or RP-18 stainless steel cartridges, 4×125 mm, 5 μm spheres, Merck (Frankfurt, Germany), injection volume 5–100 μL , syringe injection into a Rheodyne valve manually or by auto sampler (Gynkotek Gina 50)). The mobile phase was a mixture of methanol/water for the neutral compounds and methanol/water containing 10% of 0.01 M phosphate buffer, titrated to pH 2.5 for the analysis of the substituted phenols (ion suppression chromatography). Methanol/water ratios ranged from 1:1 (v/v) to 4:1 (v/v) in order to obtain capacity factors of the analytes between 2 and 5. The flow rate was 0.5–1.5 mL min^{-1} . Calibration by external standards was linear in the range from 5×10^{-12} to 2×10^{-9} mol of NAC injected. The precision of the HPLC method was typically 2

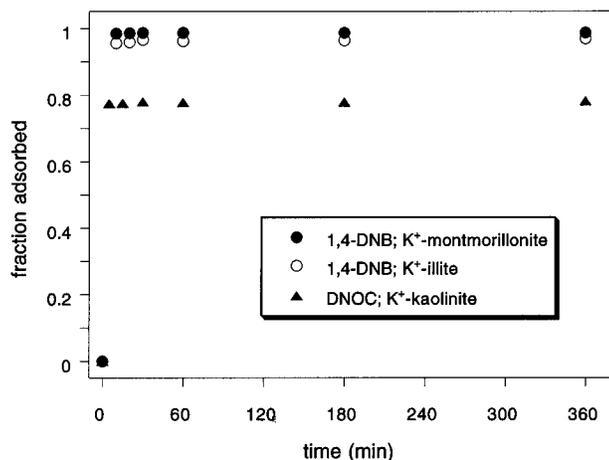


FIGURE 1. Typical examples of the adsorption kinetics of NACs in aqueous suspensions of clay minerals ($I = 0.01$ M KCl; pH = 6.5 for 1,4-DNB and 2.5 for DNOC).

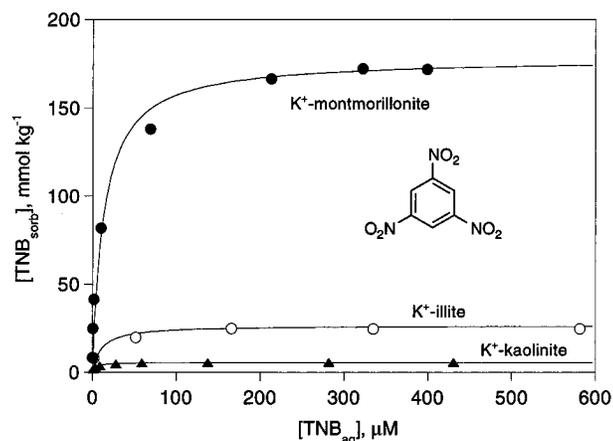


FIGURE 2. Adsorption isotherms of the explosive TNB measured in aqueous suspensions of homoionic K^+ -clays (●, K^+ -montmorillonite; ○, K^+ -illite; ▲, K^+ -kaolinite; solid lines represent Langmuir isotherms (eq 1)).

the NACs adsorb primarily at easily accessible external surface sites of the clays.

Adsorption Isotherms. Figure 2 shows a representative example of the type of adsorption isotherms obtained for strongly adsorbing NACs in aqueous suspensions of homoionic K^+ -clay minerals. Shown are results for the explosive 1,3,5-trinitrobenzene. The isotherms are convexly shaped and converge to a saturation level. The adsorption capacities, $[TNB_{sorb}]_{max}$ (mol kg^{-1}), increase in the order $[TNB_{sorb}]_{max}(\text{kaolinite}) < [TNB_{sorb}]_{max}(\text{illite}) < [TNB_{sorb}]_{max}(\text{montmorillonite})$. Qualitatively, very similar results were obtained for all NACs investigated. The adsorption capacities of a given K^+ -clay were very similar for NACs that adsorbed strongly enough to measure $[NAC_{sorb}]_{max}$. The $[NAC_{sorb}]_{max}$ values reported in Table 2 correspond (within a factor of 2) with adsorption capacities calculated for monolayer coverage and coplanar orientation of the NACs at the external siloxane surface(s) of the clays.

The shape of the isotherms can be approximated by a Langmuir equation

$$[NAC_{sorb}] = \frac{K_L [NAC_{aq}]}{1 + K_L [NAC_{aq}]} [NAC_{sorb}]_{max} \quad (1)$$

where $[NAC_{aq}]$ (mol L^{-1}) and $[NAC_{sorb}]$ (mol kg^{-1}) are the concentrations of NACs in aqueous solution and at the

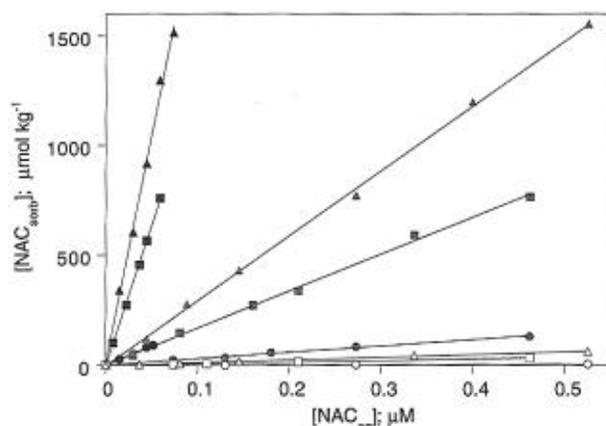


FIGURE 3. Representative examples of the linear range of adsorption isotherms of NACs for homoionic K^+ -clays at low surface coverage (triangles, montmorillonite; squares, illite; dots, kaolinite; black symbols, TNT; gray symbols, 2-A-4,6-DNT; open symbols, 4-A-2,6-DNT).

clay, respectively. K_L (L mol^{-1}) denotes the Langmuir affinity constant. However, as already discussed elsewhere (23), at low concentrations of $[NAC_{sorb}]$ the Langmuir fit generally underestimates the extend of adsorption of TNB and other NACs.

