

SORPTION OF ATRAZINE BY Al- AND Ca-SATURATED SMECTITE

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Abstract—Because of the large surface area and common occurrence of smectites in the clay fractions, they are important in sorption/desorption reactions of organic pollutants entering soils and sediments. Results of sorption and desorption of atrazine by Al- and Ca-saturated smectite reported here showed that Al-saturated smectite sorbed much higher amounts of atrazine than Ca-saturated smectite. Al-saturated smectite sorbed 3820 mg kg⁻¹ as compared to 1902 mg kg⁻¹ by the Ca-saturated smectite during 5 consecutive sorptions from 10 ppm atrazine solution. Sorption isotherms over 2–10 ppm atrazine concentration range were nonlinear in all cases. Freundlich coefficients, K_f , obtained from the sorption isotherms were much higher for Al- than Ca-saturated smectite; K_f varied from 405 to 3035 for Al-saturated and 100 to 306 for Ca-saturated. The pH values of Al- and Ca-saturated smectites were 3–4 units higher than the pK_a (1.68) of atrazine, which suggests that atrazine was sorbed as neutral molecules. Stronger H-bonding between the more polarized H₂O associated with the trivalent Al ion than the divalent Ca ion is likely responsible for the greater sorption by Al-smectite.

Key Words—Cation-Polarization, Nonionic Organics, Smectite, Surface-Hydrophobicity.

INTRODUCTION

Sorption/desorption reactions largely determine the fate and transport of organic chemicals that enter soils and sediments from industrial and agricultural operations. Because of the large surface area and common occurrence of smectites, they are important in controlling surface reactions of organic chemicals in these systems. Increasing concern with movement of these contaminants to groundwater has led to numerous investigations into their reactions and transport in soils, sediments and clay liners (Karickhoff 1980; Chiou et al. 1983; Hayes and Mingelgrin 1991; Boyd and Jaynes 1994; Pignatello and Xing 1996; Sawhney 1996). Sorption of nonionic organic compounds by soils and sediments are generally considered to be related to the organic matter contents of these sorbents. In low organic matter soils and sediments, however, clay minerals likely control the sorption/desorption interactions (Mingelgrin and Gerstl 1983; Hayes and Mingelgrin 1991). Investigations into sorption of organic contaminants of a wide range of hydrophobicities (Rebhun et al. 1992) by clays and clay-humic complexes showed that adsorption constants for humic (organic) fraction was 8 to 20 times higher than the pure clay minerals. However, in soils with the commonly encountered range of organic matter (0.5–5%) and high clay content, the contribution of the mineral fraction appeared to exceed that of the organic component.

Sorption of organic chemicals by clays decreases with increasing relative humidity (RH), and is markedly reduced in aqueous systems (Call 1957; Chiou and Shoup 1985; Thibaud et al. 1993). Decreased sorption is considered to be due to strong competition by the water molecules for the clay surfaces (Burchill

et al. 1981). Despite this competition, fairly large amounts of nonionic organic compounds are sorbed by clays at high RH and from aqueous solutions. For example, Farrell and Reinhard (1994) observed that, at 100% RH, montmorillonite SWY-1 sorbed as much as 10⁻⁵ mol g⁻¹ (1300 ppm) of various hydrocarbons. Similarly, sorption of varying amounts of di- and trichlorobenzenes by kaolinite (Schwarzenbach and Westall 1981) and montmorillonite (Rebhun et al. 1992) and of atrazine by smectites (Laird et al. 1992) in aqueous suspensions have been observed. Adsorption of the nonionic organic compounds is generally attributed to hydrophobic interactions on siloxane surfaces (Chen 1976) on basal planes of the phyllosilicates. These surfaces possess an electrostatic potential, which is equal to the sum of a short-range potential due to atoms in the charge-neutral layer, as in talc and pyrophyllite, and a long-range potential due to isomorphous substitution, as in smectite (Bleam 1990). Hydration of the interlayer exchange cations balancing the negative charge arising from isomorphous substitution imparts hydrophilicity to the siloxane surfaces at (or near) the negative charge sites. Consequently, the greater the isomorphous substitution or the layer charge of the silicate mineral, the more hydrophilic the surfaces, and vice versa. Several investigations on sorptions of nonionic organic molecules support this contention. For example, Laird et al. (1992) found that sorption of a nonionic organic pesticide, atrazine, increased with decreasing layer charge in smectites. Similarly, Jaynes and Boyd (1991) observed that increasing the hydrophobicity (decreasing the Lewis base strength, Norris et al. 1992) by replacing the hydrated inorganic exchange cations by small organic cations, or by reducing the layer charge by the well-

known Li-treatment, increased sorption of benzene and alkylbenzenes. Recently, Cox et al. (1995) also observed increased sorption of a nonionic herbicide, Thiazfluron, with decreasing layer charge in smectites.

