

Atrazine Interactions with Clay Minerals: Kinetics and Equilibria of Sorption†

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A novel technique using on-line microfiltration and HPLC analysis has been used to study sorption kinetics and sorption equilibrium of the herbicide atrazine with the clay minerals montmorillonite, kaolinite, and illite and the clay fraction of a soil. Fast and slow labile sorption have been observed for atrazine along with a reversible but kinetically slow sorption/desorption process that is consistent with diffusion of pesticide into the interior of the clay particles. Labile sorption capacity, mole fraction site coverage, labile sorption equilibrium function, and distribution coefficient were determined for the clay minerals in aqueous slurries with atrazine. The identification and quantitative descriptions of key chemical species avoid some of the commonly reported hysteresis problems. Distribution coefficients are derived from the equilibrium constants so that comparisons may be made with the results of other workers.

INTRODUCTION

Most agricultural soils are mixtures of different materials: organic matter, microbial biomass, and inorganic crystalline and noncrystalline compounds. Particle size of mineral grains varies from colloidal dimensions to pebbles. Soil-pesticide interactions may be better understood if the interactions of the soil components including organic matter, clay, and other minerals with the pesticide are better understood. Clay minerals, having small particle size and hence large surface area per unit weight, are important in the overall sorption behavior of clay soils and sediments. Large surface areas are important for sorption of pesticides (Karickhoff, 1984), but it is likely that sorption occurs most strongly at chemically or crystallographically specific sites (Karickhoff and Brown, 1978; Terce, 1983; Glass, 1987; Borggaard and Streibig, 1988; Breen, 1991; Morillo et al., 1991; Laird et al., 1992). Sites with high charge density demonstrate electrostatic attraction for ionic pesticides (Karickhoff and Brown, 1978; Glass, 1987; Morillo et al., 1991), and acidic sites can protonate nonionic pesticides at pH near the pK_a of the pesticide (Terce, 1983; Borggaard and Streibig, 1988; Breen, 1991).

Of growing concern are the effects of agricultural wastes on water quality. In Canada, the fate of pesticides used in southern Ontario, where intensive agricultural activity occurs, is an important factor affecting water quality in the Great Lakes region. In this region, micas such as illite are the most dominant mineral in the clay fraction of soils accompanied by lesser amounts of vermiculite, smectite, and chlorite. The majority of the surface soils of the region contain 25–38% clay and 32–48% sand (Kodama et al., 1992). Therefore, the clay fraction is a significant portion of the soil and undoubtedly has an important impact on interactions of these soils with pesticides.

Evidence exists that pesticides and other hydrophobic organic compounds that affect water quality interact more strongly with the clay minerals and the clay fraction of soils than with the remaining large soil particles. Richardson and Epstein (1971) have shown that DDT and methoxychlor tend to concentrate in the finer particle size

fractions of soils, whereas the more soluble endosulfan prefers coarser material. Karickhoff and Brown (1978) reported that in natural sediments, where the coarse clay fraction accounted for less than 1% of the sediment mass, it contained 50–60% of the sorbed pesticide, whereas the sand fraction, which may have accounted for as much as 99% of the sediment mass, always contained less than 10% of the sorbed pesticide. Karickhoff (1984) has noted that in nature clay mineral surfaces will most likely have organic slime, microbial biomass, humic substances, or polymeric oxide and hydroxide coverings but the sorption of hydrophobic organic chemicals is most strongly influenced by surface area. Karickhoff et al. (1979) have shown that different amounts of organic carbon (OC) are correlated with the different sediment size fractions and may be responsible for the different sorption behaviors of the size fractions. Means et al. (1982) have shown that the pesticide sorption is proportional to % OC and where % OC is low, the amount of clay, specifically montmorillonite, becomes more important in determining pesticide sorption.

The sorption behavior of specific clay minerals has been studied by several workers (Karickhoff and Brown, 1978; Terce and Calvet, 1978; Terce, 1983; Glass, 1987; Borggaard and Streibig, 1988; Singh et al., 1989; Breen, 1991; Morillo et al., 1991; Laird et al., 1992). Terce and Calvet (1978) have examined pesticide sorption to montmorillonite, illite, and kaolinite and correlated the amount of pesticide sorbed to the surface area and the cation-exchange capacity (CEC) per unit mass of the clay. Montmorillonite had the highest surface area and CEC per unit mass and thus the highest sorption of pesticides. Much of the surface area of montmorillonite is in the interior of the clay mineral particles—sites that do not exist in kaolinite. Glass (1987) has reported that glyphosate is preferentially adsorbed by clay minerals in the order montmorillonite > illite > kaolinite. Glass (1987) has also reported that glyphosate adsorption on montmorillonite decreases with the montmorillonite saturated cations in the sequence $Fe^{3+} > Cu^{2+} > Mg^{2+} > Ca^{2+} > Na^+$. Singh et al. (1989) have shown that the % OC, CEC, surface area, and amount of pesticide sorbed increased with increasing amount of clay, while the highest amount of sorbed pesticide occurred in a soil containing smectite and kaolinite. Laird et al. (1992) have shown that the sorption of atrazine on smectites decreases

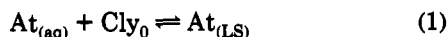
† CLBRR Contribution 92-151.

with increasing surface charge density. Laird et al. (1992) suggest that atrazine is primarily adsorbed by smectites as a neutral species.

Some sorption phenomena have not yet been fully explained. Two outstanding problems are the characterization of the sorption capacity of clay particles for labile and reversible but kinetically slow species (Gamble and Khan, 1990; Gamble and Ismaily, 1992) and the characterization of the formation of bound residues of pesticides in clays and soils (Talbert and Fletchall, 1965; Khan, 1973; Mill, 1980; Paris, 1980; Karickhoff, 1980; Freeman and Cheung, 1981; Di Toro and Horzempa, 1982; Macalady and Wolfe, 1984; Karickhoff and Morris, 1985). The objective of this work was to study the sorption kinetics and the sorption equilibrium for the labile and the reversible but kinetically slow processes that occur between atrazine and clay minerals.