At low surface coverage, i.e., for $[NAC_{sorb}] \leq 3-5\%$ of $[NAC_{sorb}]_{max}$, the isotherms were quasilinear as is illustrated by Figure 3 for various NACs and K^+ -clays. In this range of the isotherms, an adsorption constant, K_d (L kg^{-1}), i.e., the slope of the linear isotherms, can be used to describe the affinity of a given NAC to the clay mineral surface:

$$K_d = \frac{[NAC_{sorb}]}{[NAC_{aq}]} \quad (2)$$

As can be seen from the data presented in Table 3, similar to the adsorption capacities, $[NAC_{sorb}]_{max}$, the adsorption constants, K_d , of a given NAC at homoionic K^+ -clays increase in the order $K_d(\text{kaolinite}) < K_d(\text{illite}) < K_d(\text{montmorillonite})$. The following discussion on environment and compound specific factors that affect the adsorption of NACs to clay minerals will primarily be based on comparisons of K_d values of NACs measured in the quasilinear part of their adsorption isotherms.

Effect of pH on K_d . The effect of pH on the adsorption of NACs on clays was studied for neutral and ionizable NACs. Figure 4 shows adsorption edges (i.e., K_d values as a function of pH) of 1,4-DNB and of 5-methyl-2-nitrophenol (5-Me-2NP) obtained in suspensions of homoionic K^+ -illite and K^+ -montmorillonite. Similar results were obtained for K^+ -kaolinite and for other NACs (28). For neutral NACs such as 1,4-DNB, the K_d values are constant between pH 3 and 9. In contrast, for ionizable NACs such as the nitrophenols, a strong pH-dependence of the apparent K_d values was observed in the pH region corresponding to the pK_a of the compound (HA). As is illustrated by the solid lines in Figure 4, the pH-dependence of the apparent K_d values of substituted nitrophenols can be modeled satisfactorily when assuming that adsorption of the phenoxide species (A^-) is negligibly small and that the K_d value of the nondissociated species, (K_d^{HA}), is constant over the pH range considered

$$K_d(\text{pH}) = \alpha_0 K_d^{HA} \quad (3)$$

where α_0 is the fraction of the nondissociated species and

TABLE 3

Comparison of Adsorption Constants (K_d Values) of Nitroaromatic Munitions Residues and Dinitrophenol Herbicides for Homoionic K^+ -Clay Minerals

compd	K_d ($L\ kg^{-1}$)			K_d normalized to kaolinite			K_d normalized to nitrobenzene		
	K^+ -Kao.	K^+ -Illite	K^+ -Mont.	K^+ -Kao	K^+ -Illite	K^+ -Mont.	K^+ -Kao.	K^+ -Illite	K^+ -Mont.
nitrobenzene (NB)	0.6	3.5	7.2	1.0	5.8	12.0	1.0	1.0	1.0
TNT	1800	12 500	21 500	1.0	6.9	11.9	3000	3571	2986
1,2-DNB	0.4	2.5	4.2	1.0	5.8	9.8	0.7	0.7	0.6
1,4-DNB	188	1460	3100	1.0	7.8	16.5	313	417	431
2,4-DNT	690	3650	7400	1.0	5.3	10.7	1150	1043	1028
2,6-DNT	10	52	125	1.0	5.2	12.5	17	15	17
2-NT	0.3	2.7	4.6	1.0	9.0	15.3	0.5	0.8	0.6
3-NT	2.5	13	21	1.0	5.2	8.4	4.2	3.7	2.9
4-NT	4.9	24	45	1.0	4.9	9.2	8.2	6.9	6.3
2-A-4,6-DNT	300	1700	2900	1.0	5.7	9.7	500	486	403
4-A-2,6-DNT	11	70	125	1.0	6.4	11.4	18	20	17
2,6-DA-4-NT	1.1	7	10.5	1.0	6.4	9.5	1.8	2.0	1.5
DNOC	2700	16 000	37 000	1.0	5.9	13.7	4500	4571	5139
DINOSEB	6.4	nd	64	1.0	nd	10.0	10.7	nd	8.9
avg K_d				1.0	6.2 ± 1.2	11.5 ± 2.4			

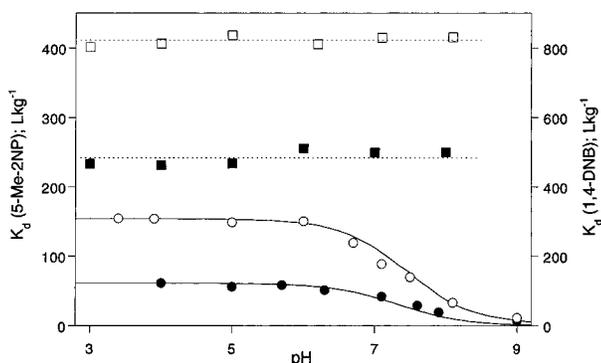


FIGURE 4. pH dependence of the adsorption of NACs in suspensions of homoionic K^+ -illite (filled symbols) and K^+ -montmorillonite (open symbols) represented by 1,4-DNB (squares) and 5-Me-2NP ($pK_a = 7.34$; dots). The solid lines represent eq 3. Experiments were performed within the linear range of the adsorption isotherms.

