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# Mechanism of Dinitrophenol Herbicide Sorption by Smectites in Aqueous Suspensions at Varying pH

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The compound 4,6-dinitro-*o*-cresol (DNOC) is an important pesticide that is strongly adsorbed by smectite clays. Because DNOC is a weak acid with an acid dissociation constant (p$K_a$) of about 4.4, pH was hypothesized to be a dominant state variable controlling sorption. In this study, we quantified the effect of pH, saturating cation ($K^+$ and $Ca^{2+}$), and freeze-drying on adsorption of DNOC by two reference smectites with different charge densities (SWy-2 and SAz-1) in dilute aqueous suspensions. The smectite–DNOC systems were adjusted from pH 3 to 7. Nearly 100% of added DNOC was adsorbed by $K^+$–saturated SWy-2 at pH 3, and sorption decreased with increasing pH to 62% at pH 7. Sorption of DNOC on $K^+$–saturated SAz-1 decreased from 94% at pH 3 to 31% at pH 7. Suspended $Ca^{2+}$–saturated SWy-2 adsorbed 82% of added DNOC at pH 3 but sorption decreased to 18% for pH 4 and above. Across the entire pH range, $Ca^{2+}$–saturated SAz-1 sorbed about 12% of added DNOC. Slightly larger amounts of DNOC were adsorbed by the "never dried" (not freeze-dried) smectites compared with the freeze-dried and rehydrated smectites. Analysis of supernatants from the $K^+$–saturated SAz-1–DNOC systems indicated co-adsorption of $K^+$ with DNOC in the phenolate form at pH values above the p$K_a$ of DNOC. At lower pH values, DNOC adsorption and complexation with interlayer $K^+$ resulted in less $K^+$ exchange by $H^+$ compared with the control without DNOC. These mechanisms explain the minimal influence of pH on the adsorption of DNOC by the $K^+$–saturated smectites.

Abbreviations: Ca-SAz-1, calcium-saturated Arizona montmorillonite reference clay (smectite); Ca-SWy-2, calcium-saturated Wyoming montmorillonite reference clay (smectite); DNOC, 4,6-dinitro-*o*-cresol; K-SAz-1, potassium-saturated Arizona montmorillonite reference clay (smectite); K-SWy-2, potassium-saturated Wyoming montmorillonite reference clay (smectite).

Out of the 18 manufactured dinitrocresols, DNOC is commercially the most important. The pesticide DNOC is used as a herbicide, fungicide, insecticide, microbiocide, and most recently in the plastics industry as an inhibitor of polymerization in styrene and vinyl (Hawley, 1981; USEPA, 1988). Although the USEPA cancelled registration of DNOC as a pesticide, existing stocks are being used around the world (International Programme on Chemical Safety, 2000). It is found as a contaminant in soils, subsoils, groundwater, and shallow aquifers (Broholm et al., 2001; Haderlein and Schwarzenbach, 1993). The development of effective strategies for remediating soils contaminated with organic molecules such as DNOC requires both an ability to quantify retention and movement of the contaminant in natural soil environments and a good understanding of the bonding mechanism between the contaminant and soil constituents.

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For neutral organic compounds, soil organic matter is commonly assumed to be the predominant sorptive phase (Chiou, 2002). In soils and subsoils, however, particularly those with low organic matter contents, clay minerals can make a substantial or even dominant contribution to sorption of certain classes of organic contaminants and pesticides including nitroaromatic compounds (NACs), triazines, and dioxins (Laird et al., 1992; Sheng et al., 2001). Among various clay minerals found in soils, smectites are very important due to their widespread occurrence (Allen and Hajek, 1989), high cation exchange capacities, large surface area, reversible interlayer expansibility, and chemically active surfaces (Laird et al., 1992). Recent studies have documented the high affinity of smectite clays for the adsorption of NACs (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weissmahr et al., 1997; Sheng et al., 2001, 2002; Boyd et al., 2001). The high adsorption of NACs by clays has been attributed to the formation of electron-donor–acceptor (EDA) complexes (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996). Accordingly, the presence of electron-withdrawing $-NO_2$ groups results in an electron-deficient aromatic ring, and negatively charged siloxane Os near sites of isomorphous substitution on the clay surface were hypothesized to contribute electrons to the electron-deficient ring system of NACs thereby forming the NAC–clay EDA complex. A quantum chemical study of the adsorption of 1, 3, 5-trinitrobenzene (TNB) on the siloxane surfaces of clay minerals, however, attributed this adsorption affinity to the existence of attractive coulombic and van der Waals forces between NACs oriented coplanar to the planar siloxane clay surface (Pelmenschikov and Leszczynski, 1999).

