

## ADSORPTION OF DINITROPHENOL HERBICIDES FROM WATER BY MONTMORILLONITES

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**Abstract**—The adsorption of two dinitrophenol herbicides, 4,6-dinitro-*o*-cresol (DNOC) and 4,6-dinitro-*o*-sec-butyl phenol (dinoseb), by two reference smectite clays (SWy-2 and SAz-1) was evaluated using a combination of sorption isotherms, Fourier transformation infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and molecular dynamic simulations. Clays were subject to saturation with various cations, and charge reduction. The DNOC adsorption decreased with increasing pH indicating that DNOC was primarily adsorbed as the neutral species. The FTIR spectra of DNOC-clay films showed that DNOC molecules are oriented parallel to the clay surface. Interlayer cations have a strong effect on adsorption depending largely on their hydration energies. Weakly hydrated cations, e.g. K<sup>+</sup> and Cs<sup>+</sup>, resulted in greater sorption compared to more strongly hydrated cations such as Na<sup>+</sup> or Ca<sup>2+</sup>. Lower hydration favors direct interactions of exchangeable cations with -NO<sub>2</sub> groups of DNOC and manifests optimal interlayer spacings for adsorption. In the presence of sorbed DNOC, an interlayer spacing for K-SWy-2 of between 12 and 12.5 Å was maintained regardless of the presence of water. This *d*-spacing allowed DNOC molecules to interact simultaneously with the opposing clay layers thus minimizing contact of DNOC with water. The charge density of clays also affected sorption by controlling the size of adsorption domains. Accordingly, DNOC adsorption by low-charge clay (K-SWy-2) was much higher than by high-charge clay (K-SAz-1) and Li-charge reduction greatly enhanced dinoseb adsorption by K-SAz-1. Steric constraints were also evident from the observation that adsorption of DNOC, which contains a methyl substituent, was much greater than dinoseb, which contains a bulkier isobutyl group. Adsorption of DNOC by K-SAz-1 was not affected in the presence of dinoseb, whereas dinoseb adsorption was greatly reduced in the presence of DNOC.

**Key Words**—Adsorption, Clay, Orientation, Pesticide, Steric Effect.

### INTRODUCTION

Recently, much attention has been given to the role of humic substances as the predominant sorptive phase in soils for neutral organic contaminants (*e.g.* Chiou *et al.*, 1979, 1983, 2000; Karickhoff *et al.*, 1979; Pignatello and Xing, 1996; Leboeuf and Weber, 1997; Chiou, 1998; Kleineidam *et al.*, 1999; Xia and Ball, 2000). Transport models commonly utilize organic matter normalized sorption coefficients ( $K_{om}$ ) to predict soil-water distribution of organic chemicals. This approach ignores the potential contribution of clay minerals to retention of organic contaminant in soils and subsoils. Earlier studies have shown that pesticides can be adsorbed by certain clays to an appreciable extent (*e.g.* Bailey and White, 1970; Mortland, 1986; Green, 1974). Subsequent attempts to define conditions under which clays may contribute substantially to pesticide/organic contaminant retention in soils concluded that this could occur when the clay to organic matter ratios in soils were greater than 5 to 30 (Hassett *et al.*, 1981; Karickhoff, 1984). In another study, the critical clay to organic carbon ratios at which mineral phase sorption accounted for 50% of

overall sorption by soils and sediments were 62 for atrazine and 84 for alachlor (Gundl and Small, 1993). Several recent studies have provided additional evidence for the potential important role of clays in pesticide retention. For example, in a study of atrazine sorption by a series of Ca-exchanged smectite clays with cation exchange capacity (CEC) ranging from 79 to 134 cmol<sub>c</sub>/kg, removal from water ranged from 0 to nearly 100%, and the logarithms of the Freundlich adsorption coefficients were inversely correlated to the CEC of the clays (Laird *et al.*, 1992). In another study, atrazine adsorption was much greater and stronger by Al-smectite than by Ca-smectite (Sawhney and Singh, 1997). Greater sorption by the Al clay was attributed to the stronger H bonding between the atrazine molecule and the more polarized waters associated with the trivalent Al ion than with the divalent Ca ion.

We recently evaluated the potential contributions of clays and soil organic matter (SOM) to the sorption of several pesticides from water (Sheng *et al.*, 2001). On a unit mass basis, SOM was a more effective sorbent than K-smectite for parathion, diuron and biphenyl, whereas the clay was more effective than SOM for the uptake of atrazine, carbaryl, dichlobenil and dinitro-*o*-cresol. Specific interactions between pesticide substituents and exchangeable cations of clay, hydrophobic interactions

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between pesticide molecules and the siloxane surfaces of clay, and steric hindrance related to the presence of large substituents in pesticide molecules were determinants of the differential adsorption of pesticides by K-smectite. It was also shown that the type of exchangeable cation and the clay CEC significantly affected atrazine uptake, possibly due to different hydration energies of cations and surface charge densities of clays. These parameters manifest different effective sizes of adsorption domains between exchangeable cations as well as different interlayer spacings. Through simple calculations using measured pesticide-clay and pesticide-SOM distribution coefficients, we concluded that in many instances soil clays have the potential to be an equal or dominant sorptive phase as compared to SOM for pesticide retention in soil.