is given by

$$\alpha_0 = \frac{1}{1 + 10^{(pH - pK_a)}} \quad (4)$$

Very similar results with respect to the effect of pH on adsorption of dissociable NACs were obtained for mixed ionic clay suspensions (data not shown). At background electrolyte concentrations ranging from $I = 0.1$ to 100 mM, and for all systems studied including binary exchanged Al^{3+}/K^+ - and Ca^{2+}/K^+ -clay minerals, adsorption of nitrophenoxide species (A^-) or eventual ion pairs ($Me^{n+}(A^-)_m$) was found to be insignificant as compared to the adsorption of the neutral NAC species, HA.

Effect of Exchangeable Cations and Ionic Strength on K_d . Table 4 illustrates the effect of adsorbed cations on the ability of the clays to adsorb NACs. Shown are adsorption constants (K_d values, log scale) of the explosive TNT measured in suspensions of homoionic K^+ - and Ca^{2+} -clay minerals. Obviously, the type of cations adsorbed to clay minerals is a crucial factor that determines their affinity for NACs. For homoionic K^+ -clays, very high adsorption constants were found, whereas the same clays were very poor sorbents when Ca^{2+} (or Na^+ , Mg^{2+} , or Al^{3+} , data not shown) was the exchangeable cation. Similar results were found for other planar NACs (data not shown).

TABLE 4

Adsorption Constants (K_d Values) of TNT for Homoionic K^+ - and Ca^{2+} -Clays as Examples for the Effect of Exchangeable Cations on the Adsorption of NACs to Clay Minerals

clay mineral	K_d ($L\ kg^{-1}$)	
	Ca^{2+} -clay	K^+ -clay
kaolinite	0.3	1800
illite	1.2	12 500
montmorillonite	1.7	21 500

Ionic strength had no measurable effect on the adsorption of NACs to homoionic clay minerals in the range of $10^{-4} M \leq I \leq 10^{-1} M$, i.e., at values that are typical of fresh water systems. Thus, K_d values measured at $I = 0.1 M$ are representative for lower ionic strength and vice versa. However, at higher background electrolyte concentrations, i.e., at $0.1 < I < 1 M$, a significant increase of K_d values with I was observed (data not shown). Most likely, the K^+ -saturation of the clays is more complete at very high ionic strength leading to higher adsorption of NACs. In addition, salting out effects may contribute to increased adsorption of neutral organic compounds at high ionic strength (21).

In order to investigate the kinetics and reversibility of cation exchange and specific adsorption of NACs, experiments were performed where the desorption of NACs from K^+ -clays ($I \leq 10^{-4} M$) was investigated after spiking the suspensions with $CaCl_2$ -electrolytes. Figure 5 shows typical results of such desorption experiments where 1,4-DNB was initially adsorbed to homoionic K^+ -illite and K^+ -montmorillonite. A few minutes after addition of the $CaCl_2$ to the suspensions, desorption of the NACs was almost completed, indicating that both the Ca^{2+}/K^+ ion exchange as well as the actual desorption of the NACs from the clay surfaces were fast processes. After the Ca^{2+}/K^+ ion exchange was at equilibrium, the recoveries of the NACs in the liquid phase were $>95\%$ for the illite and kaolinite (data not shown). Up to 90% recovery was observed for the montmorillonite systems when high $CaCl_2$ concentrations were added. At montmorillonite, a small fraction of NACs may be associated with interlamellar edge sites of the clay and therefore be affected by the relatively slow cation exchange

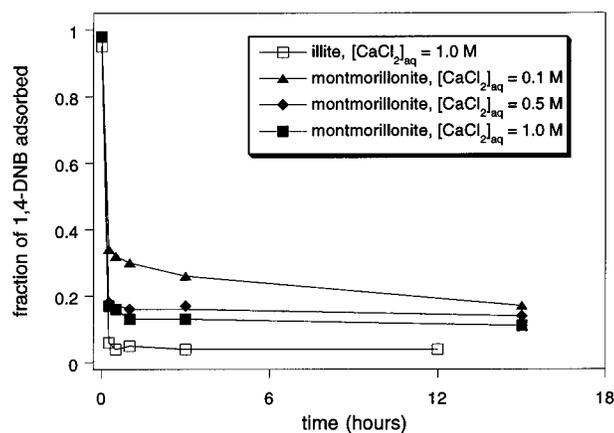


FIGURE 5. Desorption kinetics of 1,4-DNB in aqueous suspensions of K^+ -clays ($I_0 \leq 10^{-4}$ M KCl) after a single spike of $CaCl_2$ electrolyte and subsequent ion exchange of exchangeable K^+ by Ca^{2+} (concentrations have been corrected for dilution).

and swelling kinetics of expandable three-layer clays as compared to illites and kaolinites (29).