THEORY

I. Labile Surface Sorption. When pesticide is mixed with soil, it reacts with active sites that are available on the surfaces of the soil particles. The reactivities of different active sites toward pesticide molecules are different. Some are very reactive so that they can hold pesticide molecules strongly, while others are not reactive enough to hold them tightly. Upon extraction with water or an organic solvent, the loosely bound pesticide molecules will desorb. The remaining amount is not quickly extractable and contributes to the apparent "bound residue" phenomenon. This type of sorption will be discussed in more detail later on. Different soils have different labile surface sorption capacities for a given pesticide, depending on soil constituents such as clay minerals and organic matter. Gamble and co-workers (Gamble and Khan, 1990; Gamble and Ismaily, 1992; Gamble and Khan, 1992) have applied chemical stoichiometry to differentiate labile surface sorption and apparently bound residues. The chemical equation used to describe the labile surface sorption on clay is



where $\text{At}_{(\text{aq})}$ represents solution-phase atrazine, Cly_0 represents unoccupied active sites on clay, and $\text{At}_{(\text{LS})}$ represents surface labile atrazine. Before we proceed further, the labile surface sorption capacity has to be defined. In keeping with our work (Gamble and Khan, 1990, 1992), the labile surface sorption capacity is defined as the number of moles of pesticide that is reversibly sorbed by a gram of soil, measured at the saturation limit, and is given by the material balance equation

$$\theta_c = \theta_{\text{At}} + \theta_0 \quad (2)$$

in which θ_c is the labile surface sorption capacity in moles per gram of the soil and θ_{At} and θ_0 indicate occupied and unoccupied active sites, respectively, in the same units. The values of θ_c and θ_{At} can be determined experimentally, and therefore θ_0 can be readily calculated. When an equilibrium has been established in an aqueous slurry of soil particles, the law of mass action may be applied to eq 1 to give the weighted average equilibrium constant, \bar{K}_1 (Gamble and Langford, 1988).

$$\bar{K}_1 = \theta_{\text{At}}/M_{\text{At}}\theta_0 \quad (3)$$

The weighted average equilibrium constant is required here because pesticide molecules are sorbed to a heterogeneous collection of active sites.

The distribution coefficient, K_D , that is generally used in the literature is defined in terms of moles of pesticide

as follows:

$$K_D = \theta_{\text{At}}/M_{\text{At}} \quad (4)$$

This is commonly used as an empirical constant to describe the adsorbability of a pesticide to the soil. The correct meaning and real properties of K_D can be deduced, however, by the use of eqs 2 and 3, which gives rise to the simple relationship

$$K_D = \bar{K}_1(\theta_c - \theta_{\text{At}}) \quad (5)$$

Equation 5 shows that K_D decreases as θ_{At} increases.

According to the reaction described by eq 1, the net rate of atrazine loss from solution to the labile surface sites is given by the differential rate law

$$-dM_{\text{At}}/dt = k_1 M_{\text{At}}\theta_0 - k_{-1}\theta_{\text{At}} \quad (6)$$

where k_1 is the second-order rate constant for the adsorption reaction and k_{-1} is the first-order rate constant for the desorption. For adsorption to occur, a pesticide molecule has to encounter an unoccupied active site to become sorbed. In chemical kinetics, such a process is said to proceed by second-order kinetics. If the change in the amount of one of the reacting species is sufficiently small so that it remains approximately constant, then the reaction shows pseudo-first-order kinetics behavior. The desorption processes, on the other hand, require a sorbed molecule to dissociate into a free molecule and an unoccupied active site. Hence, the desorption processes are inherently first-order kinetics. For cases in which low coverage of the sorption sites gives $\theta_{\text{At}} \ll \theta_c$, then the differential rate law is simplified for two reasons. First, $\theta_0 = (\theta_c - \theta_{\text{At}})$ becomes approximately constant to give pseudo-first-order kinetics for the sorption. Second, the desorption is so small that $k_{-1}\theta_{\text{At}} \ll k_1 M_{\text{At}}\theta_0$. Equation 6 then reduces to

$$-dM_{\text{At}}/dt = k_2 M_{\text{At}} \quad (7)$$

in which k_2 is equal to $k_1\theta_0$ and has units s^{-1} . Separating variables and integrating eq 7 give the rate law

$$-\ln[M_{\text{At},t}/M_{\text{At},0}] = k_2 t \quad (8)$$

$M_{\text{At},t}$ and $M_{\text{At},0}$ are the solution-phase concentrations of atrazine at time t and time zero, respectively. Equation 8 shows that a plot of $-\ln[M_{\text{At},t}/M_{\text{At},0}]$ vs t for a first-order process will yield a straight line with a slope equal to k_2 , the pseudo-first-order rate constant for sorption. Division of k_2 by θ_0 will yield the appropriate second-order rate constant. As the sorption reaction proceeds, θ_{At} increases and M_{At} and θ_0 constantly decrease so that the above conditions may no longer be valid. The pseudo-first-order reaction becomes a second-order reaction.

II. Apparent Pesticide-Bound Residue. Bound residues may be defined as the fraction of the total amount of pesticide, initially applied to the soil, that cannot be extracted by methods commonly used in residue analyses. Many authors have reported that the initial sorption of pesticide by the soil is followed by a second stage that is much slower and not sufficiently quickly reversible to be recovered by the usual extraction methods (Talbert and Fletchall, 1965; Mill, 1980; Paris, 1980; Karickhoff, 1980; Freeman and Cheung, 1981; Di Toro and Horzempa, 1982; Macalady and Wolfe, 1984; Karickhoff and Morris, 1985). Hamaker et al. (1966) have suggested that the organic chemicals slowly diffuse into the interiors of the soil particles. This may explain the material balance loss when a sorbed pesticide is extracted from the soil by an organic solvent (Chiba, 1969; Adams, 1973; Khan, 1973). Crank (1975) gave the general case for the chemical loss by

