

# COMPREHENSIVE STUDY OF ORGANIC CONTAMINANT ADSORPTION BY CLAYS: METHODOLOGIES, MECHANISMS, AND ENVIRONMENTAL IMPLICATIONS

STEPHEN A. BOYD, CLIFF T. JOHNSTON, DAVID A. LAIRD, BRIAN J. TEPPEN, AND HUI LI

- 2.1. Introduction
- 2.2. Contributions of Clays Versus Soil Organic Matter to Sorption
- 2.3. Macroscopic Sorption Studies
- 2.4. X-Ray Diffraction
- 2.5. Vibrational Spectroscopic Studies
- 2.6. Molecular and Quantum Mechanical Simulations
- 2.7. Environmental Implications
- 2.8. Summary

## 2.1. INTRODUCTION

The publication of two papers in 1979 (Chiou et al. 1979; Karickhoff et al. 1979) marked the beginning of a major redirection of thinking regarding the sorption of neutral organic contaminants (NOCs) and pesticides in soil/sediment–water systems. Prior to these important papers, soil was generally viewed as an adsorbent containing two high-surface-area components, soil organic matter (SOM) and soil clays, that were responsible for the adsorption of NOCs and pesticides by a variety of mechanisms (e.g., H bonding, van der Waals forces) unique to the particular combination of soil and the organic solute of concern. The 1979 papers set forth a new conceptualization of NOC sorption by soils, which has come to be known as *partition theory*.

With the development of partition theory, the idea that SOM played a dominant, if not singular, role in the sorption of NOCs and pesticides by soils also gained acceptance. Soil organic matter was viewed as an organic partition

phase rather than a high-surface-area adsorbent (Pennell et al. 1995). Accordingly, organic solutes in water would essentially dissolve in amorphous SOM in much the same way that they partition from water into an immiscible organic phase such as octanol or hexane, or into organic polymers/solids such as polyurethane or rubber. The magnitude of sorption would depend directly on the amount of SOM as well as the solubility of the NOC or pesticide in water and its solubility in SOM. Solute with low water solubility partition to a greater degree into SOM manifesting a larger sorption or partition coefficient (often denoted  $K_p$  or  $K_d$ ). Sorption is quantified by this coefficient, which is in essence a simple ratio of the two concentrations:  $K_p = C_{\text{soil}}/C_{\text{water}}$ , where  $C_{\text{soil}}$  and  $C_{\text{water}}$  are the solute concentrations in SOM and water, respectively. Furthermore, when the individual  $K_p$  values (for a given NOC) among a series of soils are normalized to the corresponding fractional SOM content ( $f_{\text{om}}$ ) of the soil, the normalized values tend to converge within a factor of  $\sim 2$  (Kile et al. 1995), especially for NOCs devoid of polar functional groups. The SOM-normalized value,  $K_{\text{om}} = K_p/f_{\text{om}}$ , represents sorption per unit mass of SOM, and can for all practical purposes be considered a “constant.” Once the  $K_{\text{om}}$  of a NOC is known,  $K_p$  for soils can be easily estimated by  $K_p = K_{\text{om}}f_{\text{om}}$ , that is, simply by knowing the  $f_{\text{om}}$  of a soil. For context, owing to the semipolar nature of SOM (which has an O content of  $\sim 40\%$ – $50\%$  derived from polar functional groups such as phenolic  $-\text{OH}$  and  $-\text{COOH}$  groups), the  $K_{\text{om}}$  value of a specific NOC/pesticide is generally smaller than the corresponding octanol–water partition coefficient ( $K_{\text{ow}}$ ) by approximately an order of magnitude. Today,  $K_{\text{om}}$  is routinely used to predict  $K_p$  in NOC/pesticide leaching models;  $K_p$

defines site-specific soil–water distribution for a given NOC–soil combination.

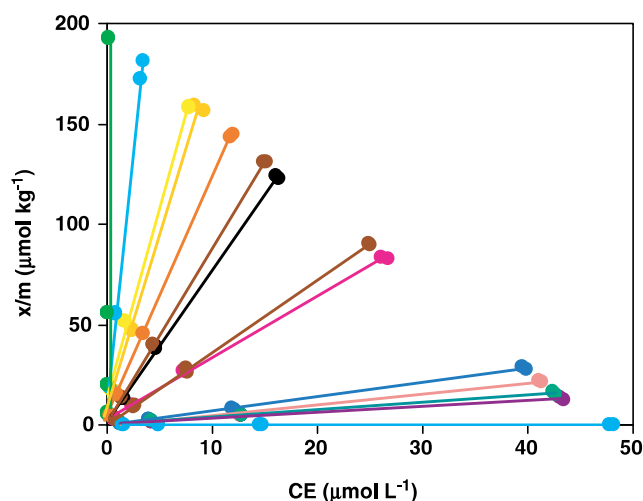
Solute partitioning, which has now gained broad acceptance as a sorption mechanism, manifests certain sorption characteristics that distinguish it from adsorption (Chiou 2002; Chiou et al. 1983). Partitioning is a process of dissolution into the partition phase, whereas adsorption involves condensation of a solute on the surface of the adsorbent. Solute partitioning manifests linear sorption isotherms, noncompetitive sorption effects in multisolute systems (two or more NOCs sorbing simultaneously), and low heat effects on sorption (i.e., low and constant enthalpies). Solute adsorption manifests (generally) nonlinear isotherms, competitive effects (negative) on sorption in multisolute systems, and comparatively large negative enthalpies (or large heat effects on sorption). Considerable evidence has been provided to demonstrate the characteristics of solute partitioning in numerous studies of sorption of NOCs from water by soils and sediments (Chiou 2002).

Further examination of NOC sorption by soil has revealed some evidence of sorption isotherm nonlinearity, and competitive effects on sorption in multisolute systems, especially at low relative solute concentrations (the ratio of concentration of solute in water to aqueous solubility of the solute). These effects, which are typically of low magnitude, have been reconciled by several theories that augment the fundamental process of solute partitioning. One such theory suggests that small amounts of high-surface-area carbonaceous materials (e.g., chars, black carbon) are responsible for the observed deviations in sorption behavior predicted from partition theory (Chiou et al. 2000). Also, SOM has been viewed as a dual sorbent containing both “hard” and “soft” components with the former responsible for the deviations from sorption characteristics predicted by strict solute partitioning (e.g., Pignatello and Xing 1996; Leboeuf and Weber 1997; Xia and Ball 2000). These ideas are best viewed as further refinements that augment the concept of solute partitioning as it pertains to NOC sorption by soils and sediments rather than a challenge to the basic idea of NOC partitioning into SOM as the dominant sorptive mechanism.

One very important manifestation of the widespread acceptance of partition theory to describe NOC sorption by soils is that most NOC/pesticide leaching models now use simple linear partition coefficients (often estimated by  $K_p = K_{om}f_{om}$ ) to predict soil–water distribution of NOCs and pesticides. This approach implicitly ignores or discounts any possible contribution of soil clays to sorption. In this context some proponents of partition theory have suggested that soil mineral surfaces are in general polar or hydrophilic in nature, and that in the presence of ambient moisture, water molecules are preferentially adsorbed on these surfaces (Chiou 2002; Chiou and Shoup 1985). Accordingly, since NOCs lack the ability to displace strongly adsorbed water molecules from the mineral surfaces, the mineral compo-

nents are in essence deactivated as adsorbent surfaces for NOCs and pesticides. Evidence has been provided to demonstrate that the addition of water to anhydrous soils results in a diminution in the overall uptake of certain NOCs and pesticides by soils. These data were interpreted to mean that mineral surfaces (e.g., clays) are active solid adsorbents for NOCs in the absence of water, and that under such conditions both mineral phase adsorption and organic matter partitioning are operative sorption processes. However, as water is added, it displaces adsorbed NOCs and pesticides from mineral surfaces (which preferentially bind water) hence sorption overall is reduced and partitioning into SOM is left as the dominant process responsible for the sequestration of NOCs and pesticides in soil–water systems.

At this point in the development of our understanding of NOC/pesticide sorption by soils, dogma held that minor “unsuppressed” sorption of NOCs to clays may occur, but that it was dwarfed by sorption to SOM. Then, in 1992 another important paper was published (Laird et al. 1992) showing that relatively pure smectite clays could effectively adsorb atrazine from water. Interestingly, atrazine adsorption by these clays ranged widely, from essentially complete removal to comparatively minimal uptake (Fig. 2.1). This variability was observed by using many different members of the group of smectite clays. These clays possess subtle differences in composition owing to differences in isomorphous substitution in the tetrahedral Si–O and/or octahedral



**Figure 2.1.** Adsorption of atrazine from water by several different reference and soil smectite clays [from Laird et al. (1992)]. Plots are of concentrations of sorbed atrazine ( $x/m$ ) versus equilibrium aqueous atrazine concentration (CE). Sorbents (in descending order) are as follows: Panther Creek beidellite, hectorite, IMV saponite, Amory montmorillonite, Wyoming bentonite, Belle Fourche montmorillonite, Upton montmorillonite, Webster smectite, Polkville montmorillonite, IMV bentonite, Chambers montmorillonite, Camp Bertean montmorillonite, Carmeron smectite/illite, and Otay montmorillonite.

**TABLE 2.1. Structural Formulas for Dioctahedral and Trioctahedral Clays with either Tetrahedral or Octahedral Isomorphic Substitution**

Substitution	Dioctahedral	Trioctahedral
Tetrahedral	Beidellite: $\text{Na}_{0.33}\text{Al}_2(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$ Nontronite $\text{Na}_{0.33}\text{Fe}_2(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$	Saponite: $\text{Na}_{0.33}\text{Mg}_3(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$
Octahedral	Montmorillonite $\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$	Hectorite $\text{Na}_{0.33}(\text{Mg}_{2.67}\text{Li}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$

Source: Adapted from Gaines et al. (1997).

Al–O sheets of the 2 : 1 clays, and the type (dioctahedral vs. trioctahedral) of octahedral sheet. Specific structures of important members of the smectite group are given in Table 2.1. Remarkably, these subtle differences manifested very large differences in the affinity of particular smectite clays for aqueous-phase atrazine. Soon thereafter, an important series of papers (Haderlein and Schwarzenbach 1993; Haderlein et al. 1996; Weissmahr et al. 1997) similarly showed that clay minerals common to soils, namely, kaolinite, illite, and smectite, could also effectively adsorb nitroaromatic compounds (NACs) from water. Among these, smectite clays were by far the most effective NAC adsorbents. From these and similar studies several questions arise: whether (1) the role of soil clays as effective adsorbents of NOCs/pesticides in soil–water systems been erroneously neglected; (2) when and under what conditions clay minerals are effective adsorbents for NOCs and pesticides in soils; (3) the specific underlying forces and mechanisms by which clays, especially smectite clays, functioned as highly effective adsorbents for NOCs; and (4) how one goes about revealing these molecular-scale forces and mechanisms?

## 2.2. CONTRIBUTIONS OF CLAYS VERSUS SOIL ORGANIC MATTER TO SORPTION

In an attempt to address the first question, we conducted a study that directly compared the potential contributions of SOM and montmorillonite clay as sorbents for several important examples of NOCs and pesticides (Sheng et al. 2001). We used an organic soil (Houghton muck) essentially devoid of clay minerals (having an organic carbon content of 49.5%) as a “surrogate” for pure SOM. This soil, where SOM was the singular (organic) sorbent for NOCs/pesticides, was compared to potassium-saturated montmorillonite, which represented a purely clay mineral adsorbent. On a unit mass basis, SOM was a more effective (to varying extents) sorbent than was K-montmorillonite for biphenyl, diuron, and parathion. However, for atrazine, carbaryl, dichlobenil, and dinitro-*o*-cresol, K-montmorillonite was more effective than SOM as a sorbent phase. Since the clay content of most mineral soils significantly exceeds the SOM content, overall sorption of certain NOCs and pesticides could plausibly be controlled by their interactions with clays, especially the expandable smectites, which possess particularly high surface areas of

~800 m<sup>2</sup>/g. Among these pesticides, specific interactions between pesticide substituents and exchangeable cations of clay, hydrophobic and/or electron donor–acceptor interactions between the aromatic rings of pesticide molecule and the siloxane surfaces of clays, and steric hindrance due to bulky substituents on the pesticide structure seemed to be important determinants of the extents of pesticide adsorption by K-montmorillonite.

The occurrence of significant clay–organic interactions observed in the study by Sheng et al. (2001) was consistent with earlier studies that had shown appreciable adsorption of certain pesticides by clays (Bailey and White 1970; Green 1974; Mortland 1986). Also, previous investigations had sought to define conditions under which clay minerals contributed significantly to NOC/pesticide retention in soils, and concluded that this could occur when clay to SOM ratios in soil 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 ca. ~62 for atrazine and 84 for alachlor (Grundl and Small 1993). In retrospect, these seem like fairly gross estimates of soil properties that could be used to benchmark the important role of clays in pesticide retention by soils. More recent studies clearly indicate a much more specific set of conditions that manifest high-affinity clay adsorbents that are unique to the particular combination of solute properties and structure as well as clay type and type of exchangeable cation associated with the clay.

Following demonstration that for several classes of important NOCs and pesticides smectite clays are equally or more effective adsorbents than SOM (compared as isolated components), the next logical line of investigation was to reveal the underlying operative mechanisms and forces responsible for adsorption by smectite clays. These clays have been the primary focus of this body of research because of their widespread occurrence, large surface areas, and reversible expandability. These clays consist of a basic 2 : 1 layer structure with an octahedrally coordinated Al–O sheet sandwiched between two tetrahedrally coordinated Si–O sheets. The specific members of this group of clays differ in being either dioctahedral or trioctahedral, and on the type, location, and extent of isomorphic substitution. For example, saponite is a trioctahedral clay (Mg–O central sheets) with nearly 100% of the isomorphic substitution

**TABLE 2.2. Characteristics of Smectite Clay Minerals Used in More Recent Studies as Adsorbents for NOCs and Pesticides**

Clay	Smectite Clay Type and Octahedral Sheet Type	Tetrahedral Charge, %	Cation Exchange Capacity cmol/kg	Surface Area m <sup>2</sup> /g	BET N <sub>2</sub> Surface Area, m <sup>2</sup> /g	OC %	Surface Charge Density, μmol/m <sup>2</sup>
SWy-2	Montmorillonite, dioctahedral	3.6	83.6	766	31.82	0.07	1.09
SAz-1	Montmorillonite, dioctahedral	~12	130	768	—	—	—
Upton	Montmorillonite, dioctahedral	1.6	113.3	730	39.8	0.06	1.55
SHCa-1	Hectorite, trioctahedral	14	86.4	743	63.19	<0.1	1.16
SapCa-2	Saponite, trioctahedral	100	97.4	750	—	0.128	1.30

Source: Adapted from Liu et al. (2009).

