

Influence of Herbicide Structure, Clay Acidity, and Humic Acid Coating on Acetanilide Herbicide Adsorption on Homoionic Clays

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Adsorption of chloroacetanilide herbicides on homoionic montmorillonite was studied by coupling batch equilibration and FT-IR analysis. Adsorption decreased in the order metolachlor > acetochlor > alachlor > propachlor on Ca²⁺- or Mg²⁺-saturated clays and in the order metolachlor > alachlor > acetachlor > propachlor on Al³⁺- or Fe³⁺-saturated clays. FT-IR spectra showed that the carbonyl group of the herbicide molecule was involved in bonding. For the same herbicide, adsorption of alachlor, acetachlor, and metolachlor on clay followed the order Ca²⁺ ≈ Mg²⁺ < Al³⁺ ≤ Fe³⁺, which coincided with the increasing acidity of homoionic clays. Adsorption of propachlor, however, showed an opposite dependence, suggesting a different governing interaction. In clay and humic acid mixtures, herbicide adsorption was less than that expected from independent additive adsorption by the individual constituents, and the deviation was dependent on the clay-to-humic acid ratio, with the greatest deviation consistently occurring at a 60:40 clay-to-humic acid ratio.

KEYWORDS: Chloroacetanilide herbicides; adsorption; sorption; montmorillonite; humic acid; complexation; alachlor; acetochlor; metolachlor; propachlor

Adsorption of pesticides on soil is one of the most important processes affecting their biological activity as well as environmental fate. The clay fraction and associated organic matter have been shown to be the primary adsorbents for pesticides in soil (1). The importance of these soil constituents in adsorption has been more directly demonstrated in studies in which model adsorbents were considered (2–7). An increasing number of studies show, however, that interactions between soil constituents can greatly affect the overall adsorption: the total adsorption is not the sum of adsorption to individual components assuming independent and additive adsorption behavior (8–12). Because clay minerals and organic matter in the soil environment are always intimately associated with each other as well as with other chemical species such as cations and anions, an understanding of constituent interactions may thus be critical for addressing pesticide adsorption in soil.

Research to understand adsorption mechanisms of pesticides is complicated by the extreme complexity and instability of soil organic matter and clay complexes. As a result, most research assesses adsorption by modeling adsorption kinetics

or correlating adsorption with soil properties (e.g., organic matter content, clay content, CEC, or pH) or pesticide properties (e.g., solubility, K_{ow} , or pK_a). The relationships between adsorption and soil properties are well established, as evidenced by many models that allow prediction of adsorption from soil parameters, for example, estimation of K_d from K_{oc} by using a soil's organic carbon content (13). On the other hand, different pesticides may be adsorbed to very different extents on the same soil. Although efforts have been made to derive equations to describe pesticide adsorption from pesticide properties such as solubility or K_{ow} , a widely applicable relationship has not been found. This indicates that solubility and K_{ow} values of pesticides may be too empirical in nature, and more descriptive, likely molecular structure or charge distribution based descriptors, should be incorporated into the models. To develop quantitative structure–adsorption relationships, it is essential to understand how a pesticide's adsorption is affected by its structure and charge characteristics at the molecular level (12, 14–15). In a previous study, we qualitatively explored the molecular basis for the relative adsorption of acetanilide herbicides on soil, Ca²⁺-clay, and a soil-derived humic acid (12). Herbicide adsorption was found to closely correlate with the type and position of the substitutions around the functional groups that were involved in bonding. In this study we further investigated the molecular basis of acetanilide herbicide adsorption by considering the effect of different exchangeable cations on adsorption on clay.

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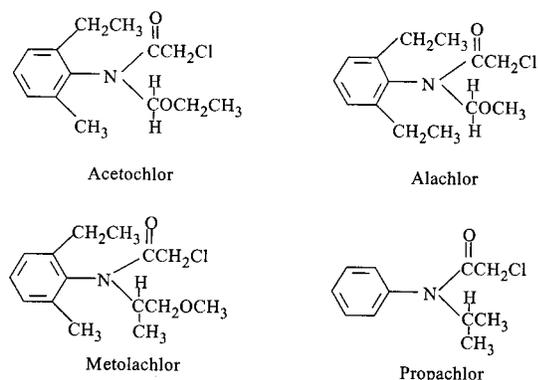


Figure 1. Chemical structures of chloroacetanilide herbicides acetochlor, alachlor, metolachlor, and propachlor.

