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## INTEGRATING MOLECULAR SIMULATIONS WITH EXPERIMENTS TO STUDY ORGANIC POLLUTANT INTERACTIONS WITH CLAY MINERALS

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# INTEGRATING MOLECULAR SIMULATIONS WITH EXPERIMENTS TO STUDY ORGANIC POLLUTANT INTERACTIONS WITH CLAY MINERALS

By

VANEET AGGARWAL

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

## DOCTOR OF PHILOSOPHY

Department of Crop & Soil Science

#### ABSTRACT

# INTEGRATING MOLECULAR SIMULATIONS WITH EXPERIMENTS TO STUDY ORGANIC POLLUTANT INTERACTIONS WITH CLAY MINERALS

#### By

#### VANEET AGGARWAL

Triazine herbicides such as atrazine and simazine have been applied for more than 40 years in the United States. Atrazine is one of the most common herbicide residues found in groundwaters of Midwest. Sorption to soil components can control the bioavailability, persistence, and transport of xenobiotics. We investigated the sorption of three triazine herbicides (atrazine, simazine, and metribuzin) by saponite and beidellite clay minerals saturated with  $K^+$ ,  $Cs^+$ ,  $Na^+$ , and  $Ca^{2+}$ . Saponite clay sorbed a larger fraction of each pesticide from aqueous solution than did beidellite clay. The lower cation exchange capacity in saponite (vs. beidellite) presumably results in a less crowded interlayer with more siloxane surface available for adsorption. Generally, Cs-saturated clays sorbed more triazines than clays saturated by  $K^+$ , Na<sup>+</sup> or Ca<sup>2+</sup>. We attribute this to the smaller hydrated radius of Cs<sup>+</sup>, which again increases the siloxane surface available for sorption. Furthermore, the relatively weak hydration of Cs<sup>+</sup> reduces the swelling of clay interlayers, thus making sorption domains less hydrated and more receptive to hydrophobic molecules. Cs-saponite manifested a sorption of more than 1% atrazine by weight above equilibrium concentrations of 6 mg/L. This is the largest sorption of neutral atrazine from water yet reported for an inorganic sorbent. Molecular dynamics simulations indicate that atrazine interacts with both clay basal planes and with multiple

cations in the clay interlayer forming both inner- and outer-sphere complexes. Similar effects of exchangeable cation on trichloroethene sorption by saponite clay were also observed, and our general concept of the factors controlling sorption of nonpolar organics by clay minerals is becoming more clear.

Molecular simulations were also used to estimate thermodynamics of polar organic sorption to montmorillonites. Our method shows promise in that simulated adsorption enthalpies for nitroaromatic compounds have the correct sign and are significantly different from that of p-xylene. Further work is still needed so that enthalpy predictions can be more precise.

# DEDICATION

To my daughter, Muskaan, wife Deepa, and parents, for everything

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## "Images in this thesis/dissertation are presented in color."

## **CHAPTER I**

# INTEGRATING MOLECULAR SIMULATIONS WITH EXPERIMENTS TO STUDY ORGANIC POLLUTANT INTERACTIONS WITH CLAY MINERALS

#### Introduction

Atrazine is one of the most commonly used agricultural herbicides in the world and has been applied for more than 30 years by corn and sorghum growers in the United States (Ribaudo and Bouzaher, 1994). In 1994, over 47 million pounds of atrazine were applied nation-wide covering about 77 % of the area cropped under corn-soybean rotation (Pike and Knake, 1996). About 2.4 million pounds of atrazine were applied on 80 % of the cropped area in Michigan, making it the most widely used herbicide in Michigan (Pike and Knake, 1996). Atrazine is also one of the most common herbicide residues found in groundwaters of Midwest (Blanchard and Donald, 1997; Burkart et al., 1999; Kolpin et al., 1998). Atrazine and two of its metabolites were detected in 26 % of 303 sampled Midwest wells in the United States (Kolpin et al., 1996) and is detected 10 to 20 times more frequently than the next most commonly detected pesticide (Belluck et al., 1991). Based on 41 land-use studies across the United Sates during 1993-1995, (Kolpin et al., 1998) indicated that of the 46 pesticide compounds examined, 39 were detected in shallow groundwater. Atrazine was the most frequently detected (38 %) followed by its decomposition product, deethylatrazine (34 %). The presence of atrazine in groundwater is a concern because of potential carcinogenic effects of s-triazines, which include atrazine, simazine, and propazine (Biradar and Rayburn, 1995). Other toxic effects of atrazine include skin irritation, respiratory effects, central nervous system disorders, and blood cell disorders (U.S. Congress, Office of Technology Assessment, 1984).

Adsorption and desorption processes on soil components are important phenomena that control the environmental fate and behavior of pesticides including bioavailability, persistence and transport of pesticides in soils and subsoils. Clay minerals

and soil organic matter (SOM) are the two chemically most active components of the soils. Generally, cultivated soils contain a larger fraction of clay than organic matter, yet most of the research conducted in the last 20 years has considered SOM as the primary sorptive phase of organic contaminants interacting with soils (Chiou et al., 1979; Chiou et al., 1983; Chiou et al., 2000; Huang et al., 1997; Kleineidam et al., 1999; Weber and Huang, 1996; Xia and Ball, 2000; Xing and Pignatello, 1997). Chiou et al. (1979) in a study with seven neutral organic molecules did not observe any indication of adsorption isotherm curvature even at concentrations approaching saturation. Therefore, they concluded that adsorption of neutral organic molecules is controlled by soil organic matter and occurs essentially by partition processes. Chiou et al. (1983) even suggested that sorption of non-ionic organic compounds on the soil mineral fraction is relatively unimportant in moist soils. Xing and Pignatello (1997) in a study with chlorinated benzenes, observed that the value of Freundlich coefficient, N, was unaffected by complete removal of mineral phase, again indicating that soil organic matter controls the sorption of such compounds in soils. It has also been found that in addition to the organic carbon content, the chemical and structural properties of soil organic matter also significantly affect the sorption of slightly polar and non-polar hydrophobic organic contaminants (Grathwohl, 1990; McGinley et al., 1993; Weber et al., 1992; Young and Weber, 1995). Geologically mature organic matter had much higher sorption capacities than relatively young humic organic matter in soils (Grathwohl, 1990; Young and Weber, 1995). Kleineidam et al. (1999) in a study with low organic matter soils observed that the reduction of organic carbon significantly decreased sorption. They therefore concluded

that organic matter dominates sorption of hydrophobic organic compounds, even in samples with very low organic carbon contents.

Clay minerals are layered aluminosilicates, most of which have structural negative charges due to cation substitution and surface areas exceeding  $10^5 \text{ m}^2 \text{ kg}^{-1}$  (Borchardt, 1989; Brown et al., 1978). The large surface area per unit weight associated with clay minerals is important for sorption of pesticides (Karickhoff, 1984). Among commonly found clay minerals, expandable 2:1 layer silicate clays are especially important due to their high surface areas, high cation exchange capacities (CECs) and surface reactivities (McBride, 1994). Smectites are important members of the expandable 2:1 layer silicate clays and contribute much of the inorganic surface areas of many soils. Therefore, smectites have a high potential for influencing the fate of pesticides in the soil environment. The sorption capacity of smectites for atrazine varies widely depending on the surface charge density of the smectite (Laird et al., 1992), the nature of the adsorbed cation (Sheng et al., 2001), and the pH of the soil (Vaz et al., 1997).

Hayes and Mingelgrin (1991) reported that in low organic matter soils and sediments, clays might control the sorption/desorption interactions. Khan et al. (1979) observed that inorganic constituents could have a dominant role in pesticide retention in low organic matter soils. Means et al. (1982) reported that pesticide sorption is proportional to the percent organic carbon and where percent organic carbon is low, the amount of clay becomes important in determining pesticide sorption. Karickhoff (1984) concluded that at clay to organic matter ratios greater than 30, the soil mineral phase becomes important for the organic contaminant sorption. Rebhun et al. (1992) reported

that sorption of organic contaminants by the organic fraction was 8 to 20 times higher than by pure clay minerals. However, in soils with the commonly encountered range of organic matter (0.5 - 5%) and high clav content, the contribution of the mineral fraction exceeded that of the organic component. In a study on the adsorption of some nitroaromatics by clay minerals, Haderlein and Schwarzenbach (1993) and Haderlein et al. (1996) found that clays with high surface areas (e.g., smectites) and exchangeable cations with low hydration energies (e.g.,  $K^+$  and  $Cs^+$ ) promoted adsorption. Boyd et al. (2001) demonstrated that the strong sorption of nitroaromatics occurs because the organic compound forms interlayer complexes with exchangeable cations of the clay. Recently, Sheng et al. (2001) reported that on a unit mass basis, some smectite clays were more effective sorbents than SOM for four out of the seven pesticides studied. Hance (1965) suggested that under field conditions in the absence of excess water, the soil mineral fraction may play an important role in adsorption. Similar results were observed for adsorption of parathion (Yaron and Saltzman, 1972), and parathion and lindane (Chiou et al., 1985) on soils. In a dry soil-hexane-parathion system the slightly polar parathion molecules efficiently compete with the apolar hexane molecules for adsorption sites (Yaron and Saltzman, 1972). Generally as the soil water content increases, parathion adsorption decreases because of the decreasing contribution of the soil mineral fraction. When soils are fully hydrated, adsorption of neutral organic solutes by soil minerals often becomes relatively insignificant compared to the uptake by partitioning into soil organic matter, presumably because water is preferentially adsorbed by minerals (Chiou et al., 1985).

#### Sorption of atrazine to soil colloids

#### a. Organic matter and clays

Talbert and Fletchall (1965) showed that atrazine adsorption to whole soils was strongly correlated with both clay content and organic matter content. However, Roy and Krapac (1994) did not find any correlation between atrazine sorption and clay content. Terce and Calvet (1977) reported little atrazine sorption by Ca-smectites. Borggaard and Streibig (1988) reported that smectites and iron oxides adsorbed little or no atrazine in the pH range of 4 – 8 and suggested that organic matter is possibly the only atrazineadsorbing constituent in many natural soils. Brouwer et al. (1990) observed a logarithmic increase of atrazine distribution coefficient with organic matter content. Wang et al. (1990) reported the preferential binding of atrazine to the higher molecular weight fraction of fulvic acids and proposed weak mechanisms of interaction such as hydrogen bonding and hydrophobic bonding to interpret their findings. On the basis of NMR spectroscopic investigation, Welhouse and Bleam (1992) concluded that due to the separation of charge within the atrazine molecule, atrazine is able to both donate and accept hydrogen bonds. On the basis of intermediate values of atrazine's donating  $(\alpha_m)$ , and accepting  $(\beta_m)$  parameters, they suggested that particularly strong complexes could be expected between atrazine and acid functional groups of humic substances (Welhouse and Bleam, 1993a) and concluded that hydrogen bonding is an important mechanism for atrazine adsorption to soil organic matter (Welhouse and Bleam, 1993b). Grundl and Small (1993) evaluated the role of mineral-phase sorption of atrazine and alachlor by different sediments and concluded that they were sorbed by both natural organic carbon

(OC) and clays. The critical clay/OC ratios at which mineral-phase sorption accounted for 50 % of the overall sorption was 62 and 84 for atrazine and alachlor, respectively. In a study with a Webster soil, Laird et al. (1994) found that organic and inorganic components were 11 and 89 % of the mass and contributed 68 and 32 % respectively, of the affinity for atrazine. Laird et al. (1992) worked in the low-concentration range up to 0.04 mg atrazine/g clay and reported that atrazine adsorption by 14 different Ca-smectites ranged from 0 to 100 %. Recently, Sheng et al. (2001) showed that a K-saturated smectite and a muck soil sorbed equal amounts of atrazine from aqueous solution.

#### b. Exchangeable cations

The type of exchangeable cation on the clay also affects pesticide sorption. Sheng et al. (2001) reported that homoionic K-montmorillonite adsorbed up to 240 mg atrazine/kg clay and is seven times more effective sorbent for atrazine than homoionic Ca-montmorillonite. They reported that the lower effectiveness of Ca-montmorillonite might be due in part to the higher hydration energy and hence larger hydrated radius of  $Ca^{2+}$  than that of K<sup>+</sup>. Thus the waters of hydration associated with  $Ca^{2+}$  obscure a greater portion of the clay surface than those associated with K<sup>+</sup>, which in turn will shrink the size of the adsorptive domains between exchangeable cations. They reported that 12.5 Å basal spacing associated with many K-smectites, as opposed to >15 Å spacing for Casmectites, may be optimal for adsorption of semiplanar aromatic pesticides like atrazine. Sawhney and Singh (1997) also reported higher atrazine adsorption by Al-smectite (3.82 mg atrazine/g clay) than by Ca-smectite (1.90 mg atrazine/g clay). They attributed higher atrazine sorption by Al-smectite to the more polarized water molecules associated with

 $Al^{3+}$  than with  $Ca^{2+}$ ; those water molecules are postulated to electrostatically attract Ngroups of atrazine. Macnamara and Toth (1970) observed that K-clay systems showed a greater adsorption capacity for linuron and malathion than Ca-, Mg-, and H/Al- clay systems. Using on-line microfiltration and HPLC technique, Gilchrist et al. (1993) observed that most of the added atrazine was rapidly and reversibly sorbed on the montmorillonite and that Na<sup>+</sup> saturated montmorillonite sorbed more atrazine than Ca<sup>2+</sup> saturated montmorillonite. The Ca<sup>2+</sup> saturated montmorillonite had a higher surface charge density than Na<sup>+</sup>.

## c. Surface charge density (SCD)

Laird et al. (1992) worked in the low-concentration range up to 0.04 mg atrazine/g clay and reported that atrazine adsorption by 14 different Ca-smectites ranged from 0 to 100 %. They reported that Panther Creek beidellite adsorbed virtually all of the added atrazine while Otay, CA montmorillonite did not adsorb any atrazine. The amount of atrazine adsorbed by the remaining 12 smectites varied between these two extremes. Panther Creek beidellite had the lowest CEC (88 cmol kg<sup>-1</sup>) while Otay, CA montmorillonite had the highest CEC (134 cmol kg<sup>-1</sup>), therefore they concluded that atrazine adsorption is inversely related with the CEC of the smectite clays. They found that 83 % of the variation in the values of the Freundlich constant (log K<sub>f</sub>) was related to the surface charge density (SCD) and surface area (SA) of the clays. Panther Creek beidellite had lower values of SCD (1.42  $\mu$ mol m<sup>-2</sup>) and SA (619 m<sup>2</sup> g<sup>-1</sup>) while Otay, CA montmorillonite had higher SCD (1.85  $\mu$ mol m<sup>-2</sup>) and SA (724 m<sup>2</sup> g<sup>-1</sup>) values. In a study with six different species of K-smectites, Sheng et al. (2001), reported that the amount of atrazine adsorbed by K-saponite was 0.25 mg/g clay and by K-montmorillonite was 0.10 mg/g clay. On the basis of adsorption coefficient values (K<sub>f</sub>), they concluded that Ksaponite (CEC 94.9 cmol/kg) is about 15 times more effective in the removal of atrazine from the solution than K-montmorillonite (CEC 130 cmol/kg). These observations are in agreement with the results of Laird et al. (1992) who concluded that atrazine sorption by clays is inversely dependent on clay properties such as SCD and CEC. Based on this evidence, they concluded that under neutral pH conditions, atrazine is dominantly sorbed on smectites as molecular species. Hamaker and Thompson (1972) suggested hydrogen bonding as a mechanism for the sorption of s-triazine herbicides to clay surfaces. Laird (1996) reported that under neutral conditions, molecular atrazine is initially sorbed on smectites by a combination of water-bridging and hydrophobic interactions. He proposed that the lone pair of electrons on the ring N atoms of atrazine molecules interact with water molecules solvating metal cations adsorbed on smectite surfaces. At the same time, the alkyl-side chains of atrazine molecules out-compete water molecules for retention on hydrophobic microsites on smectite surfaces. Hydrophobic bonding is also consistent with the observed decrease in sorption with increasing surface charge density of smectites because the amount of hydrophobic surface on smectites decreases with increasing surface charge density. One reason for this decrease in sorption with increase in SCD is that greater SCD causes the water molecules at the surface of the clays to be more strongly bound and have a more ordered structure (Gilchrist et al., 1993). Since atrazine is only sparingly water soluble (water solubility is only 30 mg/L), it is less likely to approach and adsorb to surfaces having rigid, ordered water layers than to surfaces without such layers. Barriuso et al. (1994) reported that in spite of the lower adsorption

capacity of high SCD clays, atrazine was held by stronger binding mechanisms on these clays.

#### d. pH

The extent of pesticide adsorption by clays depends strongly on the molecular structure including the basicity of the pesticides and thus on the pH of the solution, with maximum adsorption typically occurring at a pH near the pKa values of the pesticides (Weber, 1970). Atrazine has pKa of 1.68, so maximum adsorption of atrazine is expected in very acidic soils. Sorption of atrazine on acidic humic acid (pH 2.5) was ten times greater ( $K_d$  627 cm<sup>3</sup> g<sup>-1</sup>) than on neutral (pH 7.0) humic acid (Kd 62.2 cm<sup>3</sup> g<sup>-1</sup>) (McGlamery and Slife, 1966). This pH effect was attributed to increased ionic bonding caused by protonation of the amino groups on the atrazine molecule at low pH (McGlamery and Slife, 1966). Weber (1970) concluded that the adsorption of s-triazines was due to complexation of the triazine molecules with functional groups on the organic colloids and/or adsorption of s-triazine cations by ion-exchange forces. Gilmour and Coleman (1971) showed that cation exchange causes a large increase in atrazine sorption to humic acid at low pH. Charge transfer complexes have also been postulated as a possible mechanism involved in the adsorption of s-triazine herbicide onto SOM (Hamaker and Thompson, 1972). Borggaard and Streibig (1988) reported that smectites and iron oxides adsorbed no or insignificant atrazine in the pH range of 4 - 8. Madsen et al. (2000) reported that sorption of atrazine depends primarily on pH, the sorption being high at low pH (<6.7) compared with sorption at higher pH (>7.4). At lower pH, more hydrogen ions associate with the atrazine molecules giving more cationic characteristics,

which leads to increased adsorption (Frissel and Bolt, 1962). Baskaran et al. (1996) reported that as the pH increases, the proportion of atrazine cations in the solution decreases and hence the decrease in sorption with increase in pH. Clay et al. (1988) also reported that with the application of ammonium sulfate and elemental S as fertilizers to the soils, the adsorption of atrazine increased as the fertilizers decreased soil pH from 6.0 to 4.5. Atrazine is an extremely weak base (pKa of 1.68), hence little protonation of adsorptive phases can be expected at pH values 2 or more units above the pKa of the adsorbate (Hayes and Mingelgrin, 1991). Therefore, atrazine should be sorbed primarily as a neutral molecule in cultivated soils, which have a pH range of 4 - 8. Laird et al. (1992) also reported that atrazine is dominantly sorbed on smectites as a neutral species for the pH range 4.75 to 6.45.

#### e. Temperature

Harris and Warren (1964) reported that adsorption of atrazine, monuron, and simazine by bentonite was greater at 0°C than at 50°C. Adsorption by muck was similar at the two temperatures for all compounds. They concluded that bentonite had a higher bonding enthalpy than muck. Talbert and Fletchall (1965) also reported that the amount of atrazine adsorbed decreased as the temperature was raised from 0 to 50 °C. Huang et al. (1984) did not observe any effect of temperature on the adsorption of atrazine by whole soils over a temperature range of 5 to 25°C, while Lavy (1970) reported that diffusion coefficients of many triazines decreased when temperature was lowered from 25 to 5°C, coincident with decreased adsorption. The effect of temperature on the sorption of atrazine on humic acid was quite marked; sorption was nearly twice as great

at 40 °C than at 0.5 °C (McGlamery and Slife, 1966). This endothermicity would imply that sorption of atrazine to soil organic matter is governed by favorable entropy changes. Dao and Lavy (1978) reported that greater amounts of atrazine were adsorbed at 30 °C than at 5 °C on four soils at 0.1 bar moisture content. They also reported that a decrease in water: soil ratio and in soil moisture content led to an increased adsorption of atrazine. Thus, the influence of temperature on the adsorption by soils seems to be quite variable and it seems to vary with the nature of the soil components (Harris and Warren, 1964). The available data imply that sorption of atrazine to clay minerals is enthalpically favored, while sorption to organic matter is entropically favored.

## f. Fe and Al oxides

Huang et al. (1984) showed that oxides of iron and aluminum play an important role in the adsorption of atrazine by soils and that their removal drastically decreased the adsorption of atrazine by the soils. Terce and Calvet (1977) also reported similar results, while Seta and Karathanasis (1997), and Laird et al. (1994) reported that high contents of iron- and aluminum- oxyhydroxides suppressed atrazine adsorption in soils. This suppression could be due to the inhibition of smectite swelling by these oxyhydroxides. Laird et al. (1994) also observed that these free iron- and aluminum- oxyhydroxides coat silicate minerals, rendering their surfaces more hydrophilic and thus suppressing sorption of hydrophobic compounds like atrazine.