In our previous study (Sheng *et al.*, 2001), the pesticide adsorbed most strongly by clays was found to be 4,6-dinitro-*o*-cresol (DNOC). Its uptake by K-smectite was as high as 50 mg per g of the clay, ~13 times more than sorption by SOM. The high uptake of DNOC appeared to be related to the presence of strongly electron-withdrawing nitro (-NO<sub>2</sub>) groups. Haderlein *et al.* (1993, 1996) and Weissmahr *et al.* (1998) have studied the adsorption of many NO<sub>2</sub>-containing aromatic compounds by a variety of phyllosilicate clays, and proposed an electron donor-acceptor (EDA) complex formation mechanism to account for the strong adsorption of nitroaromatic compounds. Accordingly, it was hypothesized that the strong electron-withdrawing ability of -NO<sub>2</sub> substituents results in an electron-deficient aromatic ring hence promoting the formation of EDA complexes. Subsequently, we observed that increasing the electron-releasing abilities of meta- and para-substituents on nitrobenzene decreased the adsorption of such compounds, which is consistent with the EDA mechanism (Boyd *et al.*, 2001). Other, and perhaps simpler, explanations may also explain the data. Quantum calculations (Boyd *et al.*, 2001) revealed that charge on the aromatic ring of substituted nitrobenzenes remained virtually unchanged by electron-donating or withdrawing substituents, bringing the proposed EDA mechanism into question.

Another recent quantum chemical study of the 1,3,5-trinitrobenzene (TNB) siloxane complex (Pelmenchikov and Leszczynski, 1999) also challenges the EDA mechanism. In that study, no electronic evidence for EDA complexation was observed and the high affinity of 1,3,5-TNB for a model siloxane surface was attributed to attractive Coulombic and Van der Waals' forces between the surface and the planar structure of the organic guest. The variability in adsorption for a series of substituted nitrobenzenes could be largely explained by simple ideas of complexation between the nitrobenzenes and interlayer cations (Boyd *et al.*, 2001). Additive interactions of the -NO<sub>2</sub> group, and the secondary substituent, with

interlayer K<sup>+</sup> appeared to be the primary determinant of adsorption. Further recent work (Johnston *et al.*, 2001) used FTIR spectroscopy to demonstrate that interlayer cation-NO<sub>2</sub> complexation does occur, especially in K- and Cs-smectites. Thus, while the proposed EDA mechanism has not been refuted conclusively, the available data for nitroaromatic adsorption to smectites seems to be explained without recourse to such a mechanism.

The objective of this study was to investigate further the factors that influence the interactions of nitroaromatic compounds with smectite clays in aqueous systems. To do so, two reference smectite clays of different charge densities were used to adsorb two dinitrophenol herbicides of similar structures but different molecular sizes. Clays were exchanged with various cations (K<sup>+</sup>, Cs<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup>). In addition, the CEC of the clays was reduced using the Hofman-Klemen effect of charge reduction. A combination of detailed macromolecular measurements of adsorption, FTIR, XRD and molecular dynamic simulations were used to provide insight into the nature of interactions between dinitrophenol herbicides and smectite clays, and molecular scale factors that influence these interactions.

## MATERIALS AND METHODS

### *Clays and herbicides*

Two reference clays, obtained from the Clay Minerals Society Source Clay Repository (Columbia, Missouri), were used: SWy-2, a low-charge smectite, and SAz-1, a high-charge smectite. These clays were chosen to reflect the effect of charge density on herbicide adsorption. The <2 μm clay particles separated by sedimentation were subject to K<sup>+</sup> exchange. The SWy-2 was also exchanged with Na<sup>+</sup>, Cs<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup> or Al<sup>3+</sup> to evaluate cation effects on herbicide adsorption. To do so, each clay (5 g) was dispersed in a 0.1 M chloride solution (500 ml) of the respective cation. The various clay suspensions were shaken for 24 h, and fresh chloride salt solutions were used to replace the original solutions obtained after centrifugation. This process was repeated four times to ensure complete cation saturation. Distilled water (500 mL) was used to wash each clay four times to remove extra chloride salts. Clays were then freeze dried and stored for later use. The SAz-1 was also subject to charge reductions according to the procedure described by Brindley and Ertem (1971) to evaluate further the charge density effect. The Li- and Na-exchanged clays prepared following the procedures described above were mixed in various proportions according to the desired charge reduction (15Li:85Na; 30Li:70Na; 45Li:55Na; 60Li:40Na, referred to as 0.85CEC, 0.70CEC, 0.55CEC, 0.40CEC, respectively). The mixed clays (2 g each) were fully dispersed in 200 ml of distilled water using sonication for 30 min and then shaken constantly overnight. The freeze-dried clay mixtures were heated at

220°C for 12 h. The reduced-charge clays were then subject to K<sup>+</sup> saturation. The properties of these clay samples are listed in Table 1.

Two dinitrophenol herbicides, DNOC and 4,6-dinitro-*o*-*sec*-butylphenol (dinoseb), were used for the adsorption studies. They were obtained from ChemService (W. Chestnut, Pennsylvania) with a purity of 99.9%, and used as received. The water solubilities (mg/L), pK<sub>a</sub> values and log K<sub>oc</sub> values for DNOC and dinoseb are: 198 and 52, 4.35 and 4.62, and 2.64 and 2.70, respectively.