A study by Boyd et al. (2001) concluded that adsorption of several NACs is a consequence of several additive phenomena including complexation of the $–NO_2$ groups and secondary substituents (e.g., $–COOCH_3$, –CN, $–NO_2$) that interact with interlayer $K^+$ in K-smectites, hydrophobic interactions with the siloxane surfaces, and energy gained from the partitioning of NACs to the subaqueous environment of clay interlayers. A Fourier-transform infrared study showed shifts in N–O stretching frequencies of NACs due to formation of inner and outer sphere complexes with interlayer cations having comparatively low hydration enthalpies (e.g., $K^+$ or $Cs^+$ but not $Ca^{2+}$ or $Na^+$) and the $–NO_2$ groups of NACs (Johnston et al., 2001). Sheng et al. (2002) showed that sorption of two dinitrophenol herbicides was much greater by smectites exchanged with cations having comparatively lower hydration enthalpies (e.g., $K^+$, $Cs^+$, and $NH_4^+$). Molecular dynamic simulations showed DNOC interacting with $K^+$ through formation of inner sphere complexation whereby one or two Os of each $–NO_2$ group coordinated to exchangeable $K^+$ and the simultaneous interaction between $K^+$ and the phenolic O and adjacent $–NO_2$ group O. Additionally, the indirect coordination of the $–NO_2$ groups and $K^+$ ions through the intermediation of water led to the formation of outer sphere complexes. These studies established that the size of the hydration spheres of the interlayer cations as well as the charge density of the clay were important determinants of DNOC adsorption.

Chappell et al. (2005) reported that the hydration status of smectites had a large influence on sorption of atrazine, and that sample treatments such as air drying impact the sorption affinity of smectites for organic molecules. Their study showed that drying could impact the size and nature of smectite quasicrystals, thereby affecting the sorption affinity of smectites for organic molecules. Previous adsorption studies have been conducted using smectites that were rehydrated after treatment (air dried or freeze-dried). The results of Chappell et al. (2005) suggest the importance of considering the effects of drying of smectites on adsorption of aqueous-phase organic contaminants and pesticides.

Several previous studies have demonstrated high DNOC sorption at pHs below the $pK_a$ of DNOC, where DNOC exists as a neutral species. Sheng et al. (2002) showed decreasing sorption of DNOC with increasing pH (2.5–7) on K-smectite; however, some sorption was apparent even at pHs well above the $pK_a$ of DNOC. They attributed the ability of the K-smectite to adsorb anionic DNOC to surface acidity of the smectite. Smectite surface acidity has been shown to promote protonation and adsorption of weak bases at pHs above their $pK_a$ values (Mortland and Raman, 1968; Laird and Fleming, 1999), but this effect has never been clearly demonstrated for weak acids. Alternatively, electrical neutrality could also be maintained by co-adsorption of an inorganic cation with an anionic organic molecule. The evidence for specific interaction between $K^+$ and DNOC (Johnston et al., 2001) suggests the possibility that $K^+$ is co-adsorbed with DNOC.

The goal of this investigation was to test the competing hypotheses that smectite surface acidity promotes protonation and adsorption of DNOC or that $K^+$ is co-adsorbed with DNOC at pHs above the $pK_a$. The specific objectives of this study were to quantify (i) the extent of DNOC adsorption by smectites in aqueous suspensions at varying pH; (ii) the impact of the saturating cation ($K^+$ vs. $Ca^{2+}$) on DNOC adsorption; and (iii) the effect of sample treatment (freeze-dried and rehydrated vs. continuously hydrated) on adsorption of DNOC. A mechanistic interpretation for interactions between DNOC and smectites at pHs above and below the $pK_a$ of DNOC is proposed.

## MATERIALS AND METHODS

### Smectite Clays and Dinitrophenol

Reference smectites (SWy-2 and SAz-1), obtained from the Source Clays Repository of the Clay Minerals Society maintained at Purdue University, West Lafayette, IN, were used in this study. The cation exchange capacities and layer charge density of SWy-2 and SAz-1 are 82 and 125 cmolc $kg^{-1}$, and 1.09 and 1.67 $\mu mol_c\ m^{-2}$, respectively (Li et al., 2003). Approximately 500 g of SWy-2 were treated with 0.5 *M* NaOAc buffer at pH 5.0 for 2 d to remove carbonates (Gee and Bauder, 1986), and then the sample was washed with 0.5 *M* NaCl to remove excess acetate buffer and prepare a homoionic Na-montmorillonite suspension. The <2-µm clay fraction was collected by sedimentation and subsequently equal portions of the <2-µm fractions were saturated with $K^+$ and $Ca^{2+}$ by washing the clays with 0.5 *M* KCl or CaCl solutions several times. The K-SWy-2 clay suspension was dialyzed using Spectra/Por 3 membrane dialysis tubing (Spectrum Labs, Los Angeles) against a 0.1, 0.01, and 0.001 M KCl solutions for a total of 9 d, refreshing the electrolyte three to four times per day until electrical conductivity achieved a constant value. The Ca-SWy-2 clay suspension was dialyzed similarly against 0.05, 0.005, and 0.0005 *M* $CaCl_2$ solutions.

The SAz-1 clay was free of carbonates and therefore was not treated with NaOAc buffer. Otherwise, size fractionation and ion saturation to prepare the K-SAz-1 and Ca-SAz-1 suspensions were performed by the same procedures as described above. Half of each clay suspension was lyophilized, and these samples are referred to as the freeze-dried clays. The remaining halves were stored as suspensions at ~10°C and are referred to as the never-dried clay suspensions.