Atrazine adsorption-desorption is the major process affecting atrazine behavior in soils and is affected by various factors such as organic matter, clay content, pH, temperature, and iron- and aluminum- oxyhydroxides. We can see that there are many

discrepancies in the literature on the effect of inorganic fractions of soils, so atrazine adsorption to minerals needs to be further studied with new methodologies. Molecular simulations are ideally suited to contribute to our understanding of pesticide behavior in soils because they simultaneously provide mechanistic insight (that can be compared with the available spectroscopic information) and kinetic and thermodynamic estimates (that can be correlated with the many bulk measurements of pesticide diffusion, adsorption isotherms, and distribution coefficients). Thus, we propose to study the atrazine interactions with smectites using molecular simulation methods.

#### Proposal

#### A. Simulating atrazine-clay interactions

To simulate the adsorption of atrazine by clays, several types of computational studies will be performed. The minimum-energy structure for atrazine will be computed using density functional theory (Kohn et al., 1996) as implemented in the ab initio programs PQS and Gaussian98 (Frisch et al., 1998). The B3LYP functionals (Becke, 1993) were used with the 6-311G\*\* basis set (Krishnan et al., 1980). For the optimized structure, partial charges for each atom will be estimated using the CHELPG method (Breneman and Wiberg, 1990). Models for K-SWy-2 and K-SAz-1 will be created and molecular dynamics simulations of atrazine-clay complexes will be performed in order to explore the interactions between atrazine, cations and water in the interlayer region. The model for K-SWy-2 will have composition of  $K_7(Al_{42}Mg_6)(Si_{96}Al_1)O_{240}(OH)_{48}$  with a CEC of 79 cmol kg<sup>-1</sup>, while the model for K-SAz-1 will have composition of

 $K_{12}(Al_{36}Mg_{12})Si_{96}O_{240}(OH)_{48}$  with a CEC of 132 cmol kg<sup>-1</sup>. Atrazine will be added to each unit cell, with the atrazine molecular plane perpendicular to the basal planes of the clay. The interactions between atrazine, a variety of interlayer cations, and water in the interlayer region will be observed at different loading rates, that is, different numbers of atrazine molecules will be added to the unit cell. Water molecules will also be added (in random interlayer positions) so that constant-pressure simulations result in clay layer spacings corresponding to 1, 2, or 3 discrete layers of interlayer water. Target d<sub>001</sub>spacings for these simulations will be about 12.5, 15.5, and 18.5 Å, respectively. The energies will be computed using a force field developed especially for clays (Teppen et al., 1997) combined with the pcff force field (Maple et al., 1994; MSI, 2000) for the organics and water. The molecular dynamics simulation will be run in the NPT ensemble for 0.1 ns, much longer than the time required for the system volume and energy to equilibrate.

#### B. Experimental studies of atrazine-clay interactions

Adsorption of atrazine on smectites has been studied by a number of workers, but most of these studies have been limited to montmorillonite, beidellite, and nontronite, all of which are 2:1 dioctahedral clays. Only a limited number of studies have been conducted with 2:1 trioctahedral clays. Also, there have been very few studies that systematically investigated atrazine sorption to smectites as a function of the saturating cation, as has been shown to be so important in the sorption of other neutral organics (Sheng et al., 2002). These limited studies indicate that 2:1 trioctahedral clays often have higher adsorption capacities for atrazine than 2:1 dioctahedral clays. For example, Laird

et al. (1992) worked with 14 different clays and found that beidellite, hectorite, and saponite sorbed almost all of the added atrazine. We propose to conduct a laboratory experiment that will study the adsorption of atrazine by saponite, a 2:1 trioctahedral clay, saturated with  $Na^+$ ,  $K^+$ ,  $Cs^+$ , and  $Ca^{2+}$  on the exchange complex. Depending on the results, we may extend this study to include other triazines: Simazine and metribuzin are two other pesticides belonging to the class of triazines, but with very different water solubilities than atrazine. Simazine is only slightly soluble in water (5 mg/L), while metribuzin has a solubility of 1200 mg/L. Due to differences in water solubility, these triazines are expected to sorb differently in soils. If the saponite results are interesting, we may also use another clay mineral such as hectorite or beidellite to study the adsorption of these triazines: Both hectorite (a trioctahedral smectite like saponite, but differing in that hectorite has dominantly octahedral substitution) and beidellite (dominated by tetrahedral substitution, like saponite, but differing in that beidellite is dioctahedral) showed strong affinity for atrazine in Ca-saturated systems (Laird et al., 1992).

## C. Prediction of organic-clay interactions

Many of the organic pollutants in the environment were introduced years or sometimes decades ago at a time when industry and the public were not adequately aware of the scope, magnitude, and importance of environmental pollution (Alexander, 2000). Thousands of chemicals are manufactured world-over and many new chemicals are added to this ever expanding list. Many of these chemicals end up in the environment (e.g. soil, groundwater, and surface water etc.), where they are a possible source of

concern. Adsorption and transport of many of these chemicals, especially pesticides, have been studied for more than 40 years. However, it would require unfeasible financial and scientific resources to study the partition constants of such an immense range of chemicals with an equally high number of different natural phases. Thus there is interest in predictive models that can estimate the potential for a given organic compound to partition into a given sorptive phase (Goss and Schwarzenbach, 2001). We propose to use molecular dynamic simulations to estimate the adsorption energies of some chemicals that have been heavily studied from an experimental standpoint, and then correlate these adsorption energies with the adsorption coefficients obtained from the experiments. If the computed adsorption energies follow the experimental trends in adsorption coefficients, then we will have demonstrated the potential for molecular simulations to predict the sorption of neutral organic compounds to clay minerals.

To estimate the adsorption energies, we will simulate a series of nitroaromatic compounds interacting with smectite clay minerals as studied in a recent experimental dataset (Boyd et al., 2001). This experimental study is very useful for validation purposes because it reports sorption of 14 nitrobenzene compounds, differing only in the identity or location of a second functional group. A model for the K-saturated SAz-1 smectite clay mineral used in the experimental study will be created, with composition  $K_{12}(Al_{36}Mg_{12})Si_{96}O_{240}(OH)_{48}$  and a resultant cation-exchange capacity (CEC) of 132 cmol/kg. In order to prepare for molecular dynamics simulations of nitrobenzeneclay complexes, the interlayer region of the clay will be added to the unit cell, with the nitrobenzene molecular plane perpendicular to the basal planes of the clay. Water

molecules will then be added (in random interlayer positions) and molecular dynamics performed on each clay-water-organic system. The energies and forces will be computed using a force field developed especially for clays (Teppen et al., 1997) and combined with the pcff force field (Maple et al., 1994; MSI, 2000) for the organics and water. Each molecular dynamics simulations will be run in the NPT ensemble for at least 50 ps, which is about twice as long as required for the system volume and energy to equilibrate. If the initial simulation does not result in a clay layer spacing of 12.3 Å, then water molecules will either be removed or added (after expanding the clay) and the simulation re-run so that the equilibrium clay layer spacing is  $12.3 \pm 0.1$  Å, in accord with the experimental data for substituted nitrobenzenes in air-dried films of K-SAz-1 (Sheng et al., 2001; Sheng et al., 2002). A trajectory of each simulation, containing equally spaced snapshots of geometries, energies, and velocities, will be recorded for later analysis.

We will use the following algorithm to calculate the clay-organic interaction energy.

- $E_{int} = E_{tot} E_1 E_2$ ; where
- • $E_{tot}$  = Total clay–organic system energy
- • $E_1$  = Energy of system after organic has been deleted
- • $E_2$  = Energy of the system after clay and water have been deleted
- •Compute E<sub>int</sub> for at least 150 snapshots and average

Electrostatic and van der Waal components of  $E_{int}$  will be calculated the same way, in order to estimate the contributions of each component to the overall sorption energy. This clay-organic interaction energy ( $E_{int}$ ) is only a portion of the total adsorption energy, but

in the following we also propose a method for using molecular simulations to estimate the overall adsorption energy.

The typical experimental scheme for measuring total adsorption energy is

$$Clay_{(aq)} + org_{(aq)}$$
  $\longrightarrow$   $clay-org_{(aq)} + H_2O_{(aq)}$ 

where  $E_{expt}$  is the experimentally determined adsorption energy (for example, the overall free energy, enthalpy, or entropy of the transfer process). Goss and Schwarzenbach (2001) illustrated that the overall free energy change of transfer  $\Delta G_i$ , could be first decomposed into individual terms for a more mechanistic understanding of the partition process as shown in Figure 1.



Since the experimental reaction is too large and too slow to directly model with molecular simulation methods, an alternative path is proposed that is more computationally feasible and follows the spirit of Figure 1. We propose to employ the following cycle for computing the total adsorption energy:



This approach is similar to many schemes (i.e., see review in (Halperin et al., 2002)) that have been used to compare molecular simulations with experimental data for the binding of drugs to polypeptides. Since the free energy, enthalpy, and entropy are state functions (Atkins, 1998), their magnitudes should be independent of path, so that

$$E_{expt} = E_3 + E_4 + E_5$$
  
where  $E_4 = E_{i-clay} - E_{i-aqueous} = E_{(clay-cav} \longrightarrow clay-org) + E_{(org(aq)} \longrightarrow orgcav(aq))$   
 $E_4 = E_{int} + E_{(org(aq)} \longrightarrow cavity(aq))$ 

 $E_3$  is the energy for creating a cavity in the clay, by removing enough water molecules to make a cavity that can later receive the organic.  $E_3$  will be calculated in the same way as the algorithm above for  $E_{int}$ , using the smectite with a 12.3 Å d-spacing and only cations and water in the interlayer.

 $E_4$  is similar to the sum of two components as shown in Figure 1. While we are not using the gas-phase configuration that Goss and Schwarzenbach (2001) used, our term  $E_4$  can be estimated the same way. The first term in  $E_4$  is  $E_{int}$ , the energy for filling the cavity in the clay with the organic molecule. The second term in  $E_4$  is the energy for moving the organic solute out of the aqueous phase, thereby leaving an empty cavity in water.

 $E_5$  is the energy for filling this aqueous cavity with water, and  $E_5$  will again be calculated using the algorithm for  $E_{int}$  that was presented above.

We will use all of the nitroaromatic compounds from the experimental database (Boyd et al., 2001) and calculate the clay-organic interaction energies for each compound using the algorithm above for E<sub>int</sub>. Then we will fit these interaction energy values into the larger context, using the thermodynamic cycle given above to estimate the overall adsorption enthalpies for each compound. The enthalpy estimates will be checked against experimental data in two ways. In relative terms, we hypothesize that the enthalpy estimates will follow the same trends as the sorption coefficients for the nitroaromatic compounds (Boyd et al., 2001). In absolute terms, we hypothesize that our enthalpy estimates will compare favorably with experimental enthalpies recently estimated from the temperature dependence of adsorption isotherms (Li et al., 2004). If predictive capability can be demonstrated by using these nitroaromatic compounds as a training set, then we will use the methods to estimate the enthalpies of adsorption for atrazine in smectite clay minerals.

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**CHAPTER II** 

# TRIAZINE ADSORPTION BY SAPONITE AND BEIDELLITE CLAY

# MINERALS

#### Triazine adsorption by saponite and beidellite clay minerals

### Abstract

We investigated the sorption of three triazine herbicides (atrazine, simazine, and metribuzin) by saponite and beidellite clay minerals saturated with K<sup>+</sup>, Cs<sup>+</sup>, Na<sup>+</sup>, and Ca<sup>2+</sup>. Saponite clay sorbed a larger fraction of each pesticide from aqueous solution than did beidellite clay. The lower cation exchange capacity in saponite (vs. beidellite) presumably results in a less crowded interlayer with more siloxane surface available for adsorption. Generally, Cs-saturated clays sorbed more triazines than clays saturated by K<sup>+</sup>, Na<sup>+</sup> or Ca<sup>2+</sup>. We attribute this to the smaller hydrated radius of Cs<sup>+</sup>, which again increases the siloxane surface available for sorption. Furthermore, the relatively weak hydration of Cs<sup>+</sup> reduces the swelling of clay interlayers, thus making sorption domains less hydrated and more receptive to hydrophobic molecules. Cs-saponite manifested a sorption of more than 1% atrazine by weight above equilibrium concentrations of 6 mg/L. This is the largest sorption of neutral atrazine from water yet reported for an inorganic sorbent. Molecular dynamics simulations indicate that atrazine interacts with both clay basal planes and with multiple cations in the clay interlayer.

#### Introduction

Concern about the contamination of ground and surface waters by pesticides has been an area of concern for over thirty years, mainly because of the continuous use of such chemicals in agricultural production. There is a need to more accurately predict the fate and movement of pesticides and assess their risks in soil and subsurface environments. Sorption by soils/sediments is a major process that controls the transport, bioavailability, degradation and ultimately the fate of organic contaminants in the environment (Koskinen and Harper, 1990). Sorption of organic chemicals diminishes their bioavailability to target organisms (Albanis et al., 1988), affects both chemical and microbiological transformations (Armstrong and Chesters, 1968; Gamble and Khan, 1985), and reduces the leaching to groundwater (Sonon and Schwab, 1995).

Clay minerals and soil organic matter (SOM) are typically the two most chemically active components interacting with organic chemicals that enter soils and sediments. SOM has been accepted as the primary sorptive domain for the uptake of hydrophobic organic compounds (Chiou et al., 1979; Chiou et al., 2000; Huang et al., 1997; Kleineidam et al., 1999; Weber and Huang, 1996; Xia and Ball, 2000). The contaminant transport models often use soil-organic carbon-normalized sorption coefficients ( $K_{oc}$ ) to predict the distribution of organic chemicals between soil and water. This approach ignores the contribution of soil minerals to the retention of organic contaminants in soils and subsoils, based on the assumption that organic compounds cannot effectively compete with water molecules for the sorptive sites on mineral surfaces.

Clay minerals are commonly found in the soil environment, and smectites are the most important group for interacting with pesticides due to their high surface areas, moderate cation exchange capacities (CECs), and surface reactivities (McBride, 1994). Earlier studies have shown that smectite clays can adsorb many major types of pesticides such as carbamates, ureas, nitrophenols and triazines to an appreciable extent (Li et al., 2004; Li et al., 2003; Sheng et al., 2001). In a study of atrazine sorption by a series of Ca-smectite clays with CECs ranging from 79 to 134 cmol<sub>c</sub>/kg, Laird et al. (1992) reported that zero to nearly 100% of added atrazine was removed from water, with the extent of adsorption correlated inversely with the clay CEC values. Sheng et al. (2001) observed a similar relationship for sorption of atrazine by K-smectites. Sawhney and Singh (1997) reported that atrazine adsorption by Al-smectite (>1 g kg<sup>-1</sup>) was larger than that by Ca-smectite. The authors discounted protonation of atrazine and attributed the greater adsorption on Al-clay to the stronger H-bonding between atrazine and the more polarized water molecules associated with trivalent  $Al^{3+}$  versus divalent  $Ca^{2+}$ . In the present study, we have avoided Al-smectites due to the difficulty in simultaneously maintaining a homoionic Al-smectite while preventing side-reactions in which atrazine protonates and consequently adsorbs strongly by cation exchange.

Clays present in whole soils also play a major role in adsorbing triazine pesticides (Huang et al., 1984; Talbert and Fletchall, 1965). Talbert and Fletchall (1965) showed that atrazine sorption by soils was positively correlated with soil clay content as well as SOM content. Huang et al. (1984) reported that the inorganic fractions of soils with particle size  $<20 \,\mu$ m have a significant capacity to retain atrazine. Several previous studies have attempted to identify the critical ratio of clay minerals/SOM at which

sorption by the mineral phase plays an important role (Grundl and Small, 1993; Karickhoff, 1984; Means et al., 1982). Karickhoff (1984) concluded that at the ratio of swelling clays to soil organic carbon >30 the mineral phase in whole soils contributed significantly to sorption of simazine. Grundl and Small (1993) estimated that at a mass ratio near 62 for clay to organic carbon, the mineral phase accounted for half of the overall atrazine sorption.

Most studies of atrazine and simazine adsorption by smectites were conducted using smectites with negative charges originating from octahedral substitution (Gilchrist et al., 1993; Sannino et al., 1999; Sheng et al., 2001); few studies have used smectites with negative charges arising from tetrahedral sites. Also, investigations of the effect of the location of permanent negative charges on organic sorption by smectites are scarce. Compared with octahedrally substituted smectites, the negative charges in tetrahedrally substituted smectites are more localized to fewer oxygens on siloxane sheets (Farmer, 1978; McBride, 1989), resulting in differences in clay interlayer environments that may influence pesticide sorption. Beidellite and saponite clays are smectites with negative charges originating largely from tetrahedral substitution. This study was, therefore, initiated to study the adsorption of three s-triazine herbicides (atrazine, simazine, and metribuzin) by saponite and beidellite clays saturated with different cations (K<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup> and  $Ca^{2+}$ ), and to compare the results with previous studies on sorption by octahedrally substituted smectites.  $K^+$ ,  $Na^+$  and  $Ca^{2+}$  are common exchangeable cations in the soil environment, while Cs<sup>+</sup> has smaller hydrated radius relative to other cations studied here hence is expected to create a more favorable (i.e., less hydrated) clay interlayer environment for pesticide adsorption.

#### **Materials and Methods**

#### Clays and Herbicides

Two reference clays, saponite (SapCa-2, CEC 95 cmol/kg (Post, 1984)) and beidellite (SBId-1, CEC 129 cmol/kg (Hetzel and Doner, 1993)), were obtained from the Clay Minerals Society Source Clay Repository (Department of Agronomy, Purdue University, West Lafayette, Indiana, USA). The  $<2 \mu m$  clay-sized particles were separated by wet sedimentation, and then exchanged with  $K^+$ ,  $Na^+$ ,  $Cs^+$ , and  $Ca^{2+}$  to prepare homoionic clays. To do so, 25 g of clay was dispersed in a 0.1 M chloride solution (500 ml) with the respective cation. The clay suspensions were shaken for 24 h, and fresh chloride salt solutions were used to replace the original solutions after centrifugation. This process was repeated four times to ensure complete cation saturation. The excess chlorides were removed by repeatedly washing with Milli-Q water until Cl<sup>-</sup> was determined negative by reacting with AgNO<sub>3</sub> solution. The clay suspensions were then quick-frozen, freeze-dried and stored in closed containers for later use. The pH values of the smectite suspensions were 8.1 and 8.0 for Ca-saponite and -beidellite, respectively, 8.6 and 8.8 for the Na-smectites, 8.1 and 8.0 for the Cssmectites, and 8.2 and 8.0 for the K-smectites.

The three pesticides (atrazine, simazine, and metribuzin) used in the adsorption experiment were purchased from ChemService (West Chestnut, Pennsylvania) with purities of >99%, and used as received. The selected physical and chemical properties of the three pesticides along with their chemical structures are summarized in Table 1.

				Solubility		
	Structure	Molecular weight	pKa	in water (mg/L)	log K <sub>ow</sub>	λ <sub>max</sub> (nm)
atrazine	v v_c-ci v	215.69	1.70	33	2.61	220
	$C_{3H_{7}HN} - C_{N_{2}}C_{C} - NHC_{2}H_{5}$					
simazine	z- , z:	201.66	1.62	5	2.10	220.5
	C₂H₅HN − Ċ <sub>丶N</sub> ≤Ċ− NHC₂H₅ O					
metribuzin	از (CH <sub>3</sub> ) <sub>5</sub> C – ۲ <sup>ح ک</sup> ې	214.29	1.0	1050	1.60	280
	N <sub>N</sub> <sup>C</sup> -SCH <sub>3</sub>					

Table 1. Selected Physicocochemical Properties of Pesticides Used in this Sorption Study.

Given the pK<sub>a</sub> values of the herbicides and the high pH values of our clay suspensions, there was no possibility for triazine sorption as any cationic species in the present study. Rather, the triazines were all neutral, moderately hydrophobic solutes.

