TRIAZINE ADSORPTION BY SAPONITE AND BEIDELLITE CLAY MINERALS

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

Keywords—Adsorption Triazine Exchangeable cations Smectite

INTRODUCTION

Concern about the contamination of groundwaters and surface waters by pesticides has been growing steadily over the last 30 years, mainly because of the continuous use of such chemicals in agricultural production. A need exists to predict the fate and movement of pesticides and assess their risks in soil and subsurface environments more accurately. Sorption by soils/sediments is a major process that controls the transport, bioavailability, degradation, and ultimately, the fate of organic contaminants in the environment [1]. Sorption of organic chemicals diminishes their bioavailability to target organisms [2], controls chemical degradation [3,4], and reduces the leaching to groundwater [5].

Clay minerals and soil organic matter typically are the two most chemically active components interacting with organic chemicals that enter soils and sediments. Soil organic matter has been accepted as the primary sorptive domain for the uptake of hydrophobic organic compounds [6–11]. The contaminant transport models commonly 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 compete effectively 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 because of their high surface areas, moderate cation-exchange capacities (CECs), and surface reactivities [12]. 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 [13–15]. In a study of atrazine sorption by a series of Ca-smectite clays with CECs ranging from 79 to 134 cmol/kg, Laird et al. [16] reported that zero to nearly 100% of added atrazine was removed from water, with the extent of adsorption being correlated inversely with the clay CEC values. Sheng et al. [15] observed a similar relationship for sorption of atrazine by K-smectites. Sawhney and Singh [17] reported that atrazine adsorption by Al-smectite (\( >1 \) g/kg) was larger than that by Ca-smectite. Those 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\textsuperscript{3+} versus divalent Ca\textsuperscript{2+}. In the present study, we have avoided Al-smectites because of the difficulty in simultaneously maintaining a homo-ionic Al-smectite while preventing side reactions in which atrazine protonates and, consequently, adsorbs strongly by cation exchange.

Clays in whole soils also play a major role in adsorbing triazine pesticides [18,19]. Talbert and Fletchall [18] showed that atrazine sorption by soils was correlated positively with soil clay content as well as with soil organic matter content. Huang et al. [19] reported that the inorganic fractions of soils with a particle size of less than 20 \( \mu \)m have a significant capacity to retain atrazine. Several previous studies have attempted to identify the critical ratio of clay minerals to soil organic matter at which sorption by the mineral phase plays an important role [20–22]. Karickhoff [21] concluded that at a ratio of swelling clays to soil organic carbon of greater than 30, the mineral phase in whole soils contributed significantly to sorption of simazine. Grundl and Small [20] estimated that at a mass ratio of near 62 for clay to organic carbon, the mineral phase accounted for half the overall atrazine sorption.

