

Adsorption of chloroacetanilide herbicides on soil (I) Structural influence of chloroacetanilide herbicide for their adsorption on soils and its components

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Abstract: Adsorption of chloroacetanilide herbicide acetochlor, alachlor, metolachlor and propachlor on soils and soil components was determined, and the structural differences of these herbicides were used to explain the order of sorptivity. Adsorption isotherms for all herbicide-soil combinations conformed to the Freundlich equation, and K_f increased with increasing soil organic carbon content. K_d on soil humic acid was greater than that on clay, but association of humic acid with clay reduced the overall adsorption. On all soils and soil humic acids, herbicide adsorption decreased in the order: metolachlor > acetochlor > propachlor > alachlor. On Ca^{2+} -montmorillonite, the order changed to metolachlor > acetochlor > alachlor > propachlor. FT-IR spectra of herbicide-clay or herbicide-humic acid-clay mixtures showed that H-bonding and charge transfer were the primary interaction pathways between these compounds and the surface of clay or humic acids. The different moieties attached to 2-chloro-acetanilide and their unique arrangement may have influenced the binding mechanisms and thus the sorptivity of these herbicides. This study indicates that the structural difference of pesticides in the same classes may be used as a molecular probe to obtain a better understanding of sorption mechanisms of pesticides on soil.

Key words: adsorption; chloroacetanilide herbicides; soil; organic matter; clay

Introduction

Chloroacetanilide herbicides are used in large quantities for pre-emergence control of annual grasses and broadleaf weeds in corn, soybeans, peanuts, dry beans/peas, sorghum, sunflowers, and several other crops. The most commonly used herbicides in this group are acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide], alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], metolachlor [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—115 million pounds in the United States (U. S. Environmental Protection Agency, 1997). Because of their extensive usage and also their intrinsic characteristics, these herbicides have been frequently detected in ground or surface waters (Chesters, 1989; Potter, 1995).

Adsorption in soil is the most important factor for controlling pesticide transport in the soil-water environment. Adsorption of a pesticide in a given soil is governed both by the structure of the pesticide molecule and by the physico-chemical properties of the soil (Kiskinen, 1990). Consequently, most studies aiming to elucidate sorption mechanisms use the approach of correlating sorptivity with either the physico-chemical properties of pesticides (i.e., sorbate), or those of soils (e.g., sorbent). Although regression analysis using a large number of pesticides or soil types has produced many useful empirical relationships, this approach does not directly reveal the mechanisms. As such, exceptions have often been found for most empirical expressions. For instance, early investigators found that pesticide sorption in soil closely resembled partition into organic solvent, where organic matter in soil behaves like an organic solvent (Chiou, 1983). Sorptivity is therefore correlated inversely with pesticide solubility (Chiou, 1979; 1983), and

positively with the *n*-octanol-water partition coefficient K_{ow} (Hassett, 1980; Chiou, 1979; Rao, 1982). Recent studies using long equilibration terms or competitive adsorbents suggest, however, different sorption mechanisms may operate concurrently in soil, in which organic matter may act as a "glassy" polymer (Xing, 1996a; 1996b; Huang, 1997). These inconsistencies indicate the necessity to study pesticide sorption at the molecular level.

It is known that pesticides from different classes differ greatly in structure and property, while those from the same class share the same molecular core and differ only in the attached moieties or in their arrangement. Conceivably, sorption mechanisms can be explored by examining pesticides from the same class. The change in molecular structure among the derivative analogs in the same class is relatively small and gradual, and may thus be more reliably correlated with the measured sorptivity. Most sorption studies use single or randomly selected pesticides, whereas sorption measured from different soils or by different researchers is seldom comparable because of experimentation induced artifacts (Koskinen, 1991). A relatively small number of studies are conducted by examining a group of analogous pesticides under the same conditions. These studies are often shown to be more informative. For instance, sorption of methyl parathion, ethyl parathion, methyl paraoxon, and ethyl paraoxon on soils showed that the thiophosphates ($>P=S$) are predominately sorbed by soil organic matter, while the sorption of the phosphates ($>P=O$) is closely related to soil clay content (Sanchez-Martin, 1991). By comparing sorptivity of imidacloprid and its three metabolites, Cox *et al.* (Cox, 1997) found that changes in functional groups of the parent compound had profound effects on the apparent sorption. More sorption was found for compounds with $>C=NH$ than those with $>C=O$ or $>C=N-NO_2$.

In this study, we quantified the difference in adsorption of acetochlor, alachlor, metolachlor, and propachlor on three soils, one Ca^{2+} -montmorillonite, a soil-derived humic acid sample, and a clay-humic acid mixture. FT-IR analysis was used to detect the probable binding mechanisms between herbicides and clay or humic acids. The influence of herbicide structural arrangement on these binding mechanisms was analyzed, and a correlation was finally made between the structural features and sorptivity of these herbicides.