**Adsorption isotherms.** Herbicides were dissolved in 0.1 M KCl solution with concentrations up to 50% of their water solubilities. When SWy-2 clay was exchanged with a different cation, a 0.1 M chloride solution of the corresponding cation was used to dissolve the herbicides. Up to 4.4 ml of KCl (or other cation chloride) solution were pipetted into the 7 ml borosilicate glass vials containing clay (0.02 to 0.1 g). Herbicide solution was then added into each vial to make up a total volume of 5 ml. The chloride solutions acidified to pH 2.5 using HCl were used to prepare most of the herbicide solutions and to conduct most of the sorption experiments. For DNOC adsorption by K-exchanged SAz-1, different pHs were also used to determine pH effect on adsorption. The vials were rotated continuously overnight at room temperature (23 ± 1°C) to ensure complete sorption; preliminary studies showed sorption was complete within 1 h. The vials were centrifuged at 1667 g for 20 min to separate liquid and solid phases. The concentrations of herbicides in supernatants were analyzed by direct injection of supernatants (between 10 and 190 µl) on a Perkin-Elmer reverse-phase HPLC (Perkin-Elmer, Norwalk, Connecticut) fitted with an UV-visible detector set at the maximum absorption wavelength for the respective herbicide ( $\lambda_{\max}$  is 270 nm for DNOC and 271 nm for dinoseb). A platinum EPS (extended polar selectivity) C18 column was used. The mobile phase was a mixture of 70% methanol and 30% water with a flow rate of 1.0 ml/min. Herbicide recoveries in blanks not containing clays were close to 100%. The amount of herbicide sorption was calculated from the difference between the amount added and that remaining in the final solution. Curves representing sorption isotherms were not fitted to a mathematical model but were drawn to assist visualization of data.

Competitive adsorption between DNOC and dinoseb was measured by conducting adsorption experiments for DNOC in the presence of dinoseb and for dinoseb in the presence of DNOC. A KCl solution (0.1 M) containing 20 mg/L dinoseb was used as a background solution to measure DNOC adsorption, and a KCl solution (0.1 M) containing 100 mg/L DNOC was used to measure dinoseb adsorption. The pH of both solutions was adjusted to 2.5 using 1 M HCl.

**FTIR measurements.** After sampling for HPLC analysis, a portion of the remaining DNOC-K-SWy-2 suspension with an intermediate DNOC adsorption level (27 mg/g) was used for FTIR analysis. The suspension was filtered through a Millipore filter film and allowed to dry overnight. The dried DNOC-clay film was peeled off the filter film and placed on a sample holder. The sample holder was allowed to rotate so that the angle of beam incidence could be changed. A manifold controlling air humidity was used to provide moisture-saturated air (100% relative humidity) around the DNOC-clay film. The IR spectra of the DNOC-clay film were obtained using a Perkin-Elmer 1700 FTIR spectrophotometer (Norwalk, Connecticut) with 4 cm<sup>-1</sup> resolution and 72 scans at both 0° and 45° of beam incidence.

**XRD.** Basal spacings of K-SWy-2 clays with DNOC adsorbed were determined by XRD analysis. Suspensions of K-SWy-2 with various amounts of sorbed DNOC were dropped on glass slides and allowed to dry overnight at ambient conditions to obtain oriented clay films. The XRD patterns were recorded using CuK $\alpha$  radiation and a Philips APD3720 automated X-ray diffractometer (Mahwah, New Jersey) with an APD3521 goniometer equipped with a  $\theta$  compensating slit, a 0.2 mm receiving slit, and a diffracted-beam graphite monochromator, from 2 to 12°2 $\theta$ , in steps of 0.02°2 $\theta$ , at 2 s/step. The XRD patterns were re-recorded after the clay films were allowed to equilibrate with water vapor for 2 d in a closed container containing distilled water.

**Molecular simulations.** Models for K-SWy-2 and K-SAz-1 were created and molecular dynamics simulations of DNOC-clay complexes were performed in order to explore the interactions between DNOC, cations and water in the interlayer region. The model for K-SWy-2

Table 1. Physicochemical properties of clays.

Clay	CEC (cmol <sub>e</sub> /kg)	Charge density (µmol <sub>e</sub> /m <sup>2</sup> )	% tetrahedral charge
SWy-2	82	1.09	12
SAz-1	125	1.67	0
0.85Na:0.15Li	113	1.51	
0.70Na:0.30Li	95	1.27	
0.55Na:0.45Li	78	1.04	
0.40Na:0.60Li	58	0.77	

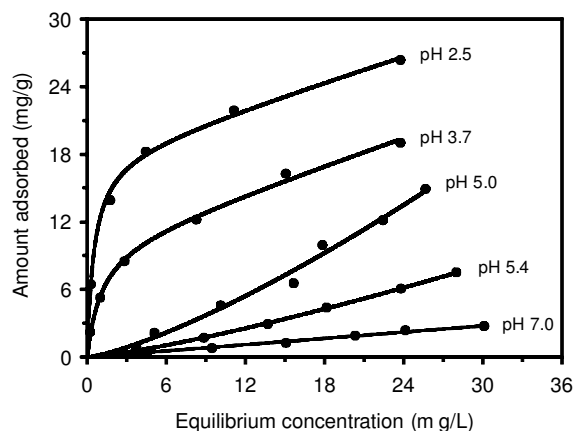


Figure 1. Effect of pH on DNOC adsorption by K-SA-z-1.