The effect of clay and humic acid complexation on herbicide adsorption was also determined, and a model that describes such interactions was developed and tested against the measured adsorption.

MATERIALS AND METHODS

Chemicals and Model Sorbents. Acetochlor [2-chloro-*N*-(ethoxy-methyl)-*N*-(2-ethyl-6-methylphenyl)acetamide] (98.1% purity), alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] (99.5% purity), metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] (98.7% purity), and propachlor [2-chloro-*N*-(1-methylethyl)-*N*-phenylacetamide] (99.5% purity) were purchased from Chem Service, Inc. (West Chester, PA). The structures of these herbicides are given in **Figure 1**.

Acid-base indicators Bromocresol Green (pH 3.8–5.4), Methyl Red (pH 4.2–6.2), Bromocresol Purple (pH 5.2–6.8), Phenol Red (pH 6.8–8.2), Thymol Blue (pH 8.0–9.2), and Thymolphthalein (pH 8.8–10.5) were all purchased from Aldrich (Milwaukee, WI). These indicators were used for measuring the internal pH of homoionic clays.

The clay used was a montmorillonite Swy-2 from Crook County, Wyoming, and was purchased from the Source Clay Minerals Repository of the Clay Mineral Society at University of Missouri, Columbia, MO. The <2 μm fraction was obtained by sedimentation. K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , and Fe^{3+} -saturated clays were prepared by repetitive treatment of the clay with 0.5 mol L^{-1} solutions of KCl, CaCl_2 , MgCl_2 , AlCl_3 , or FeCl_3 . The prepared clay samples were centrifuged, washed repeatedly with deionized water to remove nonexchanged cations and Cl^- , dried at room temperature, and ground to a fine powder. Soil humic acid (HA) was prepared from a Webster clay loam sampled from Waseca, MN. The preparation of HA followed the general procedures given by Schnitzer (16), and the detailed procedures were given elsewhere (12). Before use, the extracted HA was dialyzed in distilled water until salt-free and ground to a fine powder after drying at 40 °C. The dialysis membrane was purchased from Fisher, and the pore size was 1000 Da.

Measurement of Clay Acidity. Acidity of cation-saturated clays was measured in two ways. The external pH was measured directly in clay suspensions by using a pH meter. The clay-to-water ratio was the same as used in the following batch experiments (50 mg in 2.0 mL of water). The internal pH was determined by adding different acid-base indicators in clay suspensions and by observing for color changes after the suspension had been stirred and equilibrated for >5 min. When a change in color occurred, the suspension was centrifuged. If the color was associated only with clay particles, the color change was used to indicate the internal pH range of the clay.

Batch Adsorption Experiments. Adsorption isotherms of four herbicides on Ca^{2+} , Mg^{2+} , Al^{3+} , and Fe^{3+} -saturated montmorillonite clays were obtained by equilibrating 50 mg of adsorbent with 2.0 mL of herbicide solution in 10 mL glass vials. The sample vials were closed with Teflon-faced butyl rubber septa and mechanically shaken for 24 h at 20 ± 1 °C. Preliminary kinetic studies using multiple sampling intervals showed that >95% of the adsorption took place within the

Table 1. Adsorption Coefficients (K_d) of Selected Chloroacetanilide Herbicides on Different Homoionic Montmorillonite Clays^a

cation	K_d (L kg^{-1})			
	metolachlor	acetochlor	alachlor	propachlor
Ca^{2+}	96.7 \pm 15.6 (0.93)	44.4 \pm 3.5 (0.98)	37.3 \pm 3.5 (0.97)	32.8 \pm 3.8 (0.96)
Mg^{2+}	47.4 \pm 4.8 (0.97)	38.9 \pm 1.7 (0.99)	37.9 \pm 0.7 (1.00)	16.8 \pm 1.6 (0.97)
Al^{3+}	95.9 \pm 8.8 (0.98)	58.6 \pm 7.0 (0.96)	68.0 \pm 2.6 (1.00)	13.3 \pm 1.0 (0.98)
Fe^{3+}	110.7 \pm 6.9 (0.99)	75.8 \pm 7.6 (0.97)	106.9 \pm 6.9 (0.99)	12.0 \pm 0.6 (0.99)