The 4,6-dinitro-*o*-cresol (Fig. 1) was purchased from Aldrich Chemical Co. (Milwaukee, WI) with purity >97% and was used as received. The DNOC is a weak acid with a $pK_a$ of about 4.4 and water solubility of about 198 mg $L^{-1}$ (USEPA, 1988). A DNOC stock solution was prepared by dissolving 150 mg of DNOC in 1 L of deionized water. This solution had

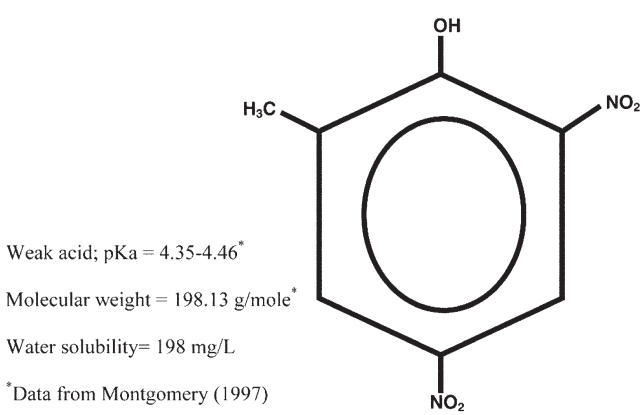


**Fig. 1. Structure and selected physicochemical properties of 4,6-dinitro-*o*-cresol (DNOC).**

a natural pH of about 3.2. To adjust the pH of the solution to the desired value, a few drops of 0.01 *M* HCl, 0.01 *M* KOH, or 0.005 *M* $Ca(OH)_2$ were added accordingly.

### Freeze-dried Resuspended Samples

Freeze-dried resuspended samples were prepared by dispersing 100 mg of $K^+$– and $Ca^{2+}$–saturated freeze-dried SWy-2 and SAz-1 in Corex tubes containing 2 mL of appropriate concentrations of KCl and $CaCl_2$ solutions so that the final ionic strength was 1.0 m*M* for the $K^+$–clay suspensions and 0.5 mM for the $Ca^{2+}$–clay suspensions. The tubes were shaken on a side-to-side shaker for 48 h at 25°C.

### Never-Dried Suspensions

The never-dried $K^+$– and $Ca^{2+}$–saturated SWy-2 and SAz-1 suspensions were adjusted to the desired solid solution concentration of 100 g clay $L^{-1}$ of electrolyte. The ionic strength for the never-dried suspensions was the same as for the freeze-dried resuspended samples. The suspensions were then shaken on a side-to-side shaker for 24 h at 25°C.

### Sample Preparation and Equilibration

The smectite suspensions and DNOC solutions were adjusted to the desired pH value by adding a few drops of 0.01 *M* HCl, 0.01 *M* KOH, or 0.005 *M* $Ca(OH)_2$. A pH-adjusted DNOC solution of 150 mg $L^{-1}$ was then added to the pH-adjusted smectite suspensions to make up a final volume of 10 mL. The final concentration of DNOC was 120 mg $L^{-1}$ with a solid solution concentration of 10 g $L^{-1}$. Triplicate samples were prepared. Blank suspensions without DNOC at each pH value were also prepared. The tubes were shaken for 24 h at 25°C. The mixtures were centrifuged at 11 951 × *g* for 25 min to separate the solid and liquid phases.

### Spectrophotometric Analysis

The pH of the supernatant from each sample was recorded, and then 9 mL of supernatant was mixed with 1 mL of 0.5 *M* potassium phosphate buffer to adjust the pH to 7. The pH-adjusted supernatant was passed through a 0.2-µm nylon filter and collected in a quartz cuvette. The DNOC concentrations were determined by measuring absorption at 268 nm, the wavelength of maximum absorbance for DNOC, with a Milton Roy Spectronic 601 spectrophotometer equipped with an UV-visible detector (Milton Roy Co., Rochester, NY). The amount of herbicide adsorbed by the smectite was calculated from the difference between the initial concentration of DNOC and the concentration of DNOC in the final solution.

### Elemental Analysis of Supernatant

Freeze-dried K-SAz-1 (150 mg) and Ca-SWy-2 (100 mg) were weighed into Corex tubes. The DNOC solutions (150 mg $L^{-1}$) were prepared by dissolving DNOC in appropriate concentrations of KCl and $CaCl_2$ solutions. A measured volume of 0.001 *M* KOH and 0.0005 *M* $Ca(OH)_2$ was added to bring the pH of the DNOC solution to 7. The smectite–DNOC systems were pH adjusted (pH 3–7) by adding an appropriate quantity of 0.01 *M* HCl such that the final volume was 10 mL with a DNOC concentration of 120 mg $L^{-1}$ DNOC in 1.0 m*M* $K^+$ or 0.5 mM $Ca^{2+}$. Controls, that is, smectites without DNOC, were prepared using the same procedure. The mixtures were equilibrated for 48 h at 25°C, then centrifuged at 11951 × *g* for 25 min. Samples were prepared in triplicate. Smectite–DNOC supernatants, supernatants of the controls (no DNOC), and the background electrolyte solutions used to prepare all of the samples were filtered through 0.2-µm nylon filters and then through 0.02-µm Anotop filters (Whatman, Brentford, UK) and pH tested. Elemental analysis ($Ca^{2+}$ and $K^+$) of the filtered supernatants was performed with a Thermo Jarrell Ash Model 61 E inductively coupled plasma–atomic emission spectrometer (Thermo Fischer Scientific, Waltham, MA).