Besides the total amount of layer charge, origin of the charge and type of the exchange cation balancing the charge also influence the sorption reactions on clay surfaces. Negative charge originating from substitution in the tetrahedral sheet resides on 3 basal oxygens, whereas charge from octahedral substitution is distributed on 10 oxygens (Farmer 1978). Localization of the tetrahedral charge and its closer proximity to exchange cations produce greater basicity of basal oxygens (Sposito 1984), resulting in stronger H-bonds between interlayer water and surface oxygens (McBride 1991). Greater basicity of smectites with tetrahedral than with octahedral charge has been illustrated by the greater reactivity of the former in protonating weak bases sorbed onto clay surfaces (Swoboda and Kunze 1968). The importance of the nature of the exchange cation (M) lies in its effect on the covalency of the M–O bond and repulsion of its solvating water proton: the higher the valence or ionic potential of the cation, the greater the proton repulsion. When the acidity of the solvated exchange cation is near or below the pK_a of the sorptive molecule, sorption of the protonated species occurs. Examples of the sorption of protonated species of NH_3 (Mortland et al. 1963; Mortland 1970), pyridine (Zachara et al. 1990) quinoline (Ainsworth et al. 1987; Traina and Onken 1991) and atrazine (Yamane and Green 1972) and others are not uncommon in the literature.

However, little protonation of an adsorptive species can be expected at pH values 2 units above the pK_a of the adsorbate (Hayes and Mingelgrin 1991). Atrazine with pK_a of 1.68 should therefore be sorbed primarily as neutral molecules by homoionic Al- and Ca-smectite with much higher pH values than the atrazine pK_a . And because the atrazine molecule contains electron donors, N and Cl, sorption of atrazine on clay surfaces can occur through H-bonding of these groups with the solvating water proton of the exchange cation. Thus, greater polarization of water solvating trivalent Al than divalent Ca as the exchange cation should result in greater sorption of atrazine by the Al-saturated smectite than by the Ca-saturated smectite.

In the present investigation, the effects of exchangeable cations Al^{3+} and Ca^{2+} on sorption of a nonionic organic chemical atrazine, a common soil pesticide, by Wyoming bentonite were determined and discussed in terms of cation solvation–water polarization and surface hydrophobicity. The cations Al and Ca were chosen because they are, respectively, the predominant exchangeable cations in the unlimed and limed soils of the temperate regions.

MATERIALS AND METHODS

Smectite clay used in this investigation came from Clay Spur, Wyoming, and was supplied by the Baroid Division of National Lead Corporation. The $<2 \mu m$ size fraction of the clay separated by sedimentation was saturated with Al or Ca ions by 5 centrifuge washings with 1 M chloride solution of the respective cation. Excess electrolyte was then removed by distilled water washings until the supernatant was free of chloride ions, as tested by $AgNO_3$ solution. The monocationic clays thus prepared were freeze-dried. The cation exchange capacity of the smectite clay was 85 meq/100 g (Singh and Kodama 1988) and the surface area of smectite from same source was determined to be $744 m^2 g^{-1}$ (Laird et al. 1992).