^a The value after the “ \pm ” is the standard error, and the value in parentheses is R^2 .

first 5 h for all adsorbent–pesticide combinations. The initial herbicide concentration ranged from 20 to 100 $\mu\text{mol L}^{-1}$, and triplicate sample vials were used for each initial concentration point. At equilibrium, the suspensions were transferred to centrifuge tubes and centrifuged at 10000 rpm for 15 min, and the supernatant was filtered through a 0.2 μm syringe filter. Herbicide concentration in solution was determined through HPLC analysis. The amount adsorbed on clay was calculated from the difference between the initial and final concentrations of herbicide in solution. Clay-free blanks were included to correct for any adsorption to the vessels.

For each herbicide, the adsorption distribution coefficient (K_d) was also determined at a single herbicide concentration (100 $\mu\text{mol L}^{-1}$) on clay–HA mixtures to determine the effect of HA–clay complexation on herbicide adsorption. The total amount of adsorbent was 50 mg, but the ratio of HA to clay was varied from 0 to 1 with a fractional increment of 0.2. Similar procedures as described above were used for determining K_d .

Analysis of herbicide concentration in supernatant was conducted on an HP 1090 HPLC equipped with a diode array detector (DAD). The column was a 250 mm \times 4.6 mm (i.d.) reversed phase Adsorbosphere HS C_{18} 5 μm (Alltech Associates, Inc., Deerfield, IL), the injection volume 10 μL , and the wavelength of detection 230 nm. Mobile phase was made of acetonitrile, methanol, and water in different proportions and acidified with 0.5% phosphoric acid. The flow rate was at 1.0 mL min^{-1} , and the external calibration method was used for quantification.

FT-IR Spectroscopy of Adsorbed Herbicides. Probable binding mechanisms during herbicide adsorption were investigated by examining shifts of characteristic FT-IR absorption bands of herbicides before and after adsorption on clay. Thin films of K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , and Fe^{3+} -saturated clays were prepared by drying 5 mL of homoionic clay suspension in a 5-cm (i.d.) ring on a polyethylene sheet at room temperature. The dried circular films of clay were then lifted off the plastic and divided into halves. Half was treated with herbicides by immersing the film in a 2% herbicide– CHCl_3 solution. After 1 day of exposure, films were removed from the solution and rinsed several times with clean CHCl_3 . The other half of the film was not treated with herbicide but was similarly washed with CHCl_3 . FT-IR spectra of the treated films were recorded using a Galaxy 4020 series FT-IR spectrometer (Mattson Instrument Co., Madison, WI). Differential spectra of adsorbed compounds were obtained by subtracting the spectra of the herbicide-treated films from those of herbicide-free films. The spectra of non-adsorbed herbicide were obtained by using KBr disks.

RESULTS AND DISCUSSION

Effect of Cations on Herbicide Adsorption on Montmorillonite. All adsorption isotherms of the acetanilide herbicides on homoionic montmorillonite were well described by either the Freundlich equation or a linear relationship. To facilitate comparison between treatments, measured concentrations in the dissolved (C_i) and adsorbed (C_s) state were fitted to a linear regression to determine the adsorption coefficient K_d (L kg^{-1}). Good correlation was consistently obtained, with $R^2 > 0.96$ (**Table 1**).

Herbicide sorption on the same homoionic clay appeared to depend on the valence of the cation. On Ca^{2+} - or Mg^{2+} -saturated