The amount of $Ca^{2+}$ and $K^+$ that was displaced from the smectite into solution in the controls (smectites without DNOC) during pH adjustment was determined. These values were calculated as the difference between the measured $K^+$ and $Ca^{2+}$ concentrations of control supernatants and the background electrolyte solutions. The amount of $Ca^{2+}$ and $K^+$ that was displaced from smectite in the smectite–DNOC system during pH adjustment was determined in the same manner. Calculating the amount of $K^+$ and $Ca^{2+}$ co-adsorbed with DNOC from the actual measured values was not possible since the individual measurements were not at exactly the same pH values in the smectite–DNOC system vs. the control. Therefore, a regression equation was calculated for the systems without DNOC to predict the $K^+$ ($y = -370.05x + 2652.9$; $R^2 = 0.98$) and $Ca^{2+}$ ($y = -35.643x^3 + 465.37x^2 - 2055x + 4162.6$; $R^2 = 0.94$) concentration at each pH of the smectite–DNOC systems being analyzed. Tabulated data represent the difference between the concentrations of $K^+$ and $Ca^{2+}$ calculated from the regression equations and the corresponding measured concentrations at each pH of the smectite–DNOC systems being analyzed.

## RESULTS AND DISCUSSION

### Dinitrophenol Sorption by Potassium and Calcium Smectites

The adsorption of DNOC by freeze-dried and never-dried homoionic K-SWy-2 and K-SAz-1 suspensions at several pH values (3–7) is shown in Fig. 2A. Adsorption of DNOC for both smectites increased with decreasing pH; the highest adsorption occurred at pH 3, the lowest pH tested. The adsorption of DNOC was higher for K-SWy-2 than for K-SAz-1 across the entire pH range. This is consistent with earlier studies showing an inverse relation between the extent of sorption and clay charge density (Lee et al., 1990; Boyd and Jaynes, 1994; Laird, 1996; Sheng et al., 2002). Nearly 100% of added DNOC was adsorbed by K-SWy-2 at pH 3; at pH 7, sorption decreased to 62%. Sorption of DNOC on K-SAz-1 decreased from 94% at pH 3 to 31% at pH 7. At pH above the $pK_a$ of DNOC (4.4), K-SWy-2 adsorbed 60 to 100% of added DNOC, whereas K-SAz-1 adsorbed 30 to 75%. For both smectites (K-SWy-2 and K-SAz-1), the never-dried suspensions sorbed more DNOC than the freeze-dried, resuspended samples.

The low-charge-density clay (SWy-2) sorbed more DNOC than the high-charge-density clay (SAz-1). In SAz-1, the size of the hydrophobic nanosites on the basal surfaces located between the negative charge sites is constrained by the comparatively higher density of these negative sites and the hydration spheres

of exchangeable cations associated with the charged sites (Lee et al., 1990; Boyd and Jaynes, 1994; Boyd et al., 2001). Crowding between the hydrated exchangeable interlayer cations may cause DNOC molecules to adopt less-than-optimal orientations (i.e., nonplanar orientations relative to the siloxane surfaces), thereby diminishing favorable adsorptive mechanisms such as $-NO_2$ interactions with the interlayer cations or van der Waals interactions with the planar hydrophobic siloxane surfaces.

Compared with K-SWy-2, DNOC sorption by Ca-SWy-2 was lower, and diminished much more rapidly as pH increased (Fig. 2B). Freeze-dried Ca-SWy-2 adsorbed 82% of added DNOC at pH 3; however, DNOC sorption decreased to 18% at pH 4 and remained constant to pH 7. The Ca-SAz-1 sorbed 12% of added DNOC across the entire pH range. The lower adsorption of DNOC observed for $Ca^{2+}$–smectite compared with the $K^+$–smectite (Fig. 2A and 2B) is attributed to the larger enthalpy of hydration, and hence larger hydration sphere, of $Ca^{2+}$ compared with $K^+$, which inhibits direct interactions between the exchangeable cations and $-NO_2$ groups of DNOC (Boyd et al., 2001; Johnston et al., 2001; Sheng et al., 2002; Li et al., 2004). The larger hydration sphere around $Ca^{2+}$ also obscures more of the neutral siloxane surface (hydrophobic nanosites), thereby reducing the average size of the adsorption domains. This results in comparatively fewer sites in $Ca^{2+}$–smectites large enough to accommodate DNOC in its most favorable orientation. Reduction in the average size of the adsorption domains also contributes to the observed lower adsorption of DNOC by the higher-charge-density clay, Ca-SAz-1 (pH 3 and 4) compared with adsorption by Ca-SWy-2, which has lower surface charge density (Fig. 2B).