(Al<sup>3+</sup> for Si<sup>4+</sup>) occurring in the tetrahedral sheets. Other smectites, such as montmorillonite, are dioctahedral with substitution (e.g., Mg<sup>2+</sup> for Al<sup>3+</sup>) primarily in the octahedral layer. Tables 2.1 and 2.2 present some key structural properties and characteristics that differentiate members of the family of smectite clays, and that serve as determinants of their affinities for NOCs and pesticides.

Nitroaromatics are an important class of compounds used widely as energetics, solvents, fragrances, and base structure for pesticide classes such as the dinitrophenols, and occur widely as environmental contaminants (e.g., in soils). They are also strongly adsorbed by smectite clays (Haderlein and Schwarzenbach 1993; Haderlein et al. 1996; Boyd et al. 2001; Sheng et al. 2002; Li et al. 2003), and for these reasons they have been subjected to several studies in an effort to understand the basis of their strong affinity for smectites. Initial studies of these compounds, which have revealed several interesting and important sorption phenomena, relied primarily on macroscopic sorption behavior. These studies revealed many important clues regarding factors that influence sorption affinity and have enabled the development of structural hypotheses for operative adsorption mechanisms, which can be subjected to further study using molecule-scale methodologies, including X-ray diffraction, vibrational spectroscopies, and molecular/quantum mechanical simulations. In the following discussion we will show what information can be gained by these complementary techniques and how, by integrating this knowledge, detailed molecular scale adsorption mechanisms can be revealed. This is the goal of our chapter, rather than a detailed review of the published literature on clay–organic interactions [for these, see Bailey and White (1970), Green (1974), Mortland (1970, 1986), and Theng 1974].

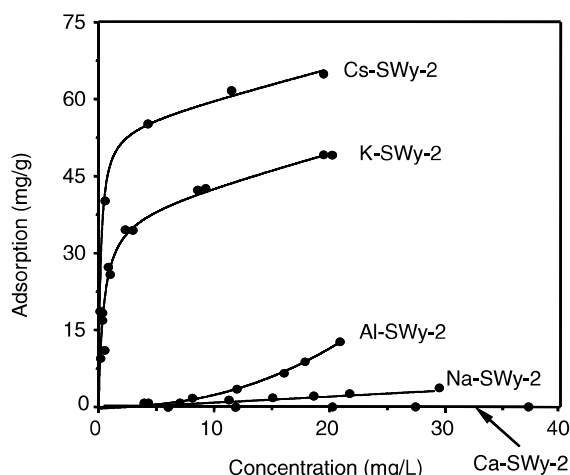
### 2.3. MACROSCOPIC SORPTION STUDIES

Early studies of organic compound–clay interactions relied heavily on macroscopic sorption data to reveal interesting phenomenologic behavior, and to begin to understand associated sorption mechanisms. Often the most dramatic change

in sorption affinity of smectite clays for NOCs is achieved by replacing naturally occurring inorganic exchangeable cations with organic cations such as quaternary ammonium and phosphonium cations (Boyd et al. 1988a–, Jaynes and Boyd 1990, 1991a,b; Lee et al. 1989; Kukkadapu and Boyd 1995; Lawrence et al. 1998; Sheng and Boyd 2000). However, the focus of this discussion is on the sorption properties for NOCs of smectites exchanged with inorganic cations since these are found in smectites as they exist in nature. As mentioned above, such smectites display high affinities for NACs (Haderlein and Schwarzenbach 1993; Haderlein et al. 1996; Weissmahr et al. 1997; Boyd et al. 2001; Sheng et al. 2002; Li et al. 2004a), and other important compounds, including atrazine (Laird et al. 1992; Aggarwal et al. 2006a), trichloroethene (Aggarwal et al. 2006b), and dioxin (Liu et al. 2009).

The affinity of smectites for NACs is strongly dependent on the nature of the inorganic cation occupying the cation exchange sites of smectites. In a study of the herbicide dinitro-*o*-cresol (DNOC), Sheng et al. (2002) showed that adsorption of DNOC from water by smectite exchanged with a series of inorganic cations decreased in the order Cs<sup>+</sup> > K<sup>+</sup> ≫ Al<sup>3+</sup> > Ba<sup>2+</sup> > Na<sup>+</sup> > Ca<sup>2+</sup> (Fig. 2.2). Calculation based on sorption isotherms showed that at a relative concentration of 0.1, Cs-SWy-2 was 1.3 times more effective than K-SWy-2, 5.5 times more effective than Al-SWy-2, 12 times more effective than Ba-SWy-2, 28 times more effective than Na-SWy-2, and 197 times more effective than Ca-SWy-2 for DNOC adsorption from water. Haderlein and Schwarzenbach (1993) and Haderlein et al. (1996) observed qualitatively similar effects of exchangeable cations on adsorption of NACs. Haderlein and co-workers attributed the strong adsorption of NACs by smectites to the formation of electron donor (negative charge sites in clays)–electron acceptor (NACs where the –NO<sub>2</sub> groups attract electron density from the aromatic π-ring system) (EDA) complexes. In a study by Boyd et al. (2001) adsorption of a series of substituted nitrobenzenes by K-SAz-1 revealed that electron-withdrawing groups did enhance sorption in a predictable manner on the basis of the Hammett substituent constant σ, and this appeared to be consistent with the proposed formation of





**Figure 2.2.** Adsorption of dinitro-*o*-cresol (DNOC) from water by SWy2 montmorillonite saturated with different exchangeable cations [from Sheng et al. (2002)]. Plots are of concentration of adsorbed DNOC versus equilibrium aqueous concentration of DNOC.

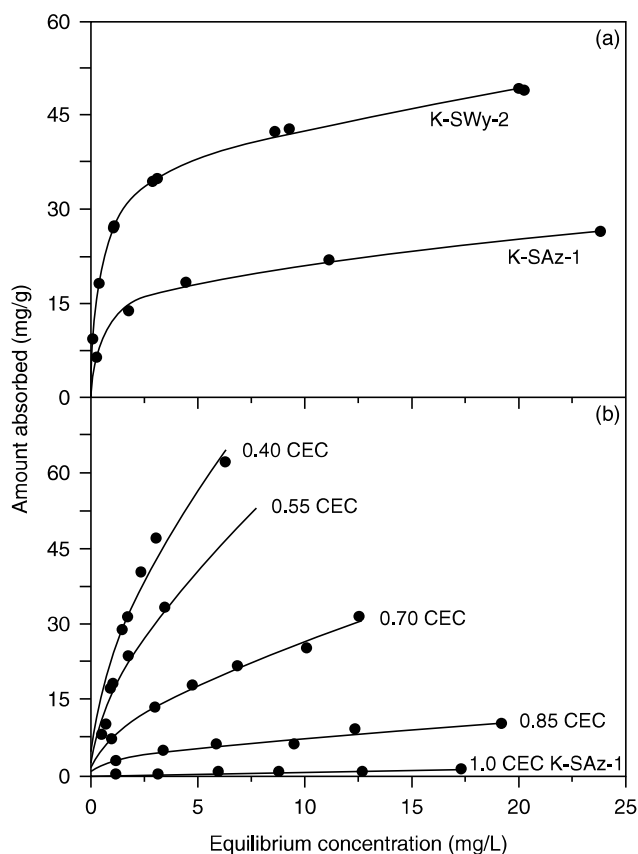
EDA complexes. However, quantum calculations of the gas-phase NACs revealed that the electron density of the aromatic  $\pi$ -ring system was unchanged among the substituted nitrobenzenes. Rather, electron density donated by a second substituent on nitrobenzene seemed to be appropriated by the  $-\text{NO}_2$  group, leaving the aromatic  $\pi$  ring relatively unaffected. Thus, the quantum calculations did not support the dominance of an EDA mechanism since there was no evidence that the aromatic ring was any more or less electron-deficient regardless of the nature of the second substituent. This observation suggested the predominance of other mechanisms and forces in the adsorption of NACs by smectite clays.

It was clear, from a cursory look at exchangeable cation ordering relative to the affinity of DNOC and other NACs, that cations with lower hydration energies, namely,  $\text{Cs}^+$  and  $\text{K}^+$ , produced higher-NAC-affinity smectites than did those saturated with cations that had higher hydration energies. This led us to hypothesize that  $-\text{NO}_2$  groups, which possess partial negative charge, might form complexes with the exchangeable cations, either directly or through the intermediation of water. Weaker cation hydration would logically favor such interactions. Furthermore, the magnitudes for adsorption of various substituted NACs by a given K-saturated smectite (Boyd et al. 2001) followed an ordering that seemed plausibly consistent with the ability of the functional groups to form complexes with interlayer  $\text{K}^+$ . In a more recent study (Liu et al. 2009), the adsorption of dibenzo-*p*-dioxin (dioxin) by saponite exchanged with different inorganic cations revealed that Cs-saponite effectively adsorbed dioxin from water, reaching nearly 1% wt/wt. In this instance there was a much larger difference in adsorption (of dioxin) by Cs- versus K-saponite, as compared to sorption of NACs.

Adsorption appeared to involve one or both of the oxygens in the dioxin ring. Dioxin adopted at least two orientations on the saponite interlayer. In one, dioxin is essentially dehydrated as it interacts with the opposing siloxane sheets and with coplanar  $\text{Cs}^+$  via one of the dioxin ring oxygens, analogous to adsorption of NACs. At higher loadings dioxin is intercalated between  $\text{Cs}^+$  and the clay surface in a tilted orientation when both oxygens of the dioxin ring interact with  $\text{Cs}^+$ . Because the negative charge character of the dioxin ring oxygens is less than that of the oxygens of  $-\text{NO}_2$  groups, the adsorptive requirement for a weakly hydrated cation, namely,  $\text{Cs}^+$ , is greater than that observed for NACs. Hence, dioxin adsorption by Cs-saponite is much higher than that by K-saponite, whereas this difference is rather smaller for NAC adsorption (Fig. 2.2).

A second important finding from macroscopic sorption studies was that smectite clays with lower charge densities were more effective adsorbents for NACs and other NOCs compared to clays with higher charge densities. This had first been observed in studies of adsorption of vapor-phase aromatic hydrocarbons (e.g., benzene, toluene) by smectites exchanged with tetramethylammonium (Lee et al. 1990). Comparison of a relatively “low-charge” smectite (SWy-2, surface charge density  $\sim 1.09 \mu\text{mol}/\text{m}^2$ ) to a “high charge” smectite (SAz, surface charge density  $\sim 1.69 \mu\text{mol}/\text{m}^2$ ) revealed that the lower-charge SWy-2 clay was a more effective adsorbent for gas-phase aromatic hydrocarbons. Also, uptake of the NOC vapor by dry clay was higher than uptake of the corresponding solute from water. Subsequent studies with similar trimethylphenylammonium clays showed the same trends for adsorption from water of a larger group of aromatic hydrocarbons (Jaynes and Boyd 1990, 1991a). Also, when the charge density of the high-charge SAz clay was chemically reduced (by the Li reduction method), adsorption was directly related to the degree of charge reduction (Jaynes and Boyd 1991b).

In our study of DNOC adsorption by K-exchanged smectites we found that the lower charged SWy-2 adsorbed more DNOC from water than the higher-charge SAz, and charge reduction of the SAz clay resulted in proportionately higher adsorption of DNOC (Sheng et al. 2002), (Fig. 2.3). So, from these macroscopic sorption studies, three key observations were made that led to the beginnings of hypotheses regarding the operative adsorption mechanisms: (1) adsorption was higher in smectites exchanged with weakly hydrated exchangeable cations, (2) adsorption of the organic vapor by the dry clay was somewhat higher than adsorption of the corresponding solute from water (i.e., water reduced uptake) and (3) adsorption by lower-charge-density clays was higher than adsorption by higher-charge-density clays. From these observations we proposed that (1) adsorption could involve the exchangeable cation via complexation with polar functional groups or structural units (e.g., with  $-\text{NO}_2$  groups of adsorbed NACs), (2) siloxane surfaces between



**Figure 2.3.** (a) Adsorption of dinitro-*o*-cresol (DNOC) by homoionic lower K-smectite (K-SWy-2) and higher (K-SAz-1) surface charge density; (b) sorption of dinitro-*o*-sec-butylphenol (Dinoseb) by charge-reduced K-SAz-1 (from 15% to 60% reduction in cation exchange capacity—denoted 0.85 CEC to 0.4 CEC) [from Sheng et al. (2002)].

exchangeable cations were nanoscale adsorption domains, and (3) water tended to decrease adsorption by hydrating the exchangeable cation—thereby reducing the potential for complex formation and by obscuring the siloxane surface; in both instances more water (i.e., more cation hydration) meant lower adsorption overall. The effects are illustrated schematically in Figure 2.4.

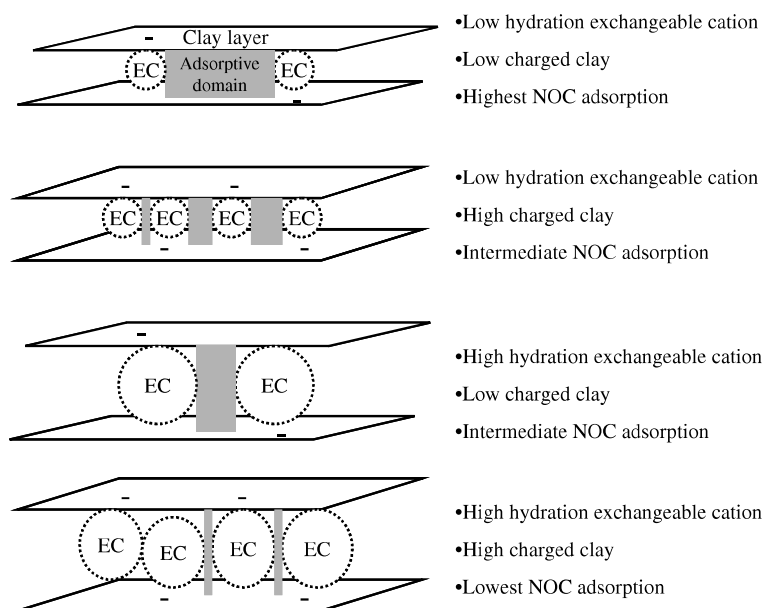
#### 2.4. X-RAY DIFFRACTION

X-ray diffraction (XRD) has provided molecule-scale information regarding the separation of the 2:1 smectite layers (i.e., the interlayer distance) in clays with and without adsorbed NOCs and pesticides. The interlayer distance of smectites is determined largely by the hydration propensities of the exchangeable cations, and to a lesser extent the layer charge. For example, homoionic K-smectites at 100% relative humidity (RH) typically exhibit interlayer spacings of 12.5–15 Å, with lower-charged smectites (e.g., SWy-2)

tending toward the higher spacings (MacEwan and Wilson 1980). Cesium-smectites have a strong tendency to equilibrate with 12.5 Å spacings, even in bulk water, due to the lower hydration energy of  $\text{Cs}^+$  compared to  $\text{K}^+$ . Smectites saturated with  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , or  $\text{Al}^{3+}$  always swell to 15 Å ( $d_{001}$ ) in aqueous suspension. Hence, exchangeable cation hydration also influences NOC/pesticide adsorption by smectite clay through its influence on the interlayer spacing of clay sheets in the clay tactoids.