Sorption of atrazine by smectite was carried out using batch-equilibration technique. Five-milligram samples of the mono-cationic clays were suspended in 5-mL portions of $4.73 \times 10^{-5} M$, $2.42 \times 10^{-5} M$ and $0.97 \times 10^{-5} M$ aqueous solutions of atrazine in glass centrifuge tubes with Teflon-lined screw caps. After 24 h, the suspensions were centrifuged at $5000 \times g$ for 20 min. Atrazine in the supernatant solution was analyzed using a high-performance liquid chromatography (HPLC) Varian Star 9050 system equipped with a UV-vis variable wavelength detector that was set at 220 nm. A 60:40 methanol:water mixture was used for atrazine elution. Atrazine sorbed was calculated from the difference between the amount of atrazine added and that remaining in solution following the reaction time. The centrifugate was resuspended in the respective atrazine solutions and the sorption process repeated 5 times to estimate sequential sorption, taking into account during each sorption the volume and concentration of atrazine solution occluded in the centrifugate.

RESULTS AND DISCUSSION

Figure 1 shows the amounts of atrazine sorbed by Al- and Ca-saturated smectites and the amounts remaining in solution following 24-h interaction in 2 consecutive sorptions, from the 3 solutions containing $0.98 \times 10^{-5} M$, $2.42 \times 10^{-5} M$ and $4.73 \times 10^{-5} M$ atrazine. Complete sorption of atrazine by Al-saturated clay occurred at the lowest concentration during the 1st sorption. The sorption isotherms show that the Al-saturated clay sorbed much higher amounts of atrazine than the Ca-saturated clay at all concentrations during both the 1st (compare Al-1 with Ca-1) and the 2nd sorption sequence (compare Al-2 with Ca-2). During the subsequent 3 successive sorptions also, the Al-clay sorbed more atrazine than the Ca-clay.

The pH values of Al- and Ca-saturated smectite suspensions were 4.95 and 5.90, respectively, which are 3 to 4 units higher than the pK_a (1.68) of atrazine. Consequently, atrazine is considered to be sorbed mainly as

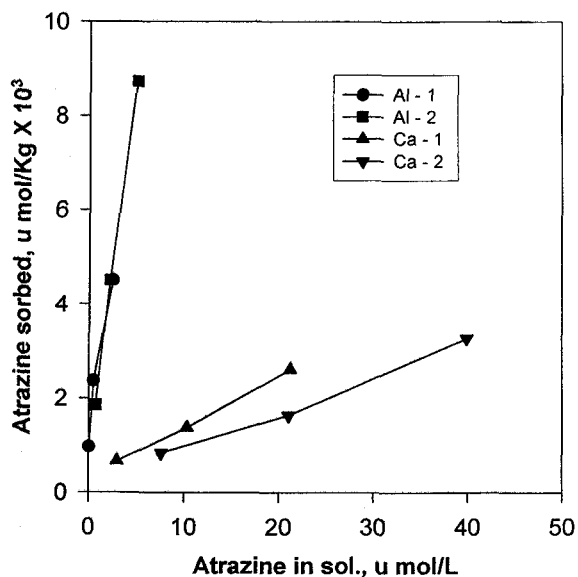


Figure 1. Sorption of atrazine by Al- and Ca-saturated smectite; 1 and 2 represent successive sorptions.

neutral molecules. Complete reversibility of atrazine sorption by a number of Ca-saturated smectites at pH ranging from 4.75 to 6.45 (Laird et al. 1992) support the above inference. Reversible sorption of atrazine by Na- and Ca-saturated montmorillonite, kaolinite and illite clay slurries at pH 5.1 has also been observed by Gilchrist et al. (1993). The absence of any dealkylated or hydrolyzed atrazine species even after the 127-d reaction period (Gilchrist et al. 1993) further corroborates the conclusion that atrazine is sorbed as neutral molecules by the homoionic smectite samples used here. A portion of the sorbed atrazine, however, was only slowly reversible, as has been observed for several organic compounds (Sawhney and Gent 1990; Aochi et al. 1992; Farrell and Reinhard 1994).

The amounts of atrazine sorbed by the Al-saturated clay in 5 successive sorptions from solutions at the 3 concentrations are shown in Figure 2. The amounts sorbed continue to increase following each successive addition, indicating that not all sorption sites are occupied even at the highest concentration. Successive atrazine sorptions by the Ca-saturated clay showed similar behavior during the 3 successive sorptions after which the amounts sorbed appeared to level off. The amounts of atrazine sorbed by the Al-saturated clay were greater than the Ca-clay and were 4 to 6 times higher after 5 successive sorptions from solutions of different concentrations.