#### Sorption Isotherm Measurements

Pesticide sorption isotherms were determined for each clay using a batch equilibration method. A series of initial pesticide concentrations was prepared by dissolving each pesticide in 0.01 M KCl, NaCl, and CsCl, and 0.005 M CaCl<sub>2</sub>. The initial solutions were then added into glass centrifuge tubes containing clay (0.01 to 0.1 g) that was saturated with the same cation in the respective pesticide initial solution, and the tubes were closed with Teflon-lined screw caps. Duplicate samples were prepared to measure sorption. The ratio of solution volume to clay amount was optimized to make sure that 20-80 % of pesticide in solution phase was sorbed by clay during the equilibration. The tubes were then shaken reciprocally for 12 hours at 40 rpm at room temperature  $(23 \pm 2 \,^{\circ}C)$ ; preliminary studies showed sorption was complete within this time. The tubes were then centrifuged at 2110 g for 20 min to separate the liquid and solid phases. The concentration of herbicide in supernatant was analyzed using a reversed-phase high-performance liquid chromatography (HPLC, Perkin-Elmer, Norwalk, CT) set at the appropriate wavelength for maximum absorption by each pesticide (Table 1). A platinum extended polar selectivity (EPS) C18 column was used. The mobile phase was a mixture of either 65% methanol (for atrazine and metribuzin) or 65% acetonitrile (for simazine) and water with a flow rate of 1.0 mL/min. Controls consisted of the initial pesticide solutions in the supporting electrolyte. Abiotic

degradation of atrazine and simazine in water at pH 7 to 9 is negligible (Comber, 1999; Noblet et al., 1996) in the absence of strong UV light. However, due to the relatively high pH values in the clay slurries and the lack of information about possible smectitecatalyzed hydrolysis, we monitored the HPLC chromatograms for peaks indicative of triazine degradation products. None were observed, and there were no significant differences between peaks or shapes of chromatograms for triazine controls versus triazine in clay suspensions. Also, no changes in solute concentrations were detected in the tubes devoid of clay within the experimental period; therefore solute mass lost in the supernatant from clay slurries was assumed to be sorbed by the clay. The amount of pesticide sorbed on the clays was calculated from the difference between the amount added and that remaining in the final equilibrated solution. Data presented are the means of duplicate samples.

## X-ray Diffraction

After supernatants were sampled for HPLC analysis, the remaining pesticide-clay suspensions were used to prepare clay films for X-ray diffraction analysis. The clay solids were resuspended with the supernatant (~ 1 to 2 mL) remaining in the vial, and then dropped onto glass slides and air-dried overnight at ambient conditions to obtain oriented clay films. X-ray diffraction patterns were recorded using Cu-K $\alpha$  radiation and a Philips APD 3720 automated X-ray diffractiometer, fitted with an APD 3521 goniometer and a  $\theta$ -compensating slit, a 0.2 mm receiving slit and a diffracted beam graphite monochromator. Diffraction patterns were recorded from 5.5 to 16.0 °2 $\theta$  at a step of 0.005 °2 $\theta$  with 4 s/step. The X-ray diffraction patterns were re-recorded after the

clay films were allowed to equilibrate with 100% relative humidity for 2 d in a closed container.

### Molecular Simulations

Molecular dynamics simulations of atrazine-clay complexation were performed in order to explore possible interaction mechanism(s) between atrazine, cations, and water in the clay interlayer regions. In this approach, electrons are not treated explicitly, but their effects are parameterized into classical (that is, non-quantum) mechanical energy functions comprising a force field. The model for K-saponite had composition  $K_9(Si_{87}Al_9)Mg_{72}O_{240}(OH)_{48}$  with a CEC of 95 cmol/kg. The smectite surfaces were constructed using methods previously detailed (Teppen et al., 1997), in which a muscovite mica layer was the starting point and Al-for-Si substitutions were random except that no two Al tetrahedral were allowed to be immediate neighbors. One molecule of atrazine was added to the unit cell, with the atrazine molecular plane perpendicular to the basal planes of the clay. The simulated loading rate was equivalent to 23 mg atrazine per g clay. Water molecules were also added (in random interlayer positions) so that constant-pressure simulations resulted in ~12.5 Å clay layer spacings, in accord with our experimental data for atrazine in films of K-saponite.

The energies were computed using a force field developed for clays (Teppen et al., 1997) combined with the polymer consistent force field (PCFF) (Maple et al., 1994; MSI, 2000) for the organics and water. As a further modification, charges on the organic solute were assigned using the COMPASS force field (Sun, 1998), which optimized organic atomic charges for condensed phase systems. In previous work (Boyd et al.,

2001; Sheng et al., 2002), we have found COMPASS charges to more faithfully reproduce quantum mechanical charges for nitrogenous organic molecules than do PCFF charges. In aqueous interfacial systems, the charges on atoms of organic solutes play a critical role in determining organic solute interactions with the clay and interlayer water and cations. In classical molecular dynamics, the nuclear charge and the local electron density are subsumed into one partial atomic charge and these charges for atrazine are illustrated in Figure 1.



Figure 1. Charges on atrazine molecule used in simulation study.

Commercial software (MSI, 2000) was used to compute the classical molecular dynamics. No constraints were imposed on our systems during their molecular dynamics except for the contents of the simulation cell: All atoms were completely free to move, and unit cell shape and volume were unconstrained. The molecular dynamics simulations were run in the NPT (constant pressure/constant temperature) ensemble for 75 ps, which is much longer than the time required for the system volume and energy to equilibrate.

# **Results and Discussion**

### Sorption Isotherm

Pesticide sorption isotherms are shown in Figure 2. The greatest sorption of atrazine was observed for Cs-saturated saponite, followed by K-, Na-, and least by Ca-saturated saponite (Figure 2a). This sorption of more than 1% atrazine by weight of clay at an aqueous atrazine concentration of 6 mg/L is by far the largest sorption of neutral atrazine from water yet reported for any inorganic material. The higher effectiveness of Cs-SapCa-2 in sorption may be due to the lower hydration energy of Cs<sup>+</sup> and hence smaller hydrated radius of Cs<sup>+</sup> compared to the other cations. The water molecules associated with exchangeable Ca<sup>2+</sup>, for example, obscure a larger fraction of the clay surface than those associated with Cs<sup>+</sup>, resulting in the reduction in the size of adsorptive domains for Ca<sup>2+</sup> saturated clays. Typical estimates of hydrated radii are 9.6 Å for Ca<sup>2+</sup> and 3.6 Å for Cs<sup>+</sup> (Evangelou, 1998). Thus the cross-sectional area of hydrated Ca<sup>2+</sup> is about 290 Å<sup>2</sup>, more than seven times that of Cs<sup>+</sup>(40 Å<sup>2</sup>); therefore, one hydrated Ca<sup>2+</sup> takes up 3.5 times as much room as do the two Cs<sup>+</sup> ions in clay interlayer. We

hypothesize that the Cs-smectites may sorb triazines more strongly because the triazines only have to compete with weakly bound water between hydrated cations, while on Ca-, K-, and Na-smectites the triazines must compete with more strongly bound water within the hydrated radii of cations. Sheng et al. (2001, 2002) also observed similar effects of exchangeable cations on the size of sorptive domains of smectite clays in pesticide sorption.



Figure 2. Sorption isotherms representing atrazine (a,b), metribuzin (c,d), and simazine (e,f) uptake from water by reference saponite (SapCa-2) and beidellite (SBId-1) clays saturated with  $Cs^+$ ,  $K^+$ ,  $Na^+$  and  $Ca^{2+}$ .

Differences in the swelling behavior between Cs- and Ca-SapCa-2 also affect the degree of pesticide adsorption. The relatively weak hydration of Cs<sup>+</sup> causes Cs-saponite to swell less in water, which again provides a more favorable sorption domain and allows the organic compound to better compete with waters for interlayer sites. Cs-smectites maintain ~12.3 Å basal spacings (monolayer of hydration) at 100% humidity (data not shown) and even in aqueous suspension (Sato et al., 1992; Suquet and Pezerat, 1987). Ca-smectites, on the other hand, swell to more than 15 Å basal spacings. The thickness of the ring of an atrazine molecule is  $\sim 3.0$  Å (Sheng et al., 2002). This would imply the lowest limit of the basal spacing for atrazine intercalation to be about 12.2 Å (the thickness of a clay layer alone for pyrophyllite is 9.2 Å). In this scenario, an atrazine molecule thus contacts both clay siloxane surfaces simultaneously (Sheng et al., 2001). This orientation favors the intercalation of organic contaminants and pesticides, because it minimizes the contact with water molecules. The efficacy of such a hydrophobic adsorption mechanism even in inorganic smectites is implied by observations (Li et al., 2004; Sheng et al., 2002) that intercalated organic solutes inhibit swelling when the smectite is exposed to water.

Our results for atrazine sorption by saponite clay compare favorably with the results reported by Sheng et al. (2001) for K-SapCa-2 and Laird et al. (1992) for another Ca-saponite (CEC = 106 cmol/kg) (Figure 3). For further comparison, isotherms measured by Sawhney and Singh (1997) and Celis et al. (1997) for atrazine sorption by other Ca-saturated reference smectites (CEC = 85 and 76 cmol/kg, respectively) are also included (Figure 3). These six datasets (except that of Celis et al. (1997)) follow the

general trend that, for a given exchangeable cation, atrazine sorption tends to increase as layer charge decreases (Laird et al., 1992).



Figure 3. Comparison of our sorption results with all earlier studies of atrazine sorption to saponites, as well as two representative montmorillonites.

The type of smectite clay does affect triazine pesticide adsorption, as illustrated by the greater atrazine adsorption by saponite than that by beidellite. (Figure 2 a and b). Sorption of atrazine by Cs-SapCa-2 was 9.2 mg/g at the aqueous concentration of 2 mg/L, and is 37 times the sorption by Cs-SBId-1 at the same aqueous concentration. Similarly, sorption of atrazine by Na- and Ca-SapCa-2 was greater than the sorption by Na-, and Ca-SBId-1 clay, respectively. These observations are again probably due to the availability of sorptive area on clay surfaces. SBId-1 clay has a CEC of 129 cmol/kg (Hetzel and Doner, 1993) while SapCa-2 clay has a relatively lower CEC (95 cmol/kg, (Post, 1984)). Generally, clay with a higher CEC retains more hydrated exchangeable cations that cover a larger portion of clay surfaces, hence results in less siloxane surface available for pesticide adsorption, as demonstrated by previous studies of an inverse relationship between clay CEC and pesticide adsorption (Laird et al., 1992; Lee et al., 1990; Sheng et al., 2001; Sheng et al., 2002). In studies of atrazine adsorption by both Ca- and K-saturated smectites, the clay with the highest CEC was consistently the least effective adsorbent for atrazine (Laird et al., 1992; Sheng et al., 2001). Celis et al. (1997) reported the similar observation that Ca-SAz-1 (CEC = 120 cmol/kg) sorbed less atrazine than Ca-SWy-1 (CEC = 76.4 cmol/kg), which is also consistent with the observation that adsorption of atrazine decreases as clay CEC increases. The current study along with previous studies supports the hypothesis that exchangeable cations (e.g.,  $Ca^{2+}$ ) with larger hydration spheres obscure more of the neutral clay siloxane surface thereby reducing hydrophobic interactions between clay surfaces and pesticides. The lower charge-density clay (SapCa-2) manifested greater adsorption compared to the higher charge-density SBId-1 clay. Lower charged clay apparently has larger exposed areas between

exchangeable cations on the neutral siloxane surfaces, which contribute more favorable pesticide adsorptive domains. Crowding interlayer cations upon pesticide adsorption may increase the electrostatic repulsion among these cations, thereby contributing as well to the reduction of pesticide adsorption by the higher charge clay.

The site of negative charges on the clay also affects sorption. Permanent negative charge on clay arises from isomorphic substitution in either tetrahedral or octahedral sites. The CEC of SBId-1 is 129 cmol/kg with the negative charges arising from mostly tetrahedral substitution, and SAz-1 has a similar CEC (130 cmol/kg) but with the negative charges primarily from octahedral substitution. Data for atrazine sorption by K-SAz-1 were reported by Sheng et al. (2001), and the atrazine sorbed by these two  $K^{+}$ saturated clays varied substantially with the much greater sorption for K-SBId-1 clay. For example, the amounts of atrazine sorbed by K-SBId-1 and K-SAz-1 were 0.79 and 0.04 mg/g, respectively, at an aqueous atrazine concentration of 8 mg/L. Since CEC values and surface areas of the two clays are similar, differences in sorption result primarily from the sites of negative charges. Compared with the charges from octahedral substitution (SAz-1), the charges from tetrahedral substitution (SBId-1) are localized to fewer surface oxygens (Farmer, 1978; McBride, 1989) resulting in more ordered distribution of exchangeable cations on mineral surfaces (Odom, 1984). These exchangeable cations (at a given hydration state) can always approach the tetrahedrallysubstituted sites more closely hence demonstrating a stronger attraction compared with octahedrally-substituted sites (Bleam, 1990). As a result, SBId-1 clay has a smaller clay layer spacing, which favors atrazine adsorption in clay interlayer environments (Chappell et al., 2005). In addition, the charge localization of tetrahedral substitution results in a

larger portion of neutral siloxane surfaces associated with mineral surfaces, which may provide large neutral surface domains for the adsorption of organic compounds.

The K-smectites studied here exhibit interesting sorption behavior. In contrast to the trend discussed above, in which sorption generally decreases as clay layer-charge increases, the higher-charged K-SBId-1 sorbs slightly more atrazine than does K-SapCa-2. Indeed, the sorption by K-SBId-1 is equivalent to that of Cs-SBId-1, while sorption by K-SapCa-2 is much below that of Cs-SapCa-2. One hypothesis is that some Cs-SBId-1 interlayers collapse and completely dehydrate even in suspension, thus rendering them unavailable for sorption of atrazine. A second hypothesis might be that K-SBId-1 sorbs like Cs-SBId-1 because the two are similarly swollen with  $\sim 12.5$ -Å d<sub>001</sub>-spacings: It is well-known (McLean and Watson, 1985) that removal of K<sup>+</sup> from an illite clay results in a tetrahedrally substituted clay mineral resembling a high-charged beidellite, while addition of  $K^+$  to these weathered illites results in  $K^+$  "fixation" to form a mica-like mineral with dehydrated interlayers. The tendency for clay minerals to fix  $K^+$  correlates with their layer charge (Sparks and Huang, 1985). While true smectites like K-beidellite should not completely dehydrate and fix K<sup>+</sup> (Sparks and Huang, 1985) because their layer charges are lower than those of illites, it is plausible that a higher-charged beidellite like K-SBId-1 would swell less than a lower-charged smectite like K-SapCa-2. Thus, despite its high charge, the interlayers of K-SBId-2 should be more likely to retain d<sub>001</sub>-spacings near 12.5-Å when fully hydrated, and thus be relatively favorable for hydrophobic interactions. Testing of these hypotheses would involve measuring  $d_{001}$ -spacings of these smectites in aqueous suspension (Chappell et al., 2005), which we hope to do in the future. In the present study we measured the  $d_{001}$ -spacings of air-dried films of K-SBId-2

and K-SapCa-2 and found them to be 10.2 and 12.0 Å, respectively, so interlayers of the K-beidellite almost completely dehydrate while K-saponite retains one layer of interlamellar water when air-dried. Thus, it is plausible that the beidellite would swell less than the saponite in suspension, as well.

The sorption of metribuzin by saponite and beidellite followed the same order as for atrazine, i.e., Cs-saturated > K-saturated  $\approx$  Ca-saturated > Na-saturated clay, but the magnitude of metribuzin sorption was smaller than atrazine sorption by both clays (Figure 2 c and d). This could be due to the higher solubility of metribuzin (1050 mg/L) compared to atrazine (33 mg/L), since we hypothesize (Boyd et al., 2001) that hydrophobic effects contribute to sorption of neutral organic solutes by smectite clays. Sorption of metribuzin by saponite clay was two to five times (Figure 2c) that by beidellite (Figure 2 d) at a given metribuzin concentration, which may again be due to the comparably lower CEC of saponite as discussed above.

The sorption of simazine by these two clays manifested similar results. Cs-SapCa-2 adsorbed appreciably higher simazine than K-, Ca- and Na-SapCa-2 (Figure 2 e), and beidellite sorbed considerably less simazine than saponite clay. This again shows that a smectite clay with a lower CEC and/or saturated with a less hydrated exchangeable cation (i.e., Cs<sup>+</sup>) usually demonstrates a greater sorption capacity. Simazine sorption by K-SBId-1 behaved like atrazine sorption in that it was almost identical to the sorption by Cs-SBId-1.

If hydrophobic effects do contribute to triazine adsorption by smectites, then at a given aqueous triazine concentration, the sorption to a given clay system should have followed the order simazine  $\approx$  atrazine > metribuzin. Simazine and atrazine are difficult

to rank, because atrazine has a slightly higher aqueous solubility (presumably because it is less symmetric) yet also has a larger octanol-water partition coefficient because it contains one more methylene group (Table 1). For the Cs-saponite at 0.1 ppm aqueous triazine, the adsorbed amounts of triazine were 2.0, 2.6, and 0.02 mg/g, for simazine, atrazine, and metribuzin, respectively (Figure 2). For K-saponite at 1.3 ppm aqueous triazine, the adsorbed amounts of triazine were 0.3, 0.1, and 0.03 mg/g, respectively. Similarly, for K-beidellite at 0.5 ppm aqueous triazine, the adsorbed amounts were 0.2, 0.2, and 0.01 mg/g, respectively. Thus, our limited data are consistent with a hydrophobic component to triazine adsorption by smectites, which implies that one role of the clay interlayer is to partially remove the hydrophobic solute from water (Boyd et al., 2001). Interlayers that perform this role most effectively, such as Cs-saponite, should then be the strongest clay mineral sorbent phases.

#### X-ray Diffraction

As the atrazine loading increased, the  $d_{001}$ -spacing (corresponding to the centroid of the diffraction peak) for the air-dried Cs-smectite increased to 12.5 Å for the 13.7 g/kg atrazine loading, from 12.1 Å for the atrazine-free clay (Figure 4). The increase in basal spacing suggests that atrazine is intercalated in the interlamellar region of the clay, with an increasing fraction of the clay domains at larger d-spacings (~12.5 Å) as the atrazine loading increases. This is consistent with our previous observations of intercalated aromatic compounds (Li et al., 2004), in which the  $d_{001}$ -spacings of air-dried K-smectite clay films increase slowly toward ~12.5 Å as the aromatic compound loading increases from zero to 200 µmol/g clay. Here, the maximum atrazine loading rate is about 65

 $\mu$ mol/g clay (Figure 4), so sorption is rather small to have a major impact on the d<sub>001</sub>spacing (Li et al., 2004), but the systematically increasing d<sub>001</sub>-spacings are consistent with our hypothesis of interlayer sorption of atrazine. The sorption of metribuzin and simazine did not result in a change in clay basal spacing compared with that in the absence of organics (data not presented). The reason is that the amount of sorbed metribuzin and simazine in clay interlayer was not sufficient to cause the swelling of clay basal spacing. Li et al. (2004) also reported that at a low amount of organic solute loadings the clay interlayer did not show the expansion.



Figure 4. X-ray diffraction patterns of air-dried Cs-SapCa-2 clay films as a function of atrazine sorption.

#### Molecular Simulations

The molecular dynamic simulation results offer structural hypotheses for atrazine interactions in the interlayer region of K-SapCa-2. Figure 5 is a representative snapshot taken from a molecular dynamics simulation. As such, it is not a minimum energy structure, but is representative of the dynamic equilibrium. The types of interactions shown in Figure 5 are comparable to others obtained during some 20 similar simulations we have done for atrazine in smectite interlayers. Within a monolayer of interlayer water between the mineral surfaces, atrazine is oriented parallel to the clay basal plane with the aromatic ring interacting with both of the opposing clay siloxane sheets. In this simulated configuration, the negatively charged ring-N atoms of atrazine also form inner-and outer-sphere complexes with multiple  $K^+$  ions. The inner-sphere complex shown is a chemically reasonable structure because a  $K^+$  ion is able to interact with two (ring N and Cl substituents) negatively charged (Figure 1) and closely spaced sites simultaneously.

Our molecular dynamic simulations also support the hypothetical interactions between atrazine and smectite siloxane surfaces that were proposed by Laird (1996): He proposed that the lone pair electrons on the ring N atoms of atrazine interact with water molecules solvating exchangeable cations associated with smectite surfaces; such complexes were indeed observed in our simulations (Figure 5). At the same time, the alkyl-side chains of atrazine molecules were hypothesized (Laird, 1996) to out-compete water molecules for retention on hydrophobic microsites on smectite surfaces. Again, this behavior is observed in the simulations (Figure 5). Such hydrophobic bonding is



Figure 5. Snapshot of a molecular dynamic simulation of atrazine in the interlayer region of homoionic K-smectite (K-SapCa-2). Clay layers were parallel to the page and have been removed in order to expose the interlayer complexes. The atom coloring scheme is K = green, O = red, H = white, C =gray, N =blue, and Cl = green (associated with the atrazine molecule).

consistent with the observed decrease in sorption with increasing clay CEC because the amount of neutral siloxane surface on smectites decreases with increasing surface charge density (SCD). On surfaces with low SCD the water molecules at the clay surface are less strongly bound and considered to have a less ordered structure (Gilchrist et al., 1993). Sparingly water-soluble organic compounds (e.g., atrazine, water solubility of 30 mg/L) are more likely to approach and adsorb to surfaces that sorb water less strongly. A lower SCD also means that there are less exchangeable cations competing for adsorption domains in the interlayer region (Sheng et al., 2002).