In a particularly revealing experiment, Sheng et al. (2002) used XRD to quantify the swelling behavior of K-SWy-2 films in the presence and absence of water vapor, and with varying amounts of adsorbed DNOC (Fig. 2.5). As expected, exposure of previously air-dried K-SWy-2 films to 100% RH caused an increase in the interlayer spacing from 11 to 15 Å. Interestingly, the presence of adsorbed DNOC restricted swelling of the rewetted clay. At higher DNOC loadings the interlayer spacings for the air-dried and rewetted (100% RH) clays were nearly equal ( $\sim 12.2$  Å). The presence of adsorbed DNOC apparently caused the monolayer (i.e., one layer of intercalated water) to be retained even though the same K-SWy-2 smectite would swell further (i.e., to 15 Å) in the absence of DNOC. Thus, the  $\sim 12$  Å spacing appeared optimal for DNOC adsorption. In this configuration, the DNOC molecules would be flat on, and parallel to, the siloxane surfaces of K-SWy-2. Furthermore, the 12 Å spacing would allow adsorbed DNOC to interact simultaneously with the opposing clay siloxane surfaces, thereby minimizing its contact with water. Considering that the free energy of hydration of many small NOCs is in the range of 10–30 kJ/mol<sup>1</sup>, removal of DNOC from bulk water on intercalation may provide sufficient energy to prevent K-SWy-2 smectite from swelling beyond the measured spacing of  $\sim 12$ –12.5 Å. This spacing provides an interlayer distance of  $\sim 3$  Å, which corresponds to the approximate thickness of DNOC. Since Cs-smectites tend to maintain a 12.5 Å spacing in water, due to the lower hydration energy of  $\text{Cs}^+$  versus  $\text{K}^+$ , the Cs-smectite is particularly well suited for intercalation of DNOC, and is a somewhat more effective adsorbent for DNOC (Fig. 2.2). It should be noted that these experiments were conducted using self-supporting clay films rather than aqueous suspensions of the K-SWy-2 clay, which are assuredly present under ambient environmental conditions, along with the particles in lesser-hydrated states. From the data of Sheng et al. (2002), it was unknown whether the clays adopt the 12 Å spacing in suspension as a result of DNOC adsorption. However, more recently developed, novel XRD techniques now enable XRD measurement of interlayer spacings in actual clay suspensions (Chappell et al. 2005; Li et al. 2007) as well as in air-dried forms.

Smectites exist as quasicrystals, which are stacks of subparallel 2:1 phyllosilicate layers with parallel *c* axes and randomly oriented *a*- and *b*-axes. In aqueous suspensions, smectite quasicrystals are dynamic in the sense that

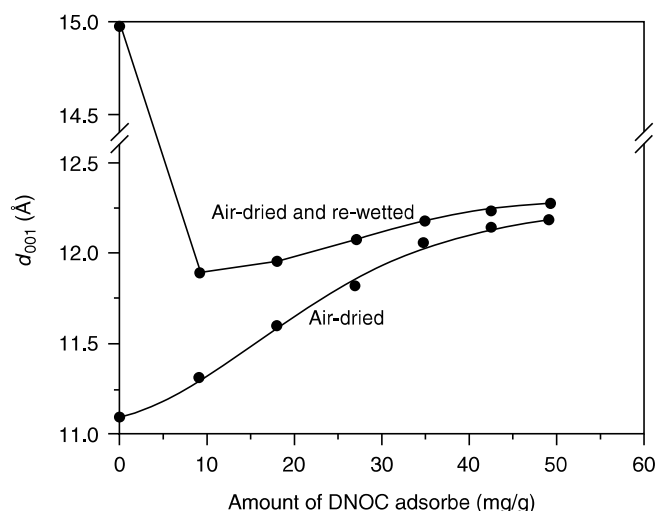


**Figure 2.4.** Availability of smectite clay interlayer domains for neutral organic contaminant (NOC) adsorption. Circles around inorganic exchangeable cation (EC) represent the hydration sphere. Lower hydration manifests larger adsorptive domains and greater potential for direct NOC–EC interactions as well as NOC interactions with the siloxane surface.

they are capable of swelling by imbibing water and/or organic molecules between layers within quasicrystals (crystalline swelling) and in the sense that large quasicrystals may cleave, producing two or more smaller quasicrystals, and conversely several smaller quasicrystals may coalesce forming a single large quasicrystal (Laird 2006). In aqueous suspensions some smectites, principally those saturated with  $\text{Na}^+$  and  $\text{Li}^+$  in dilute electrolyte solutions, are capable of

complete delamination such that the individual lamella are separated by distances 30 Å and behave as semi-independent colloids (colloids are not truly independent until the suspension is so dilute that colloid concomitant volumes do not interact). Both crystalline swelling/shrinking and the break-up/reformation of quasicrystals are inherently hysteretic processes, as energy is necessary to effect the physical rearrangements of matter that are required for both directions of both process [see Laird (2006) for a more complete discussion of smectite swelling processes].

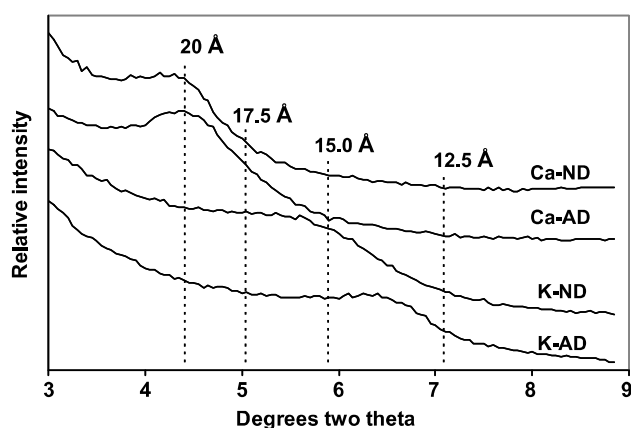
Any change in the physical state of a smectite quasicrystal in an aqueous system inherently changes the affinity of the smectite for an organic solute. Crystalline swelling, for example, can change the size of interlayer domains from 12.5 Å spacing, which is optimal for retention of many organic molecules, to a more hydrated and hence less optimal 15 or 18 Å spacings. Similarly the breakup of a large smectite quasicrystal into two or more smaller quasicrystals diminishes the number of interlayer adsorption sites and increases the number of external surface adsorption sites. Within interlayers organic molecules may interact simultaneously with the basal oxygens of two opposing siloxane surfaces, whereas organic molecules interact with only one siloxane surface on an exposed external surface. Furthermore, the permittivity of the interlayer water is lower than the permittivity of water adjacent to an external surface. Weakly polar organic molecules are partitioned from a high-permittivity aqueous phase into a low permittivity aqueous phase with the driving force being an increase in system entropy.



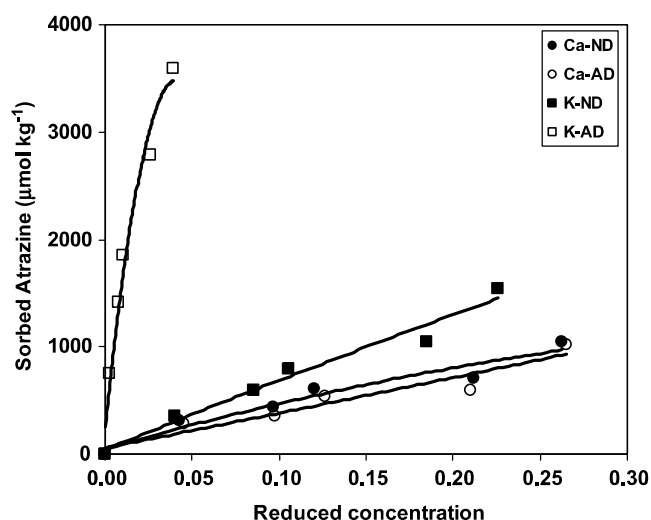
**Figure 2.5.** Basal spacings of K-smectite (K-SWy-2) clays with varying levels dinitro-*o*-cresol (DNOC) sorption in the presence and absence of water [from Sheng et al. (2001)].

The impact of crystalline swelling on adsorption of organic molecules was clearly demonstrated by Chappell et al. (2005). For the study, two suspensions of  $K^+$ -saturated Panther Creek smectite were prepared by dialysis from an original highly swollen  $Na^+$  Panther Creek biochar suspension. The two  $K$ -smectite suspensions were identical in every way except that one had been air-dried and then resuspended while  $K^+$ -saturated and the other was maintained as an aqueous suspension the entire time it was in the  $K$  form. Quasicrystals in the never-dried  $K$ -smectite ( $K$ -ND) suspension were swollen (Fig. 2.6: broad XRD peak between 15 and 17.5 Å indicating interstratification of lamellae with two or three layers of interlayer water molecules) to a greater extent than were the quasicrystals in the air-dried  $K$ -smectite ( $K$ -AD) suspension (Fig. 2.6: broad XRD peak between 12.5 and 15 Å indicating interstratification of layers with one or two layers of interlayer water molecules). This legacy in the extent of crystalline swelling from having been air-dried and then resuspended caused an order of magnitude increase in the affinity of the  $K$ -AD sample for atrazine relative to the  $K$ -ND sample (Fig. 2.7). By contrast,  $Ca$ -smectite in air-dried and never-dried ( $Ca$ -AD and  $Ca$ -ND, respectively) suspensions adsorbed similar amounts of atrazine and exhibited similar broad 20-Å XRD peaks indicating that most interlayers held four layers of interlayer water molecules regardless of the air-dried or never-dried treatments. The results (Chappell et al. 2005) demonstrate that the impact of saturating cation on the affinity of a smectite for organic molecules comes primarily from the impact of the cation on the extent of interlayer hydration, which for  $K$ -smectites is strongly influenced by the history of sample handling, or by extension, wetting–drying cycles in nature.

Comparison of XRD patterns for randomly oriented  $K$ - and  $Ca$ -smectite quasicrystals in aqueous suspensions



**Figure 2.6.** Transmission X-ray diffraction patterns for Panther Creek smectite suspensions. The smectite was saturated with  $K^+$  or  $Ca^{2+}$  and either air-dried and resuspended (AD) or never dried (ND). The patterns have been vertically offset. [The figure is adapted from data originally presented by Chappell et al. (2005)].



**Figure 2.7.** Isotherms for sorption of atrazine on Panther Creek smectite saturated with  $K^+$  or  $Ca^{2+}$  and either air-dried and resuspended (AD) or never dried (ND). *Reduced concentration* refers to the ratio of the concentration of atrazine in water to aqueous solubility of atrazine. [The figure is adapted from data originally presented by Chappell et al. (2005)].

(Shang et al. 1995) with XRD patterns for air-dried- and oven-dried-oriented films of the same smectites provided insight into the impact of the breakup and reformation of smectite quasicrystals on sorption of DNOC (Pereira et al. 2007, 2008). The phenolate form of DNOC, which is the dominant form of DNOC in solutions with  $pH \geq 4.4$ , was adsorbed primarily on external surfaces of  $K$ -smectite quasicrystals in aqueous suspensions and entered the interlayers as  $K$ -DNOC complexes when individual  $K$ -smectite layers and small quasicrystals coalesced to form large quasicrystals on drying. By contrast, in  $Ca$ -smectite suspensions ( $pH 4.4$ ) the phenolate form of DNOC was adsorbed only on external surfaces quasicrystals and there was no evidence for the formation of  $Ca$ -DNOC complexes. However, some of the phenolate DNOC became entrapped between substacks within  $Ca$ -smectite quasicrystals as the suspensions were dried to form oriented clay films. The neutral form of DNOC ( $pH \leq 4.4$ ) was adsorbed in the interlayers of a low-charge-density  $Ca$ -smectite but not in the interlayers of a high-charge-density  $Ca$  smectite, apparently due to steric restrictions.

Studies of homoionic smectite suspensions provide insight into mechanisms controlling smectite–organic interactions. However, soils and sediments invariably contain multiple types of cations, with  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $K^+$  typically being the most abundant cations in temperate region soils. Thus, in natural systems, cation exchange reactions and the adsorption/desorption of organic solutes occur simultaneously. As discussed above, both the type of cation adsorbed on the exchange complex of a smectite and the physical state of the smectite quasicrystals have a large influence on the

affinity of smectites for organic solutes. Similarly, the extent of crystalline swelling of smectites influences cation exchange selectivity, such that interlayers with 12.5 Å spacings have a distinct preference for weakly hydrated monovalent cations (e.g.,  $K^+$ ) and more expanded interlayers ( $d$  spacings of 15–20 Å) prefer more strongly hydrated divalent cations such as  $Ca^{2+}$  and  $Mg^{2+}$  (Laird and Shang 1997). Thus quasicrystal dynamics regulates interactions between cation exchange reactions and the adsorption/desorption of organic solutes, and conversely the loading of inorganic cations and organic molecules in the interlayers regulates quasicrystal dynamics (Li et al. 2004b; Chatterjee et al. 2008). Furthermore, the hysteresis that is inherent in crystalline swelling/collapse and quasicrystal formation/breakup (Laird et al. 1995) causes hysteresis in both cation exchange reactions (Laird and Shang 1997) and hysteresis in the adsorption/desorption of organic solutes (Li et al. 2004b; Chatterjee et al. 2008). Demixing of both inorganic cations and organic solutes, such that  $K^+$  and organic solutes are selectively co-adsorbed in collapsed ( $d = 12.5$  Å) interlayer domains while  $Ca^{2+}$  and water molecules are selectively co-adsorbed in expanded ( $d = 15$ – $20$  Å) interlayer domains of the same quasicrystal (Pils et al. 2007), is another implication of the interaction between quasicrystal dynamics, cation exchange reactions, and the adsorption/desorption of organic solutes.