diffusion from the plane surface of a particle into its interior. His model assumed a steady-state surface coverage for the soil particles. Crank also imposed the restriction of a "semi-infinite sink", which means that the interior of the particle does not exhibit the reverse process of diffusion out. According to Crank, the amount of pesticide that will diffuse from the particle surface into the interior is given by the expression

$$M_t = 2C_1(Dt/\pi)^{1/2} \quad (9)$$

where D is the diffusion coefficient and t is the time. C_1 is equal to θ_{At}/l , where l is a particle dimension related to diffusion. Due to the lack of detailed information about the particles' shapes and sizes, the value of l is not known. Changing units to replace M_t by θ_L allows us to rewrite Crank's equation as

$$\theta_L = [2\theta_{At}/l(D/\pi)^{1/2}]t^{1/2} \quad (10)$$

thus

$$\ln(\theta_L) = \ln(A) + 1/2 \ln(t) \quad (11)$$

in which $A = 2\theta_{At}/l(D/\pi)^{1/2}$. For this case a plot of $\ln(\theta_L)$ vs $\ln(t)$ will be a straight line with a slope equal to 0.5 and θ_L will be proportional to θ_{At} .

Equation 11 may be used as a diagnostic plot to test material balance loss data for behavior consistent with the diffusion mechanism given above. Such data have been published for atrazine in an organic soil (Gamble and Kahn, 1990) and for atrazine in a mineral soil (Gamble and Ismaily, 1992). A new plot of $\ln(\theta_L)$ vs $\ln(t)$ for the organic soil (Gamble and Kahn, 1990) has a slope equal to 0.47 ± 0.05 , which is consistent with the diffusion mechanism given above. A similar plot for the mineral soil (Gamble and Ismaily, 1992) did not yield a definitive slope. Slower diffusion and higher uncertainty due to lower θ_{At} and $M_{At,0}$ may have contributed to the nondefinitive diagnostic plot for the mineral soil. Recent results obtained by Gamble et al. (D. S. Gamble, J. Li, G. F. R. Gilchrist, and C. H. Langford, unpublished results, 1993) with more than 30 separate HPLC-MF experiments, with $M_{At,0}$ from 1×10^{-6} to 5×10^{-5} M and temperature from 5 to 35 °C, are consistent with the diffusion mechanism given above.

The general case given above is for diffusion into an infinite media from a steady-state concentration of material on the surface of a particle. For clay and soil particles, the interior may approach saturation or the rate of diffusion of pesticide out of the particle may become significant. In this case the clay or soil no longer acts as if it were an infinite sink for the pesticide and pseudo-first-order or second-order kinetics will be observed. In these cases $d\theta_L/dt$ will be lower and the slope of the diagnostic plot will be less than 0.5. Since $d\theta_L/dt$ is proportional to θ_{At} , at low θ_{At} $d\theta_L/dt$ will be indistinguishable from zero. Fracturing of clay particles along domain boundaries in the field or in the laboratory may open some of the interior channels, thereby increasing the desorption rate. A decrease in $d\theta_L/dt$ would be observed if such fracturing occurred in the laboratory while a sorption kinetic experiment was in progress.

EXPERIMENTAL PROCEDURES

Equipment. The reaction vessel was a Pyrex cylinder 7.3 cm high by 3.0 cm in diameter, with a screw cap. A Teflon-coated stir bar and magnetic stirring base were used to keep the clay minerals suspended. A thermostated circulating bath connected to double-walled Pyrex jackets were used to maintain the slurry temperature at 25 °C. HPLC analyses were performed with a

Table I. Physical and Chemical Characteristics of the Clay Samples

clay sample	short name	minor impurities by XRD	surface area, ^a m ² /g	CEC, ^a mequiv/g
sodium montmorillonite	NaMt I	quartz cristobalite	727 ± 9	1.1 ± 0.1
sodium montmorillonite	NaMt II	cristobalite	727 ± 9	1.1 ± 0.1
calcium montmorillonite	CaMt	quartz cristobalite	733 ± 14	1.1 ± 0.1
calcium kaolinite	Kaol	smectite	84 ± 3	0.18 ± 0.01
calcium illite	Illt	smectite ^b chlorite kaolinite quartz	219 ± 8	0.36 ± 0.02
<2- μ m fraction	Frac	c	378 ± 1	0.72 ± 0.03

^a Values listed are mean \pm standard deviation. ^b Smectite as an expandable layer component interstratified with illite. ^c Frac was a mixture of micas, kaolinite, quartz, and X-ray amorphous material with minor amounts of smectite, chlorite, and plagioclase and trace vermiculite.

Varian Star 9010 solvent delivery system and a Varian Star 9050 UV-vis variable-wavelength detector set to 220 nm for atrazine and to 240 nm for hydroxyatrazine. The stainless steel frits (2.0 and 0.5 μ m) and a C₁₈ guard column were used to trap solids and protect the main C₁₈ HPLC column. Microfiltration of the slurry prior to injection was done with 1-mL disposable syringes and MSI Cameo Nylon 66 0.22- μ m disposable microfilters. Further details of the equipment are given in Gamble and Kahn (1990) and Gamble and Ismaily (1992).

Reagents and Standards. Standard stock solutions of 1×10^{-4} M atrazine and 1×10^{-4} M hydroxyatrazine were prepared from the crystalline solids using distilled deionized water of 18.3 Mohms cm² resistivity. Analytical standards were prepared by serial dilution of the stock solutions.

Preparation of Clay Samples. The clays used were <2- μ m fraction of montmorillonite (Clay Spur, WY), kaolinite (Murfreesboro, AR), and illite (Fithian, IL). Homoionic clays were prepared by saturating separate clay suspensions with appropriate chloride or sulfate salts, dialyzing the clay in distilled water until free of anions, and finally freeze-drying the clay fraction. The clays used in this study were sodium and calcium montmorillonite, calcium kaolinite, and calcium illite.