Sorption on solid surfaces is generally modeled using the Freundlich equation:

$$S = K_f C^N \quad [1]$$

where S and C are the solid-phase and liquid-phase concentrations, respectively, K_f is the Freundlich co-

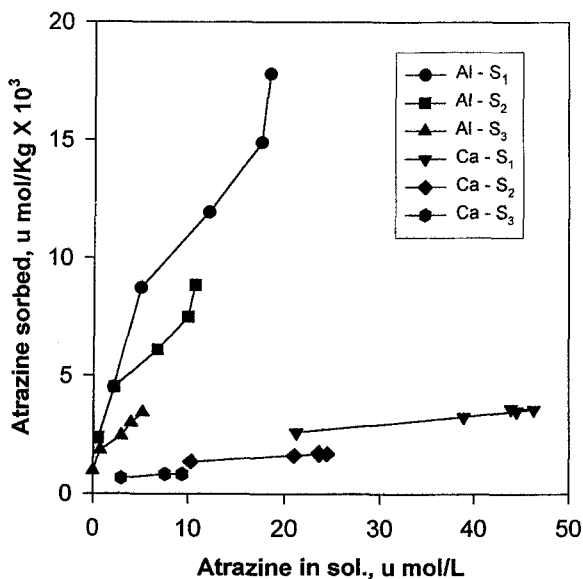


Figure 2. Atrazine sorption by Al- and Ca-saturated smectite in 5 successive sorptions from the 3 solutions: S_1 , $4.73 \times 10^{-5} M$; S_2 , $2.42 \times 10^{-5} M$ and S_3 , $0.97 \times 10^{-5} M$.

efficient and N is an empirical constant to evaluate dependence of S on C . The data obtained for atrazine sorption at the 3 concentrations by the Al- and Ca-saturated smectites were analyzed for their sorption affinity and isotherm linearity using the Freundlich equation, which assumes equilibrium conditions. The values of K_f and N thus calculated are given in Table 1. The K_f values appear to decrease with increasing occupancy of the sorption sites in both clays. However, they remain much higher for the Al-clay than for the Ca-clay. Also, the values of N deviate from unity in all cases. Variations in K_f with successive sorptions observed here clearly demonstrate that the use of equilibrium constant approach to describe short-term sorption should be made with caution.

The relative affinity of an organic compound for clay surfaces can be assessed by determining the dis-

Table 1. Freundlich parameters, K_f and N , for successive sorptions of atrazine by Al- and Ca-saturated smectite clays.

Sorption no.†	K_f	N
	Al-Clay	
1	3035	0.79
2	2430	0.79
3	731	1.12
4	667	1.10
5	405	1.30
	Ca-Clay	
1	306	0.68
2	154	0.82
3	100	0.92

† Successive sorptions.

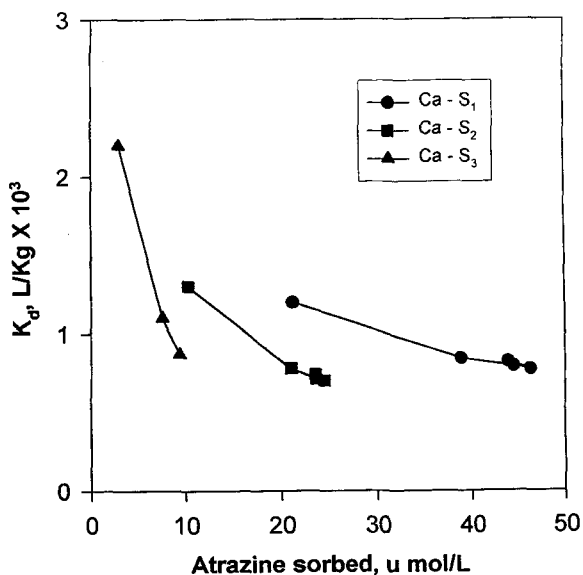
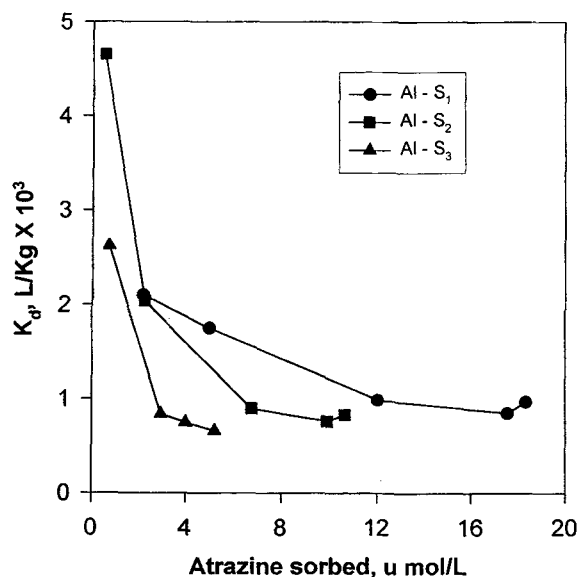