## 2.5. VIBRATIONAL SPECTROSCOPIC STUDIES

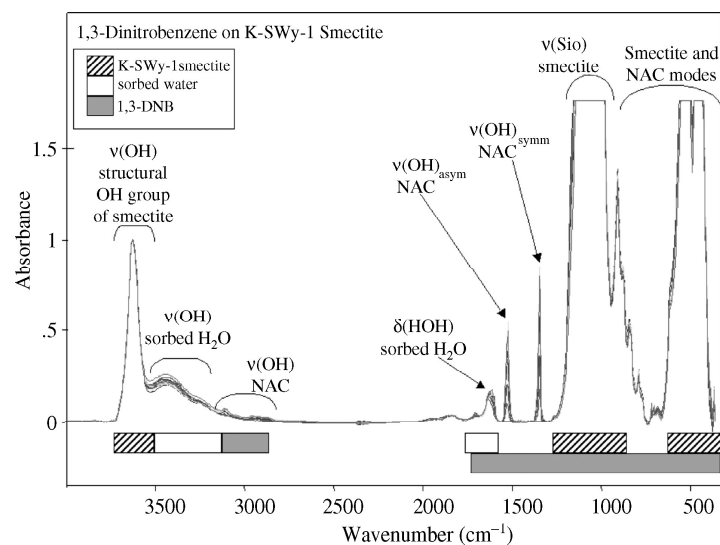
In order to achieve a mechanistic understanding of NOC interactions with soil constituents, adapted spectroscopic methods sensitive to molecular interactions are required. Sorption data are macroscopic in nature and therefore, are fundamentally insensitive to molecular phenomena (Johnston and Sposito 1987). In the case of NAC sorption to clay minerals, vibrational spectroscopy, in particular, has provided molecule-level insights about the sorption mechanisms on several different aspects. In general, NACs are well suited for clay sorption studies because selected NACs show a high affinity for smectite, and because NACs have strong IR-active vibrational modes that are sensitive to short-range intermolecular interactions (Saltzman and Yariv 1975; Weissmahr et al. 1997; Johnston et al. 2002; Sheng et al. 2002).

In the case of 1,3,5-TNB on K-SWy-2 smectite, for example, sorption values approach 400  $\mu\text{mol/g}$  (Johnston et al. 2001). The vibrational bands associated with the  $-\text{NO}_2$  groups are of particular interest in NAC surface studies. In earlier work, Yariv and co-workers (Yariv et al. 1966; Saltzman and Yariv 1975) used IR spectroscopy to study the interactions of nitrophenol and nitrobenzene with smectites. The positions of the  $-\text{NO}_2$  vibrational bands were affected by the clay surface and by the nature of the exchangeable cation when compared to the neat compound. Spectra in these

earlier studies were collected from air-dried and heated clay films to minimize the interference from water and utilized high surface loadings of the organic solute of interest. No clear spectral trends were observed from the air-dried films and evidence for inner-sphere complexation was observed for the heated films exchanged with different cations (Saltzman and Yariv 1975).

The principal bands of interest are the  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  bands along with the  $-\text{NO}_2$  deformation bands. The  $-\text{NO}_2$  group is highly electronegative, and the vibrational motions associated with  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  modes induce a large change in the induced dipole moment, which translates to intense/strong IR-active modes. Of particular benefit to clay surface studies is the fact that these vibrational modes occur in accessible spectral regions that are not obfuscated by the intense clay bands or by the presence of water (Fig. 2.8) (Johnston et al. 2001). The NACs can be considered to function as molecular probes that have diagnostic properties that are sensitive to changes in their local environment (Johnston et al. 1993). In a related way, the chemical shift of both  $^{15}\text{N}$  and  $^{17}\text{O}$  nuclei have been used to probe changes in the chemical environment around the  $-\text{NO}_2$  group resulting from intermolecular interactions.

Sorption of NAC is favored on low-charge-density clay minerals that are exchanged with less hydrated exchangeable cations (Haderlein et al. 1996; Boyd et al. 2001). On the basis of earlier studies (Jaynes and Boyd 1991b; Laird et al. 1992, 1994; Barriuso et al. 1994), increased sorption was attributed to the presence of *neutral siloxane surface* sites, which are regions on the smectite surface not in the near vicinity of exchangeable cations, waters of hydration surrounding exchangeable cations, or the isomorphic substitution sites themselves (Boyd et al. 2001; Sheng et al. 2002; Johnston et al. 2004; Li et al. 2004a). These portions of the clay surface are less hydrated and are considered to provide favorable sorption domains for semi-polar organic solutes such as NACs, atrazine, and related compounds. Haderlein and co-workers were among the first to show that a wide range of NACs showed a high affinity for smectites in sorption studies from aqueous suspension (Haderlein and Schwarzenbach 1993; Haderlein et al. 1996). Nitroaromatic compounds that show high affinities for smectites were generally found to be planar structures containing more than one nitro group (Haderlein et al. 1996). This work was extended using sorption and molecular spectroscopy [NMR, UV-visible, and *in situ* attenuated total reflection (ATR)-FTIR spectroscopy] to the study of NAC sorption mechanisms on smectite (Weissmahr et al. 1997). Although direct coordination mechanisms had been proposed in earlier NAC-smectite sorption studies (Yariv et al. 1966; Saltzman and Yariv 1975; Fusi et al. 1982) on the basis of air-dried clay films, they observed similar *in situ* ATR-FTIR results between  $\text{Cs}^+$ - and  $\text{K}^+$ -exchanged smectites. Based on the spectral similarities they concluded that the exchangeable cation did not play a

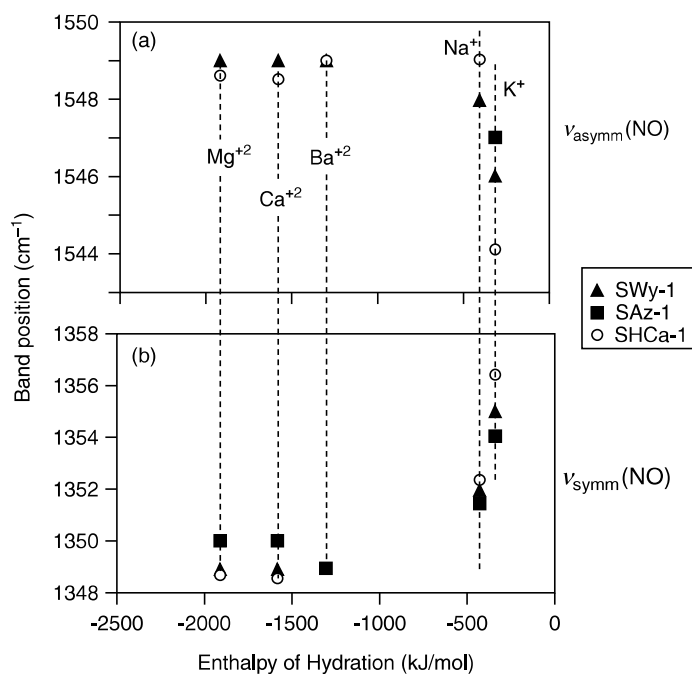


**Figure 2.8.** FTIR spectra of 1,3-dinitrobenzene sorbed to K-SWy-1 smectite. Individual band assignments are shown as well as spectral regions where IR absorption resulting from the smectite, sorbed water, and 1,3-dinitrobenzene occur [from Johnston et al. (2001)].

significant role and attributed the high affinity of certain NACs for smectites to the formation of a electron-donor-acceptor (EDA) complex discussed earlier between the  $\pi$  electrons of the NAC and the electrons of the siloxane oxygen atoms, which was not entirely consistent with the earlier

ex situ IR studies (Yariv et al. 1966; Saltzman and Yariv 1975; Fusi et al. 1982).

In order to address this apparent inconsistency further, we investigated the spectroscopic properties in the study of NACs sorption on three different smectites exchanged



**Figure 2.9.** Positions of the  $\nu_{\text{asym}}(\text{NO})$  (a) and  $\nu_{\text{sym}}(\text{NO})$  (b) bands of 1,3,5-trinitrobenzene sorbed to SAZ-1, SWy-1, and SHCa-1 smectite exchanged with Mg, Ca, Ba, Na, and Cs; the data are plotted as a function of the enthalpy of hydration of the exchangeable cation [from Johnston et al. (2001)].

with cations whose enthalpies of hydration varied from  $-315$  kJ/mol ( $\text{Cs}^+$ ) to  $-1960$  kJ/mol ( $\text{Mg}^{2+}$ ) (Evangelou 1998). Although Weissmahr et al. (1997) concluded, in light of spectral similarities between Cs- and K-exchanged smectites, that  $-\text{NO}_2$  groups were not involved in direct coordination to surface sites or exchangeable cations, the difference in the enthalpy of hydration between  $\text{Cs}^+$  ( $-315$  kJ/mol) and  $\text{K}^+$  ( $-360$  kJ/mol) is almost negligible relative to the difference of more strongly hydrated alkali-metal cations ( $\text{Li}^+$  and  $\text{Na}^+$ ) or the alkaline-earth cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ ) (Friedman and Krishnan 1973).

We found that the nature of the exchangeable cation influenced both the position and the relative intensities of the  $-\text{NO}_2$  symmetric and asymmetric stretching bands compared to their spectra obtained in aqueous solution (Fig. 2.9, Table 2.3) (Johnston et al. 2001a, 2002, 2004; Sheng et al. 2002). In the case of 1,3,5-trinitrobenzene, for example, the splitting between the asymmetric and symmetric  $\text{NO}_2$  stretching bands remained relatively constant at  $200$   $\text{cm}^{-1}$  for 1,3,5-TNB in aqueous solution and when sorbed to smectites

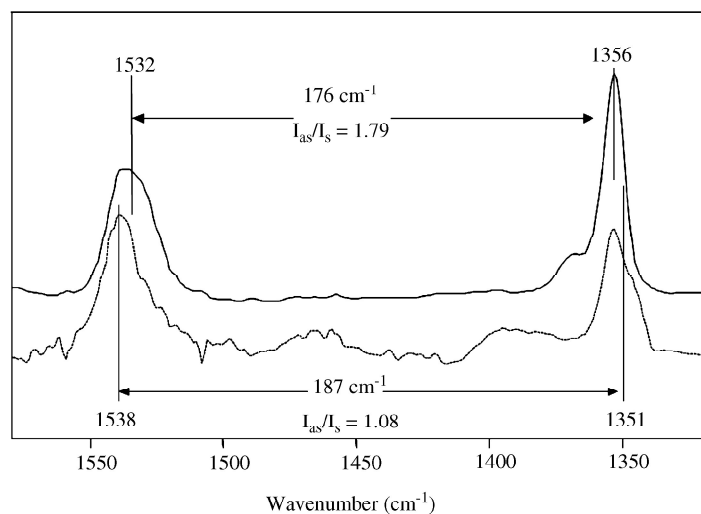
exchanged with strongly hydrated cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ). The splitting decreased to  $\sim 188$   $\text{cm}^{-1}$  for the weakly hydrated cations ( $\text{K}^+$  and  $\text{Cs}^+$ ) (Fig. 2.9). A similar decrease in the splitting between the  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  bands was observed for 1,3-dinitrobenzene (Fig. 2.10). In order to investigate this splitting further, quantum mechanical calculations of gas-phase 1,3,5-TNB, 1,3-dinitrobenzene, and inner-sphere K complexes of both NACs were undertaken (Johnston et al. 2001), using the B3LYP level of theory and the 6-311G\*\* basis set (Frisch et al. 1998). Splittings between the computed vibrational frequencies for the K complexes relative to the uncomplexed NACs showed the same shifts in direction, although of somewhat larger magnitude, that had been observed experimentally. These computational results showed that the decrease in splitting resulted from strengthened interactions between the  $-\text{NO}_2$  oxygen atoms and  $\text{K}^+$ , thus supporting the hypothesis that adsorbed NACs formed complexes with interlayer  $\text{K}^+$  ions. For more strongly hydrated exchangeable cations, the effective distance between the  $-\text{NO}_2$  group

**TABLE 2.3. Influence of Exchangeable Metal Cations on Positions ( $\nu$ ,  $\text{cm}^{-1}$ ) and Relative Intensities ( $I$ ) of  $-\text{NO}_2$  Stretching Bands of 1,3,5-Trinitrobenzene Sorbed by Different Smectite Clays (SWy-1, SAz-1, SHCa-1)**

Element(s)	$\nu_{\text{asym}}(\text{NO})$	$I_{\text{asym}}$	$\nu_{\text{sym}}(\text{NO})$	$I_{\text{sym}}$	Frequency Difference	$I_{\text{asym}}/I_{\text{sym}}$
<i>SWy-1</i>						
Mg	1549	0.78	1349	0.98	200	0.79
Ca	1549	0.93	1349	1.12	200	0.83
Ba	1549	0.99	1349	1.18	200	0.84
Al	1549	2.07	1348	2.48	200	0.83
Na	1548	3.81	1352	3.40	196	1.12
$\text{NH}_4$	1545	19.65	1349	18.79	196	1.05
K	1546	25.39	1355	22.16	191	1.15
<i>SAz-1</i>						
Mg	—	—	1350	—	—	—
Ca	—	—	1350	—	—	—
Ba	—	—	1349	—	—	—
Al	—	—	1348	—	—	—
Na	—	—	1352	—	—	—
Cs	1542	6.18	1355	6.17	187	1.00
$\text{NH}_4$	1547	—	—	8.56	197	1.05
K	1547	—	—	21.65	193	1.27
<i>SHCa-1</i>						
Mg	1549	2.47	1349	2.96	200	0.83
Ca	1549	3.09	1349	3.49	200	0.89
Ba	1549	2.43	1349	2.94	200	0.83
Al	1549	1.88	1349	2.56	200	0.73
Na	1549	2.36	1352	2.51	197	0.94
Cs	1544	22.10	1353	18.23	190	1.21
$\text{NH}_4$	1546	16.36	1350	12.65	196	1.29
K	1544	14.87	1356	10.63	188	1.40

Source: Adapted from Johnston et al. (2001).