The <2- μ m fraction of the soil GB843, taken from the Central Experimental Farm in Ottawa, ON, was separated by sedimentation. No chemical treatments were employed in the dispersion to ensure that the results relate to clays as they occur in soils. A 10-g sample of soil was washed free of soluble salts and dispersed in distilled water in a 2-L graduated cylinder by gentle manual stirring, without addition of chemical dispersing agents. The dispersion was allowed to settle until Stokes law calculation determined that the top 30 cm of the water column contained only those particles $\leq 2 \mu$ m. The top 30 cm was then removed by syphon. Dispersion and syphoning were repeated until no further yield of colloids was observed. The ≤ 2 - μ m fraction obtained was freeze-dried. The freeze-drying procedure may have caused the clay particles to fracture along domain boundaries, hence reducing the mean particle size. Since fracturing by other processes occurs in nature, freeze-drying is not perceived to be a serious limitation in our experimental technique.

Table I lists some chemical and physical properties determined for the clays used in this work. X-ray diffraction analysis showed that some of the clays had trace and minor (1–10%) impurities. Surface area was determined using ethylene glycol monoethyl ether (EGME). A monolayer distribution of EGME was sorbed onto oven-dried, desiccated, and accurately weighed clay samples. The surface area of the clay was calculated from the mass of EGME sorbed. Cation-exchange capacity (CEC) was determined by saturating the cation-exchange sites with Ca²⁺ and eluting the Ca²⁺ with Na⁺.

Procedure. A 100-mg portion of the clay sample was suspended with stirring in 20.00 mL of distilled deionized water at 25.0 °C for 3 days. After the clay mineral surfaces were sufficiently wetted, 5.00 mL of aqueous atrazine solution was

added to start the sorption reactions. Analysis of the filtrate and the slurry began immediately with each analysis bracketed by standard solution injections. Direct injection of the slurry caused the clay particles to be trapped by the stainless steel frits and the guard column where the labile sorbed atrazine was extracted by the mobile phase. Solution-phase atrazine was analyzed by microfiltration of the slurry prior to injection. In our previous work (Gamble and Khan, 1990, 1992) 0.45- μm frits and filters were used to be consistent with the U.S. EPA definition of dissolved matter (pass through a 0.45- μm filter) and suspended matter (retained by a 0.45- μm filter). In this work 0.22- μm filters were used because the smaller filter pore size should better separate material that is dissolved from material that is suspended. However, we determined that selection of 0.22- vs 0.45- μm filters had no noticeable effect on our results; hence, either size filter may be used. Filtration through either 0.22- or 0.45- μm filters produced a clear solution as filtrate. The loss of size fraction $<0.22 \mu\text{m}$ is necessary to obtain the time-resolved speciation and high extraction efficiency of this technique. In light of the identical results obtained with the two sizes of filters, it is likely that $>95\%$ of the clay particles are retained by either filter and the loss of the smallest fraction ($<0.22 \mu\text{m}$) is not a serious limitation for this technique.

Sorbed atrazine that can be extracted by water or the HPLC mobile phase is considered to be labile sorbed atrazine, determined by subtracting the microfiltrate concentration from the slurry concentration. Atrazine that cannot be extracted by the HPLC mobile phase is considered to be reversible but kinetically slow sorbed atrazine, determined by subtracting the slurry concentration from the initial concentration. Aqueous standards containing hydroxyatrazine and the dealkylated products of atrazine and hydroxyatrazine were prepared and analyzed periodically to determine if any reaction products of atrazine were formed in the clay slurries. For this work none of the above reaction products were observed in any of the clay slurries, even after 127 days. This is not surprising because the pH of the slurries remained at 5.1 ± 0.2 throughout this work.

Labile sorption capacities of the clay samples were measured by saturating the sorption sites with solutions having $M_{\text{At},0}$ of 2.5×10^{-6} and 5.0×10^{-6} M atrazine. Subtraction of the filtrate concentration from that of the slurry, the difference being equal for both experiments, gives the saturated concentration of the labile sorbed atrazine; the labile sorption capacity. It is important to note that one may obtain the labile sorption capacity and measurements of labile sorption coverage only by using a combination of on-line and off-line microfiltration and extraction (Gamble and Khan, 1990; Gamble and Ismaily, 1992).

Use of a 20- μL injection loop and a mobile-phase flow rate of 1.0 mL min^{-1} gave an extractant/clay ratio of $12.5 \text{ L g}^{-1} \text{ min}^{-1}$. Hence, for an 8-min retention time for atrazine the trapped clay particles had a relative extractant ratio of (100 L of mobile phase)/(gram of clay), which is about 4 orders of magnitude greater than the conventional volumes of extractant per gram of solid (Gamble and Khan, 1990). If the elution time, t_E , were too large relative to the retention time, t_R , then tailing and asymmetric HPLC peaks would be expected. Since only symmetric peaks were observed and the peak height and peak area were linear functions of atrazine concentration, it is likely that $t_E \ll t_R$; hence, on-line extraction of atrazine from soils and clays can be done reliably using the apparatus described here and previously (Gamble and Khan, 1990; Gamble and Ismaily, 1992).

RESULTS AND DISCUSSION

A 6-h HPLC-MF experiment using Na^+ -saturated montmorillonite and $M_{\text{At},0}$ equal to 1×10^{-6} M is shown in Figure 1. This figure shows a rapid decrease in the solution-phase concentration of atrazine (filtrate). The concentration of labile atrazine (solution phase plus labile sorbed) is measured when the slurry is injected into the HPLC, where the solids are trapped on precolumn frits (slurry). The labile atrazine concentration exhibits a small rapid decrease and then levels out. This initial loss of atrazine is consistent with the observations of Gamble and Kahn (1990) and Gamble and Ismaily (1992) and does

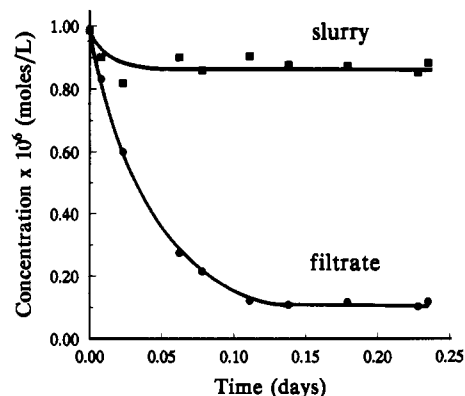


Figure 1. Results of an HPLC-MF experiment with Na^+ -saturated montmorillonite having $M_{\text{At},0} = 1.0 \mu\text{M}$. The slurry contains solution-phase atrazine and labile sorbed atrazine, while the filtrate (0.22 μm) contains only solution-phase atrazine.