In summary, we observed very strong atrazine sorption by Cs-saponite, and a lesser sorption by K-, Ca-, and Na-saponites. These results are another indication of interplay between the polar functional groups of neutral organic molecules and the hydration of interlayer cations. As the organic functional group becomes more polar, the ability to displace water from clay interlayers becomes stronger, resulting in a substantial adsorption. Thus, pesticides with multiple strongly polar functional groups like  $-NO_2$  – C=O or -C=N demonstrate a strong affiliation with K- and Cs-smectites (Boyd et al., 2001; Johnston et al., 2002; Sheng et al., 2002) due to pesticide-cation complexation. However, our results indicate that even less polar compounds (e.g., atrazine) can be strongly adsorbed by Cs-saponite, due to the optimal clay interlayer structures, i.e., maintaining  $\sim 12.5$  Å basal spacing and non-overlapping radii of hydration for Cs<sup>+</sup>. Thus, Cs-saponite interlayers contain the largest proportion of relatively hydrophobic sites, in which we hypothesize that triazines can be at least partially dehydrated, and our data are consistent with a hydrophobic component to triazine adsorption by smectites. We also found that the site of negative charge on the clay significantly influenced the

retention of pesticide. The smectite clays with the negative charge arising from tetrahedral substitution generally displayed a higher adsorption compared to smectites with octahedral substitution, presumably because tetrahedrally substituted smectites swell less in water and thereby contain narrower slit-pores that favor hydrophobic sorption. However, if the clay layer charge is large, adsorption of triazine herbicides by even tetrahedrally substituted smectites can be sharply reduced, because hydration radii for the greater number of exchangeable cations begin to overlap. Apparently, an optimal inorganic sorbent for triazine herbicides should be a Cs<sup>+</sup>-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. If true, these hypotheses should apply broadly to hydrophobic organic solutes.

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**CHAPTER III** 

# ATRAZINE INTERACTIONS WITH SMECTITE CLAYS: MOLECULAR

# SIMULATION APPROACH

### Atrazine interactions with smectite clays: Molecular Simulation approach

### Introduction

Atrazine is one of the most commonly used agricultural herbicides in the world and has been applied for more than 40 years by corn and sorghum growers in the United States (Ribaudo and Bouzaher, 1994). In 1994, over 47 million pounds of atrazine were applied nation-wide covering about 77 % of the area cropped under corn-soybean rotation (Pike and Knake, 1996). Atrazine is also one of the most common herbicide residues found in groundwaters of Midwest (Blanchard and Donald, 1997; Burkart et al., 1999; Kolpin et al., 1998), and is detected 10 to 20 times more frequently than the next most commonly detected pesticide (Belluck et al., 1991). The presence of atrazine in groundwater is a concern because atrazine is a potential carcinogen (Biradar and Rayburn, 1995), and a suspected endocrine disrupter. Toxicological concerns have resulted in the EPA setting a maximum amount of 3  $\mu$ g/L of atrazine in drinking water in the U.S. Despite restrictions, atrazine exceeds the maximum contaminant level of 3ppb at certain times in several states in the U.S.

It has been shown that adsorption of organics on smectite clays is an important phenomena that controls the bioavailability, persistence and movement of organics in soils and subsoils (Boyd et al., 2001; Laird et al., 1992; Li et al., 2003; Sheng et al., 2001). The sorption capacity of smectites for organics varies widely depending on the surface charge density of the smectite (Laird et al., 1992), the nature of the adsorbed cation (Sheng et al., 2001), the pH of the soil (Vaz et al., 1997), and the location of negative charge on the smectite.

In parallel with atrazine usage in agriculture, researchers have studied atrazine adsorption by soils and soil components for more than 40 years. Due to its long-term agronomic importance and its leaching risk, atrazine sorption processes in soils have probably been studied more than those of any other organic solute. Most studies, of course, have been phenomenological in nature, striving to characterize the extent of sorption and correlate sorption with known properties of atrazine and its related triazines, with soil properties, and with solution conditions such as pH. However, there has been continual and intense interest in mechanistically understanding the forces that drive triazine sorption.

Already by 1962, Frissel and Bolt (1962) described triazine sorption to montmorillonite as a cation exchange reaction within a few pH units of each triazine pKa. Furthermore, they speculated that >90% of triazine molecules would be adsorbed by clay-rich soils, even at neutral pH, through the action of van der Waals forces between triazines and clay siloxane surfaces (Frissel and Bolt, 1962). Weber et al. (1965) used Xray diffraction to show that prometone (a methoxy- rather than chloro-triazine, with pKa of 4.3) intercalated between clay layers. Sorption of 150 to 300  $\mu$ mol/g caused the dry clay to swell to ~13 Å, consistent with triazine rings oriented parallel to the silicate sheet. Sorption of 450  $\mu$ mol/g caused clay swelling to ~18 Å, and the authors used molecular models to postulate triazine molecules either perpendicular to the clay surfaces or arranged in double stacks in the interlayer. Most sorption to the montmorillonite was by cation exchange, since the experiments were done just 1.7 pH units above the pKa,

though the authors postulated neutral species sorption via H-bonding of triazines to siloxane surface O atoms of the clay (Weber et al., 1965).

Bailey et al. (1968) studied sorption of six triazines by Na-montmorillonite and found that sorption was generally larger for the more soluble triazines, the opposite of the expected behavior if a nonspecific, hydrophobic adsorption mechanism were operant (Hance, 1967). However, triazine cation formation can only be discounted for the three low-pKa triazines studied (including atrazine), and for those compounds there was not a consistent relationship between sorption and aqueous solubility (Bailey et al., 1968). For neutral triazines interacting with clay minerals, they hypothesized that possible adsorption mechanisms might include van der Waals interactions and H-bonding between amino N-H groups and clay siloxane O atoms.

For many years, though, the dominant mechanism for atrazine adsorption by clay minerals was thought to be cation exchange, because no sorption of uncharged ("molecular") atrazine by clays was conclusively demonstrated. However, Laird et al. (1992) argued that, at neutral pH, molecular atrazine was the species sorbing to a variety of smectites, and they showed that adsorption was inversely correlated to smectite layer charge. In a later study, Barriuso et al. (1994) measured desorption from many of these same smectites, showed that there was little hysteresis at work, and concluded that adsorption of molecular atrazine to smectites is generally reversible. As a result, they hypothesized that the atrazine sorption mechanisms were mainly van der Waals or hydrogen bonding to smectite surfaces.

The finding that atrazine adsorption was inversely correlated with smectite layer charge (Laird et al., 1992) implied a hydrophobic sorption mechanism, as had been

asserted by Jaynes and Boyd (1991) to explain their observations that benzene adsorption by smectites increased with decreasing clay layer charge. Expandable clay minerals are known to be strongly hydrophilic on a macroscopic scale (Mooney et al., 1952; Xu et al., 2000). However, on a molecular scale there are uncharged regions between the charged sites on smectite siloxane surfaces, so smectites with lower layer charges will have a greater proportion of uncharged surface. Jaynes and Boyd (1991) showed that, when smectites are saturated by organic rather than inorganic cations, the uncharged regions of the smectite surface will preferentially adsorb benzene versus water from aqueous solution, so they described these uncharged regions as hydrophobic. In smectites, these hydrophobic regions might comprise more than 40% of the total surface area (Laird, 1996).

In other contexts, the sorption of nonpolar, nonionic organic solutes is known to be controlled by "hydrophobic effects," a combination of relatively small van der Waals bonding forces and a substantial entropic gradient that drives the organic molecules out of aqueous solution (Israelachvili, 1992; Tanford, 1980; Voice and Weber, 1983). Previous studies (Boyd et al., 2001; Curtiss et al., 1986; Laird and Fleming, 1999; Mader et al., 1997; Piatt et al., 1996; Rebhun et al., 1992; Schwarzenbach and Westall, 1981; Van Bladel and Moreale, 1974) have observed that the association of organic solutes with an inorganic surface increased with decreasing aqueous solubility of the compounds.

Laird (1996) described the reversible sorption of molecular atrazine as a hydrophobic process, in which the hydrophobic alkyl side-chains of atrazine interact with the hydrophobic microsites located between smectite charge sites. At the same time, he

hypothesized (Laird, 1996), N atoms of the triazine ring may accept H-bonds from water molecules that solvate nearby cations, further stabilizing the atrazine-clay complex.

Laird (1996) predicted that, if the hydrophobic sorption mechanism for atrazine on smectites was true, then triazine sorption on montmorillonite should increase with the length of the alkyl side-chains, which had been seen in earlier data (Bailey et al., 1968; Weber, 1970) but erroneously ascribed to pKa differences. Laird and Fleming (1999) tested this hypothesis by comparing the sorption of molecular pyridine and butylpyridine at high pH: The sorption of butylpyridine was far larger than that of pyridine, thus supporting the concept of hydrophobic contributions to organic adsorption on smectites.

Spectroscopic characterization of atrazine sorption mechanisms has been limited to organic matter as a sorbent phase (Chien and Bleam, 1997; Welhouse and Bleam, 1992; Welhouse and Bleam, 1993), and we are aware of no spectroscopic studies of molecular atrazine in clays. Protonation (Cruz et al., 1968) and hydrolysis (Russell et al., 1968) of triazines on smectites have been studied by FTIR spectroscopy, but not the bonding environment of the neutral triazine.

Since atrazine adsorbs to clays as the molecular species at neutral pH (Laird et al., 1992), we wish to understand its mechanism of bonding. It is difficult to visualize the possible interactions between clay surfaces, water, and organics at the molecular level. Molecular dynamics simulations can help in understanding these interactions by providing an objective, energy-based approach to modeling the structural arrangements likely to occur and persist in smectite interlayers. Ideally, simulation results would be coupled with other molecular-scale data such as vibrational, NMR, neutron scattering, or EXAFS spectroscopies (Teppen et al., 1997) in order to employ multiple perspectives.

In the present case, we only have bulk adsorption data plus X-ray diffraction data to constrain the smectite interlayer spacing. The objective of the present study, therefore, was to couple molecular dynamics simulations with the available data in order to explore the behavior of atrazine on hydrated smectite clay surfaces.

### Materials and Methods

Molecular dynamics simulations of atrazine-clay complexes in the interlayer region were performed to explore the interactions between atrazine, exchangeable cations, and water. In this approach, electrons are not treated explicitly, but their effects are parameterized into classical (that is, non-quantum) mechanical energy functions comprising a force field.

Models for three different smectites were created, representing a Wyoming montmorillonite (lower charge due to octahedral substitution), an Arizona montmorillonite (higher charge due to octahedral substitution), and a California saponite (moderate charge due to tetrahedral substitution). The three correspond to the reference clay minerals SWy-2, SAz-1, and SapCa-2, respectively, for which we have atrazine sorption data. Homoionic versions of each smectite with K<sup>+</sup>, Cs<sup>+</sup>, or Ca<sup>2+</sup> in the interlayer were simulated. The composition of the model K-saturated Wyoming smectite (K-SWy) was K<sub>7</sub>(Al<sub>42</sub>Mg<sub>6</sub>)(Si<sub>95</sub>Al<sub>1</sub>)O<sub>240</sub>(OH)<sub>48</sub>, while that of Cs-smectite (Cs-SWy) was Cs<sub>7</sub>(Al<sub>42</sub>Mg<sub>6</sub>)(Si<sub>95</sub>Al<sub>1</sub>)O<sub>240</sub>(OH)<sub>48</sub>. The CEC of our model K-SWy was 79 cmol kg<sup>-1</sup>, and the comparable experimental value is 83 cmol kg<sup>-1</sup> (Sposito et al., 1983). We also created models for K- and Ca-saturated Arizona smectite (SAz-1). The composition of this model K-smectite (K-SAz) was K<sub>12</sub>(Al<sub>36</sub>Mg<sub>12</sub>)(Si<sub>90</sub>O<sub>240</sub>(OH)<sub>48</sub>, while that of Casmectite (Ca-SAz) was  $Ca_6(Al_{36}Mg_{12})(Si_{96})O_{240}(OH)_{48}$ . The K-SAz was a high-charged smectite, with a modeled CEC of 132 cmol kg<sup>-1</sup>, which compares with the experimental value of 130 cmol kg<sup>-1</sup> (Laird et al., 1992). The model for K-saponite had composition  $K_9(Si_{87}Al_9)Mg_{72}O_{240}(OH)_{48}$  with a CEC of 95 cmol/kg, in agreement with its experimental CEC (Post, 1984).

The smectite surfaces were constructed using methods previously detailed (Teppen et al., 1997), in which the muscovite mica structure (Brigatti and Guggenheim, 2002) was the starting point and Al-for-Si or Mg-for-Al substitutions were made to charge the layers. One molecule of atrazine was added to each unit cell of the smectite, with the atrazine ring perpendicular to the basal plane of the clay. The simulated loading rate was therefore ~24 mg atrazine per gram clay for each atrazine-smectite system. This is larger than our experimental loading rates, which are all less than 14 mg/g (see Chapter 2), but lower simulated loading rates would have required larger unit cells and therefore much slower simulations. As will be shown below, the present unit cell is large enough to allow simulation of relatively isolated atrazine molecules, while small enough to allow many different systems to be sampled. Water molecules were then added (in random interlayer positions) so that constant-pressure simulations resulted in 12.5, 15.5 or 18.5 Å clay layer spacings. One example of an initial configuration is shown in Figure 1.



Figure 1. A typical starting configuration before beginning the molecular dynamics simulation. Here, atrazine has been placed into the interlayer of Cs-SWy-2 with 55 water molecules. The equilibrium dog-spacing will eventually be 12.3 Å.

The energies and forces were computed using a force field developed for clays (Teppen et al., 1997) combined with the polymer consistent force field or pcff (Maple et al., 1994; MSI, 2000) for the organics and water. As a further modification, charges on the atrazine were assigned using the COMPASS force field (Sun, 1998), which optimized atrazine atomic charges for the condensed phase systems. In previous work (Boyd et al., 2001; Sheng et al., 2002) we have found COMPASS charges to more faithfully reproduce quantum mechanical charges for nitrogenous organic molecules than do PCFF charges. In aqueous interfacial systems, the charges on the atoms of organic solutes play a critical role in determining organic solute interactions with the clay and interlayer water and cations. In classical molecular dynamics, the nuclear charge and the local electron density are subsumed into one partial atomic charge and these charges for atrazine are illustrated in Figure 2.



Figure 2. Partial atomic charges on the atoms of the atrazine molecule, as used in all simulation studies. The total charge on the molecule sums to zero.

Commercial software (MSI, 2000) was used to compute the classical molecular dynamics, with a timestep of 0.2 fs. Ewald summation was used for both electrostatic and van der Waals forces (Karasawa and Goddard, 1989). No constraints were imposed on our systems during their molecular dynamics except for the contents of the simulation cell: All atoms were completely free to move, and unit cell shape and volume were unconstrained. The molecular dynamics simulations were run in the NPT (constant number of atoms, pressure, and temperature) ensemble for at least 50 ps, much longer than the time required for the system volume and energy to equilibrate. The unit cell volume equilibrates primarily through changes in the  $d_{001}$ -spacing, which is directly comparable to X-ray diffraction data. Note that the unit cell has a constant composition. We used periodic boundary conditions, which allow our small unit cell to more faithfully represent a condensed phase. As such, atoms are free to diffuse out of the central unit cell, but a copy of the atom will simultaneously diffuse in from the opposite side, maintaining the constant composition.

#### **Results and Discussion**

Within approximately 5 ps of simulation time, the volume of the atrazine-claywater systems was typically equilibrated, while the energy was usually equilibrated within the first 10 ps. Thus, the final 40 ps of each simulation were used as a sampling of the equilibrium dynamics of the model system. In many cases, systems of the same composition (or varying by one to a few water molecules) were simulated multiple times and the equilibrium structures were quite consistent. The molecular dynamic simulation results offer structural hypotheses for atrazine interactions in the interlayer regions of three smectites, saturated with three different cations, at three different water contents. Representative snapshots of the various equilibrated atrazine-water-clay systems taken from molecular dynamics simulations are shown in Figures 3-10. These snapshots are not minimum energy structures, but are representative of the dynamic equilibrium.

Atrazine is thought to interact with smectite surfaces through a variety of bonding mechanisms (Laird, 1996; Laird and Sawhney, 2002). Our molecular simulations revealed possible orientations of atrazine in the interlayers of our simulated smectites

with one, two, and three layers of interlayer water molecules. Figure 3 allows for comparison of the effect of water content on the atrazine molecular environment in K-SWy-2. The swelling of the smectite is a critical factor controlling atrazine adsorption: Chappell et al. (2005) recently showed that a hydrated K-smectite consisting of interstratified monolayers and bilayers (i.e., Figure 3A and 3B) adsorbed more than ten times the atrazine as did the same K-smectite when swelled to a trilayer (i.e., Figure 3C). The authors (Chappell et al., 2005) used drying-induced hysteresis to cause swelling differences, and were able to measure the K-smectite  $d_{001}$ -spacings in the suspension phase, so these spacings represent the interlayer hydration at which atrazine sorption actually occurs. These recent measurements (Chappell et al., 2005) of the effect of clay swelling on atrazine adsorption help to explain previous discoveries that addition of  $NH_4^+$ fertilizer salts to soils increases atrazine adsorption (Clay et al., 1998) and that decreasing the soil water content leads to increased atrazine sorption (Dao and Lavy, 1978). Structural trends for the monolayer, bilayer, and trilayer cases and their relation to differences in sorption will be discussed in more detail below.





# С



Figure 3. Snapshot showing the orientation of atrazine within the interlayer of a Ksaturated smectite like SWy-2 containing (A) one, (B) two, and (C) three layers of hydration water (red = oxygen, white = hydrogen, blue = mitrogen, gray = carbon, green = interlayer K<sup>+</sup> cations). Images on the left depict a side-view (x,z plane) of the atrazine-smectite interlayer complex while the images on the right depict the same from a top-view (x,y plane), having removed the silicate layers. The simulated do<sub>01</sub>-spacings for A, B, and C are 12.4, 15.5, and 17.3 Å, respectively.

Figure 4 illustrates atrazine structural relationships to cations and water within the interlayer regions of four different simulated smectites, all with  $d_{001}$ -spacings near 12.5 Å. In such smectites containing a monolayer of interlayer water, atrazine is necessarily oriented parallel to the basal surfaces and interacts directly (no intervening water molecules) and simultaneously with both opposing basal surfaces. In this simulated configuration, with its narrow  $d_{001}$ -spacing and limited volume to accommodate atrazine and several cations, the negatively charged ring-N and -Cl atoms of atrazine could hardly escape contact with multiple K<sup>+</sup> (or Cs<sup>+</sup>) ions.



Figure 4. Snapshots of molecular dynamic simulations of atrazine in the interlayer regions of four different homoionic smectites, (A) K-SWy-2, (B) Cs-SWy-2, (C) K-SAz-1, and (D) K-SapCa-2. Clay layers were parallel to the page and have been removed in order to expose the interlayer complexes. The atom coloring scheme is K = green, O = red, H = white, C = gray, N = blue, and Cl = green (associated with the atrazine molecule).

In the snapshots of Figure 4, which are typical of their respective simulations, the negatively charged ring-N and -Cl atoms of atrazine thus tended to form both inner- and outer-sphere complexes with multiple interlayer cations.

The -Cl substituent of the atrazine ring often coordinated directly to a single K<sup>+</sup> (or Cs<sup>+</sup>) ion (Figure 4) with average K (or Cs-) -Cl distances of  $3.2 \text{ Å} \pm 0.3 \text{ Å}$  (for K-SAz),  $3.9 \pm 0.2 \text{ Å}$  (for Cs-SWy),  $4.2 \pm 0.2 \text{ Å}$  (for K-SWy), and  $4.0 \pm 0.1 \text{ Å}$  (for K-SapCa-2). For example, in the Cs-SWy-2 system, approximately 5 ps of simulation time passed before Cs<sup>+</sup> and -Cl approached each other to form their inner sphere complex. Once formed, this complex remained stable over the subsequent 45 ps of simulated time (Figure 5).



Figure 5. Trajectory of the Cs – Cl inner sphere nonbonded complex in the simulated atrazine-Cs-SWy-2 system represented by Figure 4B.

Secondly, it was also typical that each ring -N- atom adjacent to the -Cl substituent of atrazine coordinated directly (inner-sphere) to a single K<sup>+</sup> (or Cs<sup>+</sup>) ion (Figure 4), with an average K (or Cs-) -N distance of 2.7 Å  $\pm$  0.2 Å (for K-SAz), 3.1  $\pm$  0.2 Å (for Cs-SWy), 3.7  $\pm$  0.2 Å (for K-SWy), and 3.2  $\pm$  0.2 Å (for K-SapCa-2). The ring -N- atom in the 5-position seems to be hindered from engaging in such complexes by the alkyl substituents in the 4- and 6-positions. Our molecular dynamic simulations also support the hypothetical interactions between atrazine and smectite siloxane surfaces that were proposed by Laird (1996): He proposed that the lone pair electrons on the ring N atoms of atrazine interact with water molecules solvating exchangeable interlayer cations; such complexes were indeed observed in our simulations. Transient states existed in which ring -N atoms (in the 1- and 3-positions) were indirectly coordinated to K<sup>+</sup> (or Cs<sup>+</sup>) ions through the intermediation of water. For example, the outer-sphere Cs -- N complex in our model SWy-2 (Figure 4B) exhibited average distance of 5.4  $\pm$  0.3 Å.