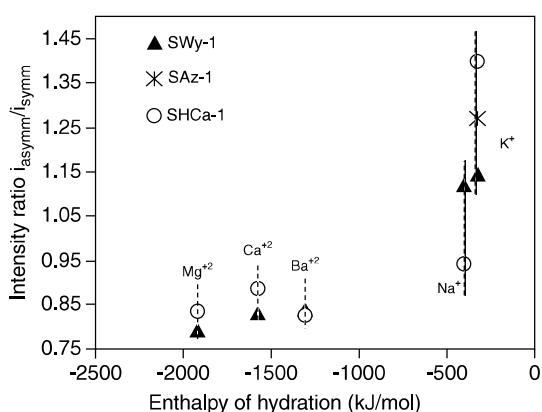




**Figure 2.10.** Comparison of the FTIR spectra of 1,3-dinitrobenzene sorbed to K-SWy-1 montmorillonite (upper spectrum) to that of 1,3-dinitrobenzene in aqueous solution (lower spectrum, dashed line); the splitting between the  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  bands is shown as well as the intensity ratio  $I_{\text{asym}}/I_{\text{sym}}$  [from Johnston et al. (2001)].

and the positively charged cation is increased, essentially turning off the site-specific interaction.

In addition to the cation-induced change in band positions of the  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  bands, the intensity ratio of  $I_{\text{asym}}(\text{NO})/I_{\text{sym}}(\text{NO})$  was also perturbed and varied as a function of enthalpy of hydration of the exchangeable cation (Fig. 2.11). In prior NAC surface studies, this intensity ratio was sensitive to different types of intermolecular interactions resulting from changes in the O–N–O angle and hydrogen bonding to oxide surfaces (Ahmad et al. 1996). Saltzman and Yariv (1975) observed that the position of the  $\nu_{\text{asym}}(\text{NO})$  band decreased and its relative intensity

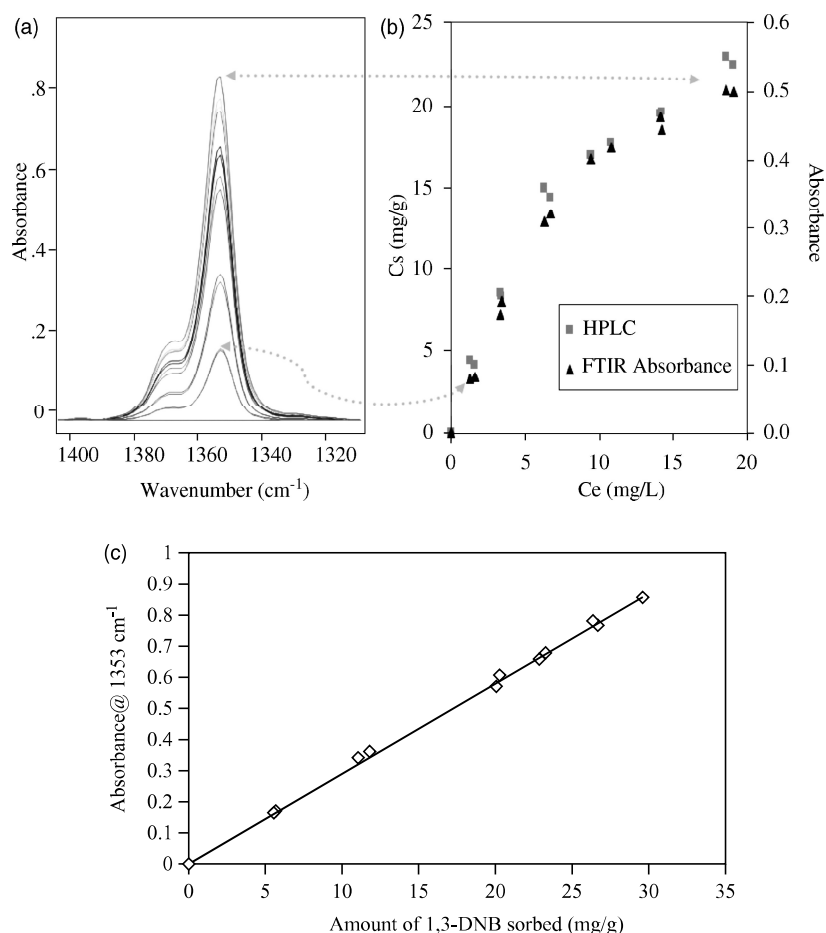


**Figure 2.11.** Intensity ratio (integrated area) of the  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  bands as a function of the enthalpy of hydration of the exchangeable cation on three smectite clays (SWy-1, SAz-1 and SHCa-1) [from Johnston et al. (2001)].

increased for *p*-nitrophenol sorbed on smectite when heated, and this was attributed to direct complexation with the exchangeable cation. Furthermore, the spectroscopic results obtained in these studies agree with the results obtained by Weissmahr et al. (1997) in that the IR data obtained for K- and Cs-exchanged smectites are similar.

The vibrational bands associated with the  $-\text{NO}_2$  group are relatively sharp and well resolved with full-width at half-maximum (FWHM) bandwidths of  $\sim 10 \text{ cm}^{-1}$ , which is quite narrow for solutes sorbed on surfaces in aqueous suspension. Although highly resolved, the band positions of the  $\text{NO}_2$  groups do not experience large shifts in position resulting from intermolecular interactions (Nyquist and Settineri 1990; Ahmad et al. 1996). In the context of prior NAC surface studies, the shift in band positions of the  $\nu(\text{NO})$  bands for the NAC-smectite complexes are some of the largest shifts reported (Conduit 1959; Urbanski and Dabrowska 1959; Jonathan 1960; Borek 1963; Baitinger et al. 1964; Green and Lauwers 1971; Nyquist and Settineri 1990; Ahmad et al. 1996).

In spectroscopic studies of environmentally relevant solutes such as NACs, it is useful to combine sorption and spectroscopic methodologies such that the amount of NAC sorbed is known. This type of information provides a direct link between the macroscopic sorption data and the molecular insights gained from spectroscopy. We conducted a series of parallel sorption and spectroscopic measurements and found that intensity of the NAC vibrational bands [ $\nu_{\text{sym}}(\text{NO})$  of 1,3-dinitrobenzene is shown in Fig. 2.12) increased linearly with increasing surface coverage as determined using HPLC (Fig. 2.12a). This confirmed the identity of the surface species as 1,3-DNB and not some

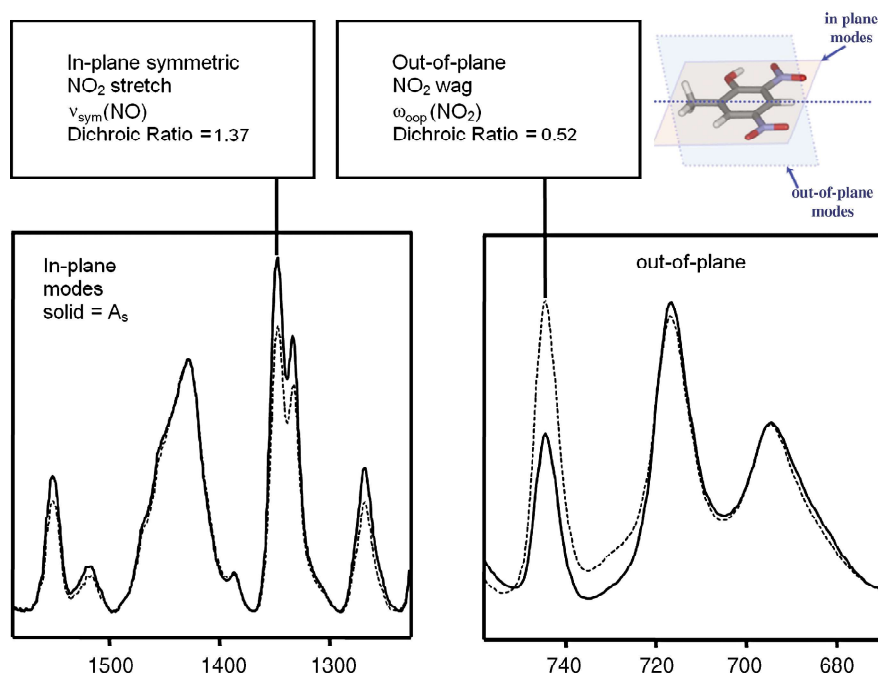


**Figure 2.12.** (a,b) Absorbance of the  $\nu_{\text{symm}}(\text{NO})$  band of 1,3-dinitrobenzene (DNB) at  $1353\text{ cm}^{-1}$  at different surface coverages (a) Each spectrum shown in (a) corresponds to a point on the HPLC-derived sorption isotherm shown in (b). Combinations of HPLC- and FTIR-derived sorption isotherms are shown in the (b). Adsorption isotherms (b) are plots of concentration of sorbed DNB ( $C_s$ ) versus equilibrium aqueous concentration of DNB ( $C_e$ ) [from Johnston et al. (2001)]. Plot of the absorbance of the  $\nu_{\text{symm}}(\text{NO})$  band of 1,3-dinitrobenzene (1,3-DNB) at  $1353\text{ cm}^{-1}$  as a function amount of 1,3-DNB sorbed by K-smectite (K-SWy-1) montmorillonite determined using HPLC methods [from Johnston et al. 2001].

degradation product. In addition, unlike traditional batch sorption methods, the surface solute is directly observed using FTIR as opposed to batch-sorption-derived data, which are based on difference in aqueous-phase concentrations measured using HPLC. In addition, the quantitative analysis of the spectroscopic data provides a measure of the limit of detection of NACs on smectite surfaces. For the data shown in Figure 2.12b, based on a minimum absorbance value of 1 milliabsorbance unit (mAU), the detection limit of 1,3-DNB would be approximately 150 nmol/g.

Polarized infrared spectroscopy can provide a direct means of determining the molecular orientation of sorbed species on oriented self-supporting film clay films (Johnston et al. 2002; Ras et al. 2003, 2007). In the case of planar organic solutes, such as many NACs, the vibrational modes

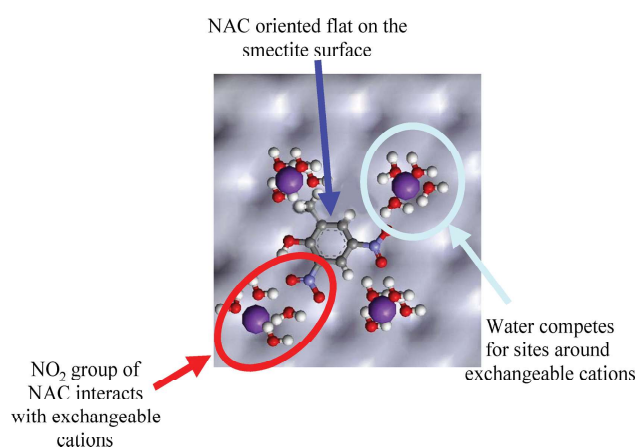
can be divided into *in-plane* and *out-of-plane* vibrational modes. The atomic motions corresponding to the  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  modes of 1,3,5-TNT, 1,3-DNB, and DNOC are aligned within same plane as the aromatic ring. In contrast, the vibrational motion of the atoms involved in the out-of-plane  $\text{—NO}_2$  deformation are oriented (as their name implies) out of plane. Because the smectite particles have a high aspect ratio, highly oriented self-supporting films can be made (Johnston and Premachandra 2001). When planar organic solutes are sorbed on smectites, linear dichroism techniques can be used to determine the molecular orientation of the sorbed species (Margulies et al. 1988). If the dichroic ratio (DR) for a particular vibrational mode is  $>1$ , the orientation of that particular vibrational mode is aligned parallel to the clay surface. The DR for the  $\nu_{\text{sym}}(\text{NO})$  band of



**Figure 2.13.** FTIR spectra of dinitro-*o*-cresol (DNOC) adsorbed by K-smectite (K-SWy-2) at 0° and 45° of beam incidence [from Sheng et al. 2002].

DNOC on K-SWy-2 is 1.32. In support of this value, the measured DR value for the out-of-plane  $\text{—NO}_2$  rock is 0.52 (Fig. 2.13). Together, these linear dichroism values indicate that the molecular plane of DNOC is parallel to the [001] plane of the clay surface (parallel to the siloxane surface as illustrated in Fig. 2.14). Interestingly, similar studies with

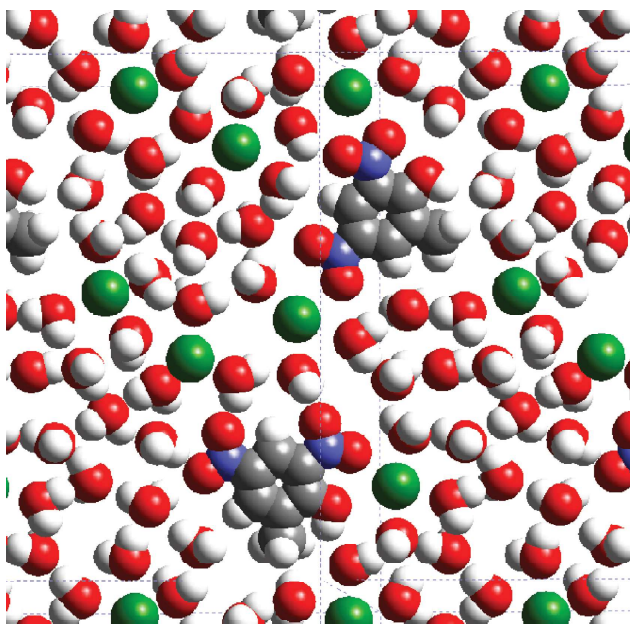
dioxin sorbed on Cs-saponite revealed that intercalated dioxin was present in orientations that were not parallel to the siloxane surface, in agreement with XRD measurements showing expanded interlayer distance of  $\sim 15.4 \text{ \AA}$  at high loadings of  $\sim 0.8\% \text{ wt/wt}$  (Liu et al. 2009).



**Figure 2.14.** Illustration of sorbed dinitro-*o*-cresol (DNOC) molecule laying flat on the siloxane surface showing the siloxane surface and water molecules surrounding the exchangeable cations. The dimensions of the DNOC molecule and the distance between the exchangeable cations are drawn to scale. The DNOC is shown as a representative nitroaromatic compound (NAC). [From Johnston et al. 2002]. (See insert for color representation of this figure.)

## 2.6. MOLECULAR AND QUANTUM MECHANICAL SIMULATIONS

In addition to the quantum chemical studies described above, molecular simulations using classical dynamics have been used (Teppen et al. 1997, 1998) to integrate experimental data and to explore the molecular mechanisms of NOC interactions with clay mineral surfaces. Clay minerals with compositions similar to various smectites were constructed (Boyd et al. 2001; Sheng et al. 2002; Chappell et al. 2005; Aggarwal et al. 2006a). Our experimental adsorption isotherms were used to choose realistic loading rates for the NOCs, and interlayer water contents were derived by inference from X-ray diffraction patterns gathered for both air-dried clay films (Sheng et al. 2002; Li et al. 2004a) and suspension-phase (Chappell et al. 2005) NOC–water–clay complexes. Water molecules and NOCs were inserted into the simulation cell at random initial positions and orientations, and the water contents were adjusted until the simulated equilibrium  $d_{(001)}$ -spacing agreed with experimental values, so that the simulated interlayer environment corre-



**Figure 2.15.** Molecular dynamics snapshot of dinitro-*o*-cresol (DNOC) in K-smectite (K-SWy-2) clay interlayer, ( $K^+$  = green, O = red, C = gray, N = blue, H = white). (See insert for color representation of this figure.)