Comparison of K_d Values at Different Clay Minerals: Surface Sites Responsible for the Adsorption of NACs. As indicated by the results presented so far and preliminary experiments with further clay minerals including other kaolinites, illites, and montmorillonites as well as nontronite, beidellite, and saponite (30), qualitatively a very similar adsorption pattern was found for all clay minerals. In all cases, NAC adsorption was strongly and consistently affected by the type of exchangeable cations adsorbed to the clay, and for the neutral species, K_d was independent of pH in the range of pH 3–9. Furthermore, the fast and fairly reversible ad- and desorption observed suggests that, irrespective of the type of clay mineral, NAC adsorption takes place primarily at easily accessible external surfaces. The conclusion that similar sites and a similar mechanism are responsible for the specific adsorption of NACs to the different clay minerals is further corroborated by the data summarized in the middle section of Table 3. Shown are normalized K_d values of NACs for three homoionic K^+ -clays scaled to the K_d values of K^+ -kaolinite. The K_d values for the various clay minerals differ by fairly constant factors, i.e., the K_d 's of a given NAC to K^+ -illite and K^+ -montmorillonite are about 6 and 12 times higher, respectively, as compared to K^+ -kaolinite. The surface properties of the clays presented in Table 2 indicate that the surface area of the external siloxane surfaces of the clay minerals differ by very similar factors (kaolinite:illite:montmorillonite = 1:6:16). The constant relative affinities of NACs to the various clay minerals suggest that EDA complex formation to kaolinite postulated in our previous and parallel work (23, 27) seems to be a general phenomena and represents an important mechanism for NAC adsorption in clay-containing environments.

Effect of Substituents on NAC Adsorption.

General Features. Figure 6 shows a plot of $\log n$ -octanol/water partition constants (K_{ow}) versus $\log K_d$ values determined for homoionic K^+ -montmorillonite of the NACs listed in Table 1. Obviously, no correlation between $\log K_d$ and $\log K_{ow}$ values exists, confirming that the hydrophobicity of a given NAC is not a significant factor in determining the specific adsorption of these compounds to clay minerals. This is in contrast to other neutral organic compounds for

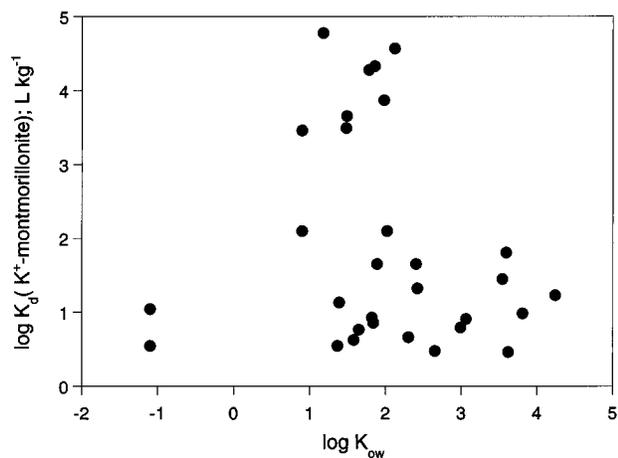


FIGURE 6. Plot of $\log K_d$ values (adsorption constants for K^+ -montmorillonite) versus $\log K_{ow}$ values (n -octanol/water partitioning constants) of the NACs (neutral species) listed in Table 1.

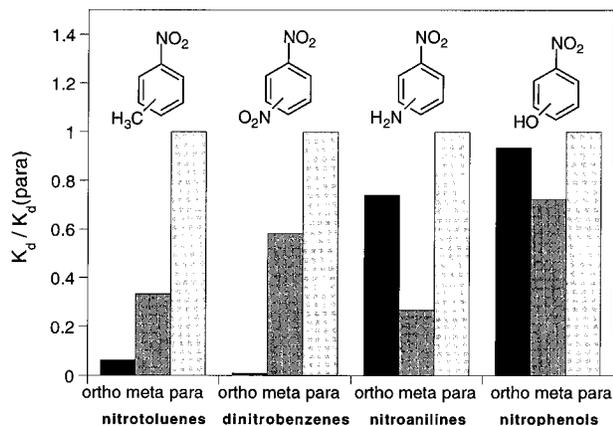


FIGURE 7. Illustration of substituent effects on the specific adsorption of NACs to K^+ -clay minerals for compounds that may/may not form intramolecular H-bonds.

which adsorption to low organic carbon sediments and to mineral surfaces can be attributed primarily to hydrophobic interactions and for which $\log K_d$ parallels $\log K_{ow}$ (16, 31). As is evident from Figure 6, there are differences of about 4 orders of magnitude between K_d values of NACs exhibiting similar K_{ow} values. This clearly indicates that type and position of substituents (i.e., electronic and steric effects) play a pivotal role for the specific adsorption of NACs to the siloxane surface of clay minerals. Figure 7 shows K_d values of isomers of some substituted nitrobenzenes, nitroanilines, and nitrophenols. Within every group of compounds, the K_d values of the isomers are scaled to the K_d of the *para*-isomer. Some distinct substituent effects that can be generalized for all NACs and all K^+ -clays investigated can be seen from these examples: (1) *ortho*-substituents such as alkyl, halogen, or even nitro groups diminish specific adsorption by steric interactions, in that they prevent complete coplanarity and thus optimal resonance of the nitro substituent(s) with the aromatic ring. The strong impact of such *ortho* substituents can further be rationalized when considering that a coplanar spatial arrangement of the acceptor compounds (NACs) and the donor sites (siloxane surfaces of clay minerals) is necessary for strong EDA complex formation (32, 33). In the following, the steric hindrance of *ortho*-substituents will be referred to as "*ortho*-effect". (2) Compounds with substituents that are able to form intramolecular H-bonds with a neighboring NO_2 group