had composition  $K_7(Al_{42}Mg_6)(Si_{96}Al_1)O_{240}(OH)_{48}$  with a CEC of  $79 \text{ cmol kg}^{-1}$ , while the model for K-SA-z-1 had composition  $K_{12}(Al_{36}Mg_{12})Si_{96}O_{240}(OH)_{48}$  with a CEC of  $132 \text{ cmol kg}^{-1}$ . Two molecules of DNOC were added to each unit-cell of K-SWy-2, while one DNOC molecule was added per unit-cell of K-SA-z-1, with the DNOC molecular plane perpendicular to the basal planes of the clay. The simulated loading rates were therefore 44 and 22 mg DNOC per g clay for the SWy-2 and SA-z-1 systems, respectively. Water molecules were also added (in random interlayer positions) so that constant-pressure simulations resulted in  $12.3 \text{ \AA}$  clay layer spacings, in accord with our experimental data for DNOC in films of K-SWy-2. The energies were computed using a force field developed especially for clays (Teppen *et al.*, 1997) combined with the pcff force field (Maple *et al.*, 1994; MSI, 2000) for the organics and water. The molecular dynamics simulations were run

in the NPT ensemble for 0.1 ns, much longer than the time required for the system volume and energy to equilibrate.

## RESULTS AND DISCUSSION

Adsorption of DNOC from water by K-SA-z-1 increased significantly with decreasing solution pH (Figure 1). The isotherm shape also changed from approximately linear at pH 7 to type III (convex to the abscissa) at pHs of 5.4 and 5.0, and to type I at pHs of 3.7 and 2.5. Considering the DNOC  $pK_a$  of 4.35, it is clear that decreasing pH from 7 to 2.5 nearly completely converts the dissociated anionic species of DNOC to the molecular (neutral) species. The observation that adsorption increases with decreasing pH indicates that DNOC is primarily adsorbed as the neutral species. At pH values less than the  $pK_a$  of DNOC, sorption is initially quite strong and the amount sorbed is substantial (*e.g.*  $>2\% \text{ wt./wt.}$ ). The anionic form of DNOC prevails at pHs  $>pK_a$ , and the electrostatic repulsion between the anionic DNOC and the negatively charged clay surfaces minimizes sorption but does not completely eliminate it. However, the acidity at clay surfaces and interlayers is known to be substantially greater than bulk solution, and this probably contributes to DNOC adsorption at pHs  $>pK_a$ . These differences in pH are more notable at lower water contents such as might exist in the interlayers of K-SA-z-1 which maintains only one layer of water (see XRD data below).

The FTIR spectra of DNOC adsorbed on self-supporting oriented clay (K-SWy-2) films at  $0^\circ$  and  $45^\circ$  of beam incidence are shown in Figure 2. Both spectra show two strong in-plane bands corresponding to the symmetric  $NO_2$ -stretching vibrations of DNOC, the

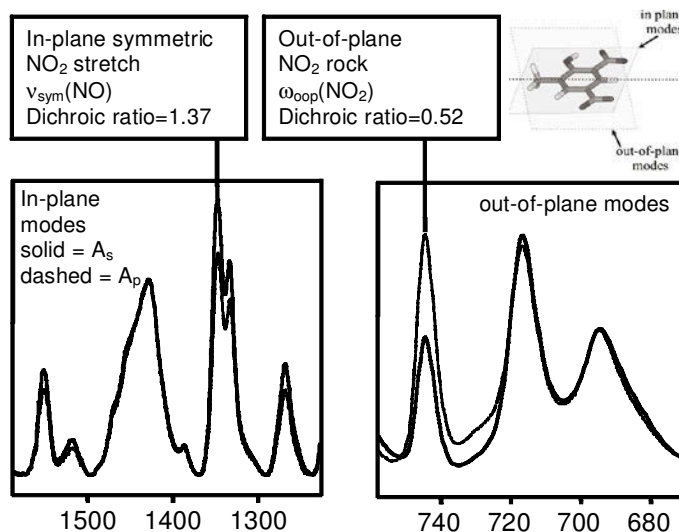


Figure 2. FTIR spectra of DNOC-K-SWy-2 at  $0^\circ$  and  $45^\circ$  of beam incidence.

bands at  $1356\text{ cm}^{-1}$  and  $1334\text{ cm}^{-1}$  correspond to symmetric N–O stretching modes (*i.e.*  $\nu_{\text{sym}}(\text{NO})$ ). The band at  $1551\text{ cm}^{-1}$  corresponds to the  $\nu_{\text{asym}}(\text{NO})$  mode (also in-plane vibration). Because the absorption intensities of the FTIR bands of oriented molecules are dependent on the angle of beam incidence, linear dichroism can be used to determine the orientation of DNOC molecules adsorbed on the clay surfaces (Prost and Chaussidon, 1969; Marguiles *et al.*, 1988). In the DNOC molecule, the dipole moments of the in-plane stretching vibrations are parallel to the ring plane, and the dipole moments of out-of-plane vibrations are perpendicular to the ring plane. The increase in the angle of beam incidence from  $0^\circ$  ( $A_s$  spectrum in Figure 2) (where the absorption intensities of in-plane vibrations are maximal and the absorption intensities of out-of-plane vibrations are minimal) to  $45^\circ$  ( $A_p$  spectrum in Figure 2) caused a decrease in the absorption intensities of in-plane vibrations and an increase in the absorption intensities of out-of-plane vibrations. This is shown most clearly when the  $A_s$  and  $A_p$  spectra are overlain (Figure 2). Comparison of the  $A_s$  and  $A_p$  spectra shows that the intensities of the in-plane bands decrease and the intensities of out-of-plane bands increase. Because the siloxane surfaces of clay in the oriented clay films are parallel to the film plane, these spectra indicate that DNOC molecules are oriented parallel to the clay surfaces. Such an orientation of trinitrobenzene molecules on clay surfaces was reported by Weissmahr *et al.* (1997).