Figure 4 shows that, for three of the four Cs- and K-smectites that we simulated, it was typical for two atrazine functional group sites (ring-N and -Cl) to simultaneously interact with one interlayer cation. These inner-sphere complexes seem to be chemically reasonable structures because a cation is able to interact with two negatively charged (-0.48 and -0.10 from Figure 2) and closely spaced sites simultaneously. We were somewhat surprised to see such complexes form, because O atoms of water have charges of -0.82 in our system and therefore ought to out-compete atrazine for coordination sites around cations. However, we see cations "complexed" to –Cl, -N- atoms, and even methyl groups of atrazine (Figure 4).

The steric conditions of crowded interlayers at 12.5-Å  $d_{001}$ -spacing may play a role in formation of such "complexes." For example, we have seen that the K -- Cl complexes in SAz-1 and SWy-2 had lengths of  $3.2 \text{ Å} \pm 0.3 \text{ Å}$  and  $4.2 \pm 0.2 \text{ Å}$ , respectively. Also, K -- N distances were 2.7 Å  $\pm$  0.2 Å and 3.7  $\pm$  0.2 Å, respectively. Part of the force driving the K-atrazine complexes closer in SAz-1 may be mutual repulsions of all the cations, since it is a higher-charged interlayer environment than is SWy-2. It is visually apparent (Figure 4C) that atrazine has disrupted the average spacing of the 12  $K^+$  ions per unit cell in SAz-1, so another reason for shorter K-atrazine complexes may simply be that atrazine is interfering with optimal interactions between interlayer cations and charged sites in the clay layers. In the simulations, we force atrazine into the K-SAz-1 interlayer, but in reality it does not need to adsorb. Thus (Sheng et al., 2001), K-SAz-1 (Figure 4C) adsorbs only about 1/6<sup>th</sup> the atrazine as does K-SWy-2 (Figure 4A), presumably because the former has higher charge, so has a more hydrophilic interlayer, so atrazine has a harder time competing with water for interlayer sites (Laird, 1996). Indeed, Laird et al. (1992) showed that atarazine sorption by Casmectites was inversely correlated with smectite layer charge.

Figures 4A and B compare the environment of atrazine in K- versus Cs-SWy-2 montmorillonite. Note that  $K^+$  cations near atrazine (Figure 4A) are more likely to have water molecules competing for them, disrupting the K-atrazine complexes, while Cs<sup>+</sup> cations (Figure 4B) are able to form two inner-sphere complexes with atrazine. This is consistent with the less favorable hydration energy of Cs<sup>+</sup>. As a result, the Cs-smectite interlayer is less hydrophilic and atrazine competes better for interlayer sites. For example, using typical estimates (Evangelou, 1998) for the hydrated radii of Cs<sup>+</sup> (3.6 Å)

and K<sup>+</sup> (5.3 Å), along with an assumed 700 m<sup>2</sup>/g basal surface area and monolayer hydration status, we compute that only 56% of the Cs-SWy-2 interlayer surface is occupied by hydrated cations while 122% of K-SWy-2 is occupied. Thus, more of the relatively hydrophobic surface should be available for atrazine sorption in the Cs-system. We know (Chapter 2) that Cs-SapCa-2 sorbs about 50 times as much atrazine as K-SapCa-2, and the saponite's layer charge is close to that of SWy-2, but we do not yet have the sorption data for Cs-SWy-2.

Given Laird's (Laird et al., 1992 and Laird, 1996) hypothesis that lower-charged smectites adsorb more atrazine because the surface charge sites are more widely separated, so a larger fraction of the smectite surface is hydrophobic, we looked to see if indeed atrazine sorbs to hydrophobic nanosites in the smectite interlayers. Figure 6 shows that most of the atrazine molecule occupies a more-hydrophobic surface site between charge sites in K-SWy-2. However, given the rather regular charge spacing in our model SWy-2, atrazine cannot quite fit completely between charged sites. For the Cs-SWy-2 (Figure 6), the atrazine ring resides almost directly over a negative site but the two alkyl sidechains occupy more hydrophobic sites.



Figure 6. Representative snapshot of the relationships of atrazine and cations to charged sites in model SWy-2 with a monolayer of water for the K- (left) and Cssaturated (right) cases. Blue octahedra are the locations of Mg-for-Al octahedral substitution sites and pink tetrahedral are the locations of Al-for-Si tetrahedral substitution sites in the montmorillonite layer. The upper clay layer and the rest of the lower clay layer have been removed for clarity.

For the more expanded smectites with two or three layers of interlayer water molecules, fewer atrazine-cation complexes formed, and the atrazine typically inclined at an acute angle relative to the basal surfaces (Figure 3B and 3C). The two alkyl side chains tended to interact directly with one basal surface each. The rest of the atrazine molecule was forced to interact with interlayer water molecules.

Figure 7 shows snapshots from four simulations of atrazine in the interlayers of hydrated smectites (both SWy and SAz), each containing a bilayer of interlayer water between the mineral surfaces. The equilibrium  $d_{001}$ -spacings of these systems were 15.5  $\pm$  0.1Å, which is a realistic interlayer spacing for smectites having two layers of





Figure 7. Snapshots of molecular dynamic simulations of atrazine in the interlayer regions of four different homoionic smectites, (A) K-SAz-1, (B) Ca-SAz-1, (C) K-SWy-2, and (D) Cs-SWy-2. Clay layers were parallel to the page and have been removed in order to expose the interlayer complexes. The atom coloring scheme is K = green, O = red, H = white, C = gray, N = blue, and Cl = green (associated with the atrazine molecule).

interlayer water. In this environment atrazine did not orient its triazine ring parallel to the clay surface during 50 ps of simulation time. In the Ca-saturated SAz-1 (Figure 7B), the negatively charged functional groups of atrazine formed only outer-sphere complexes with interlayer  $Ca^{2+}$  ions.

In the K-SWy-2 bilayer system, the negatively charged ring-N atoms of atrazine were again able to form both inner- and outer-sphere complexes with  $K^+$  ions. For example, the distance between one of the interlayer K and ring-N atoms of atrazine remained stable around  $3.1 \pm 0.3$ Å over almost all of the simulation time (Figure 8). For the Cs-SWy-2 bilayer system, just one interlayer Cs<sup>+</sup> formed an inner-sphere complex with a ring-N atom of the atrazine, compared with two inner-sphere and one outer-sphere complex in the monolayer Cs-hydrate (Figure 4B).



Figure 8. Trajectory of the K -- N inner sphere nonbonded complex in the simulated atrazine-K-SWy-2 system represented by Figure 3B and 7C.

Again, it is of interest to observe the spatial relations between adsorbed atrazine, interlayer cations, and charge substitution sites in the clay layers. Figure 9 shows that, in the K-SWy-2 bilayer system, one alkyl chain of atrazine lies in one water layer (on one basal surface) and the other alkyl chain lies in the second layer of interlayer water (on the opposite basal surface). For the Cs-SWy bilayer system, too, the two alkyl side chains interact directly (no intervening water molecules) with one basal surface each (Figure 9).



Figure 9. Representative snapshots of the relationships of atrazine and cations to charged sites in model SWy-2 with a bilayer of water for the K- (left) and Cssaturated (right) cases. Blue octahedra are the locations of Mg-for-Al octahedral substitution sites and pink tetrahedral are the locations of Al-for-Si tetrahedral substitution sites in the montmorillonite layer. The lower clay layer and the rest of the upper clay layer have been removed for clarity.

Inspection of the molecular simulation results indicates that the two alkyl chains of atrazine tend to interact with uncharged portions of the montmorillonite basal surface, just as hypothesized by Laird (1996) and Laird and Fleming (1999). Perhaps if the smectite charge distribution were more heterogeneous so that some larger uncharged domains were created, atrazine would be stable when adsorbed flat on one surface. This could be a subject for future simulations.

Finally, further simulations of atrazine in the interlayer space of SWy-2 or SAz-1 modeled even wetter conditions. Here, a trilayer of interlayer water formed between the mineral surfaces. The equilibrium  $d_{001}$ -spacing was  $18.5 \pm 0.1$ Å for Ca-SAz-1 and  $17.3 \pm$ 0.1Å for K-SWy-2. These are also realistic interlayer spacings for smectites having three layers of interlayer water. In this environment atrazine is again unable to orient parallel to the clay surface during the 50-ps simulations. Rather, the situation is similar to the bilayer case, with atrazine inclined at an even more acute angle relative to the basal surfaces, and the two alkyl side chains interacting directly with one basal surface each (Figure 10). This configuration in K-SWy-2 appears to be at least partially stabilized by H-bonds between amino hydrogens and the smectite basal oxygen atoms; two such bonds of 2.5 and 2.6 Å formed between one amino group and one basal surface and were then stable for the remainder of the simulation. The rest of the atrazine molecule is forced to interact with interlayer water molecules. As the amount of interlayer water increases, neither  $K^+$  ions nor interlayer  $Ca^{2+}$  ions are able to form inner-sphere complexes any longer. Apparently, when atrazine and the cations are not forced together into a severely limited space as in the monolayer case, water outcompetes atrazine for interlayer ions.



Figure 10. Snapshots of molecular dynamic simulations of atrazine in the interlayer regions of two different homoionic smectites, (A) Ca-SAz-1, and (B) K-SWy-2. Clay layers were parallel to the page and have been removed in order to expose the interlayer complexes. The atom coloring scheme is K = green, O = red, H = white, C = gray, N = blue, and Cl = green (associated with the atrazine molecule).

In summary, these simulations reinforce and illuminate our emerging understanding of the interactions between smectite clays and relatively nonpolar organic solutes. New X-ray diffraction evidence (Chappell et al., 2005) suggests that the strongest sorption of atrazine to smectites occurs for interlayers containing a monolayer of water. The molecular simulations of atrazine in these monolayer systems indicate that interactions of atrazine with the clay mineral surface are by full molecular contact with both basal surfaces, thus removing most of the atrazine molecule from water. It is reasonable that the entropy increase on removing atrazine from a fully hydrated state in the bulk solution to a lesser hydrated state in the smectite interlayer contributes a favorable free energy change to the system (Li et al., 2004). This effect is similar to capillary condensation of hydrophobic solutes (Corley et al., 1996), in which the free energy of sorption becomes more favorable as pores in the adsorbent become smaller. In this case, the smectite interlayer is a slit-pore and the optimal thickness for adsorption of hydrophobic molecules is approximately the molecular thickness, which corresponds (for aromatic molecules) to d-spacings near 12.5 Å. Therefore, the difference in hydration status of atrazine in the interlayers is believed to account for the dramatic effect of crystalline swelling on the affinity of smectites for atrazine (Chappell et al., 2005).

Another way of stating this is that the monolayer is an interlayer phase (Laird and Shang, 1997) that is much more conducive to hydrophobic organic solute partitioning from water than are other, more hydrated and expanded, interlayer phases. In a monolayer, water interactions with cations and two clay basal surfaces may reduce the entropy of water so significantly (Sposito and Prost, 1982) that interlayer water becomes almost a nonaqueous phase and the penalty for replacing it with a nonpolar organic solute vanishes. This may explain why our simulations showed that cation-organic complexes formed so much more readily in a monolayer of water than in the more hydrated interlayers. Such interlayer cation-organic complexes have been demonstrated spectroscopically for more polar solutes such as nitrobenzenes (Johnston et al., 2001; Johnston et al., 2002) and carbamates (manuscript in preparation), but not yet for atrazine.

As hypothesized (Laird, 1996), the simulated atrazine tended to gravitate to uncharged and therefore relatively hydrophobic portions of the smectite basal surfaces.

This is in accord with observations that, all else being equal, lower-charged smectites will adsorb more atrazine (Laird, 1996; Laird et al., 1992; Sheng et al., 2001; Chapter 2) because they have more of the hydrophobic nanosites on their surfaces and also fewer interlayer cations competing for adsorption domains in the interlayer region (Sheng et al., 2002). Even in wetter systems swollen with two or three layers of water, our simulations showed that the alkyl tails of the atrazine molecule tend to interact with the uncharged nanosites on the smectite basal surfaces, i.e., valence-satisfied basal oxygens located between charge sites.

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**CHAPTER IV** 

# ENHANCED SORPTION OF TRICHLOROETHENE BY SMECTITE CLAY

**EXCHANGED WITH CS^+** 

Enhanced sorption of trichloroethene by smectite clay exchanged with  $Cs^+$ 

### Abstract

Trichloroethene (TCE) is one of the most common pollutants in groundwater, interestingly, Cs<sup>+</sup> is a co-contaminant at many DOE sites contaminated with TCE. Smectite clays have large surface areas, are common in soils, have high affinities for some organic contaminants, hence the potential to influence the transport of organic pollutants entering soils and sediments. The exchangeable cations present near smectite clay surfaces can radically influence the sorption of organic pollutants by soil clays. This research was undertaken to determine the effect of Cs<sup>+</sup>, and other common interlayer cations, such as  $K^+$  and  $Ca^{2+}$ , on the sorption of TCE by a reference smectite clay saponite. Cs-saturated clay sorbed the most TCE, up to 3500 mg/kg, while Ca-saturated smectite sorbed the least. We hypothesize that the stronger sorption of TCE by the Cssmectite can be attributed to the lower hydration energy and hence smaller hydrated radius of  $Cs^+$ , which expands the lateral clay surface domains available for sorption. Also, Cs-smectite interlayers are only one or two water layers thick, which may drive capillary condensation of TCE. Our results implicate enhanced retention of TCE in aquifer materials containing smectites accompanied by Cs<sup>+</sup> co-contamination.

## Introduction

Chlorinated solvents such as trichloroethene (TCE, C<sub>2</sub>HCl<sub>3</sub>) are common environmental contaminants near thousands of DOE, DOD, NASA and private industry facilities. TCE has been extensively used for rocket engine flushing, metal degreasing, and organic extractions due to its effectiveness, noncorrosivity, and nonflammability. In 1994 alone, 42 million pounds of TCE were released into soil and water environments in the USA, and TCE contamination was identified in at least 852 sites among the 1416 sites proposed in the U.S. EPA National Priority list (Doherty, 2000). TCE is also one of the pollutants detected most frequently and at high concentrations in water of industrial regions (Patrick et al., 1987), and drinking water sources tested in the US in 1997 showed a wide range of TCE contamination (Griffin, 2003). The US EPA Drinking Water Standard for TCE is 0.005 mg L<sup>-1</sup> (Spitz and Moreno, 1996), which is just 0.0004% of its water solubility (water solubility of TCE is 1100 mg L<sup>-1</sup> at 25°C, (Verschueren, 2001)), therefore, even small amounts of TCE leaking into a drinking water supply can pollute a large water volume. TCE is toxic, resistant to degradation and therefore persistent in subsurface environments (Li, 2001). There is a need to accurately predict the long-term fate and movement of TCE in soils and subsurface environments.

Sorption by soils and sediments is a major process that controls the transport, bioavailability, degradation, and ultimately the fate of organic contaminants in the environment (Koskinen and Harper, 1990). Sorption of organic chemicals diminishes their bioavailability to target organisms (Alexander, 2000), affects chemical and microbiological transformations (Gamble and Khan, 1985), and reduces risk of groundwater contamination (Sonon and Schwab, 1995). Clay minerals and soil organic

matter (SOM) are typically the two most important components in controlling the fate of organic chemicals that enter soils and sediments. Most research conducted in the last two decades has indicated that SOM is the primary sorptive phase for the uptake of nonpolar or slightly polar organic contaminants (Chiou et al., 1979; Miltner et al., 1989; Ong and Lion, 1991; Wilmanski and Vanbreemen, 1990; Xia and Ball, 2000; Xing et al., 1996; Zimmer et al., 1989). Transport models often use soil-organic carbon-normalized sorption coefficients ( $K_{oc}$ ) to predict the distribution of organic chemicals between soil and water, but this approach ignores the potential contribution of soil minerals to the retention of organic contaminants in soils and subsoils. Often this approach is justified on the basis that water molecules can effectively compete with organic compounds for the sorption sites on mineral surfaces, though this has proven to be an oversimplification.

Clay minerals are abundant in soils and aquifer materials, have large surface areas, so have a great potential for sorption of organic compounds. Of the various clay minerals commonly found in the soil environment, smectites are most important for interacting with organics due to their high surface areas, moderate cation exchange capacities (CECs), and surface reactivities (McBride, 1994). Several previous studies have attempted to identify the critical ratio of clay minerals/SOM at which sorption by the mineral phase plays an important role (Farrell and Reinhard, 1994; Grundl and Small, 1993; Karickhoff, 1984). Karickhoff (1984) concluded that at critical ratio of swelling clays to soil organic C >30, the mineral phase in whole soil becomes important for sorption of simazine. Grundl and Small (1993) estimated the critical ratio of 62 for atrazine and 84 for alachlor at which mineral phase sorption accounted for half of the overall sorption. Farrell and Reinhard (1994) concluded that for high clay to natural
organic matter ratios, mineral adsorption dominates organic matter for sorption of organics.

Adsorption of TCE has been studied by a number of workers, but most such studies are limited to organo-clays (Sheng et al., 1998; Zhao and Vance, 1998), zeolites (Alvarez-Cohen et al., 1993; Farrell et al., 2003; Kleineidam et al., 2002; Li, 2001), and carbon materials (Kleineidam et al., 2002; Langer et al., 1999). Only a few studies on the interactions of clays with volatile, hydrophobic, low molecular weight halocarbons such as TCE have been conducted to date (Estes et al., 1988; Farrell and Reinhard, 1994; Rogers and McFarlane, 1981; Singhal and Singh, 1976; Werth and Reinhard, 1997). Earlier studies have shown that smectite clays can adsorb organic solvents such as TCE (1.3 mg g<sup>-1</sup> clay, (Farrell and Reinhard, 1994)), and tetrachloroethene (PCE) (5.4 mg g<sup>-1</sup> clay, (Estes et al., 1988)), to an appreciable extent. Ong and Lion (1991) observed that under oven-dried conditions the mineral fraction of whole soil plays a significant role in the sorption of TCE, but competition from water reduces TCE sorption on mineral surfaces. Based on the higher sorption by a low organic carbon containing silt fraction. Pignatello (1990) concluded that the mineral fraction of whole soil plays an important role in TCE sorption. He also concluded that mineral fraction of whole soil has a significant role in the slow release of residual fraction as organic matter in interstitial pores of particle aggregates are protected from equilibrium with bulk solution by such mineral fractions (Pignatello, 1990). Results from the few previous studies on smectites are inconsistent. For example, Farrell and Reinhard (1994) reported that montmorillonite sorbed 1300 mg kg<sup>-1</sup> TCE from the gas phase at 100% relative humidity, while Estes et al. (1988) observed little or no TCE sorption by a smectite rich soil. Rogers and

McFarlane (1981) reported that adsorption of TCE, carbon tetrachloride, and ethylene dibromide by montmorillonite was variable, ranging from 0 to17 % of the chemical added to the clay, depending on the type of the clay or interlayer cation. They reported that while Al<sup>3+</sup> saturated montmorillonite sorbed 17% of the added TCE, Ca<sup>2+</sup> saturated montmorillonite did not sorb any TCE at all.

Thus, there are some indications that the sorption of chlorinated solvents by smectites is cation-dependent. One effect of changing the interlayer cations in smectites is to change the layer-spacing of the clay. Farrell et al. (2002) indicated that TCE adsorption is energetically most favorable in pores that are just large enough to accommodate a TCE molecule. The theory of capillary phase separation says that sorption of a hydrophobic molecule into a slit-pore should become more favorable in materials with small mesopores or micropores (Corley et al., 1996). We therefore hypothesize that TCE should most effectively compete with water for sorption sites in smectite clay interlayers when the smectite layer spacing is  $\sim 12.5$  Å, as these clay interlayers are just large enough to accommodate TCE molecules. Cs<sup>+</sup> saturated smectites generally equilibrate with  $\sim 12.5$  Å layer spacings at 100% humidity and even in aqueous suspensions (Sato et al., 1992), indicating that there is just one layer of water between smectite layers. Thus, a priori, Cs<sup>+</sup>- smectites appear to possess optimal properties for TCE sorption. By the same reasoning, TCE should not be able to compete as effectively for sorption sites on  $Ca^{2+}$  saturated smectites because the strongly hydrated  $Ca^{2+}$  ions  $(\Delta G_{hvd} Ca^{2+}: -1593 \text{ kJ/mol while } \Delta G_{hvd} Cs^+: -284 \text{ kJ/mol, (Evangelou, 1998)) cause}$ greater swelling of the clay interlayers to d-spacings  $\geq 18$  Å. Sorption sites in these larger slit-pores should not be as energetically favorable for TCE condensation from water

(Corley et al., 1996), so  $Ca^{2+}$  saturated clays are expected to sorb less TCE than  $Cs^+$  saturated clays.