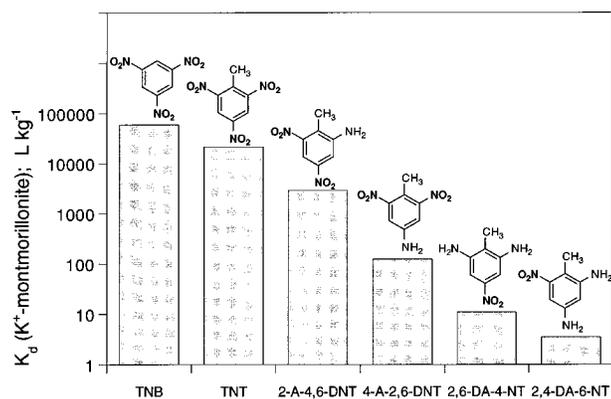
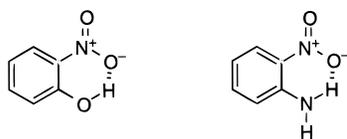


FIGURE 8. K_d values of TNT and TNB and of some common munitions transformation products for K^+ -montmorillonite.

do not show a significant *ortho*-effect. *Ortho*- and *para*-substituted isomers of such NACs have very similar K_d values. Among the various NACs considered, this is the case only for *o*-nitrophenols and *o*-nitroanilines:



(3) Substituents in the position *para* to the NO_2 group (as well as H-donating *ortho*-substituents, see above) generally have a stronger effect on K_d values than *meta*-substituents due to resonance effects.

Explosives and Munitions Residues. Figure 8 compares K_d values for K^+ -montmorillonite of the explosives TNB and TNT and of some of their most important transformation products (6). TNB has the highest K_d value among all NACs investigated since this compound can be considered as the optimal electron acceptor for EDA complexes due to its three electron-withdrawing NO_2 groups and the lack of adverse steric substituent effects. The electronic and steric effects of substituents are also reflected by the K_d values of the reduction products of TNT that are frequently encountered in munitions residues. As can be seen from Figure 8, reduction of an electron-withdrawing nitro group to an electron-donating amino group leads to a marked decrease in K_d . Furthermore, even within isomers (i.e., aminodinitro- and diaminitrotoluenes, respectively) large differences in K_d values are found due to the *ortho*-effect of the methyl group. Thus, the difference of K_d values between TNT and 2,4-diamino-6-nitrotoluene is, for instance, more than 3 orders of magnitude. For the explosive TETRYL the low K_d value found (see Table 1) is due to a combination of both *ortho*- and bulky substituent effects. These examples illustrate that the various compounds commonly present in munitions residues may exhibit very different mobilities and (bio)availabilities in subsurface environments where specific adsorption to clay minerals is a dominant sorption process. In this context, it is interesting to note that nonaromatic polynitro compounds such as RDX (1,3,5-trinitrohexahydro-1,3,5-triazine) do not show any tendency to adsorb specifically to clay minerals (cf. Table 1).

Dinitrophenol Herbicides. Figure 9 compares adsorption constants of a series of substituted dinitrophenol herbicides for K^+ -montmorillonite. All 6-alkyldinitrophenols investigated exhibit significant but quite different K_d

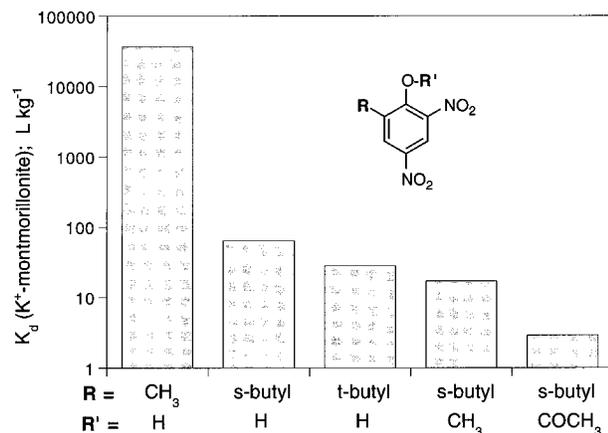


FIGURE 9. Effect of bulky substituents on the specific adsorption of NACs to K^+ -clay minerals illustrated by dinitrophenol herbicides exhibiting branched alkyl substituents.

values. A very high K_d is found for DNOC ($R = -\text{CH}_3$), whereas DINOSEB ($R = \textit{sec}$ -butyl) and DINOTERB ($R = \textit{tert}$ -butyl) have 2–3 orders of magnitude lower K_d values, despite the fact that DINOSEB and DINOTERB are much more hydrophobic than DNOC (see $\log K_{ow}$ values given in Table 1). Since the various alkyl substituents are very similar with respect to their electron-donating properties (33), steric effects must account for the big differences in K_d . Note that *n*-butyl substituents in contrast to branched butyl substituents do not show adverse effects on specific adsorption (23). The large effect of such “bulky substituents” can be rationalized by a steric hindrance of an optimal interaction between e^- -donor sites at the clay surface(s) and the NACs. The low K_d values of DINOSEB methyl ether and DINOSEB acetate shown in Figure 9 result from a superposition of both a bulky substituent effect ($R = \textit{sec}$ -butyl) and an *ortho*-effect ($R' = -\text{CH}_3$ or $-\text{COCH}_3$) at these compounds.

Other Classes of Nitroaromatic Pesticides. Table 1 also contains K_d values of some representative *N,N*-dialkyldinitroanilines and *p*-nitrophenyl thiophosphate herbicides for K^+ -montmorillonite. As is indicated by their relatively low K_d values, these compounds have little tendency to adsorb specifically to clay minerals as compared to nitrotoluene explosives and dinitrophenol herbicides. All of these compounds have bulky substituents and/or substituents *ortho* to the nitro group(s). Thus, the low K_d values of these compounds can be explained by the steric and electronic substituent effects discussed above.