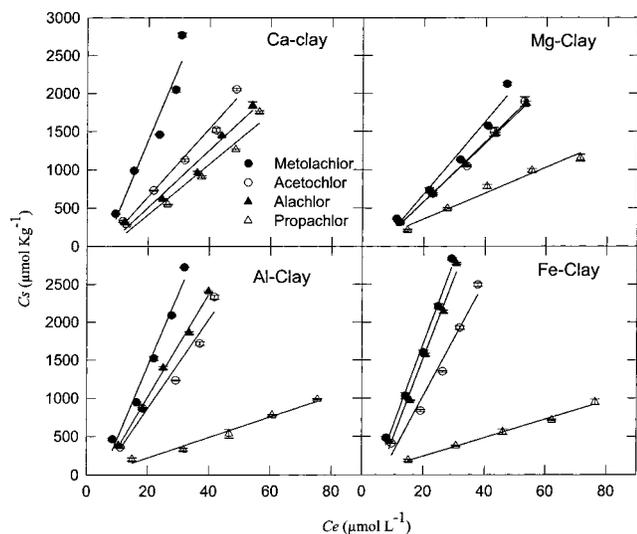


Figure 2. Adsorption isotherms of cloroacetanilide herbicides on Ca^{2+} -, Mg^{2+} -, Al^{3+} -, and Fe^{3+} -saturated montmorillonite

Table 2. Infrared Spectroscopic Absorption (ν) of the Carbonyl Group ($-\text{C}=\text{O}$) of Herbicides after Reaction with Monoionic Montmorillonite

sorbent	metolachlor		propachlor	
	ν (cm^{-1})	$\Delta\nu^a$	ν (cm^{-1})	$\Delta\nu$
herbicide	1670		1668	
K^+ -clay	1658	-12	1649	-19
Ca^{2+} -clay	1629	-41	1622	-44
Fe^{3+} -clay	1614	-56	1618	-50

^a Shift of absorption band as compared to that of pure herbicide.

clays, an order of metolachlor > acetochlor > alachlor > propachlor was observed (Table 1). On Al^{3+} - or Fe^{3+} -saturated clays, the order changed slightly to metolachlor > alachlor > acetochlor > propachlor. In a previous study, an adsorption order similar to the one for the divalent cations was found on Ca^{2+} -montmorillonite (12). This study shows that the same adsorption order may not hold for all cationic montmorillonite clays.

It was clear from both the isotherms and K_f values that for the same herbicide, adsorption generally increased in the order Mg^{2+} -clay \approx Ca^{2+} -clay < Al^{3+} -clay \leq Fe^{3+} -clay, with propachlor as the only exception (Figure 2; Table 1). The increases were more noticeable and consistent for alachlor and acetochlor. For instance, on the basis of the K_d value, adsorption on Fe^{3+} -clay for metolachlor, acetochlor, and alachlor was 57, 49, and 65% greater than that on Mg^{2+} -clay, respectively. This order coincided with the order of acidity measured in the clay suspension, which was Mg^{2+} -clay (pH 6.94) \leq Ca^{2+} -clay (pH 6.81) < Al^{3+} -clay (pH 5.71) \leq Fe^{3+} -clay (pH 4.57), as well as with that of the internal clay acidity measured with indicators, which was Mg^{2+} -clay \approx Ca^{2+} -clay (pH 8.2–9.2) < Al^{3+} -clay (pH 4.2–5.4) < Fe^{3+} -clay (pH 3.8–4.2).

Adsorption Mechanisms. Similar shifts in FT-IR absorption bands were observed for the different herbicides after adsorption on the same cationic clay. The spectra of the free and adsorbed states are shown in Figure 3 for metolachlor and in Figure 4 for propachlor. For all herbicides, after adsorption, the absorption band representing $-\text{C}=\text{O}$ vibration shifted from $\sim 1668 \text{ cm}^{-1}$ for the free molecule to a lower frequency, and the degree of shift increased in the order $\text{K}^+ < \text{Ca}^{2+} < \text{Fe}^{3+}$ (Table 2). A shift to a lower frequency suggests that the double-bond nature of $-\text{C}=\text{O}$ was weakened after adsorption, indicating the involvement of $-\text{C}=\text{O}$ in bonding to the clay. On the basis of

