

Structural Influences in Relative Sorptivity of Chloroacetanilide Herbicides on Soil

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Adsorption of the chloroacetanilide herbicides acetochlor, alachlor, metolachlor, and propachlor was determined on soils and soil components, and their structural differences were used to explain their sorptivity orders. On all soils and soil humic acids, adsorption decreased in the order: metolachlor > acetochlor > propachlor > alachlor. On Ca²⁺-saturated montmorillonite, the order changed to metolachlor > acetochlor > alachlor > propachlor. FT-IR differential spectra of herbicide–clay or herbicide–humic acid–clay showed possible formation of hydrogen bonds and charge-transfer bonds between herbicides and adsorbents. The different substitutions and their spatial arrangement in the herbicide molecule were found to affect the relative sorptivity of these herbicides by influencing the reactivity of functional groups participating in these bond interactions. It was further suggested that structural characteristics of pesticides from the same class could be used to improve prediction of pesticide adsorption on soil.

Keywords: Adsorption; sorption; acetanilide herbicides; chloroacetanilide herbicides; acetochlor; alachlor; metolachlor; propachlor; organic matter; montmorillonite; humic acid

INTRODUCTION

Chloroacetanilide herbicides are used in large quantities for preemergence control of annual grasses and broadleaf weeds in corn, soybeans, and many other crops. The most commonly used herbicides from this class are acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide], alachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide], and propachlor [2-chloro-*N*-(1-methylethyl)-*N*-phenylacetamide]. The combined sales of acetochlor, alachlor, and metolachlor in 1995 reached 100 to 115 million pounds in the United States (U. S. Environmental Protection Agency, 1997). Because of their extensive usage and also their characteristics, these herbicides have been frequently detected in ground and surface waters (e.g., Cohen et al., 1986; Chesters et al., 1989; Hallberg, 1989; Ritter, 1990; Potter and Carpenter, 1995).

Adsorption on soil is one of the most important factors for controlling pesticide movement toward groundwater (Koskinen and Harper, 1990). Thus, the relative susceptibility of groundwater to contamination from chloroacetanilide herbicides may depend closely on their relative sorptivity. Adsorption of chloroacetanilide herbicides on soil has been extensively studied (Weber and Peter, 1982; Kozak et al., 1983; Peter and Weber, 1985; Senesi et al., 1994). In these studies, however, adsorption of only one or two of these herbicides was simultaneously investigated. Because of the use of different soils and methodologies for these studies, an order of

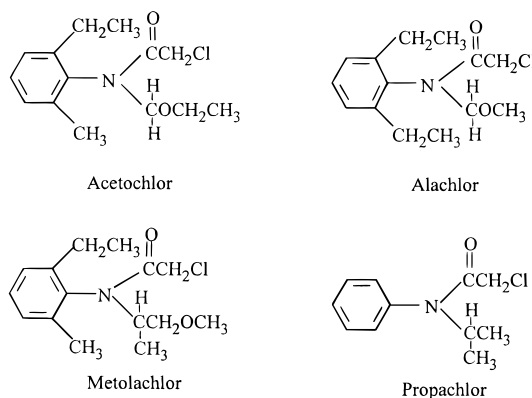


Figure 1. Molecular structures of acetochlor, alachlor, metolachlor, and propachlor.

sorptivity cannot be inferred from existing literature for these herbicides. Thus, the first purpose of this study was to determine the relative sorptivity of acetochlor, alachlor, metolachlor, and propachlor on soils, and soil mineral and humic acid components.

Chloroacetanilide herbicides share the same molecular core of 2-chloroacetanilide and differ only in the type and arrangement of substitutions (Figure 1). These structural differences should affect the reactivity of functional groups of these herbicides, and ultimately their relative sorptivity. The second purpose of this study was to identify the functional groups that may be involved in adsorption, and to evaluate possible interactions between the substitutions and these functional groups, and the influences of such interactions on herbicide sorptivity.