Figure 10 summarizes the effects of structural moieties on the specific adsorption of NACs to clay minerals. The contribution of the specific adsorption to the overall K_d value of a given NAC at K^+ -montmorillonite is illustrated by the difference between $K_d(K^+\text{-montmorillonite})$ and $K_d(\text{Ca}^{2+}\text{-montmorillonite})$. Note that for Ca^{2+} -montmorillonite specific adsorption of NACs is negligible. As is shown, electronic and particularly steric substituent effects may have a tremendous impact on the specific adsorption of NACs to clay surfaces, leading to large differences in K_d , even within classes of structurally closely related compounds.

In conclusion, the various effects of substituents described above with respect to the specific adsorption of NACs to K^+ -clays as well as spectroscopic evidence presented elsewhere (27) are perfectly consistent with EDA complex formation postulated in earlier work for the

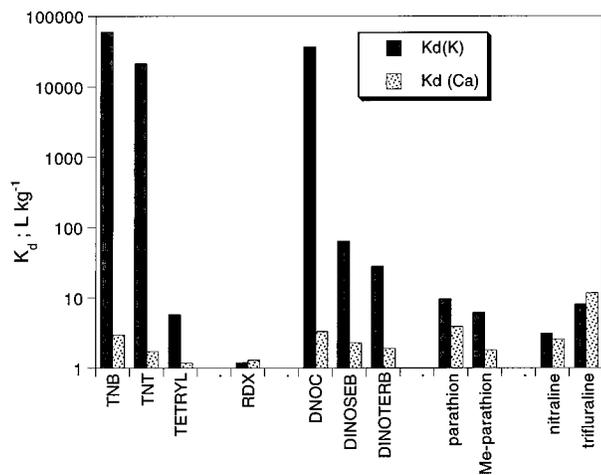


FIGURE 10. K_d values of various NACs for K^+ -montmorillonite and for Ca^{2+} -montmorillonite. The difference between the two K_d values is a measure for the tendency of a given NAC to specifically adsorb to clay minerals.

adsorption of a large number of other NACs to Cs^+ -kaolinite (23, 28). Thus, the principles derived from this model system can also be applied to other NACs and other clay minerals. Table 3 shows a comparison of K_d values of a series of NACs for homoionic K^+ -kaolinite, K^+ -illite, and K^+ -montmorillonite. The K_d values presented in the right column of Table 3 have been scaled to a reference compound (nitrobenzene; arbitrarily chosen) in order to facilitate a comparison. Two major findings can be extracted from these data: (1) The distinct substituent effects of the various NACs as discussed above for K^+ -montmorillonite were also found for K^+ -kaolinite and K^+ -illite. (2) The NB-scaled K_d values of the NACs are very similar for the three clay minerals. In other words, the relative tendency of a given NAC to specifically adsorb to clay minerals is independent of the structure of the clay minerals. Thus, the (relative) specific adsorption of NACs to sediments is independent of the composition of the matrix with respect to the type and relative abundance of clays present. Since the specific adsorption of NACs to clay minerals is governed by various steric and electronic factors, attempts to derive quantitative structure-activity relationships (QSAR's) for prediction of K_d values of NACs with molecular descriptors such as Hammett substituent constants or one-electron reduction potentials did not give satisfactory results. Further attempts to establish QSAR's based on molecular descriptors such as LUMO energies calculated with the help of quantum chemical models are currently in progress.

Environmental Significance and Applications

As demonstrated by the results presented in this study, specific adsorption to sites at the permanently negatively charged siloxane surfaces of phyllosilicates may control the extent of NAC adsorption in the subsurface. Thus, for assessing the mobility and bioavailability of NACs in soils and aquifers the degree of K^+ - (and NH_4^+)-saturation of clay minerals has to be considered as a crucial environmental factor, comparable to the role of organic matter (f_{om}) for the hydrophobic adsorption of nonpolar organic solutes.

Quantification of "Reactive" Siloxane Sites in Soils and Aquifers. In contrast to the measurement of f_{om} in solid matrices, a reliable analytical method to determine the

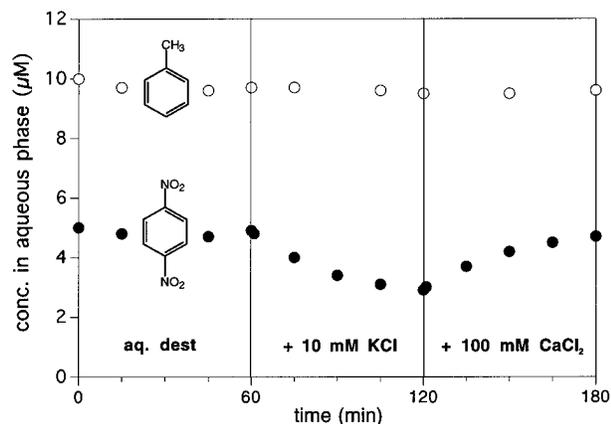


FIGURE 11. Adsorption of "probe molecules" at a sandy aquifer material as a means to distinguish hydrophobic partitioning (represented by the adsorption of toluene) from specific adsorption of NACs (represented by the adsorption of 1,4-DNB).

amount of siloxane sites that are available for specific adsorption of NACs does not exist. However, adsorption experiments with nitroaromatic probe compound(s) may be used to "calibrate" a given solid matrix with respect to its potential for specific adsorption of NACs to clay minerals in that both the actual and maximum amount of accessible surface sites may be determined.