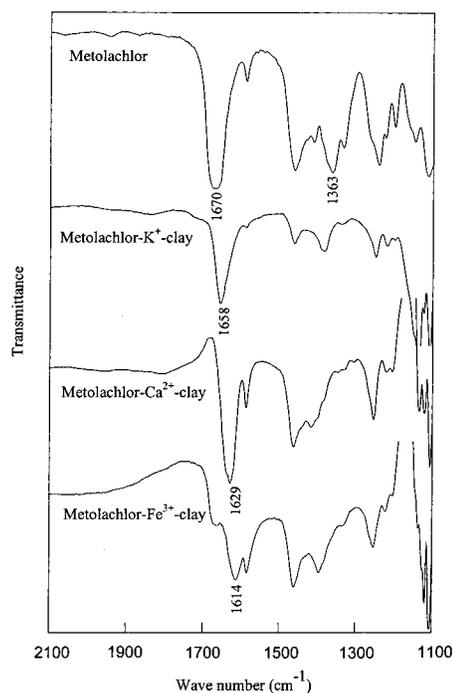


Figure 3. Infrared spectra of metolachlor on montmorillonite saturated with different cations: metolachlor; K^+ -clay; Ca^{2+} -clay; Fe^{3+} -clay. Spectra were recorded as differential spectra of herbicide-treated and untreated samples.

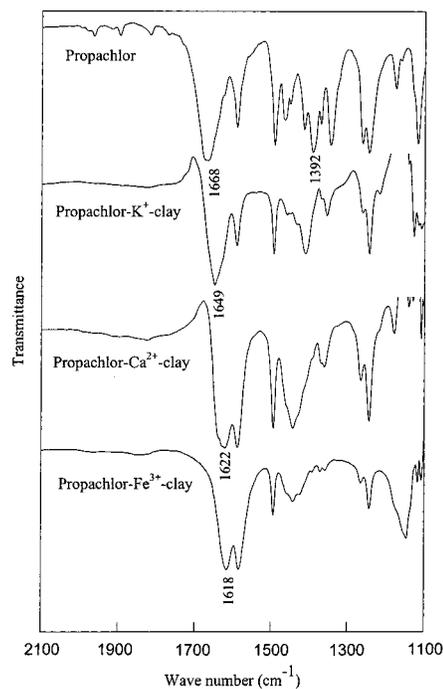


Figure 4. Infrared spectra of propachlor on montmorillonite saturated with different cations: propachlor; K^+ -clay; Ca^{2+} -clay; Fe^{3+} -clay. Spectra were recorded as differential spectra of herbicide-treated and untreated samples.

previous literature (18, 19), possible bonding interactions could include coordination bonds between $-\text{C}=\text{O}$ and the exchangeable cation, and/or H-bonds between $-\text{C}=\text{O}$ and the hydration water. Because $-\text{C}=\text{O}$ and $-\text{C}-\text{N}$ in these compounds are in a conjugation mode due to the distribution of double bonds and lone electron pairs (Figure 1), the formation of H-bonds with $-\text{C}=\text{O}$ should increase the double-bond nature in $-\text{C}-\text{N}$. This was shown in that the absorption band for $-\text{C}-\text{N}$ was shifted

to a higher frequency after adsorption and the shift was particularly clear for the K^+ -clay (Figures 3 and 4). This observation was in agreement with Bosetto et al. (17), who reported alachlor adsorption on montmorillonite by a coordination bond, through a water bridge, between the $-C=O$ group and the exchangeable cation of the clay. Hydrogen bonding has been reported for adsorption of many compounds on both clay and HA constituents (6, 17–20). Hydrogen bonding between a carbonyl group and hydration water was assumed to be the primary binding mechanism for fluzafop-butyl (21), diclofop-methyl (22), and alachlor (17) on clay. Because the tendency for the formation of both the coordination bond and the H-bond depends on the electronegativity of the carbonyl oxygen, substitutions in the herbicide molecule affect the bonding activity through their electrostatic interactions. For metolachlor, the substitutions on the ring and $-C-N$ increase the electronegativity, whereas the lack of ring substitution on propachlor decreases the electronegativity of the carbonyl oxygen (Figure 1). For acetochlor and alachlor, the lone electron pair on the oxygen of methoxy and ethoxy are in a resonance state with the lone pair on nitrogen and the double bond in $-C=O$, which delocalizes the charge distribution and thus reduces the charge density on the carbonyl oxygen. This may result in a weaker adsorption of acetochlor and alachlor compared to metolachlor on the same clay. The net effects of such interactions may have determined the relative adsorption of these herbicides on the homoionic clays.