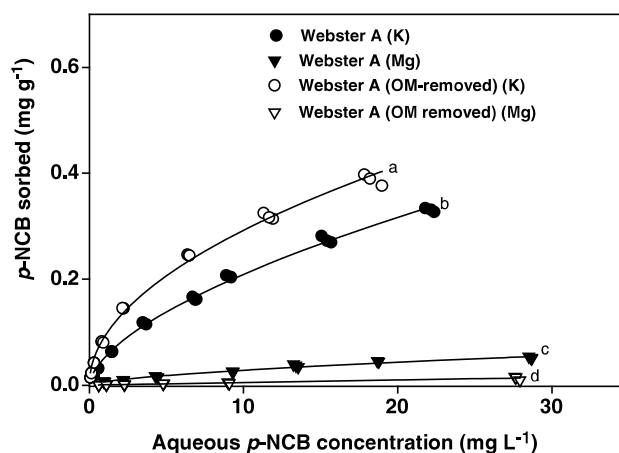
sponded as closely as possible to that of the adsorption experiments. After lengthy equilibrations, the interlayer structures were sampled. An example is shown in Figure 2.15, for which the clay layers have been removed to reveal the NAC–cation–water interactions in the interlayer region. The results are consistent with our hypotheses derived from FTIR spectroscopy in that a variety of inner- and outer-sphere NAC- $K^+$  complexes are evident. One general observation from the simulations is that such complexes are almost forced by the sterically crowded nature of the smectite interlayer region. Specifically, in a smectite interlayer of 12.5-Å  $d_{001}$  spacing as in Figure 2.5, each monovalent cation occupies only 0.5–1 nm<sup>2</sup>, while single-ring aromatic NOC molecules are at least 0.5 nm<sup>2</sup> in size. Thus, the adsorbed NOCs must be forced into close proximity to cations, and this situation will be energetically favorable only if the NOC contains O- or N-based functional groups that are at least polar enough to plausibly coordinate cations. Indeed, two or more polar functional groups are even more favorable since the NOC must fit between several cations (Fig. 2.15). For example, the close proximity of many monovalent cations can be used to rationalize why the magnitudes of nitrobenzene sorption by K-smectites follow the order 1,3,5-TNB  $\gg$  1,4-DNB  $\approx$  1,3-DNB  $\gg$  NB.

Also, dibenzo-*p*-dioxin sorbs up to 8000 mg/kg on certain Cs-smectites (Liu et al. 2009), while similar-sized PAHs that lack the oxygen functionality sorb to a much smaller extent to the same clay.

## 2.7. ENVIRONMENTAL IMPLICATIONS

The results of our studies and those others (referenced above) clearly demonstrate that NOCs and pesticides often display strong affinities for expandable 2:1-layer smectite clays, especially those saturated with weakly hydrated cation (e.g.,  $K^+$ ,  $Cs^+$ ). Most of these studies have been conducted using relatively pure reference clay specimens. In the environment, soil clay minerals and SOM are usually associated with each other. Soil organic matter might obscure clay surfaces, thereby reducing the availability and hence efficacy of soil mineral fractions for adsorption of organic compounds. Until 2005 or so, there were no studies that directly assessed the effectiveness of unisolated clay minerals in soils as adsorbents for NOCs, and specifically the extent to which mineral components are available for adsorption of NOCs.

As an initial step to approach this question, Charles et al. (2006a,b) measured sorption of several NACs by  $K^+$ - and  $Mg^{2+}$ -saturated soils and SOM-removed soils. The results showed that extraction of SOM caused an increased sorption by  $K^+$ -saturated soils (Fig. 2.16) demonstrating that SOM posed an overall negative effect on sorption of NACs (e.g. *p*-nitrocyano benzene, *p*-NCB), due to obscuration of *p*-NCB binding sites on soil clays. In contrast, sorption of *p*-NCB by  $Mg^{2+}$ -saturated Webster soil was greater than that by the  $Mg^{2+}$ -saturated SOM-removed soil (Fig. 2.16). Removal of SOM might liberate some clay surface sites; however, Mg-clays have low affinities for aqueous-phase NACs. Because clays in the  $Mg^{2+}$ -saturated SOM-removed soil were relatively inefficient sorbents for *p*-NCB, SOM was left as the principal sorbent phase, and its



**Figure 2.16.** Adsorption isotherms for *p*-nitrocyano benzene (*p*-NCB) sorption by  $K^+$ - and  $Mg^{2+}$ -saturated Webster soil (whole soil, and soil from which SOM was removed); the four isotherms (labeled *a*–*d*) are statistically different at  $p < 0.05$  [from Charles et al. (2006a)].

removal decreased sorption overall. Results such as these demonstrate that SOM and clay minerals can contribute to the sequestration of NOCs in soils, and that these contributions are interrelated.

To estimate contributions of sorption by minerals, several previous studies utilized the simple additive product of isolated SOM (e.g., humic acids) and mineral components (Pusina et al. 1992; Celis et al. 1997; Onken and Traina 1997; Li et al. 2003). However, this approach is inadequate to describe sorption of organic species by soils because it unrealistically assumes that these soil components act independently even though it is known that they are intimately associated in soils. Recognizing this, Karickhoff (1984) proposed the use of a mineral phase availability factor ( $f_a$ ) to assess the fraction of mineral surfaces (mostly clays) available for sorption of NOCs by soils, although the approach was not evaluated experimentally. This equation incorporated potential SOM blockage of sorption sites on clays by summing NOC sorption to clay and SOM:

$$Q_{\text{soil}} = f_a Q_{\text{min}} f_{\text{min}} + Q_{\text{som}} f_{\text{som}} \quad (2.1)$$

where  $Q_{\text{soil}}$  is the NOC mass sorbed per unit mass of soil,  $Q_{\text{som}}$  and  $Q_{\text{min}}$  are the SOM-sorbed and mineral-sorbed NOC per unit mass of the respective sorbent phase, and  $f_{\text{min}}$  and  $f_{\text{som}}$  are the fractional mineral and SOM contents of soil. The term  $f_a$  represents the fractional availability of sorption sites on the clay components of whole soil, that is, the fraction of mineral sorptive surfaces available in whole soil. The term  $f_a$  is a plausible refinement of simple addition of individual soil component contributions. Fractional availability ranges from 0 (unavailable) to 1 (100% available). Karickhoff (1984) equated the mineral fraction to the clay fraction owing to the high surface area of clays in general and of smectites in particular.

Using Equation (2.1) to experimentally estimate the  $f_a$  values requires knowledge of sorption by isolated soil minerals and SOM, but it is unachievable to fully separate unaltered soil components for sorption measurements. To address this deficiency, Charles et al. (2006a) developed a novel approach to determine  $f_a$  values that involves measuring the difference in sorption by soil whose cation exchange sites are saturated with different cations (i.e.,  $\text{K}^+$  vs.  $\text{Mg}^{2+}$ ) that render the clay surfaces adsorptive or nonadsorptive for NOC probe molecules. Specifically, the equation is expressed as

$$Q_{\text{K-soil}} - Q_{\text{Mg-soil}} = f_a (Q_{\text{K-min}} f_{\text{min}} - Q_{\text{Mg-min}} f_{\text{min}}) + (Q_{\text{K-som}} f_{\text{som}} - Q_{\text{Mg-som}} f_{\text{som}}) \quad (2.2)$$

where the terms are the same as those in Equation (2.1), and subscripts K- and Mg- are added to differentiate  $\text{K}^+$ - and  $\text{Mg}^{2+}$ -saturated soils or soil components.

Since  $Q_{\text{K-som}} \approx Q_{\text{Mg-som}}$  for NOCs (Charles et al. 2006a), it follows that

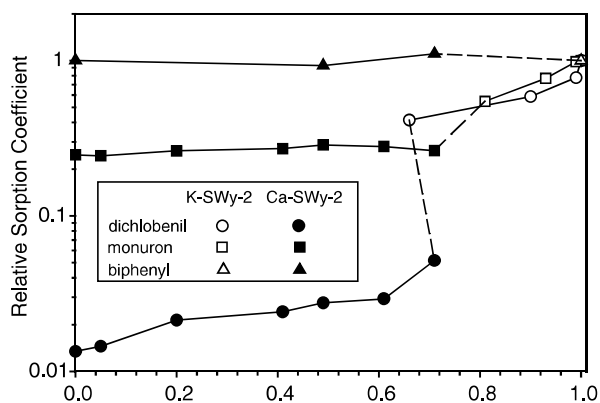
$$Q_{\text{K-soil}} - Q_{\text{Mg-soil}} \approx f_a (Q_{\text{K-min}} f_{\text{min}} - Q_{\text{Mg-min}} f_{\text{min}}) \quad (2.3)$$

Equation (2.3) eliminates the  $Q_{\text{som}}$  and  $f_{\text{som}}$  terms, which are difficult to obtain experimentally but needed in Equation (2.1). For instance, reliance on  $Q_{\text{som}}$  introduces significant errors in Equation (2.1) since  $Q_{\text{som}}$  cannot be obtained directly from sorption by isolated and unaltered SOM.

Using several NAC probe molecules, Charles et al. (2008) estimated the soil mineral availabilities of several smectitic soils. The results showed that 46%–100% of mineral surfaces in the Webster soil horizons and 35%–96% of mineral surfaces in the Clarion soil horizons were available for NOC adsorption. The  $f_a$  values were negatively correlated with the ratio of SOM/smectite contents in soils. Thus, SOM can reduce the availability of clay mineral surfaces for NOC adsorption. In soils SOM may coat clay surfaces, bridge clay packets resulting in soil aggregate formation, inhibit smectite shrinking and swelling, and partially block the entrance of NACs into interlayer regions. Our studies have revealed that, in fact,  $f_a$  is not a fixed intrinsic value for a given soil. Rather, the value depends on the type of the probe molecule used. Probe molecules with higher affinity for smectite surface adsorption sites (e.g., NACs) are more effective in accessing these sites, thereby manifesting higher  $f_a$  values. This is attributed to the more effective competition for mineral adsorptive sites by NACs than by SOM. It is apparent that a large portion of soil mineral fractions are available for adsorption of NOCs and pesticides in whole soils, particularly for adsorbates (e.g., NACs) with strong affinities for soil smectites whose cation exchange sites are partially or fully saturated with weakly hydrated cations (e.g.,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ).

It is not necessary to create fully  $\text{K}^+$ -,  $\text{Cs}^+$ -, or  $\text{NH}_4^+$ -saturated soils or sediments for significant clay mineral adsorption. The amount of weakly hydrated inorganic cations could be just sufficient to produce clay demixing of exchangeable cations. In other words, some (but not all) clay layers or regions of clay tactoids may be fully compensated with  $\text{K}^+$ ,  $\text{Cs}^+$  or  $\text{NH}_4^+$  leading to high-affinity NOC adsorption sites, while other regions are saturated with different exchangeable cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Na}^+$ ) that do not induce strong affinities for NOCs (Chatterjee et al. 2008; Li et al. 2004b).

To demonstrate this principle, adsorption of pesticides with different polarities (i.e., dichlobenil, monuron, biphenyl) was measured by homoionic K- and Ca-SWY-2 in KCl/CaCl<sub>2</sub> aqueous solutions (Li et al. 2004b). The presence of different amounts of KCl and CaCl<sub>2</sub> in solution resulted in varying populations of  $\text{K}^+$  and  $\text{Ca}^{2+}$  on the clay exchange sites as a result of cation exchange. Pesticide sorption coefficients were calculated at a relative concentration of

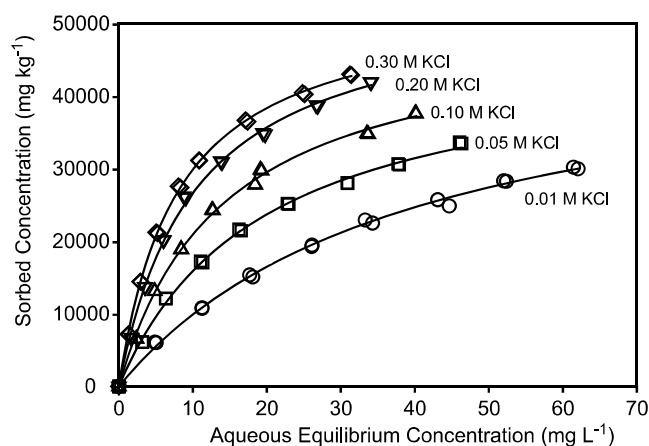


**Figure 2.17.** Sorption coefficients of pesticides normalized to the sorption coefficient by K-SWy-2 at the aqueous relative concentration (ratio of the solute concentration in water to the water solubility of solute) of 0.1 as a function of fractional  $K^+$  populations on mineral surfaces. The open (hollow) symbols represent the sorption in which  $K^+$  on homoionic K-SWy-2 was replaced by  $Ca^{2+}$ , and the solid symbols indicate the sorption in which  $Ca^{2+}$  on homoionic Ca-SWy-2 was replaced with  $K^+$  from aqueous solutions. [from Li et al. (2004b)].

0.1 (aqueous equilibrium concentration/aqueous solubility) and normalized to the corresponding sorption coefficients by homoionic K-SWy-2 (i.e., 580 L/kg for dichlobenil, 27 L/kg for monuron, and 6.4 L/kg for biphenyl). When the normalized sorption coefficients were plotted against  $K^+$  fractions ( $f_K$ ) on mineral surfaces (Fig. 2.17), sorption of the least polar biphenyl remained nearly constant (and low) across the variation of  $f_K$  on minerals from zero to one. No apparent enhancement was observed for monuron sorption on Ca-SWy-2 exchanged with KCl up to  $f_K = 0.71$ , whereas when K-SWy-2 underwent exchange with  $CaCl_2$ , sorption was reduced by about half when the fractional  $K^+$  saturation decreased from 1 to 0.81. For dichlobenil, sorption by sorbents derived from Ca-SWy-2 increased by approximately 4 times as  $f_K$  increased from zero to 0.71. Replacement of  $K^+$  from K-SWy-2 by  $Ca^{2+}$  ( $f_K = 1-0.66$ ) manifested gradually diminishing sorption of dichlobenil to  $\sim 40\%$  of that by homoionic K-SWy-2. Interestingly, dichlobenil sorption for clay derived from Ca-SWy-2 with  $f_K = 0.71$  was substantially lower than the corresponding clay derived from K-SWy-2 with  $f_K = 0.66$ . The reason for such phenomena is a tendency for preservation of the original clay structures, namely, the smectite interlayer spacings associated with K- versus Ca-smectite as cation exchange ( $K^+ \rightarrow Ca^{2+}$  vs.  $Ca^{2+} \rightarrow K^+$ ) proceeds, which can be viewed as a type of cation exchange hysteresis (Laird and Shang 1997; Laird 2006). Dichlobenil adsorbed much more strongly to  $K^+$ - rather than  $Ca^{2+}$ -saturated smectite, so that as the  $K^+ \leftrightarrow Ca^{2+}$  exchange process occurs more favorable adsorption domains persist at a given  $f_K$  when starting from the  $K^+$ -saturated end member.