MATERIALS AND METHODS

Chemicals and Soils. Acetochlor (purity 98.1%), alachlor (99.5%), metolachlor (purity 98.7%), and propachlor (purity

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Table 1. Selected Properties of Chloroacetanilide Herbicides Used^a

herbicide	MW ^b	solubility (mg L ⁻¹)	K _{ow} ^c
metolachlor	284	530	398
acetochlor	270	223	1082
propachlor	212	618	200
alachlor	270	242	794

^a The solubility values are from Worthing and Hance (1991), and K_{ow} values are from the USDA-ARS Pesticide Property Database (1998). ^b MW = molecular weight. ^c K_{ow} = octanol-water partition coefficient.

99.5%) were all purchased from Chem Service (West Chester, PA) and used as received. The structures of these compounds are shown in Figure 1, and selected properties are given in Table 1.

Three soils, Arlington sandy loam (coarse loamy, mixed, thermic, haplic Durixeralf; Riverside, CA), Linne clay loam (fine loamy, mixed, thermic, calcic pachic Haploxerolls; Paso Robles, CA), and Webster clay loam (fine loamy, mixed, mesic, typic Endoaquolls; Waseca, MN), were used in this study. Soils were collected from the surface (0–15 cm), air-dried, and passed through a 2-mm sieve. Particle size distribution of these soils was measured using the pipet method (Gee and Bauder, 1986), organic carbon content (OC) was measured by the modified Walkley-Black method (Nelson and Sommers, 1982), and cation exchange capacity (CEC) was determined by the procedure of Rhoades (1982). Soil pH was determined in slurries of soil and water (1:1, w/w). The measured soil properties are given in Table 2.

Clay and Humic Acids. The clay was a montmorillonite Swy-2 from Crook County, WY, and was purchased from the Source Clay Minerals Repository at University of Missouri, Columbia, MO. The <2- μ m fraction was obtained by sedimentation. Ca²⁺-saturated clay was prepared by repetitive treatment of the clay with 0.5 M CaCl₂ solution. The prepared clay sample was centrifuged, washed repeatedly with deionized water until Cl⁻ free, and ground to a fine powder after drying at room temperature. Humic acid (HA) was prepared from the Webster clay loam using modified procedures from Schnitzer (1982). Briefly, 0.8 kg of air-dried soil was shaken with 3.0 L of 0.5 M NaOH solution under N₂ gas in a capped bottle for 24 h. The alkaline upper solution was centrifuged at 8500 g for 15 min, and the supernatant was acidified with 6 M HCl to pH 1, followed by standing for 24 h to permit coagulation of the HA fraction. The precipitated HA was separated from the solution by centrifugation at 20 000g for 25 min, and then redissolved in a small amount of 0.5 M NaOH solution under N₂ gas. The NaOH-dissolution and HCl-precipitation of HA was repeated two more times. Finally, HA was dialyzed in distilled water until salt-free and ground to a fine powder after being dried at 40 °C.

Batch Adsorption Experiments. Batch adsorption experiments were conducted to simultaneously determine adsorption isotherms of herbicides on three soils. Ten grams of soil were equilibrated with 10 mL of 0.01 M CaCl₂-herbicide solution in closed centrifuge tubes at 20 \pm 1 °C. The initial herbicide concentration ranged from 12 to 120 μ mol L⁻¹. Triplicate sample tubes were shaken for 24 h to achieve equilibrium. A preliminary kinetic study using multiple sampling intervals showed that >95% of adsorption took place within the first 4 h for all soil-pesticide combinations. At equilibrium, the suspension was centrifuged at 20 000g for 15 min, and the supernatant was filtered through a 0.2- μ m syringe filter. Herbicide concentration in solution was determined through HPLC analysis. The concentration sorbed on soil was calculated from the difference between the initial and final concentration of herbicide in solution. Soil-less blanks were included to correct for any adsorption inside the centrifuge tubes.