The results of such an experiment performed with a sandy aquifer sediment that contains about 5% clay minerals are presented in Figure 11. Shown are the concentrations of 1,4-DNB and toluene in the aqueous phase as a function of time and composition of the background electrolyte. 1,4-Dinitrobenzene and toluene were chosen as "probes" for specific adsorption to clay minerals and hydrophobic partitioning, respectively. Note that both compounds exhibit very similar hydrophobicities but only 1,4-DNB may adsorb specifically to clay minerals. At the beginning of the experiment the sediment was suspended in distilled water. Little adsorption of 1,4-DNB and no measurable adsorption of toluene were observed. After 60 min, KCl electrolyte was added to the suspension. A steady decrease of the aqueous 1,4-DNB concentration due to adsorption to the aquifer material was observed. After another 60 min, concentrated $CaCl_2$ was added until the Ca^{2+} concentration in the background electrolyte was in large excess over the K^+ concentration. It can be seen that 1,4-DNB fairly quantitatively desorbed from the sediment while toluene was unaffected by the addition of the electrolytes.

Even though these results are preliminary and need to be supplemented by further experiments, several qualitative conclusions may already be drawn: First, the influence of varying background electrolytes on the adsorption behavior of 1,4-DNB is consistent with the results obtained for the adsorption of NACs in suspensions of pure clay minerals. Secondly, the lack of adsorption of toluene indicates that hydrophobic partitioning is negligible in this system. Thus, specific adsorption to clay minerals dominates the adsorption of NACs to this aquifer sediment. Thirdly, the rather slow sorption kinetics of 1,4-DNB observed under these conditions may be attributed to slow cation exchange processes at clay minerals that are poorly accessible due to aggregation or surface coatings. Thus, cation exchange may be a rate-limiting factor in the sorption kinetics of NACs in natural sediments. Finally, from the type of

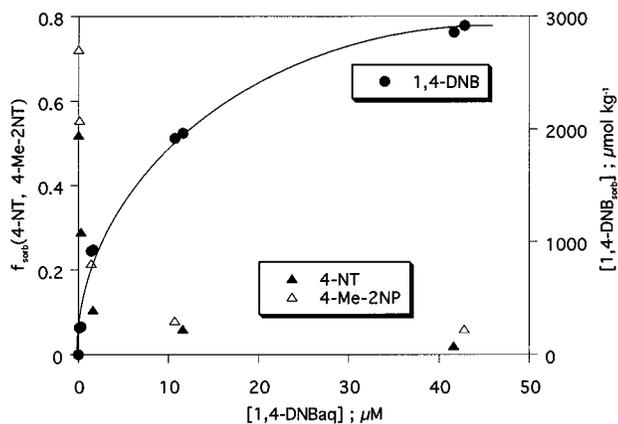


FIGURE 12. Example of competitive adsorption of NACs to clay minerals: moderately adsorbing NACs (4-Me-2NP, $K_d = 130 \text{ L kg}^{-1}$ or 4-NT, $K_d = 54 \text{ L kg}^{-1}$) desorb after addition of a strongly adsorbing NAC (1,4-DNB, $K_d = 4000 \text{ L kg}^{-1}$) to the clay suspensions (Cs^+ -kaolinite, $\text{pH} = 5.0$, $I = 0.1 \text{ M CsCl}$).

experiments shown in Figure 11, prediction of K_d values for other NACs can be achieved by relating the K_d value(s) of the probe(s) to the compounds of interest. The contribution of specific adsorption at clay minerals to the K_d of the target NACs can be assessed from a set of relative reactivities as given in Table 3 for various NACs. Furthermore, the (potential) contribution of hydrophobic partitioning to the overall adsorption can be calculated from the ratio of the $\log K_{ow}$ values of the target compound and the probe using an appropriate $\log K_{om}/\log K_{ow}$ relationship (21, 34).

Implications for Remediation Measures. The potential of strong and reversible retention of NACs due to specific adsorption at natural clay minerals may have some significant implications for remediation measures and the choice of remediation schemes at contaminated sites. The mobility of NACs such as TNT and its byproducts at those sites may be controlled by manipulating the K^+ -saturation of the clay minerals present. On the one hand, a ready release of adsorbed NACs from contaminated sediments may be desirable as is the case in *ex-situ* treatment(s) of the sediments or *in-situ* pump and treat or funnel and gate remediation schemes (35). In such situations, the fraction of NACs in the mobile phase and thus also their bioavailability may be enhanced by the exchange of (naturally adsorbed) K^+ -cations by strongly hydrated cations such as Na^+ or Ca^{2+} . On the other hand, immobilization of NACs due to enhanced adsorption may be considered to protect groundwater wells or to gain time for further evaluation of the contaminated sites. In those situations, addition of K^+ to the systems may significantly enhance the adsorption of certain NACs.

Competitive Adsorption: Implications for the Mobility of NACs at Heavily Contaminated Sites. At contaminated sites, e.g., in the vicinity of munitions plants, mixtures of dozens of nitroaromatic contaminants may be present at high concentrations (up to their aqueous solubilities) in soils and aquifers (5). Technical grade TNT contaminated with various byproducts (e.g., dinitrotoluenes) and transformation products of these compounds such as nitro-toluidines are major contaminants at such sites (7). Among these compounds TNT exhibits by far the highest affinity to clay minerals (see above).