1 Materials and methods

1.1 Chemicals and soils

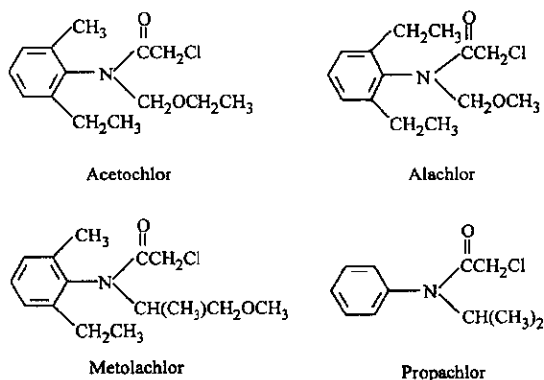


Fig. 1 Molecular structure of acetochlor, alachlor, metolachlor and propachlor

Acetochlor (purity 98.1%), alachlor (99.5%), metolachlor (purity 98.7%), and propachlor (purity 99.5%) were all purchased from Chem Service (West Chester, PA), and used as received. The structures of these compounds are shown in Fig. 1.

Three soils, sandy loam soil A, clay loam soil B, and clay loam soil C, 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, 1986), organic carbon content by the modified

Walkley-Black method (Nelson, 1986), and cation exchange capacity (CEC) by the procedure of Rhoades (Rhoades, 1986). Soil pH was determined in slurries of soil and water (1:1, w/w). The measured soil properties are given in Table 1.

Table 1 Selected physical and chemical properties of soils

Soil	OC, %	Clay, %	Sand, %	Silt, %	pH	CEC
Clay loam soil A	3.48	28.75	35.39	35.85	5.22	25.79
Clay loam soil B	2.51	31.30	36.67	32.03	6.80	29.86
Sandy loam C	0.92	7.40	74.63	17.97	6.73	5.95

1.2 Clay and humic acids

The clay was a montmorillonite Swy-2 from Crook County, Wyoming, and was purchased from the Source Clay Minerals Repository at University of Missouri-Columbia, MO. The $<2\mu\text{m}$ fraction was obtained by sedimentation. Ca^{2+} -saturated clay was prepared by repetitive treatment of the clay with 0.5 mol/L CaCl_2 solution. The prepared clay samples were 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 (Schnitzer, 1982). Briefly, 0.8 kg of air-dried soil was shaken with 3.0 L of 0.5 mol/L NaOH solution under N_2 gas in a capped bottle for 24 h at room temperature. The alkaline upper solution was centrifuged at 10000 g for 15 min, and the supernatant was acidified with 6 mol/L HCl to pH 1, followed by standing for 24 h to permit coagulation of the HA fraction. The precipitated HA was separated from the supernatant solution by centrifugation at 18000 g for 25 min, and then re-dissolved in a small amount of 0.5 mol/L NaOH solution under N_2 gas. The NaOH-dissolution and HCl-precipitation of HA was repeated for two more times. Finally, HA was dialyzed in distilled water until salt-free, and ground to a fine powder after drying at 40 °C.

1.3 Adsorption

Adsorption isotherms of herbicides on soils were determined by equilibrating 10.0 g of air-dried soil with 10 ml of 0.01 mol/L CaCl_2 -herbicide solution in closed centrifuge tubes at $20 \pm 1^\circ\text{C}$. The initial herbicide concentration ranged from 12 to 120 $\mu\text{mol/L}$. 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 15000 g 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 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.

Herbicide adsorption was separately measured on Ca^{2+} -clay, HA, and HA and Ca^{2+} -clay mixture at $20 \pm 1^\circ\text{C}$. The amount of adsorbent was always 50 mg, and the volume of 0.01 mol/L CaCl_2 -herbicide solution was 5.0 ml. The initial herbicide concentration in solution was 100 $\mu\text{mol/L}$. For adsorption on HA-clay mixture, 5 mg of HA and 45 mg of Ca^{2+} -clay were added into the herbicide solution before shaking. After shaking for 24 h, the suspension was centrifuged at 20000 g for 15 min and filtered through 0.2 μm 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) 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 C_{18} (5 μm , Alltech, Deerfield, IL), injection volume was 20 μl , and wavelength of detection was 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 always maintained at 1.0 ml/min. External calibration was used for quantification.

1.4 Adsorption mechanisms

Adsorption mechanisms were investigated by using FT-IR analysis of self-supporting films of herbicide- Ca^{2+} -clay and herbicide-HA- Ca^{2+} -clay complexes. Self-supporting films of clay or HA-clay were prepared by evaporating 5 ml of Ca^{2+} -clay or HA(10%) + Ca^{2+} -clay(90%) suspension in a 5-cm (i.d.) ring on polyethylene sheet at room temperature. These air-dried films, about 50 mg in weight, 5 cm in diameter, 10 μm in thickness, were cut into two halves. One half was treated with herbicides by immersing the film in 2% herbicide- CHCl_3 solution. After 1d of treatment for clay films or 2d for HA-clay films, 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 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. All FT-IR spectra of the pure and adsorbed compounds are reported between 3500 and 600/ cm .