Adsorption was affected by the type of exchangeable cation on the clay (Figure 3). Among the cations tested,  $\text{K}^+$ - and  $\text{Cs}^+$ -exchanged SWy-2 clays were much more effective than  $\text{Al}^{3+}$ -,  $\text{Ba}^{2+}$ -,  $\text{Na}^+$ - and  $\text{Ca}^{2+}$ -exchanged SWy-2 clays for DNOC adsorption. Calculation shows that at the relative concentration (equilibrium concentration/water solubility) of 0.1,  $\text{Cs}^+$ -exchanged SWy-2 is  $\sim 1.3$  times more effective than K-SWy-2, 5.5 times more effective than Al-SWy-2, 12 times more effective than

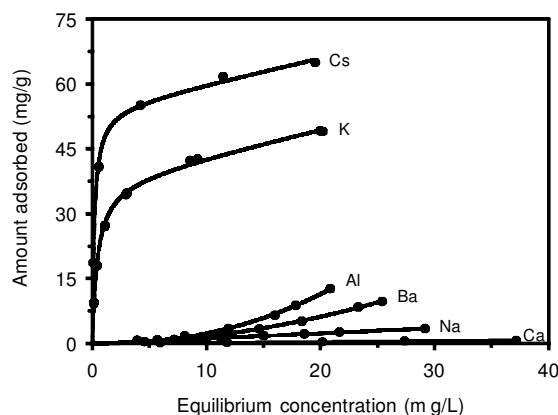


Figure 3. Effect of exchangeable cations on DNOC adsorption by K-SWy-2.

Ba-SWy-2, 28 times more effective than Na-SWy-2, and 197 times more effective than Ca-SWy-2, for DNOC adsorption. Haderlein and Schwarzenbach (1993) and Haderlein *et al.* (1996) observed similar effects of exchangeable cations on adsorption, and attributed the difference in adsorption to differences in the degree of hydration of the exchangeable cations. The parallel orientation of DNOC molecules relative to the clay layers manifests a requirement for adsorption domains of sufficient size on the siloxane surfaces between exchangeable cations. The cations ( $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) that result in low effectivenesses of the corresponding clays for DNOC adsorption have greater hydration energies than those of  $\text{Cs}^+$  and  $\text{K}^+$ . This results in larger hydration spheres for  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  compared to  $\text{Cs}^+$  and  $\text{K}^+$ . The larger sizes of highly hydrated cations may obscure a greater portion of the siloxane surfaces and shrink the size of the effective adsorption domains so that fewer sites are of sufficient size to accommodate DNOC molecules. Furthermore, the  $-\text{NO}_2$  groups of DNOC are likely to have weaker electrostatic interactions with more strongly hydrated cations which presumably maintain their waters of hydration. In contrast, for a weakly hydrated exchangeable cation such as  $\text{K}^+$ , FTIR studies (Boyd *et al.*, 2001; Johnston *et al.*, 2001) and molecular dynamic simulations (see discussion below) provide evidence for direct K- $\text{NO}_2$  interactions. As such, the DNOC adsorption isotherm is linear for SWy-2 exchanged with  $\text{Ca}^{2+}$  or  $\text{Na}^+$ , type III with  $\text{Ba}^{2+}$  or  $\text{Al}^{3+}$ , and type I with  $\text{K}^+$  or  $\text{Cs}^+$ , indicating progressively stronger interactions.

One further effect of the exchangeable cation on sorption of DNOC is through its influence on the interlayer spacing of the clay films. Homoionic K-smectites in aqueous suspension typically exhibit layer spacings of 12.5 to 15 Å (MacEwan and Wilson, 1980), and perhaps even 18 Å, with lower-charged smectites such as SWy-2 tending toward the higher spacings. In general, clay films exposed to 100% relative humidity need not have the same basal spacings as dispersed clays in aqueous solution, but the swellings tend to be similar for K-smectites (MacEwan and Wilson, 1980). The swelling behavior of K-SWy-2 films in the presence and absence of water vapor and varying amounts of adsorbed DNOC is shown in Figure 4. Exposure of previously air-dried K-SWy-2 films to 100% relative humidity caused an increase in the interlayer spacing from 11 Å to 15 Å, as is commonly observed (MacEwan and Wilson, 1980). Interestingly, the presence of sorbed DNOC restricted swelling of the re-wetted clay. At the higher DNOC loadings, the interlayer spacings for the air-dried and the re-wetted clays were nearly equal (12.2 Å). Apparently, the presence of DNOC caused the monolayer structure to be retained even in cases (*e.g.* K-SWy-2) where the smectite would swell further in the absence of DNOC. It is quite reasonable that the 12 Å spacing would be



optimal for DNOC sorption. Presumably, this would allow the herbicide molecule to contact the opposing clay surface simultaneously, thereby avoiding contact with most water molecules. Considering that the free energy of hydration of many small organic molecules is in the range of 10 to 30 kJ/mol, removal of DNOC from water may provide sufficient energy to prevent K-smectite from swelling beyond 12 to 12.5 Å. Since we were unable to measure the swelling of aqueous K-SWy-2 suspensions containing adsorbed DNOC, it is unknown whether the clays adopt a 12 Å *d*-spacing in suspension as a result of DNOC adsorption. It is clear, however, that DNOC adsorption inhibits the rehydration of previously air-dried K-SWy-2 films. Cs-smectites have a strong tendency to equilibrate with 12.5 Å spacings, even in aqueous suspension (MacEwan and Wilson, 1980), due to the low hydration energy of Cs<sup>+</sup>. The natural clay swelling thus creates an interlayer thickness that is optimally sized for removing DNOC from the solution phase, hence Cs-SWy-2 is an even more effective adsorbent of DNOC than K-SWy-2.