The measured adsorbed and solution concentrations were fitted to the Freundlich equation:

$$C_s = K_f C_e^{1/n} \quad (1)$$

where C_s (μ mol kg⁻¹) is herbicide concentration in the solid phase at equilibrium, C_e (μ mol L⁻¹) is herbicide concentration in the solution phase at equilibrium, and K_f and 1/n are empirical constants. K_{oc} (g mL⁻¹), the adsorption constant after normalization over soil organic carbon content, was calculated by dividing K_f by soil organic carbon content.

$$K_{oc} = (K_f/OC\%) \times 100 \quad (2)$$

Herbicide adsorption at a single concentration was separately measured for each herbicide on Ca²⁺-clay, HA, and a mixture of HA and Ca²⁺-clay at 20 \pm 1 °C. Adsorption was determined using 50 mg of adsorbent and 5.0 mL of 0.01 M CaCl₂-herbicide solution (100 μ mol L⁻¹), using three replicates for each herbicide-sorbent combination. For adsorption on HA-clay mixtures, 5 mg of HA and 45 mg of Ca²⁺-clay were added into the herbicide solution before shaking. After the suspension was shaken for 24 h, it was centrifuged at 20 000g for 15 min and filtered through 0.2- μ m syringe filters. The final solution was analyzed on HPLC for herbicide concentration.

Analysis of herbicide concentration in supernatant was conducted on a HP 1090 HPLC (Hewlett-Packard, Wilmington, DE) equipped with an auto-injection system and a diode-array detector (DAD). The column was a 250-mm \times 4.6-mm (i.d.) reverse-phase Adsorbosphere HS C₁₈ (5 μ m, Alltech, Deerfield, IL), injection volume was 20 μ L, and wavelength of detection was 230 nm. Mobile phase was a mixture of acetonitrile-methanol-water (60:10:30) that was acidified with 0.5% phosphoric acid. The flow rate was maintained at 1.0 mL min⁻¹ for all herbicides. External calibration was used for quantification.

FT-IR Analysis. Probable bond interactions between herbicides and sorbents were investigated by comparing FT-IR spectra of herbicides adsorbed on thin films of Ca²⁺-clay and HA-Ca²⁺-clay mixture. Self-supporting films of clay or HA-clay were prepared by evaporating 5 mL of Ca²⁺-clay or HA-(10%) + Ca²⁺-clay(90%) suspension in a 5-cm (i.d.) ring on a polyethylene sheet at room temperature. These air-dried films, about 50 mg in weight, 5 cm in diameter, 10 μ m in thickness, were cut into two halves. One half was treated with herbicides by immersing the film in 2% herbicide-CHCl₃ solution. After 1 d of treatment for clay films or 2 d for HA-clay films, films were removed from the solution and rinsed several times with CHCl₃. The other half of the film was not treated with herbicide, but was similarly washed with CHCl₃. FT-IR spectra of the treated films were recorded at 3500–600 cm⁻¹ by using a Galaxy 4020 FT-IR spectrometer (Mattson Instrument Co., Madison, WI). All FT-IR spectra of the pure and adsorbed compounds were measured under the same conditions. Differential spectra of adsorbed compounds were obtained by subtracting on the same scale the spectra of the herbicide-treated films from those of herbicide-free films. Because subtraction was between samples that originated from the same film and received identical treatments, differences were unlikely to be attributable to artifacts.

RESULTS AND DISCUSSION

Adsorption on Soil and Model Components. All adsorption isotherms were well described by the Freundlich equation for the selected concentration range, with $r \geq 0.99$ (Table 3, Figure 2). The 1/n value was significantly less than 1.0 in every case, ranging from 0.75 to 0.84. Nonlinearity has been widely observed in adsorption of organic compounds on soil (e.g., Rao and Davidson, 1980). The fact that 1/n is smaller than unity implies that as the initial concentration in the system increases, adsorption will decrease, or, the mobility of pesticides will increase. This can be seen in the changes of K_d (g mL⁻¹), the adsorption coefficient defined for a single concentration. For instance, K_d of alachlor in