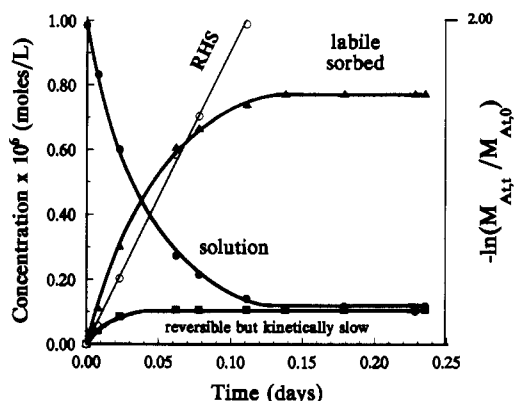


Figure 2. Chemical speciation of atrazine from Figure 1 (left abscissa); first-order rate law for depletion of atrazine from solution (RHS = right abscissa).

not fit the diagnostic plot for diffusion into the interiors of the particles (eq 11). From the start of the experiment to 0.1 day the concentration of solution-phase atrazine decreases while the concentration of labile sorbed atrazine increases. For the period 0.1–0.2 day the concentration of solution-phase atrazine was $0.11 \pm 0.01 \mu\text{M}$ and the total concentration of atrazine was $0.88 \pm 0.01 \mu\text{M}$; the difference, $0.77 \pm 0.02 \mu\text{M}$, equals the concentration of labile sorbed atrazine. The concentration of reversible but kinetically slow sorbed atrazine equals the difference between $M_{\text{At},0}$ and the slurry concentration. The difference between $M_{\text{At},0}$ and the slurry concentration of atrazine in the 0.1–0.2-day region is $0.11 \pm 0.01 \mu\text{M}$.

Figure 2 shows the concentrations (left-hand axis) of solution-phase atrazine, labile sorbed atrazine, and reversible but kinetically slow sorbed atrazine, determined from the data in Figure 1. A plot of $-\ln[M_{\text{At},t}/M_{\text{At},0}]$ vs t [right-hand axis (RHS)] for the solution-phase atrazine is also shown. Equation 9 shows that the pseudo-first-order rate constant, equal to the slope of the straight line in Figure 2, is $(2.07 \pm 0.09) \times 10^{-4} \text{ s}^{-1}$. The corresponding second-order rate constant is $22.7 \pm 1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($90.8 \pm 3.9 \text{ g mol}^{-1} \text{ s}^{-1}$). Later it will be shown that for this work the assumption of pseudo-first-order kinetics is valid.

Figure 3 shows the results of an HPLC-MF experiment done using Na^+ -saturated montmorillonite with $M_{\text{At},0}$ equal to 5×10^{-7} M. The solution-phase concentration of atrazine falls below the system limit of detection ($\text{LD} = 3 \times 10^{-8}$ M) within 22 min, showing that $k_c \geq (1.6 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$. After this time, atrazine is no longer detectable in the solution phase of the slurry. The total concentration of labile atrazine (labile sorbed plus solution phase) has

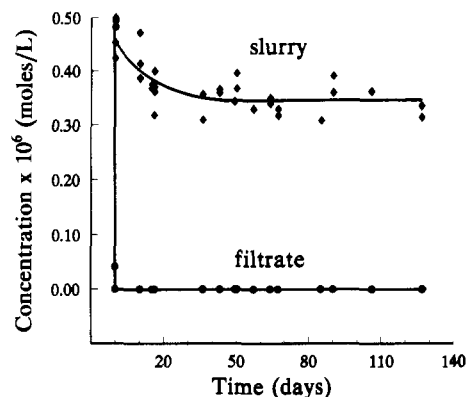


Figure 3. Results of an HPLC-MF experiment with Na⁺-saturated montmorillonite having $M_{At,0} = 0.5 \mu\text{M}$. The slurry contains solution-phase atrazine and labile sorbed atrazine, while the filtrate ($0.22 \mu\text{m}$) contains only solution-phase atrazine.

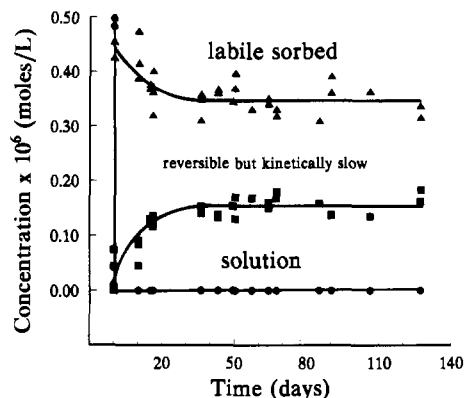


Figure 4. Chemical speciation of atrazine from Figure 3.

an initial fast drop, like that observed in Figure 1, followed by a slower decrease for a period of 15 days, and then remains constant for 120 days.