Most studies of atrazine and simazine adsorption by smectites were conducted using smectites with negative charges originating from octahedral substitution [15,23,24]; few studies have used smectites with negative charges arising from tetrahedral sites. Also, investigations regarding 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 [25,26], resulting in differences in the clay interlayer environments that may influence pesticide sorption. Beidellite and saponite clays are smectites with negative charges originating largely from tetrahedral substitution. Therefore, the present study was initiated to examine the adsorption of three \( \sigma \)-triazine herbicides (atrazine, simazine, and metribuzin) by saponite and beidellite clays saturated with different cations (\( \text{K}^{+} \), \( \text{Na}^{+} \), \( \text{Cs}^{+} \), and \( \text{Ca}^{2+} \)) and to compare the results with those of previous studies on sorption by octahedrally substituted smectites. Potassium, \( \text{Na}^{+} \), and \( \text{Ca}^{2+} \) are common exchangeable cations in the soil environment, whereas \( \text{Cs}^{+} \) has a smaller hydrated radius relative to those of the other cations studied here and, 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 from Ballarat, California, USA (\( \text{SapCa}-2; \text{CEC}, 95 \text{ cmol/kg} \) [27]), and beidellite from Silver City, Idaho, USA (\( \text{SBId}-1; \text{CEC}, 129 \text{ cmol/kg} \) [28])—were obtained from the Clay Minerals Society Source Clay Repository (Department of Agronomy, Purdue University, West Lafayette, IN, USA). The clay particles less than 2 \( \mu \text{m} \) in size were separated by wet sedimentation and then exchanged with \( \text{K}^{+} \), \( \text{Na}^{+} \), \( \text{Cs}^{+} \), and \( \text{Ca}^{2+} \) to prepare homo-ionic clays. To do so, 25 g of clay were 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 repeated washing with Milli-Q\textsuperscript{®} (Millipore, Bedford, MA, USA) water until \( \text{Cl}^- \) was determined to be negative by reacting with \( \text{AgNO}_3 \) 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 Cs-smectites; 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 Chem Service (West Chester, PA, USA) with purities of greater than 99% and were used as received. The selected physical and chemical properties of the three pesticides, along with their chemical structures, are summarized in Table 1. Given the \( \text{pK}_a \) values of the herbicides and the high pH values of our clay suspensions, no possibility existed 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 \( \text{KCl} \), \( \text{NaCl} \), or \( \text{CsCl} \) or 0.005 M \( \text{CaCl}_2 \). The initial solutions were then added into glass centrifuge tubes containing clay (0.01–0.1 g) that was saturated with the same cation in the respective pesticide initial solution, and the tubes were closed with Teflon\textsuperscript{®}-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 to 80% of pesticide in the solution phase was sorbed by clay during the equilibration. The tubes were then shaken reciprocally overnight at 40 rpm at room temperature (23 ± 2°C); preliminary studies showed sorption was complete within this time. The tubes were then centrifuged at 2,110 \( \text{g} \) for 20 min to separate the liquid and solid phases. The concentration of herbicide in the supernatant was analyzed using reversed-phase, high-performance liquid chromatography (HPLC; Perkin-Elmer, Norwalk, CT, USA) set at the appropriate wavelength for maximum absorption by each pesticide (Table 1). A platinum extended polar selectivity 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 [29,30] in the absence of strong ultraviolet light. Because of the relatively high pH values in the clay slurries and the lack of information about possible smectite-catalyzed hydrolysis, however, we monitored the HPLC chromatograms for peaks indicative of triazine degradation products. None was ob-

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Table 1. Selected physicochemical properties of pesticides used in the sorption study

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Molecular weight</th>
<th>( \text{pK}_a )</th>
<th>Solubility in water (mg/L)</th>
<th>( \text{Log } K_{ow} )</th>
<th>( \lambda_{max} ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>215.69</td>
<td>1.70</td>
<td>33</td>
<td>2.61</td>
<td>220</td>
</tr>
<tr>
<td>Simazine</td>
<td>201.66</td>
<td>1.62</td>
<td>5</td>
<td>2.10</td>
<td>220.5</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>214.29</td>
<td>1.0</td>
<td>1050</td>
<td>1.60</td>
<td>280</td>
</tr>
</tbody>
</table>
served, and no significant differences were found 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 the amount remaining in the final equilibrated solution.

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 (~1–2 ml) remaining in the vial and then dropped onto glass slides and air-dried overnight at ambient conditions to obtain oriented clay films. The x-ray diffraction patterns were recorded using Cu-Kα radiation and a Philips Automated Powder Diffraction (APD) 3720 x-ray diffractometer (PANalytical, Almelo, The Netherlands) fitted with an APD 3521 goniometer and a θ-compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator. Diffraction patterns were recorded from 5.5 to 16.0 °2θ at a step of 0.005 °2θ with 4 s/step. The x-ray diffraction patterns were rerecorded 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 to explore possible interaction mechanisms 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 (i.e., nonquantum) mechanical energy functions comprising a force field. The model for K-saponite had the composition K9(Si87Al9)Mg72O240(OH)48, with a CEC of 95 cmol/kg. The simulation of a unit cell and Al-for-Si substitutions were random, except that no two Al tetrahedra were allowed to be immediate neighbors. One molecule of atrazine was added to the unit cell, with the atrazine molecular plane being perpendicular to the basal planes of the clay. The simulated loading rate was equivalent to 23 mg atrazine/g clay. Water molecules also were added (in random interlayer positions) so that constant-pressure simulations resulted in approximately 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 [31] combined with the polymer consistent force field [32,33] for the organics and water. As a further modification, charges on the organic solute were assigned using the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field [34], which optimized organic atomic charges for condensed phase systems. In previous work [35,36], we have found COMPASS charges to reproduce more faithfully the quantum mechanical charges for nitrogenous organic molecules than the polymer consistent force field 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. Commercial software [33] 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 constant number of atoms, pressure, and temperature (NPT) ensemble for 75 ps, which is much longer than the time required for the system volume and energy to equilibrate.