The above assumption for bond formation would also support the observed effects of different exchangeable cations on herbicide adsorption on clay. First, the strength of the coordination bond between $-C=O$ and the exchangeable cation of clay should increase as the polarizing power of the cation increases from bivalent to trivalent. Second, H-bonding should be highly favored in the acidic interlayer of Fe^{3+} - or Al^{3+} -saturated clay as compared to that containing Ca^{2+} or Mg^{2+} . The internal pH values in Fe^{3+} - and Al^{3+} -clays were only 3.8–4.2 and 4.2–5.4, respectively. Linear regression confirmed that the shift of the $-C=O$ vibration band after adsorption was closely related with the external pH of homoionic clay, and the coefficient of correlation was >0.87 (Table 2). Dependence of adsorption on clay acidity was reported previously for a number of other pesticides. For instance, clay adsorption of dimepate (18), triclopyr (9), and thiazafurion (4) was found to increase with the acidity of homoionic clays.

The influence of cation on the adsorption of propachlor appeared to be the opposite. As the cation changed from Ca^{2+} to Fe^{3+} , K_d decreased from 32.8 to 12.0, or a decrease of 68%. Therefore, other binding sites may have been involved in propachlor adsorption. One of the potential sites is the $-C-N$, where the lone pair on the N can form a coordination bond with cations. This interaction should be the strongest for propachlor due to its lack of substitutions or steric hindrance. For the same reason, the smaller radius of Ca^{2+} or Mg^{2+} should enhance, whereas the larger radius of Al^{3+} or Fe^{3+} should inhibit, such an interaction.

Effect of Humic Acid Association on Herbicide Adsorption on Montmorillonite. Adsorption coefficients (K_d) on Ca^{2+} -clay and HA mixtures of different ratios were measured to determine the effect of HA association on herbicide adsorption on clay. Herbicide adsorption on pure HA was 1.76–2.37 times greater than that on pure Ca^{2+} -clay. Herbicide adsorptions on mixtures of HA and Ca^{2+} -clay, however, all deviated significantly from what could be expected by assuming independent and additive adsorption on the individual components (shown in Figure 5

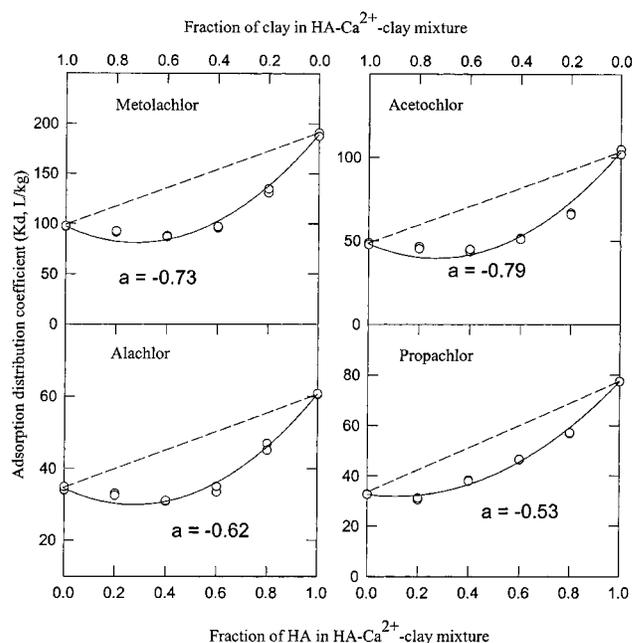


Figure 5. Adsorption coefficients of acetanilide herbicides on clay and humic acid mixtures in different ratios.

as dotted lines). This indicates that complexation of HA and Ca^{2+} -clay resulted in smaller surface areas or fewer sites available for adsorption or that complexation changed the properties of the adsorbents in such a manner that the overall adsorption was reduced. In an aqueous medium consisting of f_m fraction of clay and f_{HA} fraction of HA, the total adsorption would be the sum of their individual adsorption terms if complexation had no effect on adsorption:

$$K_d = f_m K_m + f_{HA} K_{HA} \quad (1)$$

K_m is the adsorption coefficient for clay, and K_{HA} is the adsorption coefficient for HA. Application of eq 1 would give the dotted lines in Figure 5 for the tested herbicides and adsorbents. If complexation between clay and HA results in a different adsorption capacity for the HA-clay complexes, then sorption follows eq 2:

$$K_d = f_m K_m + f_{HA} K_{HA} + a f_m f_{HA} (K_m + K_{HA}) \quad (2)$$

The third term in eq 2 represents the deviation from the independent adsorption scenario, with a reflecting the relative change in adsorption capacity of the HA-clay complexes. If $a < 0$, complexation reduces adsorption. In contrast, if $a > 0$, complexation enhances adsorption. When $a = 0$, eq 2 would reduce to eq 1, and complexation would have no effect on adsorption.