Smectites saturated with Ca<sup>2+</sup>, Ba<sup>2+</sup> or Al<sup>3+</sup> always swell to >15 Å in aqueous suspension and they adsorb much less DNOC (Figure 3). According to the hypothesis presented above, the interlayer region of smectites saturated by these strongly hydrated cations is too thick (>6 Å) to remove the 3 Å thick DNOC from the aqueous phase. Presumably the energy penalty for dehydrating these cations is too large to allow any phase change that would accommodate DNOC more favorably.

The size of the adsorption domains is also dependent on the charge density of the clay mineral (as reflected by CEC). Assuming that the negative charges are regularly distributed on 750 m<sup>2</sup> g<sup>-1</sup> of clay surface, that the *d*-spacings are 12.3 Å, and using the clay charge densities from Table 1, calculations show the spacing between adjacent K<sup>+</sup> ions to be 7.1 Å for K-SAz-1 and 8.7 Å for K-SWy-2. The larger adsorption domains in

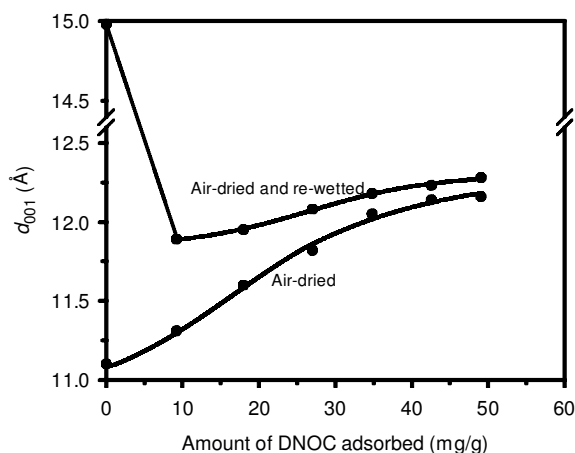


Figure 4. Basal spacings of DNOC-adsorbed K-SWy-2 clays in the presence and absence of water.

low-charge K-SWy-2 result in a greater degree of adsorption of DNOC by K-SWy-2, as compared to the high-charge K-SAz-1 with its smaller adsorption domains (Figure 5a). From the isotherms, K-SWy-2 is 2.2 times more effective than K-SAz-1 for DNOC adsorption at the relative concentration of 0.1.

To examine further the effect of charge density on adsorption, reduced-charge K-SAz-1 clays were used to adsorb dinoseb. Dinoseb contains a secondary butyl group instead of a methyl group as in DNOC, and therefore it is a structurally similar but larger molecule compared to DNOC. Sorption of dinoseb by the high-charge SAz-1 is depressed substantially compared to the low-charge SWy-2 (Figure 5). Charge reduction reduces the number of exchangeable cations on the clay surfaces, and thus provides larger adsorption domains for herbicide adsorption. The measured CECs for reduced-charge SAz-1 clays are linearly correlated to the percent of Na-clay after it was mixed with Li-clay and prior to heating (Table 1) although the maximum theoretical reduction (based on %Li) was not reachable. Based on the measured CECs of the Li-treated clays, the spacing between adjacent K<sup>+</sup> ions is 7.1, 7.4, 8.1, 8.9 and 10.4 Å for the original SAz-1 and the progressively reduced-charge clays, respectively. The adsorption of dinoseb by these reduced-charge clays shows that charge reduction significantly enhances dinoseb adsorption (Figure 5b). A

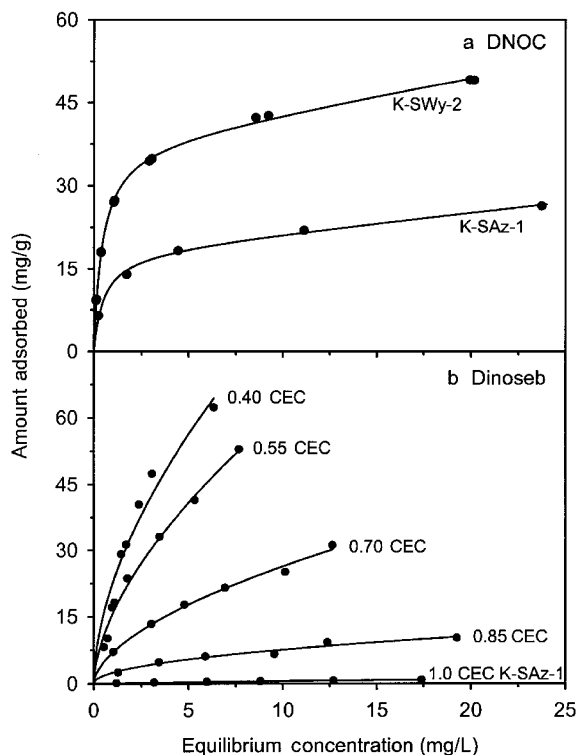


Figure 5. (a) Effect of CEC of clays on DNOC adsorption by K-SWy-2 and K-SAz-1. (b) Effect of charge reduction of SAz-1 on dinoseb adsorption by K-saturated clays.