RESULTS AND DISCUSSION

Pesticide sorption isotherms are shown in Figure 2. The greatest sorption of atrazine was observed for Cs-saturated saponite, followed in decreasing order by K-, Na-, and Ca-saturated saponite (Fig. 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, to our knowledge, for any inorganic material. The higher effectiveness of Cs-SapCa-2 in sorption may be caused by the lower hydration energy of Cs+ and, hence, the smaller hydrated radius of Cs+ compared to that of the other cations. The water molecules associated with exchangeable Ca2+, for example, obscure a larger fraction of the clay surface than do those associated with Cs+, resulting in the reduction in the size of adsorptive domains for Ca2+ compared to Cs+. Typical estimates of hydrated radii are 9.6 Å for Ca2+ and 3.6 Å for Cs+ [37]. Thus, the cross-sectional area of hydrated Ca2+ is approximately 290 Å2, which is more than sevenfold that of Cs+ (40 Å2); therefore, one hydrated Ca2+ takes up 3.5-fold as much room as do the two Cs+ ions in the 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 whereas on Ca-, K-, and Na-smectites, the triazines must compete with more strongly bound water within the hydrated radii of cations. Sheng et al. [15,36] also observed similar effects of exchangeable cations on the size of sorptive domains of smectite clays in pesticide sorption.

Differences in the swelling behavior between Cs- and Ca-SapCa-2 also affect the degree of pesticide adsorption. The relatively weak hydration of Cs+ causes Cs-saponite to swell less in water, which again provides a more favorable sorption domain and allows the organic compound to compete better
with waters for interlayer sites. The Cs-smectites maintain approximately 12.3 Å basal spacings (monolayer of hydration) at 100% humidity (data not shown) and even in aqueous suspension [38,39]. The Ca-smectites, on the other hand, swell to more than 15 Å basal spacings. The thickness of the ring of an atrazine molecule is approximately 3.0 Å [36]. This would imply the lowest limit of the basal spacing for atrazine intercalation to be approximately 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 [15]. 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
and Singh [17]; \[15\]); interactions between clay surfaces and pesticides. The lower-neutral clay siloxane surface, thereby reducing hydrophobic (e.g., Ca\(^{2+}\)) clay CEC increases. The present study (along with previous with the observation that adsorption of atrazine decreases as arising primarily from octahedral substitution. Data for atrazine sorption by K-SAz-1 were reported by Sheng et al. [15], and the atrazine sorbed by these two K\(^{2+}\)-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. Because 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 [25,26], resulting in more ordered distribution of exchangeable cations on mineral surfaces [42]. These exchangeable cations (at a given hydration state) can always approach the tetrahedrally substituted sites more closely, hence demonstrating a stronger attraction compared with that of octahedrally substituted sites [43]. As a result, SBId-1 clay has a smaller clay layer spacing, which favors atrazine adsorption in clay interlayer environments [44]. 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 the clay layer-charge increases, the higher-charged K-SBId-1 sorbs slightly more atrazine than the K-SapCa-2 does. Indeed, sorption by K-SBId-1 is equivalent to that of Cs-SBId-1, whereas sorption by K-SapCa-2 is much less than 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 approximately 12.5 Å \(d_{001}\)-spacings. It is well-known [45] that removal of K\(^{+}\) from an illite clay results in a tetrahedrally substituted clay mineral resembling a high-charge beidellite, whereas 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 [46]. Whereas true smectites like K-beidellite should not dehydrate completely and fix K\(^{+}\) [46], 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-1 should be more likely to retain \(d_{001}\)-spacings near 12.5 Å when fully hydrated and, thus, be relatively favorable for hydro-

![Fig. 3. Comparison of the present sorption results with those of all earlier studies of atrazine sorption to saponites as well as two representative montmorillonites.](Image 42x563 to 282x738)