This hypothesis is of environmental interest, since TCE and  $Cs^+$  co-contamination has been reported in groundwater plumes at a number of DOE sites (Brigmon et al., 1998; McKinley et al., 2001; Riley and Zachara, 1992; Zachara et al., 2002). As one example, mixed liquid waste containing both  $Cs^+$  and TCE was injected through a single well into the Snake River Plain aquifer at Idaho National Engineering and Environmental Laboratory from 1953 to 1972 (National Research Council, 2000).

Based on these hypotheses and observations, this study was initiated to study the adsorption of TCE by saponite, a 2:1 trioctahedral clay, saturated with different exchangeable cations ( $K^+$ ,  $Cs^+$  and  $Ca^{2+}$ ).  $K^+$  and  $Ca^{2+}$  were selected, as they are common exchangeable cations in the soil environment.  $Cs^+$  was selected primarily because TCE and  $Cs^+$  co-contamination has been reported in groundwater plumes at a number of DOE sites (Brigmon et al., 1998; McKinley et al., 2001; Riley and Zachara, 1992; Zachara et al., 2002). Secondly,  $Cs^+$  has a smaller hydrated radius compared with other cations studied here, hence is expected to create a more favorable interlayer environment (i.e. less hydrated) for TCE sorption. The negatively charged sites on saponite clay originate largely from tetrahedral substitution.

#### **Materials and Methods**

Clays

The reference clay, saponite (SapCa-2, CEC 95 cmol kg<sup>-1</sup>) used in the adsorption study, was purchased from the Clay Minerals Society Source Clay Repository (Department of Agronomy, Purdue University, West Lafayette, Indiana, USA). The < 2  $\mu$ m clay-sized particles were separated by wet sedimentation, and then exchanged with K<sup>+</sup>, Cs<sup>+</sup>, and Ca<sup>2+</sup> to prepare homoionic clays. To do so, 25 g of clay were dispersed in a 0.1 M chloride solution (500 ml) of the respective cation. The clay suspensions were shaken for 24 h, and fresh chloride salt solutions were used to replace the original solutions after centrifugation. This process was repeated four times to ensure complete cation saturation. The excess chlorides were removed by repeatedly washing with Milli-Q water until Cl<sup>-</sup> was determined negative by reacting with AgNO<sub>3</sub> solution. The clay suspensions were then quick-frozen, freeze-dried and stored in a closed container for later use.

# Solute

Analytical grade TCE used in the adsorption experiment was purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin) with a purity of >99%, and used as received. The selected physicochemical properties of TCE are as follows: molecular weight 131.4 g mol<sup>-1</sup>, vapor pressure at 30°C is 12.5 kPa, boiling point 87 °C, density 1.45 g cm<sup>-3</sup>, log K<sub>ow</sub> at 25°C is 2.53, dipole moment 0.9 Debye, molar volume 89.87 cm<sup>3</sup> mol<sup>-1</sup> at 25°C, and average molecular diameter is 6.8 Å (Farrell and Reinhard, 1994).

# Determination of Henry's Law Constant

The equilibrium headspace technique was used to determine Henry's Law constant of TCE in different electrolytes, which is similar to the method reported by Garbarini and Lion (1985) and Lincoff and Gossett (1984). Determinations of Henry's Law constant as well as sorption isotherms were conducted using 20 mL capacity glass headspace GC-vials. Bottle volume was determined by weight by filling to capacity with water at room temperature  $(23 \pm 2 \degree C)$ . Three different TCE concentrations were prepared in 0.1 M KCl and CsCl, and 0.05 M CaCl<sub>2</sub>. Same volume (25 µL) of stock TCE solution (prepared immediately prior to their use) (500 mg  $L^{-1}$ ) was injected into the vials containing different volumes of each electrolyte solution to create different concentrations. Vials were capped immediately with Teflon-lined silicone septa and aluminum crimp caps to minimize volatile loss of TCE. The vials were then shaken reciprocally overnight at 40 rpm at room temperature  $(23 \pm 2 \degree C)$ ; preliminary studies showed that equilibrium was achieved within this time-period. TCE concentration in the headspace of each vial was analyzed using a Varian 3700 gas chromatograph with flame ionization detector (GC-FID) connected with a HP 19395A Headspace Autosampler. The dimensionless Henry's Law constant (H<sub>C</sub>) was calculated (Lincoff and Gossett, 1984) as:

$$H_{c} = \frac{C_{g2}V_{l2} - C_{g1}V_{l1}}{C_{g1}V_{g1} - C_{g2}V_{g2}}$$
(1)

where  $C_{g1}$  and  $C_{g2}$  are the TCE concentrations in gas phase of vials 1 and 2,  $V_{g1}$  and  $V_{g2}$ are the gas volumes in vials 1 and 2, and  $V_{11}$  and  $V_{12}$  are the solution volumes in vials 1 and 2. The experiment was performed in triplicate, and at least duplicate results are presented. We used these values of Henry's Law constant to calculate the distribution of TCE in the sorption experiments, as Henry's Law was dependent on the cation in solution.

### Sorption Isotherm Measurement

TCE sorption isotherms were determined using a batch equilibrium headspace technique (Garbarini and Lion, 1985). Freeze-dried clay (0.1 to 0.6 g) was suspended in 5.0 mL of electrolyte solution (0.1 M for CsCl and KCl, and 0.05 M for CaCl<sub>2</sub>). A series of initial TCE concentrations (0.5, 1.0, 2.0, 5.0, 10, 20, 40, 70 and 100 mg L<sup>-1</sup>) were prepared by injecting different volumes of stock TCE solution (500 mg L<sup>-1</sup>) (prepared immediately prior to their use in respective electrolyte solution) into vials using a syringe. Vials were capped immediately with Teflon-lined silicone septa and aluminum crimp caps to minimize volatile losses of TCE. The vials were then shaken reciprocally overnight at 40 rpm at room temperature ( $23 \pm 2$  °C); preliminary studies showed that equilibrium was achieved within this time. TCE concentration in headspace of the vials was analyzed using a Varian 3700 GC-FID as above. All isotherm experiments were performed in triplicate, and at least duplicate results are presented.

After reaching partitioning equilibria, TCE distributions in air, solution and clay were determined by comparing two systems, viz. systems containing clay and systems without clay. The same solution volume  $(V_l)$ , gas volume  $(V_g)$ , total mass of TCE  $(M_T)$ was applied to both systems. Under such circumstances, sorption equilibria were evaluated using the following relationships:

a. System without clay (at equilibrium):

$$M_{T} = C_{l1}V_{l} + C_{g1}V_{g}$$
(2)

b. System with clay (at equilibrium):

$$M_{T} = C_{12}V_{l} + C_{g2}V_{g} + C_{clay}M_{clay}$$
(3)

where  $C_{l1}$  and  $C_{l2}$  are the equilibrium TCE concentrations in solution phase of systems without and with clay, respectively,  $C_{g1}$  and  $C_{g2}$  are equilibrium TCE concentrations in the gas phase of systems without and with clay, respectively,  $C_{clay}$  is the TCE concentration in the clay phase, and  $M_{clay}$  is the mass of clay (g) added to the system. Since the same amounts of TCE were added into both systems, equations (2) and (3) are equal, thus:

$$C_{l1}V_{l} + C_{g1}V_{g} = C_{l2}V_{l} + C_{g2}V_{g} + C_{clay}M_{clay}$$
(4)

From Henry's Law, we know that:

$$C_{l} = \frac{C_{g}}{H_{c}}$$
(5)

and we determined  $H_c$  for each electrolyte using equation (1) as described above. Substituting  $C_l$  from equation (5) into equation (4), we get:

$$\frac{C_{g1}}{H_c}V_l + C_{g1}V_g = \frac{C_{g2}}{H_c}V_l + C_{g2}V_g + C_{clay}M_{clay}$$
(6)

From equation (6) the amount of TCE sorbed on the clay ( $C_{clay}$ ) can be determined as:

$$C_{clay} = \frac{(C_{g1} - C_{g2})^* [(V_l / H_c) + V_g]}{M_{clay}}$$
(7)

 $C_{g1}$  and  $C_{g2}$  are determined using a Varian 3700 GC-FID. The TCE concentrations in aqueous solution and clay phases were calculated using equation 5 and 7, respectively.

# X-ray Diffraction

Clays were mixed with water to form suspensions, which were used to prepare clay films for X-ray diffraction analysis. The suspensions were dropped onto glass slides and air-dried overnight at ambient conditions to obtain oriented clay films. The clay films were then allowed to equilibrate with water vapor for 2 d in a closed container containing distilled water to expose the clay films at 100% relative humidity. X-ray diffraction patterns were recorded using Cu-K $\alpha$  radiation and a Philips APD 3720 automated X-ray diffractionmeter, fitted with an APD 3521 goniometer and a  $\theta$ -compensating slit, a 0.2 mm receiving slit and a diffracted beam graphite monochromator. Diffraction patterns were recorded from 5.5 to 16.0 °2 $\theta$  at a step of 0.005 °2 $\theta$  with 4 s/step.

#### **Results and Discussion**

# Henry's Law Constant

Henry's Law constant of TCE was found to be different in the three different electrolyte solutions used for the sorption study. The values of Henry's Law constant were determined to be 0.61 for 0.1 M KCl, 0.74 for 0.05 M CaCl<sub>2</sub>, and 0.92 for 0.1 M CsCl, which are all different from the value (0.40) in the pure water-air system (Verschueren, 2001). The presence of salt in the water phase makes the aqueous solution more unfavorable for the dissolution of TCE; thereby enhancing the Henry's Law constant. Since these differences are large and since the Henry's Law constant plays a significant role in the calculation of sorption (eqs 5 and 7), we measured these values of Henry's Law constant for each salt solution and used these values of Henry's Law constant to calculate the TCE aqueous concentrations in the relevant electrolyte solutions in our sorption experiments.

### Sorption Isotherm

TCE sorption isotherms are shown in Figure 1. The data points are the average values of equilibrium concentration (X-axis) and amount of TCE sorbed (Y-axis), and the error bars show the standard deviations. Ca-saturated saponite sorbed the least TCE (Figure 1a) and Cs-saturated saponite sorbed the most TCE (Figure 1b). K-saturated saponite sorbed roughly twice that amount of the Ca-saponite (Figure 1a). The sorption of 0.34% (wt./wt.) TCE by the Cs-smectite at an equilibrium concentration of 90 mg L<sup>-1</sup> is the largest TCE sorption reported for any clay mineral that we know of, though Alvarez-Cohen et al. (1993) observed 20% TCE sorption for a low-charge zeolite, and Farrell et

al. (2003) observed up to 50% TCE sorption for another low-charge zeolite under both dry air and 100% relative humidity, while Farrell and Reinhard (1994) reported 0.13% (wt./wt.) TCE sorption by montmorillonite and Rogers and McFarlane (1981) did not observe any TCE sorption by Ca<sup>2+</sup> saturated montmorillonite. While solute transport models generally assume no TCE sorption to clays in aquifer materials, Figure 1 shows that there might be significant sorption of TCE to aquifer smectites especially if Cs<sup>+</sup> is a co-contaminant in the plume.



Equilibrium Concentration of TCE, mg/L

Figure 1. Sorption isotherms representing trichloroethene uptake from water by reference saponite (SapCa-2) clay saturated with (a) calcium, and potassium, and (b) cesium.

The lower effectiveness of Ca-SapCa-2 may be due in part to the larger enthalpy of hydration of  $Ca^{2+}$ . The larger hydration sphere around  $Ca^{2+}$  causes Ca-saponite to swell in water, thus expanding the slit-pore and decreasing the energy gained by removing TCE from aqueous solution (Corley et al., 1996). Also, the larger hydration sphere of  $Ca^{2+}$ obscures a larger fraction of the lateral siloxane surface between exchangeable cations compared to those associated with either  $Cs^+$  or  $K^+$ , and thereby effectively shrinks the size of the adsorptive domains for  $Ca^{2+}$  saturated clays. Conversely, the higher effectiveness of Cs-SapCa-2 in sorption may be due in part to the lower hydration energy of  $Cs^+$  and hence smaller hydrated radius of  $Cs^+$  compared to  $K^+$  or  $Ca^{2+}$ . The relatively weak hydration of Cs<sup>+</sup> also causes Cs-saponite to swell less in water, which potentially provides a more favorable sorption domain (Corley et al., 1996), and allows the organic to compete better with water for interlayer sites. The fewer water molecules associated with exchangeable Cs<sup>+</sup>, for example, obscure a smaller fraction of the clay surface than those associated with  $Ca^{2+}$ , resulting in the increase in the adsorptive domains for  $Cs^{+}$ saturated clays. Zhu et al. (2004) also reported high sorption of polycyclic aromatic hydrocarbons (PAHs) by Cs-saturated clays. They hypothesized that relatively weak hydration of  $Cs^+$  resulted in stronger cation- $\pi$  interaction ensuring higher sorption of PAHs, while bivalent cations like  $Ca^{2+}$  having high hydration energies induced weak cation- $\pi$  interactions, resulting in low sorption. While 'hydrated radii' are poorly defined, typical estimates of hydrated radii are 9.6 Å for  $Ca^{2+}$ , 5.3 Å for K<sup>+</sup>, and 3.6 Å for Cs<sup>+</sup> (Evangelou, 1998). Thus the cross-sectional area of hydrated  $Ca^{2+}$  is about 290 Å<sup>2</sup>, more than seven times that of  $Cs^+$  (40 Å<sup>2</sup>); therefore one hydrated  $Ca^{2+}$  takes up 3.5 times as much room 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<sup>-1</sup> and the 95 cmol kg<sup>-1</sup> CEC of saponite SapCa-2, we compute that the hydrated radii of Ca<sup>2+</sup> or K<sup>+</sup> must overlap in the interlayer regions of homoionic SapCa-2, meaning that TCE would have to compete with strongly bound water for interlayer sorption sites, which it apparently does not do very well. On the other hand, Cs<sup>+</sup> and its hydration shells are projected to occupy only about 67% of the interlayer space, implying that TCE has to compete only with less strongly bound water in the Cs-smectite interlayers. This may explain why the Cs-smectite is a much more effective sorbent for TCE. Sheng et al. (2001; 2002) also observed similar effects of cation exchange on domain size for the sorption of atrazine and DNOC by SWy-2 clay.

Of the cations studied here, Cs-smectite is most likely to have a 12.5 Å layer spacing, even in aqueous suspension. If so, and assuming TCE sorption is in the interlayer, then at most a monolayer of TCE can sorb and the system should exhibit Langmuir-type behavior. The best-fitting Langmuir parameters are a monolayer coverage of about 4500 mg kg<sup>-1</sup>, and Langmuir K of about 0.032. This Langmuir function does not fit the data particularly well at low concentrations because of the upward curvature of the isotherm data, but the Freundlich curve is even worse for the same reason. Similarly, a Langmuir isotherm does not fit well for K-smectite at low concentrations, but can be fit at high concentrations (Figure 1a). The Ca-system on the other hand will never have a 12.5 Å layer spacing in suspension, so sorption of a simple monolayer of TCE is unlikely in the Ca-smectite interlayer. For the Ca-system there was no evidence of an adsorption plateau, so there is no way to fit the Langmuir equation. Therefore, we report Freundlich parameters for our Ca-system:  $K_f (mg^{1-N} L^N kg^{-1})$ , the Freundlich sorption coefficient is

3.11, and N (unitless) is 1.16. The N value > 1.0 for Ca-smectite is consistent with earlier results (Li et al., 2003; Sheng et al., 2001) for hydrophobic compound sorption to Ca-smectites.

# X-ray Diffraction

Differences in the swelling behavior between Cs- and Ca-SapCa-2 may also contribute to their differential adsorption of organic compounds. Many Cs-smectites equilibrate with ~12.5 Å layer spacings (hydrate monolayer structures) at 100% humidity and even in aqueous suspension (Sato et al., 1992). All Ca-smectites, on the other hand, swell to more than 15 Å in suspension. Our results show that Cs-saturated saponite swells to 12.1 Å at 100% humidity (K-saturated saponite swells to 12.2 Å), while Ca-saturated saponite swells to 14.9 Å at 100% humidity (Figure 2). Of course, the d-spacings of these clay films may be smaller than those of the smectites in aqueous suspension when the adsorption experiments were carried out, although the clay films were exposed to 100% RH. Teppen et al. (1998) concluded that, for idealized siloxane surfaces of layer charge zero, the most stable mode of TCE sorption occurs by full molecular contact, coplanar with the clay surface. They further concluded that this kind of interaction is suppressed by increasing water loads. The average molecular diameter of TCE is 6.8 Å (Farrell and Reinhard, 1994) and the thickness perpendicular to the molecular plane is only about half that. We propose that in a system with a monolayer of water  $(K^+, and Cs^+)$ -saturated clays near 12-Å d-spacings as in Figure 2), TCE intercalates into clay interlayers and, coplanar with the clay basal surfaces, interacts with two opposing clay layers by full molecular contact with both via van der Waals and electrostatic forces. That is, TCE like many

planar aromatic molecules is only about 3 to 3.5 Å thick so fits very well between two smectite layers at d-spacings of 12-12.5 Å (Sheng et al., 2002). Thus Cs-smectite, which can reasonably be expected to have a 12.5-Å d-spacing even in aqueous suspension (Berend et al., 1995; Kawano and Tomita, 1991; MacEwan and Wilson, 1980; Suquet and Pezerat, 1987; Suquet et al., 1975; Suquet et al., 1977), may have the optimal slitpore to maximize the energy of TCE condensation from solution (Corley et al., 1996), because if the interlayer region was any more narrow than 12 Å, then TCE could no longer intercalate at all because it simply could not fit.



Figure 2. X-ray diffraction pattern of reference saponite (SapCa-2) clay in oriented clay films as a function of different cation saturation at 100% humidity.

Given a 3-Å thick interlayer region, 33% of the basal surface not covered by Cs<sup>+</sup> hydration shells as described above, and the TCE molar volume cited above, we predict that the Cs-saponite might be able to sorb up to 10% TCE by weight if all interlayer volume outside primary Cs<sup>+</sup> hydration shells were filled with TCE. Since we observed only 0.34% sorption (Figure 1), our assumptions may be simplistic in that a) The kinetics of tortuous TCE diffusion to many interlayer sites may be slow, or b) TCE is not able to displace other interlayer water outside primary Cs<sup>+</sup> hydration shells. In this regard, a tetrahedrally substituted clay may have been an inopportune choice in that tetrahedral charge is much more localized on fewer surface oxygens (McBride, 1989) and exchangeable cation ordering is only found in tetrahedrally substituted smectites (Odom, 1984). The exchangeable cations (at a given hydration state) can always approach a tetrahedral site more closely than an octahedral site (Bleam, 1990), and thereby strengthen the hydrogen bonding of interlayer water to the siloxane surface itself (Yariv, 1992).

Sorption isotherms for Cs-, K-, and Ca-saturated saponite are nonlinear (Figure 1 a and b). This nonlinearity could be due to several possible causes: 1) The heterogeneous distribution of sorption sites on the clays, 2) Equilibrium was not achieved during the course of the study, or 3) At least some of the postulates of a Langmuir-type sorption are satisfied, particularly the presence of a finite number of sorptive sites that, when fully occupied, constitute a 'monolayer' of adsorbate coverage. Li and Werth (2001) concluded that since sorbate molecules first occupy those sorption sites that have the highest adsorption potential, therefore sorption isotherms of TCE on two different natural solids were nonlinear. Similarly, Estes et al. (1988) and Hamaker and Thompson (1972)

did not observe equilibrium for sorption of organic on montmorillonite clay over a period of 30 days and concluded that slow changes in clay surface that resulted in the continuous exposure of new adsorption sites were the primary reason for the failure to achieve equilibrium. If our hypotheses about TCE sorption to the Cs-saponite are correct, then the smectite interlayer should behave very nearly like an ideal Langmuir system because the 12-Å d-spacing allows only monolayer coverage in the interlayer and the lateral adsorption domains between hydrated cations are only a fraction of a finite smectite basal surface area.