Figure 3. a) Distribution coefficients (K_d) for atrazine sorption by Al-smectite for 5 successive sorptions at 3 concentrations listed in Figure 2 and b) same for atrazine sorption by Ca-smectite.

tribution coefficient, K_d , defined simply as the ratio of its concentration in the solid phase to that in the liquid phase. The approach is empirical and has the advantage that no equilibrium is assumed. Distribution coefficients determined from the 5 successive sorptions from the 3 atrazine solutions giving 15 K_d estimates for each clay are shown, as a function of the solution concentrations, in Figure 3. The distribution coefficients for both Al- and Ca-saturated smectites varied over a wide range, increasing with decreasing solute concentration. In Al-saturated clay, K_d varied over almost an order of magnitude, whereas in Ca-

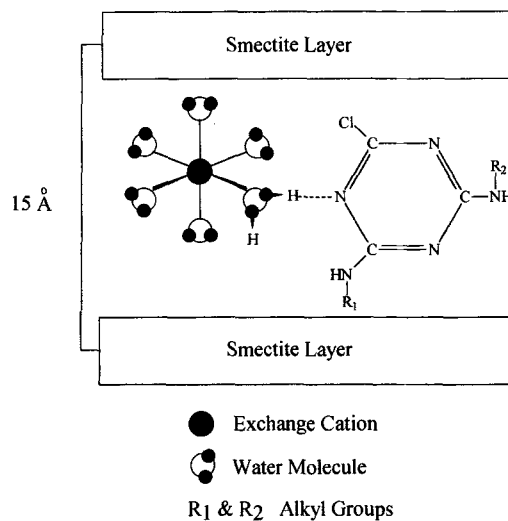


Figure 4. Schematic illustration of H-bonding and hydrophobic interaction between atrazine molecule and smectite interlayer surface.

saturated clay, K_d varied over a 3-fold range only. Furthermore, values of K_d for the Al-clay were much higher than Ca-clay. In both clays, K_d decreased on successive sorptions and tended to level off eventually. Different values of distribution coefficient for atrazine sorption by monocationic clays at different degrees of sorption site occupancy have also been reported by Gilchrist et al. (1993).

Apparently, the greater sorption of atrazine by Al- than by Ca-saturated smectite results from stronger H-bonding between more polarized H_2O associated with trivalent Al than divalent Ca. Although no spectroscopic analysis to establish H-bonding was done in this investigation, recent nuclear magnetic resonance (NMR) investigations by Ukrainczyk and Smith (1996) strongly support the H-bonding mechanism for sorption of nonionic organic compounds by smectite. In a detailed solid state ^{15}N NMR study of pyridine adsorption by homoionic K-, Ca-, Mg- and Al-hectorite, these authors showed that pyridine interacted primarily through H-bonding to the interlayer H_2O solvating the exchange cation. Furthermore, the greater the polarity of hydration water of the exchange cation, the stronger was the H-bonding. Mobility of the sorbed pyridine, thus, decreased in the order $K^- > Ca^- > Mg^- > Al^-$ -saturated hectorite. H-bonding between exchange-cation solvating water and nonionic dichloroethylene (DCE) molecules has been also inferred in infrared (IR) analysis of DCE sorption by hectorite (Siantar et al. 1994). It is suggested, therefore, that the sorption of a nonionic organic molecule, as atrazine, occurs mainly by H-bonding.