Figure 2A indicates that K-smectite suspensions adsorbed substantial amounts of DNOC at pHs well above the $pK_a$ of DNOC, where the anionic (phenolate) form of the molecule predominates. In this pH range, electrostatic repulsion between anionic DNOC and the negatively charged sites on the smectite surfaces should inhibit DNOC sorption. Our data demonstrate, however, that substantial amounts of DNOC were adsorbed. Two phenomena might help resolve this observation. First, clay surface acidity might catalyze protonation of the phenolate form of DNOC. Surface acidity has been shown to promote protonation of weak bases one or two pH units above their $pK_a$ values (Mortland and Raman, 1968; Laird and Fleming, 1999). Second, anionic DNOC might be co-adsorbed with $K^+$, resulting in the formation of a neutral K–DNOC complex. The co-adsorption of anionic DNOC and $K^+$ is consistent with previous studies suggesting inner sphere interactions between $K^+$ and $-NO_2$ groups of DNOC in the interlayers of smectites (Boyd et al., 2001; Johnston et al., 2001; Sheng et al., 2002), and with the observation that high sorption of DNOC at pHs above the $pK_a$ occurred only for the K-smectite and not for Ca-smectite.

To test the hypothesis that $K^+$ is co-adsorbed with anionic DNOC, the release or uptake of $K^+$ and $Ca^{2+}$ accompanying pH change in the presence and absence of DNOC was evaluated for the K-SAz-1 and Ca-SWy-2 systems. The amount of solution-phase $K^+$ or $Ca^{2+}$ would be expected a priori to increase with decreasing pH, assuming ion exchange of $K^+$ or $Ca^{2+}$ by $H^+$. Interestingly, as HCl was added to lower the solution pH (pH range 3–7), substantially more $K^+$ was displaced from the K-smectite into solution in the control systems (smectite without DNOC) than the smectite–DNOC systems (Fig. 3A). These results indicate co-adsorption of $K^+$ and anionic DNOC or that more $K^+$ is retained on the clay in the presence of adsorbed DNOC. Both explanations seem plausible, since K–DNOC complexes have been shown to form in the interlayers of K-smectite accompanied by significant negative enthalpies of interaction (Boyd et al., 2001; Johnston et al., 2001; Li et al., 2004). In contrast, we observed little or no difference in the amount of $Ca^{2+}$ displaced from Ca-smectite into solution

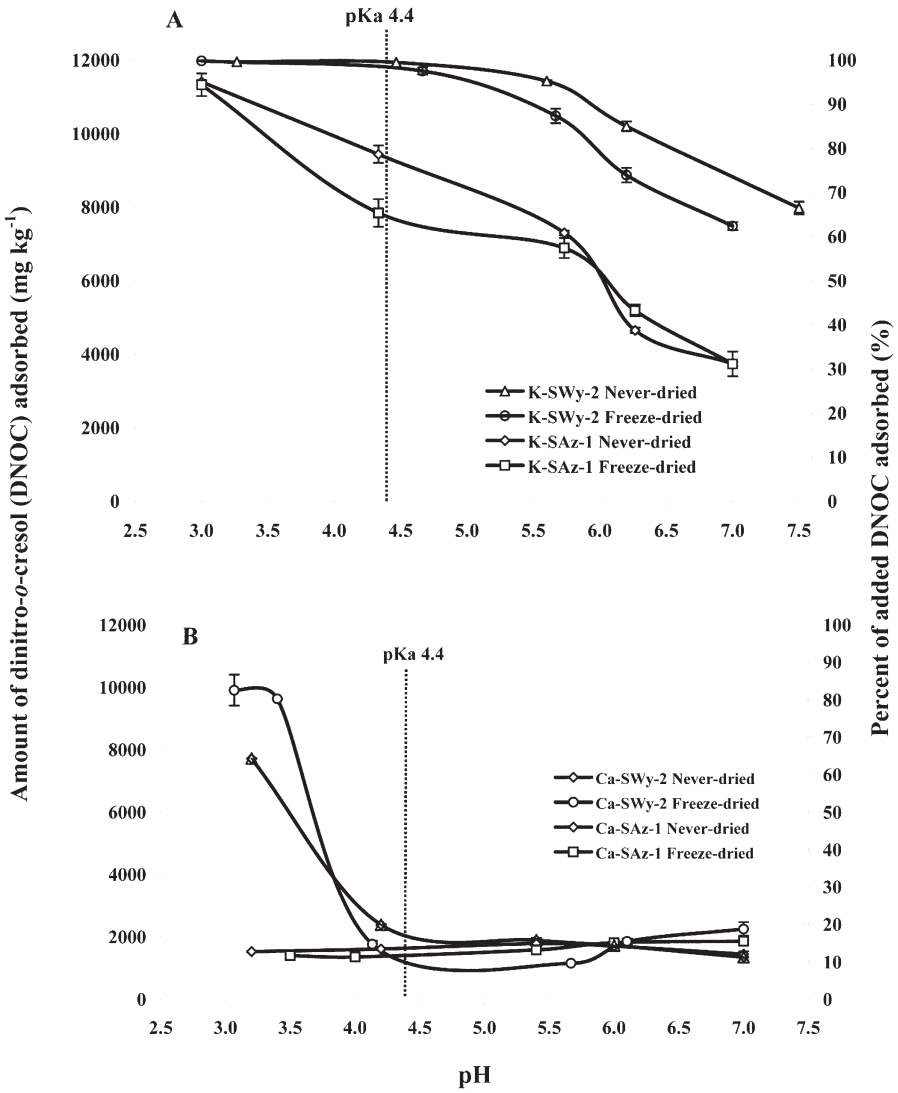


**Fig. 2. Adsorption of dinitro-*o*-cresol (DNOC) by (A) untreated and freeze-dried $K^+$–saturated smectite suspensions (K-SWy-2 and K-SAz-1), and (B) untreated and freeze-dried $C^{2+}$–saturated smectite suspensions (Ca-SWy-2 and Ca-SAz-1) as a function of pH.**