Figure 4 shows the calculated species curves for the experimental data shown in Figure 3. The slower 15-day decrease in the total concentration of atrazine is probably due to reversible but kinetically slow sorption. This sorption may be due to diffusion of atrazine molecules into the mineral grains at boundaries, lattice imperfections, or other structural features. Diffusion occurs when the thermal energy of a molecule causes it to move from sorption site to sorption site on the interior surfaces of a mineral grain. This random diffusion will carry the molecule into or out of the interior of a particle. Early in the sorption reaction, when the surface (labile) concentration is high and the interior (reversible but kinetically slow) concentration is low, diffusion into the particle is more probable than diffusion out of the particle. The enthalpy of sorption presents an energy barrier, which must be overcome by the thermal energy of the molecule for diffusion to occur. This process is called retarded intraparticle diffusion. Equations 9–11 describe diffusion into a volume from a steady-state concentration on the surface of that volume. Equation 11 shows that for the above case a plot of $\ln(\theta_L)$ vs $\ln(t)$ will have a slope of 0.5. A plot of $\ln(\theta_L)$ vs $\ln(t)$ for the reversible but kinetically slow sorption in Figure 4 has a slope of 0.25 ± 0.05 , which is not consistent with the diffusion model given above. However, for $M_{At,0}$ equal to $1.0 \mu\text{M}$ the slope of the diagnostic plot is 0.45 ± 0.08 , which is consistent with the diffusion model.

The plateau in the reversible but kinetically slow sorbed species curve from 20 to 127 days (Figure 4) may be due to the establishment of equilibrium for the diffusion of

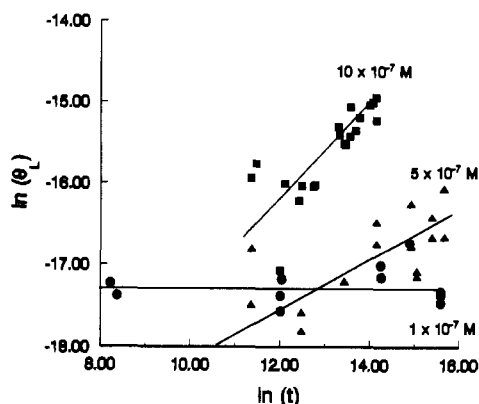


Figure 5. Diagnostic plot for intraparticle diffusion.

atrazine into and out of the clay particles. The amount of atrazine taken up by reversible but kinetically slow sorption in the plateau region increases with increase in $M_{At,0}$. This increase is consistent with the proposed equilibrium, but the equilibrium function cannot be calculated since the intraparticle sorption capacity is not known.

Figure 5 shows plots of $\ln(\theta_L)$ vs $\ln(t)$ for sorption experiments using kaolinite and $M_{At,0}$ values of 0.1, 0.5, and $1.0 \mu\text{M}$. Reversible but kinetically slow (intraparticle) sorption is not observed for the lowest $M_{At,0}$, and the slope of the diagnostic plot is 0.24 ± 0.09 for the next higher $M_{At,0}$. For $M_{At,0}$ equal to 1.0 (shown) and $2.0 \mu\text{M}$ (not shown) the diagnostic plots have slopes of 0.48 ± 0.09 and 0.45 ± 0.15 , respectively. Figure 5 shows that the slope of the diagnostic plot is dependent on θ_{At} . Since labile site coverage is related to $M_{At,0}$ through the law of mass action, the discrepancy in the diagnostic plot for $M_{At,0} \leq 0.5 \mu\text{M}$ may be an artifact of the low labile site coverage.

If reversible but kinetically slow sorption occurs by intraparticle diffusion, then the labile sorbed species may supply atrazine for the diffusion process. It follows that the observed initial fast sorption, that is kinetically slow to desorb, occurs while both the solution/surface and the surface/intraparticle concentration gradients are highest. The remainder of the reversible but kinetically slow sorption occurs after these concentration gradients have been established, so that intraparticle diffusion proceeds under heterogeneous equilibrium between the solution phase and the labile sorbed phase. Hence, an increase in θ_{At} causes an increase in the rate of intraparticle diffusion, making it rapid enough to be observed during the kinetic experiments. Systems having θ_{At} too low will not have intraparticle diffusion observable by the methods described here, but observation for longer time should reveal intraparticle diffusion.

Table II shows the results of the labile and reversible but kinetically slow (intraparticle) sorption kinetic experiments, with results correlated with $M_{At,0}$ and the equilibrium value for the mole fraction of labile site coverage, $\chi_1 = \theta_{At}/\theta_c$. Kaolinite and the $<2\text{-}\mu\text{m}$ fraction do not have observable intraparticle sorption at the lowest χ_1 values, but at higher χ_1 values fast intraparticle sorption is observed. Kaolinite and the $<2\text{-}\mu\text{m}$ fraction also have slow intraparticle sorption for higher χ_1 values. As discussed earlier, if the reversible but kinetically slow sorption is due to retarded intraparticle diffusion, then the labile sorbed layer supplies atrazine to the diffusion process. For low χ_1 the rate $d\theta_L/dt$ is too low to allow observable loss of atrazine. The relation between χ_1 and intraparticle sorption (columns 4, 5, 9, and 10 of Table II) shows that $d\theta_L/dt$ is a function of χ_1 and that for low rates

Table II. Sorption Kinetics Characteristics

clay	$M_{At,0}$	X_1	general trends ^a				values for intraparticle sorption		
			intraparticle		labile		initial, μM	$d\theta_L/dt, \mu\text{M} \times 10^9$	$\ln \theta_L$ vs $\ln t$
			fast	slow	fast	slow			
NaMt									
I	0.5	0.045	Y	Y	Y	N	0.085	-0.94	0.25
	1.0	0.084	Y	Y	Y	Y	0.095	-3.0	0.45
II	2.0	0.180	Y	Y	Y	Y	0.129	ND ^b	ND
CaMt	0.5	ND	N	N	Y	N	0.0	0.0	0.0
	1.0	ND	N	N	Y	N	0.0	0.0	0.0
	2.0	0.260	N	N	Y	N	0.0	0.0	0.0
Kaol	0.1	0.0085	N	N	Y	N	0.002	0.0	0.0
	0.5	0.035	Y	Y	Y	N	0.013	-1.8	0.24
	1.0	0.063	Y	Y	Y	N	0.070	-11	0.48
	2.0	0.18	Y	Y	Y	N	0.055	-16	0.45
Illt	0.5	0.069	Y	Y	Y	N	0.050	0.0	0.0
	1.0	0.112	Y	Y	Y	N	0.027	0.0	0.0
	2.0	0.207	Y	Y	Y	N	0.020	0.0	0.0
Frac	0.5	0.033	N	N	Y	N	0.0	0.0	0.0
	1.0	0.041	N	Y?	Y	N	0.02	-1.9	0.0
	2.0	0.083	Y	Y	Y	N	0.12	-5.5	0.59

^a Y, yes; N, no. ^b ND, not determined.