Just as cation exchange processes on smectites alter adsorption of NOCs, changes in aqueous solution conditions such as ionic strength could also influence adsorption via their effects on clay quasicrystal structures. In aqueous solution, smectite clays are often present as quasicrystals consisting of stacks of clay platelets separated by interlayers filled with exchangeable cations and water molecules. Sorption of NOCs must effectively compete with interlayer water molecules to access adsorption domains on clay siloxane surfaces. Increasing aqueous salt concentration can promote the formation of clay aggregates, and reduce the amount of water between clay layers, thereby manifesting smaller interlayer distances in the formed quasicrystals and facilitating intercalation of NOCs. For example, sorption of 1,3-DNB by K-SWy-2 increased with increasing KCl aqueous concentration (Fig. 2.18). At a relative 1,3-DNB aqueous concentration of 0.05, sorption by K-SWy-2 increased approximately 1.4, 1.7, 2.0 and 2.2 times as the KCl concentration increased from 0.01 M to 0.05, 0.10, 0.20, and 0.30 M, respectively (Li et al. 2007). Similar results were also observed for pesticide adsorption (Li et al. 2006). The small reduction in 1,3-DNB solubility due to the “salting out” effect was shown to be incapable of causing such a large increase in 1,3-DNB sorption by K-SWy-2. X-ray diffraction patterns and light absorbance of K-clay suspensions indicated the aggregation of clay particles and the formation of quasicrystal structures as KCl ionic strength increased, which is believed to be responsible for the enhanced adsorption of NACs and pesticides at higher ionic strength.

For adsorption of NOCs by smectites, the type of exchangeable cation is the primary determinant of the size of sorptive domains in the clay galleries, clay interlayer distances, and the formation of complexes with NOCs. Cation exchange reaction ( $K^+ \leftrightarrow Ca^{2+}$ ) on smectite generates a range of  $K^+$ -saturated fractions or domains in the clay,



**Figure 2.18.** Sorption isotherms of 1,3-dinitrobenzene (1,3-DNB) by K-SWy-2 from 0.01, 0.05, 0.10, 0.20, and 0.30 M KCl aqueous solutions [from Li et al. (2007)].

resulting in enhanced or reduced NOC adsorption (Chatterjee et al. 2008; Li et al. 2004b). Such simple cation exchange processes could be used as geochemical modulator in the development of environmentally friendly protocols to control the sorption, mobility, and bioavailability of NOCs in smectitic soils or soils amended with smectite clays. For example, Roberts et al. (2007a, 2007b) demonstrated the successful application of  $K^+/Ca^{2+}$  exchange reactions on smectite clays as a means to modulate the retention and release of NACs, and hence their toxicity to plants. Ionic strength is another plausible way to control clay interlayer environment, thereby modulating the degree of NOCs sorption/desorption in environmental systems. These simple geochemical controls on the adsorption/desorption of toxic NOCs could be used in bioremediation/phytoremediation to modulate the bioavailability and toxicity of NOCs to microorganisms and plants.

## 2.8. SUMMARY

Sorption of NOCs by smectites can assume values along a continuum from zero up to 100 g NOC per kg clay. The critical factors that control sorption are a complex interplay among the functional groups of the NOC, the layer charge of the clay mineral, and the hydration of interlayer cations (Fig. 2.14):

1. The clay layer charge plays an important role because it controls the lateral distance between strongly hydrated interlayer cations. While "hydrated radii" are poorly defined, typical estimates of hydrated radii are 9.6 Å for  $Ca^{2+}$ , 5.3 Å for  $K^+$ , and 3.6 Å for  $Cs^+$  (Evangelou 1998). Thus the cross-sectional area of hydrated  $Ca^{2+}$  is about 2.9 nm<sup>2</sup>, more than 7 times that of  $Cs^+$  (0.4 nm<sup>2</sup>), so one hydrated  $Ca^{2+}$  takes up 3.5 times as much surface area in the clay interlayer as do the two  $Cs^+$  ions that  $Ca^{2+}$  replaces. Using these hydrated radii along with an idealized smectite basal surface area of 750 m<sup>2</sup>/g and a 95 cmol/kg CEC, we compute that the hydrated radii of  $Ca^{2+}$  or  $K^+$  must overlap in the interlayer regions, meaning that the lateral adsorption domains (Fig. 2.4) are very small and the NOC would have to compete with strongly bound water for interlayer sorption sites. On the other hand,  $Cs^+$  and its hydration shells are projected to occupy only about 67% of the interlayer space; that is, about one-third of the surface area in a Cs-smectite may consist of lateral sorption domains (Fig. 2.4), implying that NOCs need compete only with weakly bound water in the Cs-smectite interlayers. This may explain why the Cs-smectite is the more effective adsorbent for essentially all NOCs studied. This idea of lateral domains is supported by several observations (Lee et al. 1990; Jaynes and Boyd 1991b; Laird et al. 1992; Sheng et al. 2001, 2002) of an inverse relationship between the CEC of clays and the amount of the organic solute adsorbed, since fewer interlayer cations per unit surface area mean larger lateral adsorption domains available for organic solutes (Fig. 2.4). When layer charge is quite large, adsorption of even polar NOCs by smectites can be sharply reduced, because hydration radii for the greater number of exchangeable cations begin to overlap. In contrast, even Ca-smectites with low layer charges exhibit a strong sorption of atrazine (Laird et al. 1992).
2. As the organic functional group becomes more polar, the ability of the NOC to displace water from clay interlayers becomes stronger, apparently due to enhanced inner- and/or outer-sphere complexation between the NOC and interlayer cations, resulting in increased adsorption. Thus, pesticides with multiple strongly polar functional groups like  $-NO_2$ ,  $-C=O$  or  $-C\equiv N$  exhibit a strong sorption to K-smectites (Sheng et al. 2001; Boyd et al. 2001), even though the hydrated radii of the  $K^+$  ions are expected to overlap. Such polar functional groups apparently allow the NOC to form pesticide-cation complexes that are strong enough to displace water from the hydration shells of interlayer cations.
3. Compounds with functional groups that are less polar (e.g., atrazine, TCE, dioxin) are less strongly bound by K-smectites but can still be strongly adsorbed by Cs-smectites, apparently because these NOCs are still able to displace the more weakly bound interlayer water found in the adsorptive domains (Fig. 2.4) between the hydrated Cs ions. The propensity for less polar NOCs to occupy these sites is further enhanced when the clay basal spacing is optimized at approximately 12.5 Å, as in the cases of Cs- and certain K-smectites, as discussed above. In these cases, the NOCs can be mostly dehydrated, and a hydrophobic component contributes to NOC adsorption by smectites (Li et al. 2004a; Chappell et al. 2005). In this context, the site of negative charge on the clay can influence the retention of pesticide, presumably because tetrahedrally substituted smectites swell less in water and thereby contain narrower-slit pores that favor hydrophobic sorption (Aggarwal et al. 2006a,b). Additionally, the negative charges are more localized in tetrahedrally substituted smectites affording more neutral (hydrophobic) siloxane surface area for NOC adsorption.

Apparently, then, an optimal inorganic sorbent for NOCs should be a  $Cs^+$ -saturated smectite with a low layer charge resulting from tetrahedral substitution. These criteria maximize adsorption domains parallel to the clay surfaces while



optimizing (near 12.5 Å) the adsorption domains perpendicular to the clay surfaces. Such clays may adsorb 10% of their weight for an NOC such as TNB with multiple, strongly complexing functional groups. In contrast, such clays adsorb some 1% by weight of more hydrophobic NOCs of lesser ability to form complexes with interlayer cations.

## ACKNOWLEDGMENTS

This project was supported by grant P42 ES004911 from the National Institute of Environmental Health Science (NIEHS), National Institute of Health (NIH), and National Research Initiative Competitive Grants from the USDA National Institute of Food and Agriculture. The contents are solely the responsibility of the authors and do not necessarily represent the official views of these federal agencies.

## REFERENCES

- Aggarwal, V., Li, H., and Teppen, B. J. (2006a), Triazine adsorption by saponite and beidellite clay minerals, *Environ. Toxic. Chem.* **25**, 392–399.
- Aggarwal, V., Li, H., Boyd, S. A., and Teppen, B. J. (2006b), Enhanced sorption of trichloroethene by smectite clay exchanged with Cs<sup>+</sup>, *Environ. Sci. Technol.* **40**, 894–899.
- Ahmad, I., Dines, T. J., Rochester, C. H., and Anderson, J. A. (1996), IR study of nitrotoluene adsorption on oxide surfaces, *J. Chem. Soc. Faraday Trans.* **92**, 3225–3231.
- Bailey, G. W. and White, J. L. (1970), Factors influencing the adsorption, desorption, and movement of pesticides in soil, in *Residue Reviews: Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds*, Gunther, F. A. and Gunthereds J. D. eds., Vol. 32, Springer-Verlag, New York, PP. 29–92.
- Baitinger, W., Schleyer, P. V. R., Murty, T. S. S. R., and Robinson, L. (1964), Nitro groups as proton acceptors in hydrogen bonding, *Tetrahedron* **20**, 1635–1647.
- Barriuso, E., Laird, D. A., Koskinen, W. C., and Dowdy, R. H. (1994), Atrazine desorption from smectites, *Soil Sci. Soc. Am. J.* **58**, 1632–1638.
- Borek, F. (1963), Effect of p-CH<sub>2</sub>X substituents on vibrational frequencies of the aromatic nitro group, *Naturwissenschaften* **50**, 471–472.
- Boyd, S. A., Mortland, M. M., and Chiou, C. T. (1988b), Sorption characteristics of organic compounds on hexadecyltrimethylammonium smectite, *Soil Sci. Soc. Am. J.* **52**, 652–657.
- Boyd, S. A., Lee, J. F., and Mortland, M. M. (1988c), Attenuating organic contaminant mobility by soil modification, *Nature* **333**, 345–347.
- Boyd, S. A., Sun, S., Lee, J. F., and Mortland, M. M. (1988a), Pentachlorophenol sorption by organoclays, *Clays Clay Miner.* **36**, 125–130.
- Boyd, S. A., Sheng, G., Teppen, B. J., and Johnston, C. T. (2001), Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays, *Environ. Sci. Technol.* **35**, 4227–4234.
- Celis, R., Cox, M. C., Hermosin, M. C., and Cornejo, J. (1997), Sorption of thiazafuron by iron- and humic acid-coated montmorillonite, *J. Environ. Qual.* **26**, 472–479.
- Chappell, M. A., Laird, D. A., Thompson, M. L., Li, H., Teppen, B. J., Aggarwal, V., Johnston, C. T., and Boyd, S. A. (2005), Influence of smectite hydration and swelling on atrazine sorption behavior, *Environ. Sci. Technol.* **39**, 3150–3156.
- Charles, S. M., Li, H., Teppen, B. J., and Boyd, S. A. (2006a), Quantifying the availability of clay surfaces in soils for adsorption of organic contaminants and pesticides, *Environ. Sci. Technol.* **40**, 7751–7756.
- Charles, S. M., Teppen, B. J., Li, H., Laird, D. A., and Boyd, S. A. (2006b), Exchangeable cation hydration properties strongly influence soil sorption of nitroaromatic compounds, *Soil Sci. Soc. Am. J.* **70**, 1470–1479.
- Charles, S. M., Teppen, B. J., Li, H., and Boyd, S. A. (2008), Fractional availability of smectite surfaces in soils for adsorption of nitroaromatic compounds in relation to soil and solute properties, *Soil Sci. Soc. Am. J.* **72**, 586–594.
- Chatterjee, R., Laird, D. A., and Thompson, M. L. (2008), Interactions among K<sup>+</sup>-Ca<sup>2+</sup> exchange, sorption of m-dinitrobenzene, and smectite quasicrystal dynamics, *Environ. Sci. Technol.* **42**, 9099–9103.
- Chiou, C. T. (2002), *Partition and Adsorption of Organic Contaminants in Environmental Systems*, Wiley, Hoboken, NJ.
- Chiou, C. T. and Shoup, T. D. (1985), Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity, *Environ. Sci. Technol.* **19**, 1196–1200.
- Chiou, C. T., Peters, L. J., and Freed, V. H. (1979), A physical concept of soil-water equilibria for nonionic organic compounds, *Science* **206**, 831–832.
- Chiou, C. T., Porter, P. E., and Schmedding, D. W. (1983), Partition equilibria of nonionic organic compounds between soil organic matter and water, *Environ. Sci. Technol.* **17**, 227–231.
- Chiou, C. T., Kile, D. E., Rutherford, D. W., Sheng, G., and Boyd, S. A. (2000), Sorption of selected organic compounds from water to a peat soil and its humic-acid and humin fractions: Potential sources of the sorption nonlinearity, *Environ. Sci. Technol.* **34**, 1254–1258.
- Conduit, C. P. (1959), Ultraviolet and infrared spectra of some aromatic nitro-compounds, *J. Chem. Soc.* 3273–3277.
- Evangelou, V. P. (1998), *Environmental Soil and Water Chemistry: Principles and Applications*, Wiley, New York.
- Friedman, H. L. and Krishnan, C. V. (1973), Thermodynamics of ionic hydration, in *Water: A Comprehensive Treatise*, Vol. 3, *Aqueous Solutions of Simple Electrolytes*, Franks, F., ed, Plenum, New York, PP. 1–118.
- Frisch, M. J., Trucks, G. W., et al. (1998), *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh, PA.
- Fusi, P., Ristori, G. G., and Franci, M. (1982), Adsorption and catalytic decomposition of 4-nitrobenzenesulphonylmethylcarbamate by smectite, *Clays Clay Miner.* **30**, 306–309.