The type of smectite clay also affects TCE sorption. For example, our results show that Ca-saturated saponite sorbed  $\sim 460 \text{ mg TCE/kg}$  at the highest equilibrium concentration, but Rogers and McFarlane (1981) in a study with Ca-saturated montmorillonite (dioctahedral, CEC 80 cmol/kg) did not observe any apparent sorption of TCE. Two possible reasons for these differences are: (i) differences in the CEC of the clays, and (ii) type of the clay. However, we can ignore the differences in CEC to be responsible for the differences in sorption of TCE by these two clays. Generally, the lower the CEC of clay, the smaller is the clay surface occupied by the exchangeable cations, which makes more clay siloxane surface area available for sorption. Several workers have reported an inverse relationship between the CEC of the clay and the amount of the organic adsorbed (Laird et al., 1992; Lee et al., 1990; Sheng et al., 2001; Sheng et al., 2002). Based on these results, Ca-saturated montmorillonite of Rogers and McFarlane (1981) should have sorbed more TCE than that observed in the present investigation. Therefore, it seems that differences in TCE sorption may be related to the source of negative charge on the clays and not to differences in the CEC of the clays. The

negative charge on the saponite clay arises from isomorphous substitution in tetrahedral structures. Generally, for a given layer charge, clays with negative charge from tetrahedral substitution sorb more organics than do clays where negative charge develops from octahedral substitution. Compared to smectites with negative charges from octahedral isomorphous substitution, the 2:1 smectites with negative charges from tetrahedral isomorphous substitution exhibit less swelling of the interlayer space in water. The theory of capillary phase separation (Corley et al., 1996) thus implies that sorption of hydrophobic molecules from water should be more favorable in tetrahedrally versus octahedrally substituted smectites (for a given layer charge and interlayer cation), and such behavior has been observed (Laird et al., 1992; Sheng et al., 2001) though not explained.

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**CHAPTER V** 

# MOLECULAR SIMULATIONS TO ESTIMATE THERMODYNAMICS OF POLAR ORGANIC SORPTION TO MONTMORILLONITE

# Molecular simulations to estimate thermodynamics of polar organic sorption to montmorillonite

# Introduction

The list of anthropogenic organic chemicals that enter the environment expands continually. Soils and sediments are important environmental sinks for these chemicals and often contain the bulk of such chemicals after release. Hence, the potential for sorption to solid phases is a key parameter in estimating the environmental risk and fate of these chemicals, and has therefore been the subject of intensive investigation (Bailey and White, 1970; Boyd et al., 2001; Chiou, 1998; Chiou et al., 1979; Haderlein and Schwarzenbach, 1993; Karickhoff and Morris, 1985; Karickhoff et al., 1979; Sheng et al., 2002; Weissmahr et al., 1999).

Soil adsorption coefficients can be determined by batch equilibrium methods, but these can be difficult and expensive procedures. Despite 40 years of experimental work, soil sorption coefficients are in many cases unavailable even for high-production-volume chemicals (Sabljic et al., 1995). Even when sorption data are available for a given compound, they pertain to only a very limited number of sorbents. It would require unfeasible financial and scientific resources to measure adsorption coefficients for all pertinent chemicals interacting with all relevant natural phases. Thus there is interest in predictive models that can estimate the potential for organic compound sorption to a given solid phase (Andersson et al., 2002; Goss and Schwarzenbach, 2001). Such models could aid our prediction of contaminant transport and fate, while potentially even prescreening the probable fates of new compounds in order to minimize environmental risk.

For neutral organic compounds (NOCs), a breakthrough in predictive sorption modeling came with the realization that their sorption from water to soil organic matter (SOM) is analogous to partitioning into a bulk organic phase (Chiou et al., 1979; Karickhoff et al., 1979). Numerous approaches to estimate  $K_{oc}$  (the soil organic Cnormalized linear sorption coefficient) and therefore sorption to SOM have been published during the last 25 years, such as estimation of Koc based on water solubility (Briggs, 1981; Chiou et al., 1983; Gerstl, 1990; Karickhoff, 1981), n-octanol/water partition coefficient (Briggs, 1981; Chiou et al., 1983; Gerstl, 1990; Gerstl and Mingelgrin, 1984; Karickhoff, 1981), reversed-phase high-performance liquid chromatographic (RP-HPLC) capacity factor (Guo et al., 2002; Kanazawa, 1989; Muller and Kordel, 1996), topological indices (Gerstl, 1990; Sabljic et al., 1995), molecular parameters and linear solvation energy relationships (Gramatica et al., 2000; Huuskonen, 2003; Kanazawa, 1989; Lohninger, 1994), fragment constants and structural correction factors (Tao et al., 1999), and one-parameter linear free energy relationships (LFER) (Goss and Schwarzenbach, 2001). However, there are drawbacks with most of these approaches. For example, estimation of K<sub>oc</sub> based on water solubility and octanol/water partition coefficients can be very difficult for very hydrophobic substances (Gawlik et al., 1997). Furthermore, Goss and Schwarzenbach (2001) argued that the predictive power of one-parameter LFERs (i.e., K<sub>ow</sub>) is limited, because no single parameter can completely describe all the molecular interactions that determine environmental phase partitioning processes.

For NOCs with polar functional groups, specific interactions between adsorbate and adsorbent seem most likely to impact sorption. For example, the strong sorption of

nitroaromatic compounds to certain smectites (swelling clay minerals) seems to be driven by complexation of interlayer cations by solute -NO<sub>2</sub> groups (Boyd et al., 2001; Johnston et al., 2001; Johnston et al., 2002). In addition to such complexation, hydrogen bonding (Laird, 1997) and hydrophobic interactions (Boyd et al., 2001; Jaynes and Boyd, 1991) appear to play a role in NOC sorption to clay minerals, and evidence has been marshaled for other forces such as cation-pi bonding (Zhu et al., 2004) and electron donor-acceptor complexes (Haderlein and Schwarzenbach, 1993; Weissmahr et al., 1997). Since smectites have large surface areas and can contribute to and even dominate (Sheng et al., 2001) the sorption of many NOCs, it would be useful to be able to predict the strength of NOC sorption to smectites. To do so, however, it is apparent that many different types of molecular interactions need to be considered.

Molecular modeling techniques, therefore, may be appropriate tools to estimate smectite-NOC sorption affinities. Molecular simulations can help interpret experimental observation, discriminate among competing models to explain macroscopic or spectroscopic data, integrate bulk (P,V,T) and molecular properties, and test or generate scientific hypotheses (Bleam, 1993; Cygan, 2001; Lasaga and Gibbs, 1990; Sauer and Ahlrichs, 1990; Teppen et al., 1998). In particular, classical molecular simulations (often termed molecular mechanics) that parameterize all electronic effects have been used successfully to study heterogeneous clay mineral systems (Chang et al., 1997; Cygan, 1998; Delville, 1991; Greathouse et al., 2000; Kalinichev et al., 2000; Skipper, 1998; Skipper et al., 1991; Smith, 1998; Sutton and Sposito, 2001; Teppen et al., 1997). Such simulation methods are most commonly used to probe structural properties, because it is much more difficult to accurately compute energy relations (Schafer et al., 1990).

Nonetheless, the methods are reaching a reasonable level of maturity where it may be fruitful to test the ability of molecular mechanics methods to compute adsorption energies.

# Choice of compounds

Several experimental studies (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weissmahr et al., 1999; Weissmahr et al., 1997) indicated that nitroaromatic compounds adsorb strongly to smectite clay minerals, especially when the smectite is saturated with K<sup>+</sup> or Cs<sup>+</sup> counterions. In comparing molecules of very different organic functionality, there were indications that planar compounds with polar functional groups that might complex hydrated interlayer cations were most favorably adsorbed (Sheng et al., 2001). To test and refine this concept, Boyd et al. (2001) measured the adsorption from water of a planar series of para- and meta-substituted nitrobenzenes (SNBs) by the K-saturated Arizona smectite clay mineral SAz-1, a high-charge montmorillonite. Fourier transform infrared (FTIR) spectroscopy revealed shifts in the -NO<sub>2</sub> vibrational modes of 1,3,5-trinitrobenzene (TNB) (Boyd et al., 2001) and other SNBs (Johnston et al., 2001; Sheng et al., 2002) upon adsorption to K<sup>+</sup>-smectite, results that are consistent with the complexation of  $K^+$  by  $-NO_2$  groups. Such vibrational shifts were absent or less pronounced for smectites saturated with more strongly hydrated cations (i.e.,  $Na^+$ ,  $Mg^{2+}$ , Ca<sup>2+</sup>, Ba<sup>2+</sup>). Molecular dynamic simulations of dinitrobenzene systems (Boyd et al., 2001; Sheng et al., 2002) predicted that each -NO<sub>2</sub> group interacted with one or more different interlayer K<sup>+</sup> counterions. The experimental adsorption data (Boyd et al., 2001)

indicated that, among the nitrobenzenes tested. Freundlich complexation constants were strongest for the carboxylic methyl ester functional group, and decreased in the order:  $R-COOCH_3 > R-NO_2 > R-COCH_3 > R-CN > R-CHO > R-OCOCH_3 > R-OCH_3 > R-NH_2$ where R = nitrobenzene. Such an ordering is plausible from a complexation standpoint, considering both the presence and steric availability of atoms that can interact favorably with  $K^{+}$ . Two hypotheses that have been presented (Boyd et al., 2001) to explain this selectivity sequence for nitroaromatic molecules are 1) Additive complexation interactions between organic molecule functional groups and multiple interlayer cations, and 2) Hydration energy differences between the various organic molecules. Recently, enthalpies were measured (Li et al., 2004) for the adsorption of three nitroaromatic solutes to smectites. Thus, the nitroaromatic compounds are a promising system for developing molecular simulation methods to study adsorption energies, because systematic bulk adsorption data (Boyd et al., 2001), spectroscopic (Johnston et al., 2001) and X-ray diffraction (Li et al., 2004; Sheng et al., 2002) investigations of interlayer environments, and adsorption enthalpy data (Li et al., 2004) are all available. A simulation model is of potential importance since it might enable us to estimate the adsorption energies of new chemicals even before they are synthesized. If we are successful, it might be possible in the future to screen interesting chemicals (i.e., pesticides) for their soil sorption and leaching potentials even before chemical synthesis and biological efficacy testing are done.

Our goal in the present study is to develop and test two methods that use molecular dynamic simulations to estimate the enthalpies of adsorption for several NOCs interacting with smectites, and then correlate these enthalpy predictions with

experimental enthalpies and adsorption coefficients. The objectives of this study are to simulate a series of these nitroaromatic molecules in the interlayer region of montmorillonite clay, to use the molecular dynamics results to compute the relative adsorption energies for these nitroaromatics, and to determine the dominant components of the adsorption energies.

# **Materials and Methods**

A model for K-SAz-1 was created and molecular dynamics simulations of parasubstituted nitrobenzene-clay complexes were performed in order to estimate the adsorption energies for a series of nitroaromatic compounds. In this approach, electrons are not treated explicitly, but their effects are parameterized into classical (that is, nonquantum) mechanical energy functions comprising a force field. The clay model had the composition  $K_{12}(Al_{36}Mg_{12})Si_{96}O_{240}(OH)_{48}$  with a CEC of 132 cmol/kg. The smectite surfaces were constructed using methods previously detailed (Teppen et al., 1997), in which a muscovite mica layer was the starting point and octahedral Mg-for-Al substitutions were random except that no two Mg octahedra were allowed to be immediate neighbors. In order to prepare for molecular dynamics simulations of nitrobenzene-clay complexes, the interlayer region of the clay was expanded to 20 Å and one molecule from the series of substituted nitrobenzene was added to the unit cell, with its molecular plane perpendicular to the basal planes of the clay in an attempt to avoid biasing the final structure. The simulated loading rate was equivalent to 18 mg nitroaromatic per g clay. Water molecules were also added (in random interlayer positions) so that constant-pressure simulations resulted in 12.3 Å clay layer spacings. If

the simulation did not result in a clay layer spacing of 12.3 Å, then water molecules were either removed or added (after expanding the clay) so that the equilibrium clay layer spacing was  $12.3 \pm 0.1$  Å, in accord with the experimental data for substituted nitrobenzenes in air-dried films of K-SAz-1.

The energies were computed using a force field developed for clays (Teppen et al., 1997) combined with the polymer consistent force field (PCFF) (Maple et al., 1994; MSI, 2000) for the organics and water. As a further modification, charges on the organic solute were assigned using the COMPASS force field (Sun, 1998), which optimized organic atomic charges for condensed phase systems. In previous work (Boyd et al., 2001), we computed quantum mechanical charges for a series of nitroaromatic solutes and found COMPASS charges to more faithfully reproduce the quantum charge estimates than did PCFF charges. The charges on organic solute atoms are the most important force field parameters in determining interactions with the clay surface, interlayer water, and aqueous cations. In a typical force field, the nuclear charge and the local electron density around a given atom are subsumed into one atom-centered partial atomic charge, and the COMPASS charges for nitroaromatic solutes are illustrated in Figure 1. Commercial software (MSI, 2000) was used to compute the classical molecular dynamics. No constraints were imposed on our systems during their molecular dynamics except for the contents of the simulation cell: All atoms were completely free to move, and unit cell shape and volume were unconstrained.



Figure 1. Charges on para-dinitrobenzene molecule used in simulation study.

The molecular dynamics simulations were run in the NPT ensemble for 50 ps, much longer than the time required for the system volume and energy to equilibrate. Trajectories were saved from each molecular dynamics simulation, and snapshots from the post-equilibrium portion of each dynamic trajectory were used to estimate clayorganic interaction energies by computing the difference between the total energy of the system and the energies of the hydrated clay and the organic separately. A scripting program was written to automate the energy calculation for many snapshots of a given system. We used two different algorithms for converting simulation energies to predictions for experimental adsorption enthalpies.

# Computational algorithm 1

The typical experimental scheme for measuring adsorption of aqueous organics to clays is

where  $H_{expt}$  is the experimentally determined adsorption energy (for example, the overall free energy, enthalpy, or entropy of the transfer process). The experimental reaction is too difficult to simulate directly, since diffusion kinetics are slower than the *ns* timescales that are accessible to molecular simulations. Instead, we propose an alternative path that is more computationally feasible and follows the spirit of many schemes that have been used to simulate the binding of drugs to polypeptides (Gohlke and Klebe, 2002; Halperin et al., 2002). We employ the following thermodynamic cycle for computing the energy of adsorption of an aqueous organic molecule to a hydrated clay mineral:

 $Clay-cavity_{(aq)} + org_{(aq)} + H_2O \longrightarrow clay-org_{(aq)} + cavity_{(aq)} + H_2O$ 

Since the free energy, enthalpy, and entropy are state functions (Atkins, 1998), their magnitudes should be independent of path, so that

$$\Delta H_{expt} = \Delta H_3 + \Delta H_4 + \Delta H_5$$
<sup>[3]</sup>

This thermodynamic cycle is very similar in spirit to a recent study by Goss and Schwarzenbach (2001) where the free energy change  $\Delta G_i$  for partitioning of a compound between two phases is decomposed to enable a more mechanistic understanding of the partition process (Figure 2).



Similarly, Scmidt (Schmidt et al., 2002) proposed that the free energy of transfer of a molecule between two bulk phases 1 and 2,  $\Delta_{1,2}G$ , depends on the cohesive energy of both phases and the interactions of the molecule with both surrounding phases (van der Waals and H-bond interactions). All these interactions need to be taken into consideration when comparing the partitioning of a set of molecules between various organic phases and water. The transfer of a molecule into a bulk phase requires a cavity to be formed to accommodate the molecule (and therefore depends on the size of the molecule). For the formation of the cavity, the intermolecular interactions of the bulk phase molecules are interrupted. Thus, the stronger the cohesive interactions in the bulk phase, the more energy is required to form a cavity in the phase.

To relate  $\Delta H_4$  of our thermodynamic cycle to Figure 2, we recognize that

$$\Delta H_4 = \Delta H_{i-clay} - \Delta H_{i-aqueous} = \Delta H_{(clay-cavity \rightarrow clay-org)} + \Delta H_{(org(aq) \rightarrow water cavity(aq))}$$
[4]

That is,  $\Delta H_4$  is the sum of the energy changes for transferring the organic compound out of a cavity in the aqueous solution and into a cavity in the clay interlayer region. We estimated each energy term in equation 4 by equilibrating the entire organic-water (clay) system and then calculating interaction energies between subsets of the system. For example, we used the following algorithm to calculate  $\Delta H_{i-clay}$  (the interaction energy between organic compound *i* and its environment in the hydrated smectite interlayer) of Figure 2:

$$\Delta H_{i-clay} = \Delta H_{tot} - \Delta H_1 - \Delta H_2; \text{ where}$$
 [5]

- $\Delta H_{tot} =$  Total clay-organic system energy
- $\Delta H_1$  = Energy of system after organic has been deleted
- $\Delta H_2$  = Energy of the system after clay layers, interlayer cations, and water have been deleted
- Compute ∆H<sub>i-clay</sub> for many (≥ 150) snapshots to compile an estimate for the ensemble average value

Using this same general algorithm, we also computed  $\Delta H_{i-aqueous}$  (the interaction energy between the organic compound and its environment in aqueous solution),  $\Delta H_3$ (the interaction energy between the clay phase and the water molecules taken from the clay interlayer to create a cavity the size of the organic compound:  $\Delta H_3$  was calculated by removing water molecules from the smectite with 12.3 Å layer spacing but no interlayer organic compound – see Figure 2), and  $\Delta H_5$  (the energy required to fill the cavity in water that previously held the organic compound – see Figure 2). Once the four energy terms  $\Delta H_{i-clay}$ ,  $\Delta H_{i-aqueous}$ ,  $\Delta H_3$ , and  $\Delta H_5$  were computed, we were able to estimate  $\Delta H_{cxpt}$ as illustrated in cycle [2].

Note that we have neglected two necessary terms in the total energy. Both  $\Delta H_3$ and  $\Delta H_5$  can be though of as containing two separate components (Gallicchio et al., 2000), one for creating a cavity in water and a second component for the interaction of the cavity contents with its environment. Calculation of the first component, cavitation, for  $\Delta H_3$  presents some special problems: Most studies (Gallicchio et al., 2000; Höfinger and Zerbetto, 2003; Sandberg et al., 2002) of cavitation in water work with bulk aqueous phases that can expand to accommodate the cavity without any fundamental change to
the phase at distance from the cavity. In contrast, smectite clays might not be able to add a cavity to their interlayer volume without swelling and thus becoming a new phase. In our molecular dynamics methods, we use periodic boundary conditions to allow a relatively small unit cell (here, just 700 atoms) represent a condensed phase by replicating the unit cell to infinity. In such a case, the composition of the unit cell is typically fixed and water cannot leave the interlayer region (for example, in response to a growing cavity). In principle, we could do a realistic simulation by constructing a reasonable clay fragment consisting of multiple smectite layers embedded in a much larger unit cell containing an aqueous solution. Then, as a cavity grew, water could actually leave the interlayer region and enter the bulk aqueous phase. We leave such a simulation for the future, as we anticipate very slow simulations due to a huge number of atoms and also slow kinetics of water diffusion out of the clay. Indeed, with such a system one might have better luck actually trying to get an organic solute to adsorb into or desorb from the interlayer region and track the enthalpy changes directly through time. For the present study, we will use literature estimates for the cavitation components of both  $\Delta H_3$ , and  $\Delta H_5$ , and simulate just the water addition or removal from the cavity.

The molar volume of solid 1,4-dinitrobenzene is 103.5 cm<sup>3</sup>/mol (Lide, 1995), implying a molecular volume of 172 Å<sup>3</sup>/molecule, which should be a lower limit for the molecular volume in any other phase since crystalline 1,4-dinitrobenzene packing should be maximally efficient. This is about six times the molecular volume of liquid water (30 Å<sup>3</sup>/molecule), so any cavity for insertion of 1,4-dinitrobenzene into another phase should require removal of more than six water molecules. Our clay-water system (containing no 1,4-dinitrobenzene) that gave clay layer spacing of 12.3 Å contained 55 water molecules

per unit cell while our clay-1,4-dinitrobenzene-water system of the same  $d_{001}$ -spacing required 45. This difference of 10 water molecules per 1,4-dinitrobenzene is reasonable given packing inefficiency, and was adopted as an empirical estimate for the number of water molecules that must be removed in order to make a cavity for the nitroaromatic solutes here. Values of H<sub>3</sub> (equation 2) were computed by removing 10 continuous water molecules out of the 55 originally present in the clay-water system (containing no organic) with  $d_{001}$ -spacing of 12.3 Å (same clay layer spacing as our clay-organic-water system), while the values of H<sub>5</sub> (equation 2) were computed by removing 10 waters out of the 252 originally present in a periodic box of water (containing no clay or organic) (see Figure 2). The same estimates for H<sub>3</sub> and H<sub>5</sub> were used for each compound.