similar observation was made by Weissmahr *et al.* (1998) regarding the adsorption of 4-nitrotoluene. These results demonstrate the importance of charge density in determining the size of adsorption domains, which appear to exist primarily between hydrated exchangeable cations in the clay interlayers. They are consistent with earlier studies which established the inverse relation between sorption and layer charge, and the effect of layer charge on adsorption domain size (Jaynes and Boyd, 1990, 1991; Lee *et al.*, 1990; Laird *et al.*, 1992; Boyd and Jaynes, 1994; Laird, 1996).

Once the size of the adsorption domains is defined, molecular size also exerts a steric effect on adsorption. This is illustrated by the observation that the adsorption of dinoseb by K-SAz-1 is lower than that of DNOC (Figure 6). Based on the mole concentration of herbicide adsorbed per unit mass of K-SAz-1, DNOC is adsorbed 37 times more than dinoseb at the highest measured adsorption. Thus, even subtle changes in pesticide structure, in this case substitution of isobutyl for methyl, can dramatically impact sorption. The difference in affinity is also illustrated by the competitive adsorption between DNOC and dinoseb (Figure 6). Adsorption of DNOC by K-SAz-1 remains unchanged in the presence and absence of dinoseb. In contrast, in the presence of DNOC, dinoseb adsorption is significantly reduced. These results demonstrate that dinoseb cannot effectively compete with DNOC for adsorption sites due to steric constraints imposed by the secondary butyl group of dinoseb.

The molecular dynamics simulation results illustrate possible interactions of DNOC in the interlayer regions of K-SWy-2 and K-SAz-1 (Figure 7). Within a monolayer of interlayer water, DNOC has little choice but to orient its molecular plane parallel to the clay basal planes, in agreement with the FTIR findings. In this environment, the simulated DNOC molecules readily complex multiple  $K^+$  ions with their  $-NO_2$  groups and commonly, their  $-OH$  groups as well. The snapshots in

Figure 7 are typical of the overall simulations, and show that DNOC interacts readily with  $K^+$  ions through several types of inner-sphere and outer-sphere complexes. Often, both O atoms of one  $-NO_2$  group are directly coordinated to a single  $K^+$  ion with an average  $K-O$  distance of  $3.0 \pm 0.2$  Å in K-SWy-2 ( $2.9 \pm 0.2$  Å in K-SAz-1). Another common complex (two instances are shown in Figure 7) is for the phenolic O and one O of the neighboring  $-NO_2$  group to simultaneously coordinate  $K^+$  at these same distances. The third type of inner-sphere complex is between a single O of a  $-NO_2$  group and  $K^+$ , usually more transient and with somewhat longer  $K-O$  distances of 3.2 to 4.5 Å. Finally, transient states existed in which  $-NO_2$  groups were indirectly coordinated to  $K^+$  ions through the intermediation of water. These outer-sphere complexes exhibited radial distribution functions with peak distances of  $5.0 \pm 0.3$  Å and  $6.5 \pm 0.5$  Å between  $K^+$  ions and the O atoms of DNOC. Note (Figure 7) that in the confined interlayer space of the K-smectites, each DNOC molecule always interacted with multiple  $K^+$  ions simultaneously. Such interactions are largely additive, which helps explain the strong adsorption of many nitrobenzenes by K-exchanged clay minerals. This idea of multiple complexation interactions between nitroaromatic pesticides and interlayer cations may seem to conflict with observations (Figure 5a) that the higher-charged clay adsorbs less pesticide. This apparent conflict can be qualitatively reconciled by looking at Figure 7 and considering the crowding of interlayer  $K^+$  in the K-SAz-1. Adding another DNOC molecule to the interlayer region while maintaining the 12.3 Å layer spacing would require the average spacing between those cations to decrease further, causing the electrostatic repulsion energy to increase. Based on the configurations in Figure 7, the aqueous phase (excluding the DNOC) of the interlayer fluid in the K-SAz-1 system is already approaching a  $K^+$  concentration of 14 mol  $L^{-1}$ , while that of K-SWy-2 is  $<10$  mol  $L^{-1}$ . Another possible explanation (D.A. Laird, pers. comm.) for decreased DNOC adsorption by K-SAz-1 is that interlayer water is more strongly bound by smectites of higher charge density, due to increases in both numbers of cations and layer charge density, so DNOC is less likely to displace that water.