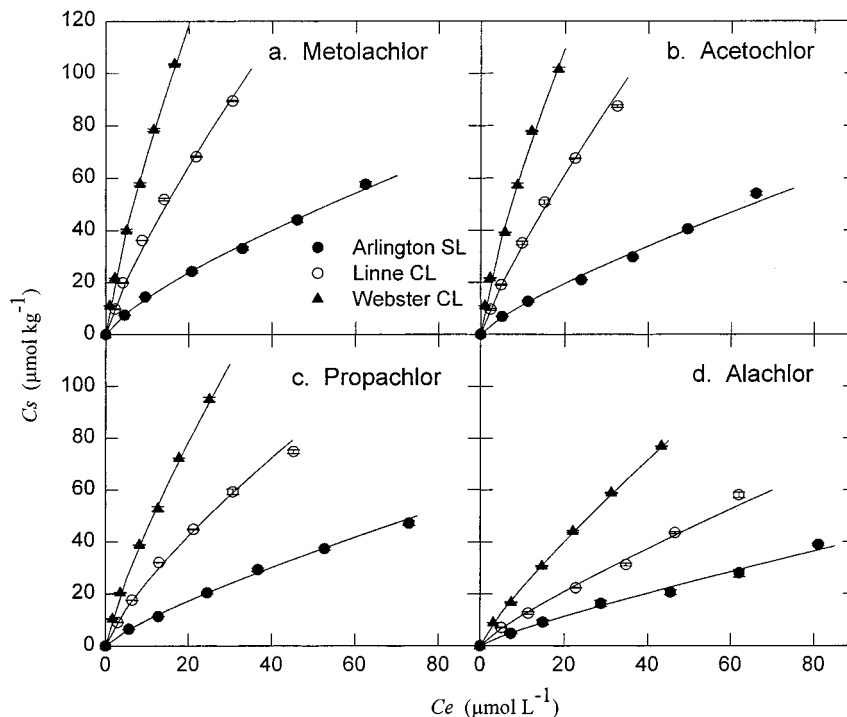


Figure 2. Adsorption isotherms of acetanilide herbicides on Arlington sandy loam, Linne clay loam, and Webster clay loam: (a) metolachlor; (b) acetochlor; (c) alachlor; and (d) propachlor.

Table 2. Selected Physical and Chemical Properties of Soils

soil	OC(%)	clay(%)	sand(%)	silt(%)	pH ^a	CEC ^b
Webster clay loam	3.48	28.8	35.4	35.8	5.22	25.9
Linne clay loam	2.51	31.3	36.7	32.0	6.80	29.9
Arlington sandy loam	0.92	7.4	74.6	18.0	6.73	5.9

^a Measured in 1:1 soil/water slurry. ^b In cmol kg⁻¹.

Webster clay loam was 1.77 g mL⁻¹ at 120 μmol L⁻¹, which was considerably smaller than that measured at 12 μmol L⁻¹ ($K_d = 2.78$ g mL⁻¹). As the water solubility of many acetanilide herbicides is relatively high (e.g., 223–618 mg L⁻¹ for the four herbicides used in this study), it is important to specify the concentration ranges under which K_d is measured.

For the same herbicides, K_f always decreased in the order of Webster clay loam > Linne clay loam > Arlington sandy loam (Table 3, Figure 2), which coincided with the decreasing order of soil organic matter content (Table 2). Previous studies using soil components suggest that all humic substances, except humin, exhibited a high affinity for acetanilide herbicides (Kozak et al., 1983; Senesi et al., 1994). Our study confirmed the positive effect of soil organic matter on adsorption of chloroacetanilide herbicides, as often observed in previous studies (Rao et al., 1986; Wood et al., 1987). This was further shown in that K_{oc} values calculated for the three soils studied (1.2–1.6 times different) were less scattered than the corresponding K_f values (3.6–5.9 times different) for the same herbicide. The role of soil organic matter was more directly validated in herbicide adsorption on HA extracted from soil (Table 4). Besides soil organic matter, however, significant adsorption also occurred on Ca²⁺-montmorillonite clay (Table 4). In comparison to HA, adsorption on Ca²⁺-clay was 1.7 to 2.4 times smaller. This was