The measured K_d values in Figure 5 were fitted to eq 2 for each herbicide, and the derived nonlinear regression lines (shown as solid lines in Figure 5) accurately depicted the measurements for all herbicides, with correlation coefficients $R^2 > 0.98$. The a values are -0.73 , -0.79 , -0.62 , and -0.53 for metolachlor, acetochlor, alachlor, and propachlor, respectively. The relative deviation of adsorption from eq 1, $D\%$, can be calculated as

$$D\% = a f_m f_{HA} (K_m + K_{HA}) / (f_m K_m + f_{HA} K_{HA}) \times 100 \quad (3)$$

Solving eq 3 using the regression and finding the maximum allowed the calculation of the clay-to-HA ratio at which the greatest decrease in adsorption occurred. This ratio was found

to be 0.6:0.4 for all herbicides. At this clay-to-HA ratio, the actual adsorption was 37.5, 40.9, 31.6, and 27.7% less than that predicted by independent adsorption for metolachlor, acetochlor, alachlor, and propachlor, respectively. Thus, HA and clay complexation affected differently the adsorption of different herbicides, although the greatest effect occurred at the same clay-to-HA ratio for all of the herbicides.

Reduced adsorption was also observed by Pusino et al. (8) for metolachlor after Ca^{2+} - or Na^{2+} -montmorillonite was mixed with different proportions of HA.

In studying the adsorption of thiazafurion on montmorillonite, Celis et al. (10) observed that coating with iron species, commercial HA, or soil HA all decreased herbicide adsorption on the clay, whereas removing the coating restored the adsorption. It is well-known that the surface chemistry and activity of clay minerals can be drastically modified after complexation with certain organic species. For instance, the polarity change after coating clay with large organic cations such as long-chain alkylamides was found to greatly enhance the clay's adsorption toward nonionic organic compounds (23, 24). In soil, it is estimated that from 52 to 98% of all soil carbon occurs as clay-soil organic matter complexes (25). It is clear from this and other studies that the intimate association between individual soil constituents causes modification of their sorptive properties toward pesticides. Understanding the direction, degree, and causes of this modification on pesticide adsorption would be important both for elucidating adsorption mechanisms and for estimating adsorption a priori by using soil compositions. As clay and organic matter interactions may be subject to various processes under natural conditions, the influence of variables such as time, temperature, and the origin and nature of clay and organic matter constituents on the modification of adsorption caused by constituent complexation should be further examined.

Conclusion. Adsorption of acetanilide herbicides on the same cationic montmorillonite decreased in the order metolachlor > acetochlor > alachlor > propachlor. For all herbicides, adsorption on clay after cation saturation followed $\text{Mg}^{2+} \leq \text{Ca}^{2+} < \text{Al}^{3+} \leq \text{Fe}^{3+}$. Both adsorption trends can be explained by the specific molecular structure of the herbicides and their interactions with clay cations. This further confirms that the structural differences between analogous compounds in the same class may be used as molecular probing information to gain a better understanding of adsorption mechanisms.

Adsorption of herbicides on HA-clay complexes deviated significantly from an independent and additive adsorption behavior, indicating that complexation of individual constituents modified the overall adsorption properties. Under the experimental conditions, HA-clay complexation reduced adsorption for all herbicides. The clay-to-HA ratio at which the greatest decrease in adsorption occurred was 0.6:0.4 for all herbicides. However, at this ratio, greater decreases in adsorption were observed for metolachlor and acetochlor than for propachlor. The underlying mechanisms for these effects were not known from this study. Given the fact that clay and organic matter are always intimately associated in soil, understanding the influence of these interactions on pesticide adsorption may provide useful information on adsorption mechanisms and may also allow quantitative predictions of adsorption by using information of soil compositions.

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