H-bonding between the atrazine molecule and the hydrated exchange cation, Ca, is illustrated in Figure 4. The H-bonding likely occurs at the more electro-

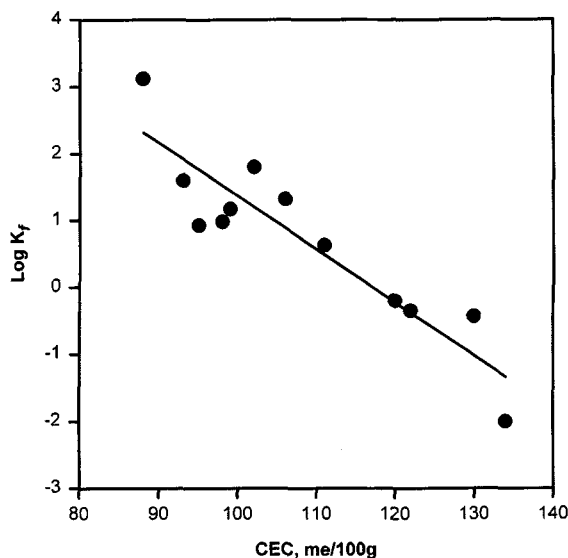


Figure 5. Relationship between logarithm of the Freundlich constant for atrazine sorption and CEC of smectite clays (adapted from Laird et al. 1992).

negative N rather than at the less electronegative Cl atom in the atrazine molecule. The side chain amino groups are even less electronegative because of delocalization of their lone-pair electrons into the atrazine ring (Welhouse and Bleam 1992). Thus, H-bonding at NH groups with the exchange-cation solvating water is unlikely.

While H-bonding appears to be a major mechanism of atrazine sorption on smectite surfaces, the increased sorption of atrazine with decreasing layer charge of smectites (Figure 5) suggests that hydrophobic interactions also occur with the low charge density surfaces. Laird et al. (1992) attributed the increased atrazine sorption with decreasing layer charge to more favorable competition with water for sorption on low charge density siloxane surfaces. Possible orientation of the atrazine molecules on the siloxane surface was not addressed, however. In IR analysis of the sorption of the herbicide Thiazfluron by layer silicates, Cox et al. (1995) observed a shift in the NH-stretching bond in the adsorption spectra to a higher frequency. They attributed the shift to the formation of H-bonds between the NH of amide group in Thiazfluron and the oxygens of the siloxane surfaces in layer silicates, as smectite. While such interactions in atrazine sorption have not been determined, it has been suggested that compounds with electron withdrawing substituents can sorb onto siloxane surfaces where π system of the aromatic compound acts as an electron acceptor and the oxygens of the surface as electron donors (Mortland 1970; Haderlein and Schwarzenbach 1993).

Increased atrazine sorption with decreasing layer charge (increasing hydrophobicity), and appreciable

sorption by high layer charge (strong surface hydration) smectites (Laird et al. 1992) led Laird (1996) to suggest that atrazine sorption involves both hydrophobic sorption and H-bonding. Occurrence of both hydrophobic and hydrophilic sorption sites on siloxane surfaces can be explained as follows. Localization of the negative layer charge originating from isomorphous substitution (Bailey 1966; Sposito 1984; McBride 1991), and thus of interlayer exchange cations, produces hydrophilic centers where H-bonding of atrazine can occur. The distal siloxane surfaces away from the negative charge influence provide hydrophobic sorption sites (Bleam 1990). Thus, low-charge smectite where charges are farther apart would have more hydrophobic sites. Calculations based on the assumption that the radius of hydrophilic region around a unit charge is about 0.5 nm (Laird 1996), show that nearly 50% of the siloxane surface of the smectite ($SCD = 1.15 \mu\text{mol}_c \text{ m}^{-2}$) used here is hydrophobic. The relative effect of the hydrophobic surface on atrazine sorption in this investigation is not known. However, the contribution of hydrophobic sorption should be similar in the Al- and Ca-saturated samples. The effect on atrazine sorption, if any, of the greater interlayer sorption surface for Al- than Ca-smectite, because of $\frac{2}{3}$ as many Al as Ca ions in the interlayers, should be small. We therefore conclude that a major factor in greater sorption of atrazine by the Al- than Ca-saturated smectite is the stronger H-bonding between the more polarized hydration water associated with the interlayer Al ion.

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