Table 3. Freundlich Constants K_f (g mL⁻¹), 1/n, and Estimated K_{oc} (g mL⁻¹) for Adsorption of Four Acetanilide Herbicides on Three Soils (Mean ± Standard Deviation)^a

herbicide	K_f	1/n	K_{oc}
Webster clay loam			
metolachlor	11.77 ± 0.05	0.77 ± 0.01	338
acetochlor	10.83 ± 0.06	0.77 ± 0.02	311
propachlor	7.03 ± 0.05	0.81 ± 0.01	202
alachlor	3.25 ± 0.03	0.84 ± 0.01	93
Linne clay loam			
metolachlor	5.86 ± 0.08	0.81 ± 0.02	233
acetochlor	4.93 ± 0.08	0.84 ± 0.02	196
propachlor	4.10 ± 0.05	0.78 ± 0.01	163
alachlor	1.68 ± 0.07	0.84 ± 0.02	67
Arlington sandy loam			
metolachlor	2.50 ± 0.05	0.75 ± 0.01	273
acetochlor	1.82 ± 0.06	0.79 ± 0.02	198
propachlor	1.54 ± 0.04	0.81 ± 0.01	167
alachlor	0.89 ± 0.10	0.84 ± 0.03	97

^a The correlation coefficient r was ≥ 0.99 for each treatment.

Table 4. Distribution Coefficient K_d (g mL⁻¹) of Acetanilide Herbicides on Humic Acid (HA) Extracted from Soil, Ca²⁺-Saturated Montmorillonite Clay, and HA–Clay Mixture (10:90, w/w). (mean ± Standard Deviation)^a

herbicide	soil HA	Ca ²⁺ -clay	HA–Ca ²⁺ -clay
metolachlor	189.2 ± 1.7	97.3 ± 0.4	92.1 ± 0.6
acetochlor	103.3 ± 1.7	48.2 ± 0.4	45.8 ± 0.6
propachlor	77.4 ± 0.1	32.7 ± 0.1	32.9 ± 0.4
alachlor	60.2 ± 0.3	34.5 ± 0.5	30.2 ± 0.1

^a The correlation coefficient r was ≥ 0.99 for each treatment.

in agreement with Sethi and Chopra (1975), who reported a contribution of clay minerals to the adsorption of alachlor.

Herbicide adsorption on all soils, soil HA, and HA–Ca²⁺-clay mixture invariably followed the order: metolachlor > acetochlor > propachlor > alachlor (Tables 3 and 4). On Ca²⁺-montmorillonite, however, the order

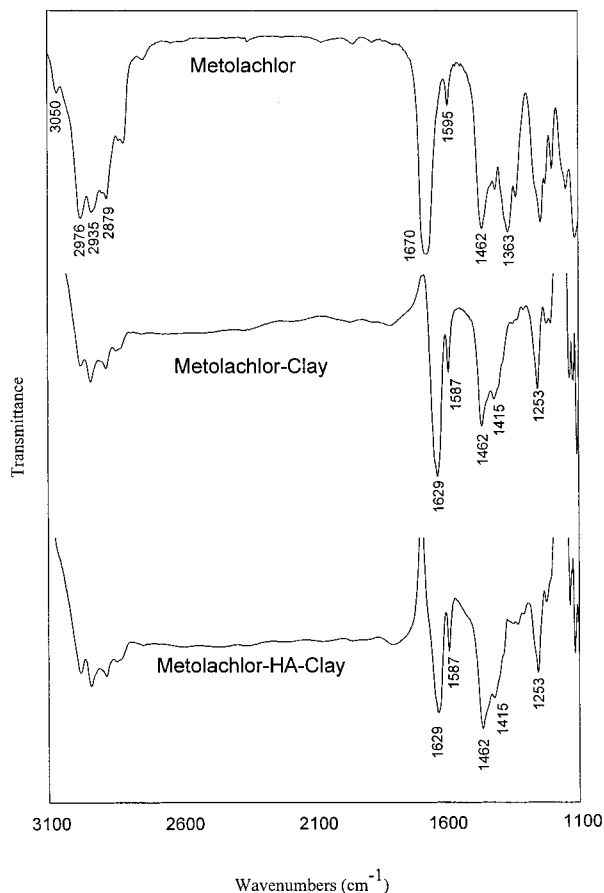


Figure 3. Differential FT-IR spectra. (a) metolachlor; (b) metolachlor sorbed on Ca^{2+} -montmorillonite; and (c) metolachlor sorbed on humic acid (10%) and Ca^{2+} -montmorillonite (90%).