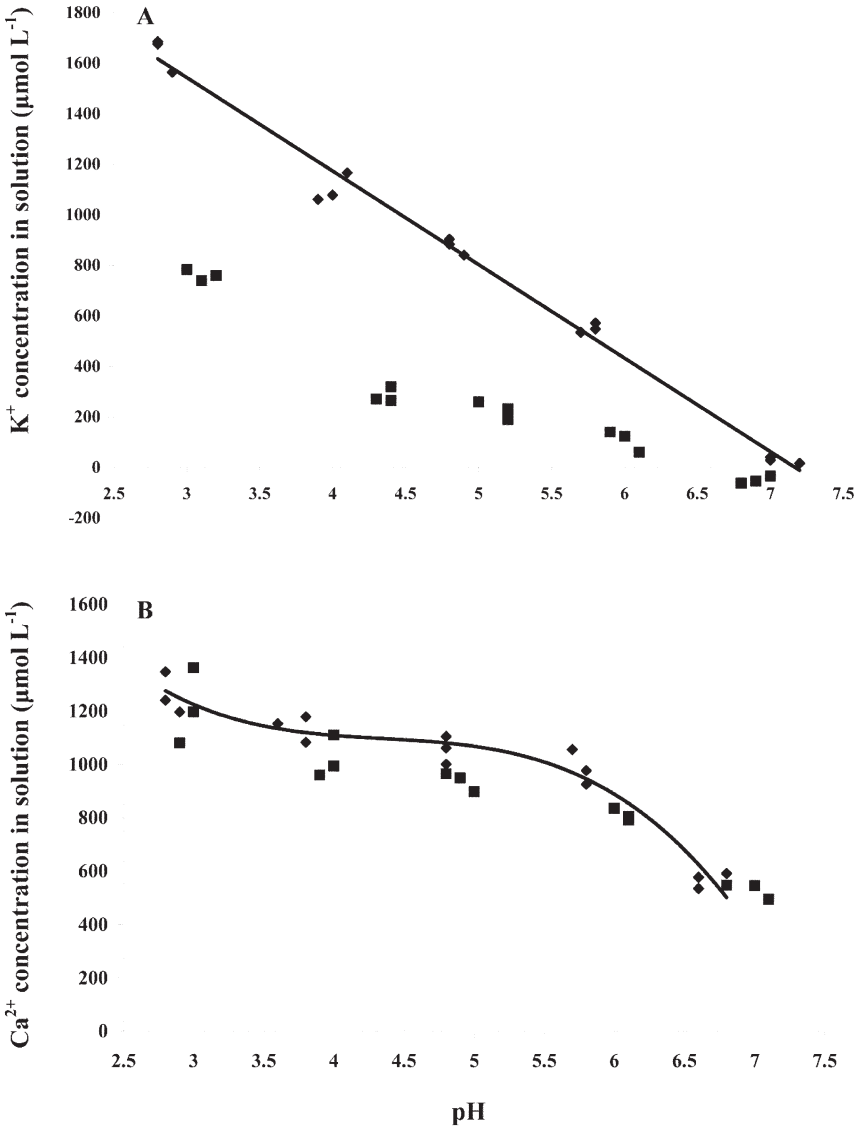


**Fig. 3. (A) The $K^+$ concentration in solution minus background electrolyte representing $K^+$ derived from $K^+$–saturated SAz-1 smectite in the presence (■) and absence (♦) of dinitro-*o*-cresol (DNOC), and (B) the $Ca^{2+}$ concentration in solution minus background electrolyte representing $Ca^{2+}$ derived from $Ca^{2+}$–saturated SWy-2 smectite in the presence (■) and absence (♦) of DNOC as a function of pH.**

**Table 1. Quantities of dinitro-o-cresol (DNOC) and additional $K^+$ and $Ca^{2+}$ (relative to the control without DNOC) adsorbed on $K^+$–saturated SAz-1 smectite and $Ca^{2+}$–saturated SWy-2 smectite at pH 3 to 7. The sorbed amounts of cations and DNOC were obtained from two separate experiments.**

| Additional cation adsorbed† | System pH | DNOC adsorbed | DNOC system pH |
|---|---|---|---|
| μmol $kg^{-1}$ | | μmol $kg^{-1}$ | |
| | $K^{\pm}$ system | | |
| 74 (±3.1) | 3.1 | 57 (±1.5) | 3 |
| 75 (±4.3) | 4.4 | 40 (±1.8) | 4.3 |
| 53 (±2.6) | 5.1 | 35 (±1.3) | 5.7 |
| 33 (±1.4) | 6 | 26 (±0.8) | 6.3 |
| 15 (±5.1) | 6.9 | 19 (±1.7) | 7 |
| | $Ca^{2\pm}$ system | | |
| 2 (±15.3) | 2.9 | 50 (±2.5) | 3.1 |
| 9 (±8.1) | 3.9 | 9 (±0.6) | 4.1 |
| 14 (±2.9) | 4.9 | 6 (±0.1) | 5.7 |
| 5 (±0.7) | 6.1 | 9 (±0.5) | 6.1 |
| −15 (±9.2) | 6.9 | 11 (±1.1) | 7 |