To investigate the impact of compound mixtures on the specific adsorption of NACs, adsorption experiments were performed with binary mixtures of NACs in clay mineral

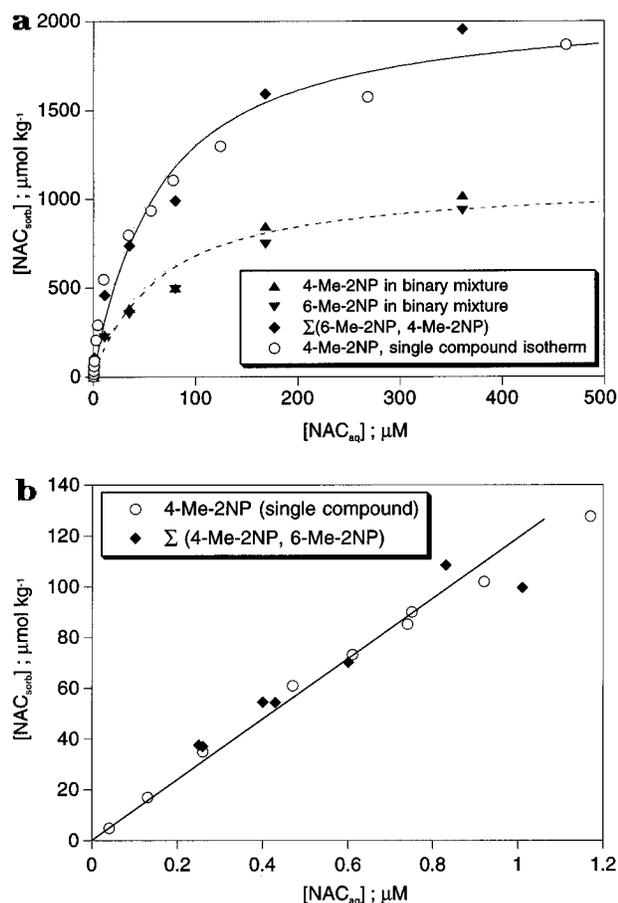


FIGURE 13. Example of competitive adsorption among NACs that exhibit similar K_d values. Adsorption isotherms of 4-Me-2NP ($K_d = 130 \text{ L kg}^{-1}$) measured in single solute experiments are compared with isotherms measured in the presence of binary mixtures of the 4-Me-2NP and 6-Me-2NP ($K_d = 120 \text{ L kg}^{-1}$): (a) saturation isotherms; (b) linear range of isotherms (sorber: Cs^+ -kaolinite, $\text{pH} = 5.0$, $I = 0.1 \text{ M CsCl}$).

suspensions. Figure 12 shows results of experiments where a strongly adsorbing compound (1,4-DNB, $K_d = 4000 \text{ L kg}^{-1}$) was added to suspended clays that already had adsorbed a more weakly adsorbing NAC (4-NT, $K_d = 54 \text{ L kg}^{-1}$ or 4-Me-2NP, $K_d = 130 \text{ L kg}^{-1}$). With increasing amounts of 1,4-DNB adsorbed, more and more of 4-NT or 4-Me-2NP desorbed from the clay mineral. In the saturation range of the 1,4-DNB-isotherm, 4-NT and 4-Me-2NP were almost quantitatively desorbed from the kaolinite. Thus, the competition efficiency of the NACs parallels their relative affinities (K_d -values) to the clay mineral(s) even though different "classes" of NACs (i.e., substituted nitrobenzenes and nitrophenols) were applied.

Figure 13 shows the results of experiments where the competition among two NACs exhibiting similar adsorption constants was studied. The NACs were applied at similar (initial) aqueous concentrations. Binary adsorption isotherms of the two NACs (4-Me-2NP, 6-Me-2NP) are compared with isotherms where 4-Me-2NP was adsorbed independently. Figure 13a depicts saturation isotherms obtained for both type of experiments. In the binary adsorption experiments the adsorption capacity, $[\text{NAC}_{\text{sorb}}]_{\text{max}}$, of each of the two isomers (dashed line) was about half of the adsorption capacity of the control experiment where 4-Me-2NP (and 6-Me-2NP, data not shown) were adsorbed individually (solid line). The adsorption calculated for the sum of the two NACs matched

very well the control isotherm obtained for the independent adsorption of 4-Me-2NP. Figure 13b shows the linear range of the isotherms. As is evident, at low surface coverage the NACs adsorbed quasi-independently.

The results of these competition experiments demonstrate that competition of adsorbed NACs is negligible only in very dilute systems. Beyond the linear range of the adsorption isotherms, the relative affinities of NACs to the clay minerals determine their effectiveness in competing for surface sites with other NACs. The results obtained with binary mixtures of NACs suggest that the adsorption capacity as well as the linear range of the isotherms at clay minerals remain constant regardless of whether a single compound or mixtures of NACs are present.

In the light of these results, nitro-reduction, an important transformation pathway of NACs in the subsurface (6), may not only enhance the mobility of contaminants due to the lower K_d values of the resulting (nitro)aniline products but also by the weaker competition behavior of these compounds as compared to their (poly)nitrated precursors.

Several investigations have shown that at elevated surface concentrations of organic contaminants enhanced adsorption of such solutes may occur when present in mixtures due to altered surface properties of the sorbent(s) and cooperative adsorption (36–38). However, from the results presented in this study, such cooperative adsorption may not be expected for the specific adsorption of NACs at clay minerals.

Outlook. The results of this study form a basis for understanding and quantifying the sorption behavior of NACs in subsurface environments. Specific adsorption of NACs to clay minerals and its implications, particularly the effects of exchangeable cations at clay minerals, convex adsorption isotherms of NACs, effects of substituents, and

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