In summary, dinitrophenol herbicides are adsorbed by smectite clays as neutral species. The DNOC molecules are intercalated by smectite clays and oriented parallel to clay surfaces. The properties of both clays and herbicide molecules affect adsorption. A decrease in the size of adsorption domains on the clay surfaces due to increasing hydration of exchangeable cations and/or charge density reduces adsorption. Adsorption from water is favored by weakly hydrated exchangeable cations (*e.g.*  $K^+$ ,  $Cs^+$ ) that manifest interlayer spacings of 12.5 Å, which appears optimal for adsorption. Here the herbicide molecule contacts both clay surfaces, which minimizes

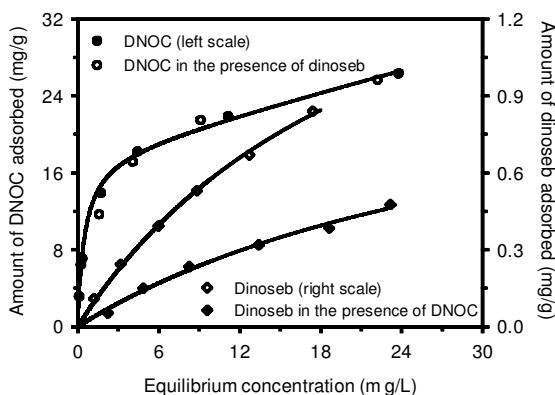


Figure 6. Effect of molecular size of herbicides on adsorption by K-SAz-1, and competitive adsorption between DNOC and dinoseb.

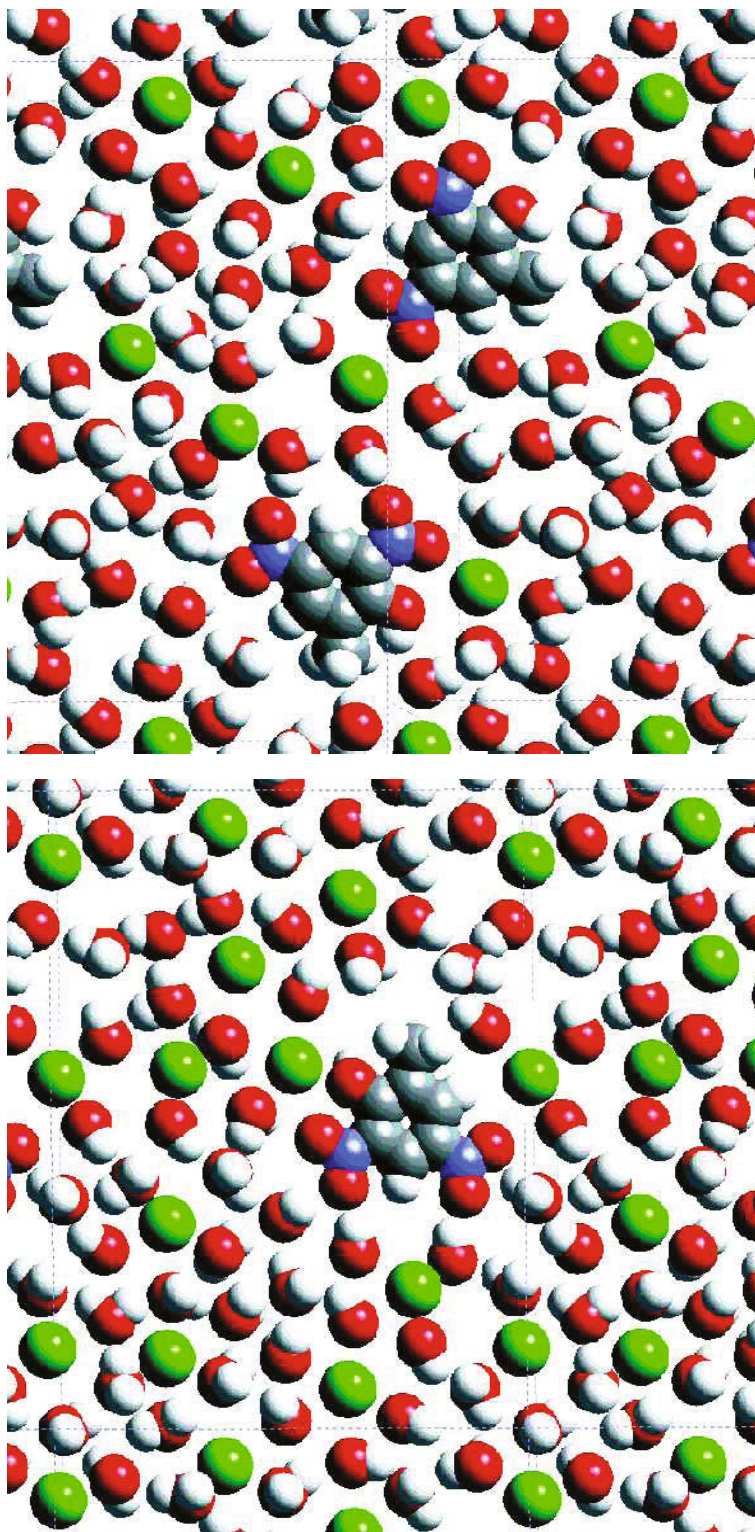


Figure 7. Snapshots of molecular dynamics simulations of DNOC in the interlayer regions of K-SWy-2 (upper) and K-SAz-1 (lower). Clay layers were parallel to the page and have been removed in order to expose the interlayer complexes. The atom coloring scheme is K = green, O = red, H = white, C = gray and N = blue.



its interaction with water. Lower cation hydration also favors direct interaction of  $-NO_2$  groups with interlayer cations. Exchangeable cations with larger hydration energies cause larger interlayer spacings ( $>15 \text{ \AA}$ ), interact less effectively with  $-NO_2$  groups, and the corresponding clays are less effective adsorbents. An increase in the molecular size of herbicides diminishes adsorption due to steric constraints.

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