- Gaines, R. V., Skinner, H. C. W., Foord, E. E., Mason, B., and Rosenzweig, A. (1997), *Dana's New Mineralogy*, Wiley, New York.
- Green, J. H. S. and Lauwers, H. A. (1971), Vibrational spectra of benzene derivatives — XIII The nitrobenzenes, *Spectrochim. Acta*. **27A**, 817–824.
- Green, R. E. (1974), Pesticide-clay-water interactions, in *Pesticides in Soil and Water*, Guenzi, W. D. ed., Soil Science Society of America, Madison, WI PP. 3–37.
- Grundl, T. and Small, G. (1993), Mineral contributions to atrazine and alachlor sorption in soil mixtures of variable organic carbon and clay content, *J. Contam. Hydrol.* **14**, 117–128.
- Haderlein, S. B. and Schwarzenbach, R. P. (1993), Adsorption of substituted nitrobenzenes and nitrophenols to mineral surface, *Environ. Sci. Technol.* **27**, 316–326.
- Haderlein, S. B., Weissmahr, K. W., and Schwarzenbach, R. P. (1996), Specific adsorption of nitroaromatic explosives and pesticides to clay minerals, *Environ. Sci. Technol.* **30**, 612–622.
- Hassett, J. J., Banwart, W. L., Wood, S. G., and Means, J. C. (1981), Sorption of  $\alpha$ -naphthol: Implications concerning the limits of hydrophobic sorption, *Soil Sci. Soc. Am. J.* **45**, 38–42.
- Jaynes, W. F. and Boyd, S. A. (1990), Trimethylphenylammonium-smectite as an effective adsorbent of water soluble aromatic hydrocarbons, *J. Air Waste Manage. Assoc.* **40**, 1649–1653.
- Jaynes, W. F. and Boyd, S. A. (1991a), Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays, *Soil Sci. Soc. Am. J.* **55**, 43–48.
- Jaynes, W. F. and Boyd, S. A. (1991b), Hydrophobicity of siloxane surface in smectites as revealed by aromatic hydrocarbon adsorption from water, *Clays Clay Miner.* **39**, 428–436.
- Johnston, C. T. and Sposito, G. (1987), Disorder and early sorrow: Progress in the chemical speciation of soil surfaces, in *Future Developments in Soil Science Research*. Boersma, L. L. ed., Soil Science Society of America, Madison, WI, PP. 89–100.
- Johnston, C. T. and Premachandra, G. S. (2001), Polarized ATR-FTIR study of smectite in aqueous suspension, *Langmuir* **17**, 3712–3718.
- Johnston, C. T., Sposito, G., and Earl, W. L. (1993), Surface spectroscopy of environmental particles by Fourier transform infrared and nuclear magnetic resonance spectroscopy, in *Environmental Particles*, Vol. 2 in Environmental Analytical and Physical Chemistry Series, Buffle J. and van Leeuwen, H. P., eds., Lewis, Boca Raton, FL, PP. 1–36.
- Johnston, C. T., Boyd, S. A., Teppen, B. J., and Sheng, G. (2004), Sorption of nitroaromatic compounds on clay surfaces, in *Handbook of Layered Materials*, Auerbach, S. M., Carrado, K. A., and Dutta, P. K., eds., Marcel Dekker, New York, PP. 155–189.
- Johnston, C. T., De Oliveira, M. F., Teppen, B. J., Sheng, G., and Boyd, S. A. (2001), Spectroscopic study of nitroaromatic-smectite sorption mechanisms, *Environ. Sci. Technol.* **35**, 4767–4772.
- Johnston, C. T., Sheng, G., Teppen, B. J., Boyd, S. A., and de Oliveira, M. F. (2002), Spectroscopic study of dinitrophenol herbicide sorption on smectite, *Environ. Sci. Technol.* **36**, 5067–5074.
- Jonathan, N. B. H. (1960), Relations between force constants, bond orders, bond lengths, and bond frequencies for some nitrogen-oxygen bonds, *J. Molec. Spectrosc.* **4**, 75–83.
- Karickhoff, S. W. (1984), Organic pollutant sorption in aquatic systems, *J. Hydraul. Eng.* **110**, 707–735.
- Karickhoff, S. W., Brown, D. S., and Scott, T. A. (1979), Sorption of hydrophobic pollutants on natural sediments, *Water Resour. Res.* **13**, 241–248.
- Kile, D. E., Chiou, C. T., Zhou, H., Li, H., and Xu, O. (1995), Partition of nonpolar organic pollutants from water to soil and sediment organic matters, *Environ. Sci. Technol.* **29**, 1401–1406.
- Kukkadapu, R. K. and Boyd, S. A. (1995), Tetramethylphosphonium- and tetramethylammonium-smectites as adsorbents of aromatic and chlorinated hydrocarbons: Effect of water on adsorption efficiency, *Clays Clay Miner.* **43**, 318–323.
- Laird, D. A. (2006), Influence of layer charge on swelling of smectites, *Appl. Clay Sci.* **34**, 74–87.
- Laird, D. A. and Shang, C. (1997), Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 phyllosilicates, *Clays Clay Miner.* **45**, 681–689.
- Laird, D. A., Shang, C., and Thompson, M. L. (1995), Hysteresis in crystalline swelling of smectites, *J. Colloid Interface Sci.* **171**, 240–245.
- Laird, D. A., Barriuso, E., Dowdy, R. H., and Koskinen, W. C. (1992), Adsorption of atrazine on smectites, *Soil Sci. Soc. Am. J.* **56**, 62–67.
- Laird, D. A., Yen, P. Y., Koskinen, W. C., Steinheimer, T. R., and Dowdy, R. H. (1994), Sorption of atrazine on soil clay components, *Environ. Sci. Technol.* **28**, 1054–1061.
- Lawrence, M. A. M., Kukkadapu, R. K., and Boyd, S. A. (1998), Adsorption of phenol and chlorophenols by tetramethylammonium- and tetramethylphosphonium-exchanged montmorillonite, *Appl. Clay Sci.* **13**, 13–20.
- Leboeuf, E. J. and Weber, W. J. (1997), A distributed reactivity model for sorption by soils and sediments. 8. Sorbent organic domains: Discovery of a humic acid glass transition and an argument for a polymer-based model, *Environ. Sci. Technol.* **31**, 1697–1702.
- Lee, J. F., Crum, J., and Boyd, S. A. (1989), Enhanced retention of organic contaminants by soils exchanged with organic cations, *Environ. Sci. Technol.* **23**, 1365–1372.
- Lee, J. F., Mortland, M. M., Chiou, C. T., Kile, D. E., and Boyd, S. A. (1990), Adsorption of benzene, toluene, and xylene by 2 tetramethylammonium-smectites having different charge-densities, *Clays Clay Miner.* **38**, 113–120.
- Li, H., Teppen, B. J., Johnston, C. T., and Boyd, S. A. (2004a), Thermodynamics of nitroaromatic compound adsorption from water by smectite clay, *Environ. Sci. Technol.* **38**, 5433–5442.
- Li, H., Teppen, B. J., Laird, D. A., Johnston, C. T., and Boyd, S. A. (2004b), Geochemical modulation of pesticide sorption on smectite clay, *Environ. Sci. Technol.* **38**, 5393–5399.
- Li, H., Sheng, G., Teppen, B. J., Johnston, C. T., and Boyd, S. A. (2003), Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes, *Soil Sci. Soc. Am. J.* **67**, 122–131.
- Li, H., Teppen, B. J., Laird, D. A., Johnston, C. T., and Boyd, S. A. (2006), Effects of increasing potassium chloride and calcium chloride ionic strength on pesticide sorption by K- and Ca-smectite, *Soil Sci. Soc. Am. J.* **70**, 1889–1895.

- Li, H., Pereira, T. R., Teppen, B. J., Laird, D. A., Johnston, C. T., and Boyd, S. A. (2007), Ionic strength-induced formation of smectite quasicrystals enhances nitroaromatic compound sorption, *Environ. Sci. Technol.* **41**, 1251–1256.
- Liu, C., Li, H., Teppen, B. J., Johnston, C. T., and Boyd, S. A. (2009), Mechanisms associated with the high adsorption of dibenzo-p-dioxin from water by smectite clays, *Environ. Sci. Technol.* **43**, 2777–2783.
- MacEwan, D. M. C. and Wilson, M. J. (1980), Interlayer and intercalation complexes of clay minerals, in *Crystal Structures of Clay Minerals and Their X-Ray Identification*, Brindley, G. W. and Brown, G., eds., Mineralogical Society, London, PP. 197–248.
- Margulies, L., Rozen, H., and Banin, A. (1988), Use of X-ray powder diffraction and linear dichroism methods to study the orientation of montmorillonite clay particles, *Clays Clay Miner.* **36**, 476–479.
- Mortland, M. M. (1970), Clay-organic complexes and interactions, *Adv. Agron.* **22**, 75–117.
- Mortland, M. M. (1986), Mechanisms of adsorption of non-humic organic species by clay, in *Interactions of Soil Minerals with Natural Organics and Microbes* (special publication 17.), Huang, P. M. and Schritzer, M., eds., Soil Science Society of America, Madison, WI, PP. 59–76.
- Nyquist, R. A. and Settineri, S. E. (1990), Infrared study of substituted nitrobenzenes in carbon tetrachloride and chloroform solutions, *Appl. Spectrosc.* **44**, 1552–1557.
- Onken, B. M. and Traina, S. J. (1997), The sorption of pyrene and anthracene to humic acid-mineral complexes: Effect of cosolute, *J. Environ. Qual.* **26**, 132–138.
- Pennell, K. D., Boyd, S. A., and Abriola, L. M. (1995), Surface area of soil organic matter reexamined, *Soil Sci. Soc. Am. J.* **59**, 1012–1018.
- Pereira, T. R., Laird, D. A., Johnston, C. T., Teppen, B. J., Li, H., and Boyd, S. A. (2007), Mechanism of dinitrophenol herbicide sorption on smectites in aqueous suspensions at varying pH, *Soil Sci. Soc. Am. J.* **71**, 1476–1481.
- Pereira, T. R., Laird, D. A., Thompson, M. L., Johnston, C. T., Teppen, B. J., Li, H., and Boyd, S. A. (2008), Role of smectite quasicrystal dynamics in adsorption of dinitrophenol, *Soil Sci. Soc. Am. J.* **72**, 347–354.
- Pignatello, J. J. and Xing, B. (1996), Mechanisms of slow sorption of organic chemicals to natural particles, *Environ. Sci. Technol.* **30**, 1–11.
- Pils, J. R. V., Laird, D. A., and Evangelou, V. P. (2007), Role of cation demixing and quasicrystal formation and breakup on the stability of smectitic colloids, *Appl. Clay Sci.* **35**, 201–211.
- Pusina, A., Liu, W., and Gessa, C. (1992), Influence of organic matter and its clay complexes on metolachlor adsorption on soil, *Pesticide Sci.* **36**, 283–286.
- Ras, R. H. A., Schoonheydt, R. A., and Johnston, C. T. (2007), Relation between s-polarized and p-polarized internal reflection spectra: Application for the spectral resolution of perpendicular vibrational modes, *J. Phys. Chem. A* **111**, 8787–8791.
- Ras, R. H. A., Johnston, C. T., Franses, E. I., Ramaekers, R., Maes, G., Foubert, P., de Schryver, F. C., and Schoonheydt, R. A. (2003), Polarized infrared study of hybrid Langmuir-Blodgett monolayers containing clay mineral nanoparticles, *Langmuir* **19**, 4295–4302.
- Roberts, M. G., Rugh, C. L., Li, H., Teppen, B. J., and Boyd, S. A. (2007a), Reducing bioavailability and phytotoxicity of 2,4-dinitrotoluene by sorption on K-smectite clay, *Environ. Toxic. Chem.* **26**, 358–360.
- Roberts, M. G., Rugh, C. L., Li, H., Teppen, B. J., and Boyd, S. A. (2007b), Geochemical modulation of bioavailability and toxicity of nitroaromatic compounds to aquatic plants, *Environ. Sci. Technol.* **41**, 1641–1645.
- Saltzman, S. and Yariv, S. (1975), Infrared study of the sorption of phenol and p-nitrophenol by montmorillonite, *Soil Sci. Soc. Am. J.* **39**, 474–479.
- Shang, C., Laird, D. A., and Thompson, M. L. (1995), Transmission X-ray diffraction technique for measuring crystalline swelling of smectites in electrolyte solutions, *Clays Clay Miner.* **43**, 128–130.
- Sheng, G. and Boyd, S. A. (2000), Polarity effect on dichlorobenzene sorption by hexadecyltrimethylammonium-clays, *Clays Clay Miner.* **48**, 43–50.
- Sheng, G., Johnston, C. T., Teppen, B. J., and Boyd, S. A. (2001), Potential contributions of smectite clays and organic matter to pesticide retention in soils, *J. Agric. Food Chem.* **49**, 2899–2907.
- Sheng, G., Johnston, C. T., Teppen, B. J., and Boyd, S. A. (2002), Adsorption of dinitrophenol herbicides from water by montmorillonites, *Clays Clay Miner.* **50**, 25–34.
- Teppen, B. J., Rasmussen, K., Bertsch, P. M., Miller, D. M., and Schäfer, L. (1997), Molecular dynamics modeling of clay minerals. 1. Gibbsite, kaolinite, pyrophyllite, and beidellite, *J. Phys. Chem. B* **101**, 1579–1587.
- Teppen, B. J., Yu, C.-H., Miller, D. M., and Schäfer, L. (1998), Molecular dynamics simulations of the sorption of organic compounds at the clay mineral/aqueous solution interface, *J. Comput. Chem.* **19**, 144–153.
- Theng, B. K. G. (1974), *The Chemistry of Clay-Organic Reactions*, Wiley, New York.
- Urbanski, T. and Dabrowska, U. (1959), The influence of the conjugation on the position of the infra-red band of the nitro group in some aromatic nitro-compounds, *Bull. Acad. Polonaise Sci.* **7**, 235–237.
- Weissmahr, K. W., Haderlein, S. B., Schwarzenbach, R. P., Hany, R., and Nuesch, R. (1997), *In situ* Spectroscopic investigations of adsorption mechanisms of nitroaromatic compounds at clay minerals, *Environ. Sci. Technol.* **31**, 240–247.
- Xia, G. S. and Ball, W. P. (2000), Polanyi-based models for the competitive sorption of low-polarity organic contaminants on a natural sorbent, *Environ. Sci. Technol.* **34**, 1246–1254.
- Yariv, S., Russell, J. D., and Farmer, V. C. (1966), Infrared study of the adsorption of benzoic acid and nitrobenzene in montmorillonite, *Israel. J. Chem.* **4**, 201–213.