became metolachlor > acetochlor > alachlor > propachlor (Table 4). All differences were significant at $P = 0.01$. These orders of sorptivity cannot be correlated to herbicide solubility, which follows: propachlor (618 mg L^{-1}) > metolachlor (530 mg L^{-1}) > alachlor (242 mg L^{-1}) > acetochlor (223 mg L^{-1}) (Worthing and Hance, 1991) (Table 1). Nor can they be correlated with the octanol-water partition coefficients (K_{ow}) of these compounds, which follows the order of acetochlor (1082) > alachlor (794) > metolachlor (398) > propachlor (200) (U.S. Department of Agriculture, Agricultural Research Service, 1998) (Table 1). Both solubility and K_{ow} would suggest a sorptivity order of acetochlor > alachlor > metolachlor > propachlor.

Adsorption Mechanisms. To understand the mechanisms that define the observed relative sorptivity, we obtained differential FT-IR spectra of herbicides sorbed on Ca^{2+} -clay and HA-clay mixture. Similar FT-IR spectra were obtained for metolachlor, alachlor, and acetochlor sorbed on clay or HA-clay; the spectra for propachlor were somewhat different. The spectra of metolachlor and propachlor are shown in Figures 3 and 4.

From comparing FT-IR spectra of herbicides before and after adsorption, it was evident that coordination bonds might have formed between herbicide carbonyl oxygen and cations on clay (Figures 3 and 4). This was reflected for metolachlor in a shift of C=O absorption band from 1670 cm^{-1} for the pure herbicide to 1629 cm^{-1} for the adsorbed herbicide (Figure 3), and for propachlor in a similar shift from 1668 cm^{-1} for the pure herbicide

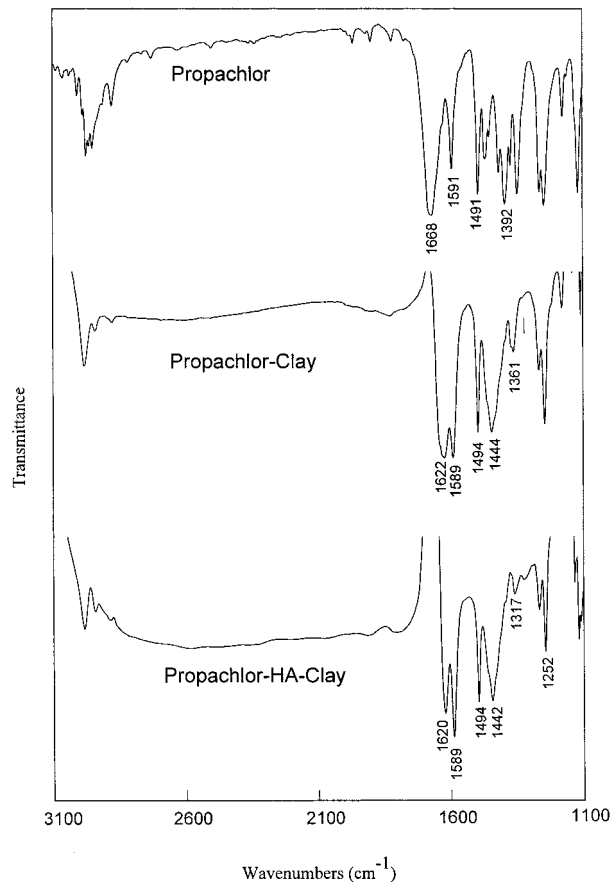


Figure 4. Differential FT-IR spectra. (a) propachlor; (b) propachlor sorbed on Ca^{2+} -montmorillonite; and (c) propachlor sorbed on humic acid (10%) and Ca^{2+} -montmorillonite (90%).

to 1622 cm^{-1} after adsorption (Figure 4). Formation of coordination bonds was proposed to occur between C=O of alachlor and hydrated cations of clay minerals by Bosetto et al. (1993) also.