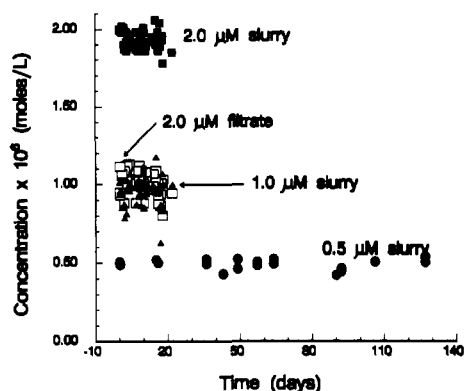


Figure 6. Results of an HPLC-MF experiment with Ca^{2+} -saturated montmorillonite having $M_{At,0} = 2.0 \mu\text{M}$. The slurry analyses for Ca^{2+} -saturated montmorillonite having $M_{At,0} = 0.5$ and $1.0 \mu\text{M}$ are also shown.

of intraparticle sorption the diffusion model is not fulfilled. The amount of atrazine taken up by a fast intraparticle sorption, which is complete in a matter of minutes, is shown in column 8. This surge of atrazine to the intraparticle sorption sites may be due to the surge of atrazine to the labile sorption sites (column 6). The rapid accumulation of labile sorbed atrazine will set up a steep concentration gradient with respect to the intraparticle sorption sites for atrazine, and the fast intraparticle sorption may serve to establish a new concentration gradient inside the particles.

All of the systems tested, except Na^+ -saturated montmorillonite, had fast labile sorption that reached equilibrium within 2 min of the beginning of the experiment. For the experiments shown here this process has a minimum k_c value of about $8 \times 10^{-4} \text{ s}^{-1}$ or a k_1 value of $3000 \text{ g mol}^{-1} \text{ s}^{-1}$. (The results for Na^+ -saturated montmorillonite were discussed earlier.)

Figure 6 shows the results of an HPLC-MF experiment performed using Ca^{2+} -saturated montmorillonite having $M_{At,0}$ equal to $2.0 \mu\text{M}$ along with the slurry analysis for $M_{At,0}$ equal to 0.5 and $1.0 \mu\text{M}$. Ca^{2+} -saturated montmorillonite had or showed no kinetically slow sorption over the duration of this experiment. Figure 6 shows 100% material balance for atrazine for a period of 127 days. This demonstrates that the HPLC-MF technique is free from determinate experimental errors with respect to material balance. From Figure 6 and the negative test

results for chemical reaction products of atrazine discussed earlier, it can be concluded that for the conditions reported here no hydrolysis or dealkylation of labile atrazine occurred during this work.

Table III shows the labile sorption capacity, the equilibrium solution-phase concentration, the equilibrium labile site coverage, the weighted average equilibrium function, and the distribution coefficient for different initial concentrations of atrazine. For Na^+ -saturated montmorillonite, kaolinite, and illite the labile site coverage plus the solution-phase concentration ($C_{At} + M_{At}$) is less than $M_{At,0}$. This material balance loss is due to reversible but kinetically slow sorption as seen in Figures 1 and 3 and Table II. The ability of the HPLC-MF technique to separately determine C_{At} and M_{At} has allowed this reversible but kinetically slow sorption to be measured directly during the sorption reaction and at equilibrium. The chemical speciation information produced by the experimental method has made it possible to define and calculate the sorption equilibrium function in terms of the labile sorption alone, rather than some unknown combination of the labile sorption and the reversible but kinetically slow sorption. This avoids some of the hysteresis problems commonly reported in the literature. The montmorillonite samples have much larger θ_c than the other clays, and Terce and Calvet (1978) have proposed that pesticides may be sorbed to the interlamellar surfaces in montmorillonite, resulting in the observed higher sorption. Na^+ -saturated montmorillonite not only has greater θ_c than Ca^{2+} but also has a larger \bar{K}_1 , showing that the labile sorbed atrazine is more strongly bound to Na^+ -saturated montmorillonite than to Ca^{2+} -saturated montmorillonite. The differences in θ_c and \bar{K}_1 may be due to the difference in charge density of the interlayer cations, Na^+ and Ca^{2+} , with ionic radii of 0.97 and 0.67 \AA , respectively. The higher charge density will cause Ca^{2+} to have a more highly ordered and strongly bound hydration sphere, which may prevent much of the atrazine from entering the interlayer spaces.

Comparison of Table I with Table III shows qualitatively that the labile sorption capacity of the clays increases with increasing surface area and CEC. Sodium and calcium montmorillonite, however, have the same surface area and CEC but different sorption capacities. Figure 7 shows that θ_c decreases with increasing surface charge density (CEC/surface area), which is similar to the observations of Laird et al. (1992). One possible explanation for the

Table III. Equilibrium Characteristics

clay	$C_c, \mu\text{M}$	$\theta_c, \mu\text{m/g}$	$M_{At,0}, \mu\text{M}$		$M_{At,t}, \mu\text{M}$	$C_{At,t}, \mu\text{M}$	$\theta_{At,t}, \mu\text{m/g}$	$K_1/10^3$	K_D
			nominal	actual					
NaMt									
I	9.12	2.28	0.5	0.498	<0.03	0.414	0.103	1500+	13.4
			1.0	0.986	0.110	0.770	0.191	830	7.0
II			2.0	2.00	0.203	1.668	0.414	1020	7.6
CaMt	4.0	1.0	0.5	0.498	ND ^a	ND	ND	ND	ND
			1.0	1.01	ND	ND	ND	ND	ND
			2.0	2.00	1.04	0.957	0.260	338	0.92
Kaol	1.28	0.32	0.1	0.0991	0.085	0.011	0.0027	97	0.12
			0.5	0.592	0.534	0.044	0.0113	77	0.090
			1.0	1.11	0.750	0.050	0.0115	56	0.071
			2.0	1.99	1.77	0.068	0.021	40	0.039
Illt	1.40	0.35	0.5	0.497	0.401	0.099	0.024	187	0.247
			1.0	1.00	0.818	0.158	0.039	154	0.193
			2.0	2.00	1.690	0.290	0.073	125	0.172
Frac	1.88	0.47	0.5	0.493	0.432	0.061	0.015	78	0.14
			1.0	0.990	0.744	0.079	0.019	57	0.11
			2.0	1.98	1.72	0.157	0.039	52	0.090

^a ND, not determined.