### Computational algorithm 2

The overall enthalpy change for adsorption of NACs to mineral surfaces from an aqueous phase can be expressed by combining equation 3 and 4 to give:

$$\Delta H_{expt} = \Delta H_{3cav} + \Delta H_{3int} + \Delta H_{i-clay} - \Delta H_{i-aqueous} + \Delta H_{5cav} + \Delta H_{5int}$$
<sup>[6]</sup>

Summing just the fourth and fifth terms of equation 6 yields approximately the dehydration enthalpy (that is, the negative of the hydration enthalpy  $\Delta H_{hyd}$ ) of the NAC, since hydration involves creating a cavity in water and placing the organic solute in the cavity (Goss and Schwarzenbach, 2001). Thus,

$$\Delta H_{expt} = \Delta H_{3cav} + \Delta H_{3int} + \Delta H_{i-clay} - \Delta H_{hyd} + \Delta H_{5int}$$
<sup>[7]</sup>

The purest measure for hydration of a compound is normally defined (Plyasunov and Shock, 2000) as transfer of the compound from its ideal gas (where it has no energetic interactions with its environment) to its aqueous solution. For example:

1,4-dinitrobenzene (g) 
$$\leftrightarrow$$
 1,4-dinitrobenzene (aq) [8]

Note that this reaction is the sum of the dissolution reaction

1,4-dinitrobenzene (s) 
$$\leftrightarrow$$
 1,4-dinitrobenzene (aq) [9]

and the reaction

$$1,4-\text{dinitrobenzene}(g) \leftrightarrow 1,4-\text{dinitrobenzene}(s) \qquad [10]$$

Reaction 10 is the reverse of the sublimation reaction, so the hydration enthalpy can be expressed as (Plyasunov and Shock, 2000)

$$\Delta H_{hyd} = \Delta H_{dis} - \Delta H_{subl}$$
[11]

Fortunately, estimates for sublimation enthalpies  $\Delta H_{subl}$  have been published (Chickos and Acree, 2002) for several of the NACs studied here, and are listed in Table 3. This allows equation 7 to be rewritten

$$\Delta H_{expt} = \Delta H_{3cav} + \Delta H_{3int} + \Delta H_{i-clay} + \Delta H_{subl} - \Delta H_{dis} + \Delta H_{5int}$$
<sup>[12]</sup>

Now, when  $\Delta H_{hyd}$  (equation 7) or  $\Delta H_{subl}$  and  $\Delta H_{dis}$  (equation 12) can be looked up or estimated for any compound, it becomes easier to estimate an experimental adsorption enthalpy for that compound.

## **Results and Discussion**

### Algorithm 1 validation

As a first test of our overall method and specific algorithms, we have computed adsorption enthalpies for the two nitrobenzene derivatives ( $R-NO_2$  and  $R-COOCH_3$ , where R=nitrobenzene) that adsorbed most strongly to the smectite in the experimental study (Boyd et al., 2001) and compared them with that of p-xylene, which is of similar size but lacks the polar functional groups that might enable complexation with interlayer cations so is expected to sorb with a much less favorable enthalpy (Table 1).

Table 1. Estimated and measured enthalpies of reaction (kJ/mol) as defined by the equation designated as cycle [2] and Figure 2. The same estimates for  $\Delta H_3$  and  $\Delta H_5$  were used for each compound.

-			:				- - -	81
Compound	ΔH i-clay	-AH i-aqueous	ΔH₃	ΔH <sub>3</sub>	ΔHs	ΔHs	Estimated	Measured
(R=nitrobenze			cavity	insertion	cavity	insertion	$\Delta H_{expt}$	$\Delta H_{\text{expt}}$
R-NO.	-154 + 16	+149 + 71	+60.0	+560 to	-60.0	-600 to	-5 + 77	-18+1
		17 7 / 1 1		+750		-720		
R-COOCH3	-108 ± 14	+114±16	+60.0	560-750	-60.0	-600-720	+6±22	1
TNB	-235 ± 17	+227 ± 23	+60.0	560-750	-60.0	-600-720	<b>-</b> 8 ± 29	<b>-</b> 28 ± 4
<i>p</i> -xylene	+38 ± 11	+40±9	+60.0	560-750	-60.0	-600-720	+78 ± 15	:
<sup>a</sup> (Li et al., 2004)								

Note that the clay-organic interaction enthalpies are quite favorable for all nitrobenzene solutes but not for p-xylene. The value of  $\Delta H_{i-clay}$  for 1,4-dinitrobenzene adsorption to K-SWy-2 smectite was recently estimated to be -93 kJ/mol (Li et al., 2004), compared with our estimate (Table 1) of -154 kJ/mol. The same paper estimated  $\Delta H_{i-clay}$  for 1,3,5trinitrobenzene adsorption to K-SWy-2 smectite at -124 kJ/mol (Li et al., 2004), again much smaller than our estimate (Table 1) of -235 kJ/mol. The only other estimates we know of for related systems are quantum mechanical: -38 kJ/mol for 1,3,5trinitrobenzene interacting with a single, neutral 2:1 clay surface (Pelmenschikov and Leszczynski, 1999), and -49 kJ/mol for nitrobenzene interacting with two waters of hydration at the surface of a Na-smectite fragment (Gorb et al., 2000). The values of  $\Delta H_{i-clay}$  for 1,4-dinitrobenzene and 1,3,5-trinitrobenzene computed here by molecular mechanics are about 65 and 90% larger, respectively, than the values estimated from experimental data (Li et al., 2004), and thus may indicate some deficiency in either the force field or the structural model used in our simulations. Electrostatic interactions account for >100% of  $\Delta H_{i-clay}$  for 1,4-dinitrobenzene (Table 2), so the forcefield perhaps overpredicts the tendency of 1,4-dinitrobenzene to form inner-sphere complexes with K<sup>+</sup>. On the other hand, the molecular dynamics estimates for  $\Delta H_{1-aqueous}$  were done in the absence of any ionic species, yet the water-organic interaction enthalpies are also strong and favorable, so  $-\Delta H_{i-aqueous}$  values are large and positive for the nitrobenzenes.

chemical structure	K <sub>f</sub> , Freundlich coefficient (l/g)	ΔH <sub>electrostatic</sub>	∆H <sub>vdw</sub> – kJ/mol	ΔH <sub>int</sub>	ΔG of solvation
NO, NH2	0.0499	-137	40	-98	13.0
NO2	0.182	-91	5.0	-86	6.2
NO2	0.452	-75	17	-58	13.8
NO2-СНО	1.05	-107	6.0	-101	10.4
NO2-COOCH3	3.28	-103	-5.0	-108	14.4
NO2 COCH3	2.62	-104	5.0	-99	12.0
	1.16	-129	24	-106	11.1
NO <sub>2</sub> -NO <sub>2</sub>	2.87	-167	14	-154	19.3
H <sub>3</sub> C		20	19	38	15.8
TNB		-236	2.0	-235	15.8

# Table 2. The Freundlich adsorption coefficients for substituted nitrobenzenes andthe adsorption energies of the corresponding substituents.

The values of  $\Delta H_{i\text{-}aqueous}$  for all solutes in Table 1 are within a few percent of their analogous values  $\Delta H_{i\text{-}clay}$  in the clay phase. This is really quite surprising given that the clay interlayer contains a 12 mol/L solution of K<sup>+</sup> while the bulk aqueous phase contained only water and the organic solute. From these results, we anticipate that Algorithm 1 will be difficult to make useful, because  $\Delta H_{i\text{-}clay}$  and  $\Delta H_{i\text{-}aqueous}$  differ by less than their standard deviations. Thus, the overall adsorption enthalpy  $\Delta H_{expt}$  (a relatively small number) has to be predicted by subtracting two rather uncertain large numbers, a situation that does not allow for statistically significant predictive power.

Literature estimates are available for comparison with some values of  $-\Delta H_{1-aqueous}$ in Table 1, but none of them are direct. Sandberg et al. (2002) predict 73 kJ/mol for  $-\Delta G_{i-aqueous}$  of *p*-xylene. To convert this to a  $-\Delta H_{i-aqueous}$  value, we note that Gallicchio et al. (2000) estimate that, for a range of 11 alkanes, the ratio of  $\Delta H_{i-aqueous} / \Delta G_{i-aqueous}$ averages  $1.17 \pm 0.04$ . This implies that  $-\Delta H_{j-aqueous}$  should be near 85 kJ/mol for *p*-xylene, which is about twice our estimate. Estimates for the values of  $-\Delta H_{i-aqueous}$  for the substituted nitrobenzenes have to begin with nitrobenzene, since we know of no estimates for di- or trinitrobenzenes. The  $-\Delta G_{i-aqueous}$  for nitrobenzene is estimated as 76 kJ/mol (Sandberg et al., 2002). Furthermore, adding a nitro-substituent to benzene, toluene, or phenol result in consistent changes of  $-\Delta G_{i-aqueous}$  of 23 kJ/mol (Sandberg et al., 2002), so reasonable guesses for  $-\Delta G_{i-aqueous}$  values of 1,4-dinitrobenzene and 1,3,5-trinitrobenzene are 99 and 122 kJ/mol, respectively. Scaling these values by 1.17 (Gallicchio et al., 2000) converts them to crude approximations of 116 and 143 kJ/mol for the  $-\Delta H_{i-aqueous}$  of 1,4-dinitrobenzene and 1,3,5-trinitrobenzene, respectively, compared with 149 and 227 kJ/mol in Table 1. Our simulated estimates of  $-\Delta H_{i-aqueous}$  for *p*-xylene are too low while

those for the nitrobenzenes appear to be too large in comparison with previous estimates (Sandberg et al., 2002) that were also based on molecular simulations. A possible explanation is that force filed parameters used in either the previous study, the present study, or both were inaccurate or at least disagreed. For example, we used charges of  $\pm 0.6170$  on N and -0.4280 on O atoms in  $-NO_2$  groups, while the previous study (Sandberg et al., 2002) used 0.58 and  $\pm 0.33$ , respectively. Apparently, they (Sandberg et al., 2002) scaled the OPLS-AA forcefield (Price et al., 2001) charges ( $\pm 0.65$  and  $\pm 0.37$ ) by 0.9 in order to improve their fits to experimental free energies of hydration. Our previous quantum mechanical study (Boyd et al., 2001) of 15 small gas-phase nitroaromatic compounds fit atomic partial charges to the molecular electrostatic potentials and found that charges on N were  $\pm 0.66 \pm 0.01$  and those on O were  $\pm 0.40 \pm 0.01$ . In condensed phases like water, these charges would probably be larger in magnitude due to polarization caused by interactions with solvent molecules.

Relevant estimates for the cavitation component of  $\Delta H_5$  have been published, but they are again indirect since  $\Delta G_5$  values are more commonly available. Molecular dynamics simulations have been used several times, the first being (Postma et al., 1982), to estimate free energies for cavity formation in water, and the numbers come to a reasonable consensus. Taking cyclohexane as an example (density of the liquid at 20 °C is 0.779 g/cm<sup>3</sup> (Lide, 1995) so molecular volume is 180 Å<sup>3</sup>, similar to dinitrobenzene), three recent estimates for  $-\Delta G_5$ , the free energy required to form a cavity in water that can hold cyclohexane are 66 (Gallicchio et al., 2000), 64 (Sandberg et al., 2002), and 72 kJ/mol (Höfinger and Zerbetto, 2003). Furthermore, Gallicchio et al. (2000) estimated the enthalpic contribution for the first time and found that, for a range of eight C<sub>4</sub>- to C<sub>6</sub>-

alkanes, the ratio of  $\Delta H_5 / \Delta G_5$  averages 0.58 ± 0.03. Pertinent to Table 1, Sandberg et al. (2002) predict -68 kJ/mol for  $\Delta G_5$  of p-xylene, and using  $\Delta H_5 / \Delta G_5 = 0.58$  (Gallicchio et al., 2000) implies that the cavitation component of  $\Delta H_5$  for p-xylene should be near -39 kJ/mol. Consider another way to make this estimate: The cavitation free energy  $\Delta G_5$  for a single water molecule is estimated at  $15.6 \pm 0.2$  kJ/mol (Sandberg et al., 2002). Converting this to  $\Delta H_5$  using the 0.58 (Gallicchio et al., 2000) conversion factor yields 9.0 kJ/mol per water molecule. Given that the molecular volume of p-xylene (203 Å<sup>3</sup>, (Lide, 1995) is about seven times that of water, and given that cavitation energies depend predominantly on molecular volume and surface area (Gallicchio et al., 2000; Höfinger and Zerbetto, 2003), the cavitation enthalpies  $\Delta H_5$  for all the solutes considered here should be near -60 kJ/mol. A third way to estimate the cavitation energy is through use of an equivalent spherical radius. Again, cavitation energies like  $\Delta H_3$  are thought to depend more on volume than on any particular shape (Höfinger and Zerbetto, 2003), and polynomials that are quadratic or cubic in equivalent spherical radius of the cavity often fit molecular estimates well (Höfinger and Zerbetto, 2003; Sandberg et al., 2002). For pxylene, with a volume of 203  $Å^3$ , the equivalent spherical radius is 3.65 Å and a polynomial fit to alkanes (Sandberg et al., 2002) yields 100 kJ/mol for  $\Delta G_5$  to form that sphere in water. Applying  $\Delta H_5 / \Delta G_5 = 0.58$  (Gallicchio et al., 2000) again implies that  $\Delta H_5$  for p-xylene should be about -58 kJ/mol. Since all the solutes of Table 1 are roughly the same size, -60 kJ/mol should be a reasonable estimate for all  $\Delta H_5$  cavitation values and were also used for the cavitation component of  $\Delta H_5$  in the clay since we know of no relevant estimates there. Thus we assume for now that cavitation energy differences in

the two phases will be insignificant, which looks like a reasonable assumption given the magnitudes of some of the other energy terms in Table 1.

The second components (for the interaction of the cavity contents with its environment) of  $\Delta H_3$  (the enthalpy required to take water out of a cavity in the clay interlayer) and  $\Delta H_5$  (the enthalpy change for filling an aqueous cavity with water – see Figure 2) require comment. These numbers were obtained by applying algorithm [5] to one or more water molecules, then normalizing the resultant interaction energy to the 10 water molecules considered to be leaving the interlayer cavity or entering the aqueous phase cavity. The range of values in Table 1 comes from ten or more estimates, each time choosing different subsets, for both the clay phase and the aqueous phase. The variability and overlap in these values that is evident in Table 1 would again seem to preclude their use as part of a sum to estimate relatively small adsorption energies.

Are the estimates (Table 1) for interaction of water inserted into an aqueous cavity reasonable? We know of no previous studies that tried to estimate  $\Delta H_3$ , but  $\Delta H_5$ values can be estimated. As discussed above, +9.0 kJ/mol is a reasonable estimate for the cavitation component of  $\Delta H_5$ , but what about this interaction component. The sum of the two components should just be the hydration enthalpy (Gallicchio et al., 2000), which is -44.0 kJ/mol (Lide, 1995). This implies by difference that the interaction component of  $\Delta H_5$  for insertion of water into an aqueous cavity should be -53 kJ/mol. Our estimates of -60 to -72 kJ/mol are somewhat more negative than this value, but within reason. Our value may be a bit large because we did not allow the water molecules bordering the cavity to reorient their H-bonding patterns during our estimate: We simply deleted a cavity of water molecules and recalculated the energy.

The sum of  $\Delta H_3$  and  $\Delta H_5$  might be compared with experimental data, since  $\Delta H_3 + \Delta H_5$  should approximate the energy required to move water out of the smectite interlayer and into bulk water. That is, the sum of  $\Delta H_3 + \Delta H_5$  refers to the reaction (equation 2)

$$Clay_{(aq)} + cavity_{(aq)} \leftrightarrow Clay-cavity_{(aq)} + H_2O_{(aq)}$$
 [13]

which is equivalent to

$$cavity_{(aq)} \leftrightarrow cavity_{(clay)}$$
[14]

which seems equivalent to

$$H_2O_{(clay)} \leftrightarrow H_2O_{(aq)}$$
[15]

The measured heat of immersion for the first layer of water loading on Ksmectites is about -1 to -4 kJ/mol of water (Berend et al., 1995), for an average of about -2.5 kJ/mol, so  $\Delta H_3 + \Delta H_5$  should be about +2.5 kJ/mol of water. Thus, for the 10 water molecules used to represent each cavity, we would expect the magnitude of the insertion component of  $\Delta H_3$  to be about 25 kJ/mol larger than that of  $\Delta H_5$ . Instead, there is little difference and, if anything, the central tendency of  $\Delta H_3$  is to have a slightly smaller magnitude, although any differences are again swamped out by the overall variability.

The preliminary results of Table 1 are encouraging in that a) our algorithm yields adsorption enthalpies of the correct sign for for agreement with the experimental data (Li et al., 2004) for 1,4-dinitrobenzene and 1,3,5-trinitrobenzene (and, for what it is worth, the standard deviations for the computed estimates overlap with the experimental

estimates), and b) adsorption enthalpies for nitroaromatics and p-xylene are predicted to be significantly different, even at this preliminary stage. A significant challenge in the path to making the algorithm useful is the size of the error bars at each step because they cause the overall  $E_{expt}$  estimates to have an uncertainty that will often be larger than the value itself. Further work is needed to understand and minimize the sources of uncertainty in the energy estimates.

The interaction energy was dominated by electrostatic rather than van der Waals terms (Table 2), in accordance with the earlier concepts that complexation interactions between interlayer cations,  $K^+$  in this case, and the nitroaromatic molecules are critical. These complexation energies also seem to dwarf the aqueous solvation energies of the nitroaromatics as a contributor to the overall adsorption energy.

To test the validity of the algorithm 1, we used the data from Boyd et al. (2001) (Figure 3). The numbers along the right hand side are our simulated interaction energies between organic and the smectite. Note that they follow a reasonable trend with strong interaction energy for strongly sorbing ones and smaller interaction energy for poorly sorbing ones, although some of them are out of order. But, in general, the trend of predicted energies for experimental sorption results is promising.



Figure 3: Validity of algorithm with experimental data.

For comparison, p-xylene, which is dimethylbenzene, which has an interaction energy of +38 kJ/mol. A positive number tells us that it is unfavorable and most of the nitro compounds are favorable. Xylene cannot form complexes and so its interaction energy is positive. (All the calculation energies are for monolayer systems where complexation interactions will be maximum.)

 $\Delta H_{int}$  values were quite favorable for all nitroaromatic compounds but unfavorable for p-xylene. Thus, the algorithm shows promise for computation of useful  $\Delta H_{int}$  values, but the adsorption energies depend on factors other than  $\Delta H_{int}$ . For example, the energies for removal of the organic from aqueous solution must be a component of the adsorption energy, and this factor shows a range of 6 to 19 kJ/mol (see Table 2).

In our simulations, the energies for removing organics from their cavities in bulk water were estimated at +149  $\pm$  21 kJ/mol for p-NO<sub>2</sub>, +114  $\pm$  16 kJ/mol for p-COOCH<sub>3</sub>, +227  $\pm$  23 kJ/mol for TNB, and +40  $\pm$  9 kJ/mol for p-xylene (Table 1). Therefore, adsorption enthalpies are estimated to be -5  $\pm$  27 for p-NO<sub>2</sub>, +6  $\pm$  22 for p-COOCH<sub>3</sub>, -8  $\pm$ 29 for TNB, and +78  $\pm$  15 for p-xylene.

A goal of each simulation was a 12.3 Å d-spacing for the clay-water-organic system. Using p-COOCH<sub>3</sub> as a test for the sensitivity of  $\Delta$ Hint, four different simulations were performed at three water contents that each resulted in a 12.3 Å d-spacing (Figure 4). Variability in  $\Delta$ Hint was about 2 kJ/mol for a given water content but ~21 kJ/mol among the different water contents. Within a given simulation, standard deviations for  $\Delta$ Hint among the 150 observations were ~ 17 kJ/mol.



Figure 4. Sensitivity Analysis.

#### Algorithm 2 validation

In applying algorithm 2, we can make use of our discovery using algorithm 1 that  $\Delta H_{3int}$  and  $\Delta H_{5int}$  cancel each other (Table 1). This simplifies the estimation of an experimental adsorption enthalpy because only simulations of the clay phase are necessary, using

$$\Delta H_{expt} = \Delta H_{3cav} + \Delta H_{i-clay} + \Delta H_{subl} - \Delta H_{dis}$$
[16]

Table 3 shows the results of applying algorithm 2 to the two nitroaromatic compounds for which we have measured the thermodynamics of adsorption to K-smectite (Li et al., 2004). Note that, while the predictions are not quantitative, they again have the proper sign and now have the advantage that the predicted adsorption enthalpy values themselves are larger than their standard deviations.

asured <sup>b</sup> xpt	± 1
Mea AHe	-18
Estimated ΔH <sub>expt</sub>	<b>-</b> 25 ± 16
ΔH <sub>dıs</sub> <sup>b</sup>	25
$\Delta H_{subl}{}^{a}$	94 ± 1
ΔH <sub>i-clay</sub>	-154 ± 16
$\Delta H_{3cav}$	+60
Compounds	p-NO <sub>2</sub>

**-**28 ± 4

-91 ± 17

53

 $107 \pm 1$ 

-235 ± 17

<del>1</del>60

TNB

61

 $38 \pm 11$ 

<del>1</del>60

p-xylene

Table 3. Application of algorithm 2 to estimate experimental adsorption enthalpies.

<sup>a</sup> (Chickos and Acree, 2002) <sup>b</sup> (Li et al., 2004)

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Thus, we conclude that the method for simulating adsorption enthalpies shows promise. For example, predictions for nitroaromatic compounds versus p-xylene are significantly different. Further work is needed that will attempt to isolate and minimize sources of uncertainty to find out how precise the enthalpy predictions can become.

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