† Compared with the amount adsorbed in the absence of DNOC.

between the control and DNOC-added systems (Fig. 3B), consistent with previous results indicating the inability of $Ca^{2+}$ to form complexes with DNOC in Ca-smectites (Boyd et al., 2001; Johnston et al., 2001). As pH increases, there should be a systematic decrease in the amount of displaced $Ca^{2+}$ (Fig. 3B), approaching zero at pH 7; however, the measured value of displaced $Ca^{2+}$ at pH 7 was about 500 μmol $L^{-1}$. This excess displaced $Ca^{2+}$ probably represents residual $CaCl_2$ in the freeze-dried Ca-SWy-2 due to incomplete dialysis.

The difference in the total amounts of $K^+$ and $Ca^{2+}$ present in supernatants of the controls (smectite without DNOC) and smectite–DNOC systems as a function of pH are shown in Table 1. The difference represents the amount of additional $K^+$ or $Ca^{2+}$ that was removed from solution by the clay, or not released from the clay, concomitantly with DNOC adsorption. These values are compared with the total amount of DNOC adsorbed by the clay across the same pH range (Table 1). Interestingly, $K^+$ uptake (or retention) associated with DNOC adsorption occurred at all pHs tested. In general, slightly more $K^+$ than DNOC was adsorbed. Deviation from the expected equivalence of these species is attributed to the slightly different experimental methods, and separate experiments, used to obtain the adsorbed DNOC values compared with the adsorbed $K^+$ values.

Approximately 15% of added DNOC was adsorbed by both Ca-SWy-2 and Ca-SAz-1 across the tested pH range of 4 to 7 (Fig. 2B). These results suggest the existence of a limited number of pH-independent sites in Ca-smectite that adsorb the anionic form of DNOC. These sites are probably along the lateral edges of the smectite layers. Structural Al atoms exposed along the crystallite edges are hydrolyzed to aluminol groups (Al–OH). These groups carry half a negative charge (Al–$OH^{-1/2}$) and on protonation carry half a positive charge (Al–$OH_2^{1/2}$). The point of zero net charge for aluminol groups is about 7, so they should be dominantly positively charged across the studied pH range. The phenolate form of DNOC can interact with such Al–$OH_2^{+1/2}$ edge sites through charge neutralization reactions and can therefore be adsorbed. Also, ligand exchange reactions resulting from direct (inner sphere) bonding between DNOC and an exposed Al along the edges of smectites could contribute to adsorption.

The freeze-drying treatment (Fig. 2) did not have as large an impact on the affinity of the smectites for DNOC as in a previous study where air-drying treatments were shown to

substantially influence atrazine (2-chloro-4-ethylamine-6-isopropylamino-S-triazine) sorption (Chappell et al., 2005). Air drying (Chappell et al., 2005) might have promoted the formation of larger quasicrystals (with greater effectiveness as adsorbents) than the freeze-drying procedure used in this study (Oetjen and Haseley, 2003).

In summary, we observed that, as the K-smectite suspension pH increased, excess $K^+$ was held by the clay in the presence of DNOC, compared with the same systems devoid of sorbed DNOC. It seems plausible that anionic DNOC is co-adsorbed with $K^+$ as a neutral K–DNOC complex by smectites in aqueous suspensions at pH values above the $pK_a$ of DNOC. This could explain the observed sorption of large amounts of DNOC by K-smectites at pHs well above the $pK_a$ of DNOC, where it would exist largely in the anionic form. At pH values below the $pK_a$ of DNOC, excess $K^+$ on the clay (compared with the control without DNOC) is probably due to the favorable energy associated with the formation of the K–DNOC complexes in the interlayers (Li et al., 2004). In these instances, the net effect of the presence of DNOC in the interlayer of SWy-2 is to enhance the nominal selectivity of $K^+$ vs. $H^+$, since the formation of K–DNOC complexes in smectite interlayers is energetically favorable (Li et al., 2004). Larger amounts of DNOC are adsorbed by low-charge-density smectites than by high-charge-density smectites. The difference is related to the size of the hydrophobic nanosites on smectite surfaces between exchangeable cations, which function as planar adsorption domains. The existence of adsorption sites of sufficient size for optimal DNOC orientation and adsorption diminishes with increasing surface charge density. A limited amount of DNOC is also adsorbed by Ca-smectites independent of pH or surface charge density. Exposed aluminol groups along the lateral edges of the smectite layers are the probable sites for this limited sorption.

Since DNOC is a weak acid, pH was expected a priori to be the dominant state variable controlling sorption and movement of DNOC in contaminated soils. Our results show, however, that pH is only one of many variables to consider when developing remediation strategies. In temperate regions, most soils have a pH well above the $pK_a$ of DNOC and are dominated by $Ca^{2+}$, conditions that limit sorption of DNOC by soil clays. Our results suggest that the injection of $K^+$ into a contaminant plume may be an effective means of promoting sorption and hence preventing the movement of DNOC and possibly other nitroaromatic contaminants into groundwater.