On soil HA, two types of bond formation might have occurred. (1) Formation of hydrogen bonding between carbonyl oxygen (C=O) and amide nitrogen (C-N) of herbicides and hydroxyl and carboxyl groups of HA. Interaction at C=O was indicated by a shift of C=O absorption band from 1670 cm^{-1} for pure metolachlor to 1629 cm^{-1} after adsorption on HA-clay (Figure 3), and from 1668 cm^{-1} for pure propachlor to 1620 cm^{-1} for adsorbed propachlor (Figure 4). Interaction at C-N was reflected in the disappearance of the C-N stretching band at 1363 cm^{-1} for pure metolachlor and 1392 cm^{-1} for pure propachlor after adsorption on the HA-clay mixture. Multi-functional hydrogen bonding was previously suggested to occur in adsorption of alachlor and metolachlor on organic substances in other studies (Weber and Peter, 1982; Kozak et al., 1983; Senesi, 1992; 1994). (2) Formation of π - π charge transfer bonds between the benzene ring of herbicides and aromatic nuclei of HA. This was evident especially for propachlor, where an increase of the relative strength of absorption around 1591 cm^{-1} (representing $-\text{C}=\text{C}-$ vibration) was seen after adsorption on HA-clay (Figure 4). Charge transfer (π) was postulated as one of the bonding possibilities for alachlor and humic acids extracted from regular and sewage-sludge-amended soils (Senesi et al., 1994).

Relationship between Herbicide Structure and Sorptivity. Differences in herbicide structure might

have affected sorptivity by influencing the reactivity of the functional groups participating in the bond formation. The carbonyl oxygen and amide nitrogen can conjugate, thereby increasing electron density on N. This should enhance the potential for coordination (on both amide-N and carbonyl-O) with clay cations. From Figure 1, substitutions on the side chain would increase nitrogen electron density in the order of metolachlor [$-\text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$] > acetochlor ($-\text{CH}_2\text{OCH}_2\text{CH}_3$) > alachlor ($-\text{CH}_2\text{OCH}_3$) > propachlor [$-\text{CH}(\text{CH}_3)\text{CH}_3$]. Alkyl substitutions on the ring would increase nitrogen electron density in the order of alachlor \approx metolachlor \approx acetochlor > propachlor. These substitutions together may have determined the order of reactivity of carbonyl oxygen and amide nitrogen on clay: metolachlor > acetochlor > alachlor > propachlor, which coincided with the order of sorptivity on clay.

On soil or HA, similar influences of substitutions should also occur for hydrogen bonding between herbicides and the sorbent. In addition to hydrogen bonding, however, charge-transfer bonds might have formed between the benzene ring of the herbicide and the aromatic nuclei of soil organic-matter fractions. This interaction should be most significant for propachlor, because it has the least steric hindrance due to its lack of alkyl substitution on the ring. The latter interaction may be just significant enough to cause a switch between propachlor and alachlor of their sorptivity on soils, HA, and HA-clay mixture, resulting in an overall order of metolachlor > acetochlor > propachlor > alachlor.

CONCLUSIONS

Adsorption of acetanilide herbicides was shown to follow specific orders. On soil or humic acids extracted from soil, the order was metolachlor > acetochlor > propachlor > alachlor; whereas on clay, the order changed to metolachlor > acetochlor > alachlor > propachlor. These orders could not be explained from the solubility or K_{ow} values of these compounds. From FT-IR analysis and existing information, two functional groups, carbonyl oxygen and amide nitrogen, were assumed to contribute to bond formation between clay and herbicides. On soil HA, carbonyl oxygen, amide nitrogen, and benzene ring were proposed to participate in the bond formation. The observed sorptivity orders could be adequately explained by examining the interactions of substitutions with these reactive sites. Such an evaluation of the relationship between herbicide structures and sorptivity further strengthened our understanding of adsorption mechanisms of these herbicides as a class. Because structural differences in the classes are generally more gradual than between classes, they may be better related to sorptivity, as shown in this study. This hypothesis is worthy of further testing using pesticides from other families.

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