- K-SapCa-1 (Sheng et al. [15]); \(\ast\) = Ca-sapone (Laird et al. [16]); \(\ast\) = Ca-montmorillonite (Sawhney and Singh [17]); \(\ast\) = Ca-montmorillonite (Cels et al. [40]).
phobic interactions. Testing of these hypotheses would involve measuring $d_{001}$-spacings of these smectites in aqueous suspension [44], 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 that interlayers of the K-beidellite almost completely dehydrate whereas 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 that for atrazine (i.e., Cs-saturated > K-saturated > Ca-saturated > Na-saturated clay), but the magnitude of metribuzin sorption was smaller than that of atrazine sorption by both clays (Fig. 2c and d). This could be a result of the higher solubility of metribuzin (1.050 mg/L) compared to that of atrazine (33 mg/L), because we hypothesize [35] that hydrophobic effects contribute to sorption of neutral organic solutes by smectite clays. Sorption of metribuzin by saponite clay was two- to fivefold (Fig. 2c) that by beidellite (Fig. 2d) at a given metribuzin concentration, which again may be a result of the comparably lower CEC of saponite as discussed above.

The sorption of simazine by these two clays manifested similar results. The Cs-SapCa-2 adsorbed appreciably higher simazine than did K-, Ca-, and Na-SapCa-2 (Fig. 2e), and beidellite sorbed considerably less simazine than did 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') usually demonstrates a greater sorption capacity. Simation 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 = 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 (Fig. 2). For K-saponite at 1.3 ppm of 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 of 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 remove, in part, the hydrophobic solute from water [35]. Interlayers that perform this role most effectively, such as Cs-saponite, then should be the strongest clay mineral sorbent phases.

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 of atrazine loading from 12.1 Å for the atrazine-free clay (Fig. 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 $d_{001}$-spacings (~12.5 Å) as the atrazine loading increases. This is consistent with our previous observations of intercalated aromatic compounds [14], in which the $d_{001}$-spacings of air-dried K-smectite clay films increase slowly toward approximately 12.5 Å as the aromatic compound loading increases from zero to 200 μmol/g clay. Here, the maximum atrazine loading rate is approximately 65 μmol/g clay (Fig. 4), so the sorption is rather small to have a major impact on the $d_{001}$-spacing [14]. The systematically increasing $d_{001}$-spacings, however, 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 the clay interlayer was not sufficient to cause the swelling of clay basal spacing. Li et al. [14] also reported that at a low amount of organic solute loadings, the clay interlayer did not show the expansion.

The molecular dynamics 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, rather, 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 (Fig. 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 [47]: He proposed that the lone pair of electrons on the ring N atom of atrazine interact with water molecules solvating exchangeable cations associated with smectite surfaces; such complexes were, indeed, observed in our simulations (Fig. 5). At the same time, the alkyl-side chains of atrazine molecules were hypothesized [47] to outcompete water molecules for retention on hydrophobic microsites on smectite surfaces. Again, this behavior is observed in the simulations (Fig. 5). Such hydrophobic bonding is 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. On surfaces with low-surface-charge density, the water molecules at the clay surface are less strongly bound and considered to have a less ordered structure [23]. Sparingly water-soluble organic compounds (e.g., atrazine [water solubility, 30 mg/L]) are more likely to approach and adsorb to surfaces that sorb water less strongly. A lower surface-charge density also means that less exchangeable cations are competing for adsorption domains in the interlayer region [36].

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 -NO₂, -C=O, or -C≡N demonstrate a strong affinity with K- and Cs-smectites [35, 36, 48] because of pesticide–cation complexation. The present results, however, indicate that even less polar compounds (e.g., atrazine) can be adsorbed strongly by Cs-saponite because of the optimal clay interlayer structures (i.e., maintaining approximately 12.5 Å basal spacing and nonoverlapping radii of hydration for Cs⁺).

Thus, Cs-saponite interlayers contain the largest proportion of relatively hydrophobic sites, in which we hypothesize that atrazines can be at least partially dehydrated, and our present 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 that of smectites with octahedral substitution, presumably because tetrahedrally substituted smectites swell less in water and, thereby, contain narrower slit pores that favor hydrophobic sorption. If the clay layer charge is large, however, then adsorption of triazine herbicides by even tetrahedrally substituted smectites can be reduced sharply, 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⁺-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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Triazine sorption by smectite clays