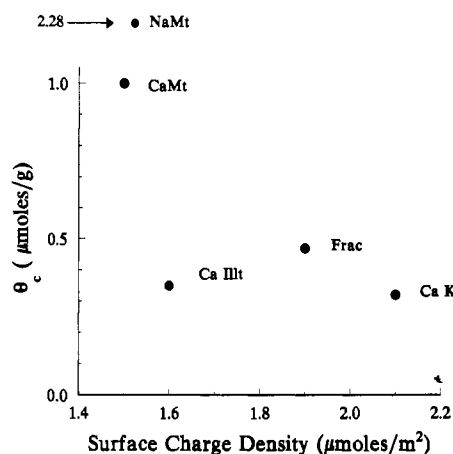


Figure 7. Labile sorption capacity, θ_c , vs surface charge density for the clays used in this work. See Table I for definitions.

observed behavior is that greater surface charge density, like greater charge density, causes the water molecules at the surface to be more strongly bound and have a more ordered structure. Since atrazine is only sparingly hydrophilic (water solubility in the micromolar range), it will be less likely to approach and adsorb to surfaces having rigid, ordered water layers than to surfaces without such layers. The binding and order of the surface water layer cause the observed decrease in θ_c with increase in surface charge density. This effect is similar to that observed for Ca^{2+} - and Na^+ -saturated montmorillonite, where differences in charge density affect θ_c . Kaolinite, illite, and the <2- μm fraction have similar values of θ_c . For these clays the mean value and standard deviation for θ_c is $0.38 \pm 0.08 \mu\text{mol/g}$, which is less than that reported for an organic soil (Gamble and Kahn, 1990) but similar to that reported for a mineral soil (Gamble et al., 1992).

Figure 8 shows that K_1 and K_D decrease with increasing χ_1 for all samples and the K_1 and K_D values for kaolinite, illite, and the <2- μm fraction have similar values for similar χ_1 values. The clay samples used in this study contained no organic matter, so that sorption is due only to interaction between the clay and atrazine. Correlation of θ_c and K_1 for the clay samples and the mineral soil suggests that labile sorption occurs by the same mechanism for these two cases. Table III shows the relation between solution-phase concentration and labile site coverage. Table III is consistent with the observations of Karickhoff and Morris (1985) for low site coverage. This relation can be ade-

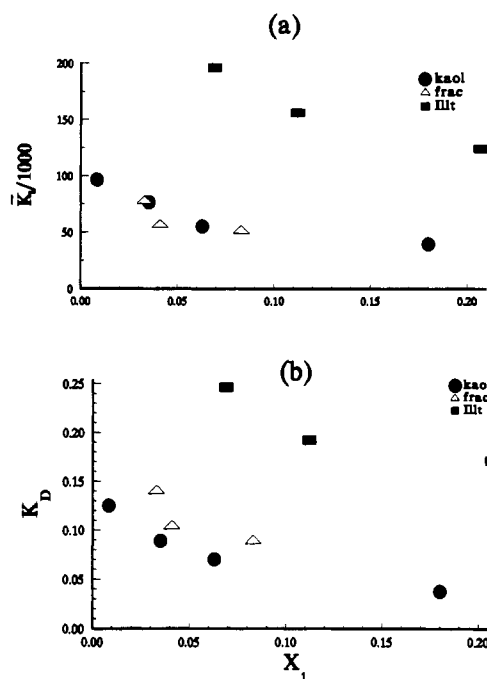


Figure 8. Effect of labile site coverage: (a) K_1 vs χ_1 ; (b) K_D vs χ_1 . See Table I for definitions.

quately described by the law of mass action or the Freundlich equation; however, only the law of mass action can describe the sorption behavior near saturation of the labile sorption sites.

The distribution coefficient for atrazine in the water/clay system, K_D , is equal to M_{At}/C_{At} or $K_1\theta_0$; hence, even if K_1 were constant, K_D would be a function of χ_1 : $\chi_1 = (\theta_c - \theta_0)/\theta_c$. Current hydrology and pesticide fate models use a fixed value of K_D to describe pesticide distribution between phases. This work shows that with the appropriate laboratory determinations K_D may be calculated from knowledge of K_1 and θ_0 or χ_1 and θ_c .

CONCLUSIONS

Clay minerals are an important soil component with respect to pesticide-soil interactions. Results presented here show that under conditions of low labile sorption site coverage and dilute solution the kinetic and equilibrium phenomena for sorption are general for a variety of clay minerals and soil components. First-order, pseudo-first-order, and second-order kinetics along with the law of mass

action can be applied to sorption of atrazine by clay minerals. Labile sorption of low concentrations of atrazine by clay particles is rapid enough to establish equilibrium in a matter of minutes. Reversible but kinetically slow sorption of atrazine may be due to diffusion of atrazine into domain boundaries within the clay particles and hence may be labile on a longer time scale. Labile sorption capacity and site loading are important factors in pesticide-clay kinetics and equilibrium. The sorption capacity appears to be related to the charge density of interlayer cations present in expandable clays and the surface charge density of clays.

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Received for review September 22, 1992. Revised manuscript received April 1, 1993. Accepted June 21, 1993.*

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.