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## REFERENCES

Allen, B.L., and B.F. Hajek. 1989. Mineral occurrences in soil environments. p. 199–278. In J.B. Dixon and S.B. Weed (ed.) Minerals in soil environments. 2nd ed. SSSA Book Ser. 1. SSSA, Madison, WI.

Boyd, S.A., and W.F. Jaynes. 1994. Role of layer charge in organic contaminant sorption by organo-clays. p. 48–77. In A.R. Mermut (ed.) Layer charge characteristics of 2:1 silicate clay minerals. Clay Miner. Soc. Worksh. Lectures 6. Clay Miner. Soc., Boulder, CO.

Boyd, S.A., G. Sheng, B.J. Teppen, and C.T. Johnston. 2001. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. Environ. Sci. Technol. 35:4227–4234.

Broholm, M.M., N. Tuxen, K. Rügge, and P.L. Bjerg. 2001. Sorption and degradation of the herbicide 2-methyl-4,6-dinitrophenol (DNOC) under aerobic conditions in a sandy aquifer in Vejen, Denmark. Environ. Sci. Technol. 35:4789–4797.

Chappell, M.A., D.A. Laird, M.L. Thompson, H. Li, B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2005. Influence of hydration and swelling on atrazine sorption behavior. Environ. Sci. Technol. 39:3150–3156.

Chiou, C.T. 2002. Partition and adsorption of organic contaminants in environmental systems. John Wiley & Sons, Hoboken, NJ.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383–411. In A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Haderlein, S.B., and R.P. Schwarzenbach. 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces. Environ. Sci. Technol. 27:316–326.

Haderlein, S.B., K.W. Weissmahr, and R.P. Schwarzenbach. 1996. Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. Environ. Sci. Technol. 30:612–622.

Hawley, G.G. 1981. The condensed chemical dictionary. 10th ed. Van Nostrand Reinhold Co., New York.

International Programme on Chemical Safety. 2000. Effect on humans. Section 8. In Dinitro-ortho-cresol. Environ. Health Criteria 220. Available at www.inchem.org/documents/ehc/ehc/ehc220.htm#_Toc478363972 (accessed 20 Sept. 2005; verified 16 Apr. 2007). IPCS, World Health Organ., Geneva.

Johnston, C.T., M.F. De Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2001. Spectroscopic study of nitroaromatic–smectite sorption mechanisms. Environ. Sci. Technol. 35:4767–4772.

Laird, D.A. 1996. Interactions between atrazine and smectite surfaces. p. 86–100. In M.T. Meyer and E.M. Thurman (ed.) Herbicide metabolites in surface water and groundwater. ACS Symp. Ser. 630. Am.Chem. Soc., Washington, DC.

Laird, D.A., E. Barriuso, R.H. Dowdy, and W.C. Koskinen. 1992. Adsorption of atrazine on smectites. Soil Sci. Soc. Am. J. 56:62–67.

Laird, D.A., and P.D. Fleming. 1999. Mechanisms for adsorption of organic bases on hydrated smectite surfaces. Environ. Toxicol. Chem. 18:1668–1672.

Lee, J.F., M.M. Mortland, C.T. Chiou, D.E. Kile, and S.A. Boyd. 1990. Adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities. Clays Clay Miner. 38:113–120.

Li, H., G. Sheng, B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2003. Sorption and desorption of pesticides by clay minerals and humic acid–clay complexes. Soil Sci. Soc. Am. J. 67:122–131.

Li, H., B.J. Teppen, C.T. Johnston, and S.A. Boyd. 2004. Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. Environ. Sci. Technol. 38:5433–5442.

Mortland, M.M., and K.V. Raman. 1968. Surface acidities of smectites in relation to hydration, exchangeable cation and structure. Clays Clay Miner. 16:393–398.

Oetjen, G.W., and P. Haseley. 2003. Changes of structure in freezing or frozen products. p. 74–96. In Freeze-drying. 2nd ed. Wiley-VCH, Weinheim, Germany.

Pelmenschikov, A., and J. Leszczynski. 1999. Adsorption of 1,3, 5-trinitrobenzene on the siloxane sites of clay minerals: Ab initio calculations of molecular models. J. Phys. Chem. B 103: 6886–6890.

Sheng, G., C.T. Johnston, B.J. Teppen, and S.A. Boyd. 2001. Potential contributions of smectite clays and organic matter to pesticide retention in soils. J. Agric. Food Chem. 49:2899–2907.

Sheng, G., C.T. Johnston, B.J. Teppen, and S.A. Boyd. 2002. Adsorption of dinitrophenol herbicides from water by montmorillonites. Clays Clay Miner. 50:25–34.

USEPA. 1988. Health and environmental effects profile for dinitrocresols. NTIS PB 88–220769. USEPA, Cincinnati, OH.

Weissmahr, K.W., S.B. Haderlei, R.P. Schwarzenbach, R. Hany, and R. Nuesch. 1997. In situ spectroscopic investigations of adsorption mechanisms of nitroaromatic compounds at clay minerals. Environ. Sci. Technol. 31:240–247.