2 Results and discussion

2.1 Sorption on soil and model components

Data from soil adsorption experiments were fitted to the logarithmic Freundlich equation:

$$\log C_s = \log K_f + n_f \log C_e, \quad (1)$$

where C_s ($\mu\text{mol/kg}$) is the herbicide concentration in the solid phase at equilibrium; C_e ($\mu\text{mol/L}$) the herbicide concentration in the solution phase at equilibrium, and K_f and n_f are empirical constants representing the intercept and slope of the isotherm, respectively. K_∞ (g/mL) the adsorption constant after normalization over soil organic carbon content, was calculated by dividing K_f over the fraction of organic C in soil:

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

All adsorption isotherms are L-shaped (Fig. 2). Although these isotherms appear to be Langmuirian, the Freundlich equation was preferred because it is more realistic for systems as heterogeneous as soils. All data fit the Freundlich equation for the selected concentration range, with $r_2 > 0.983$ (Table 2). The n_f value was significantly < 1.0 in every case, ranging from 0.752 to 0.844. Non-linearity is widely observed in adsorption of organic compounds in soil (Rao, 1980). Recent kinetic studies attribute the slow adsorption to sorption on the fraction of soil organic matter that resembles condensed, glassy polymers (Xing, 1996a; 1996b). In reality, the fact that n_f is considerably smaller than unity implies that as the initial concentration (C_i) in the system increases, K_d , the adsorption coefficient measured at single concentrations, will decrease, or the mobility of pesticides will increase. For instance, K_∞ of alachlor in Webster CL at $C_i = 120$ $\mu\text{mol/L}$ was 51, which was much smaller than that measured at $C_i = 12$ ($\mu\text{mol/L}$) ($K_\infty = 80$). As the water solubility of many acetanilide herbicides is relatively high (e.g., 223–618 mg/L for the four herbicides used in this study), it is important to specify the concentration ranges under which K_d or K_∞ is measured.

Similar observation was made by Cox *et al.* (Cox, 1997) for imidacloprid adsorption in soils. Depending on the initial concentration used for measuring K_d , imidacloprid can be arbitrarily classified as a "leacher" or "non-leacher".

For the same class herbicides, K_f always decreases in the order of Webster CL > Linne CL > Arlington SL, which coincides with the decreasing order of soil organic matter content. Previous studies using soil components suggest that all humic substances, except humin, exhibit a high affinity for acetanilide herbicides (Kozak, 1983). Our study confirms the positive effect of soil organic matter on pesticide adsorption, as established widely by many other researchers. Under the assumption that the mineral components are not significantly active in the adsorption process and all

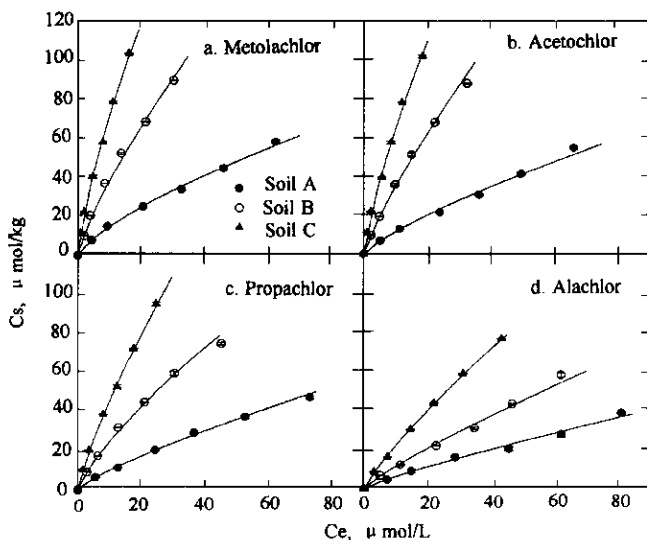


Fig. 2 Adsorption isotherms of chloroacetanilide herbicides on three soils
(a) metolachlor; (b) acetochlor; (c) alachlor; (d) propachlor

the soil organic matter has the same adsorptive characteristics, the adsorption constant K_f should be linearly dependent on the organic content of soil. The validity of this equation is supported by observation that, for a given herbicide, K_{oc} values obtained on different soils (1.2—1.6 times different) are less scattered than the corresponding K_f values calculated on the total soil weight basis (3.6—5.9 times different).

The fact that K_{oc} is still somewhat scattered after normalization over soil OC content indicates however, that some other factors have apparently contributed, though to a lesser extent, to the overall adsorption. A support to such a hypothesis is given by an examination of the adsorption of these four herbicides on Ca^{2+} -clay and HA extracted from Webster CL (Table 3). Significant herbicide adsorption was observed on both HA and Ca^{2+} -clay, and the adsorption on HA was 1.7—2.1 times stronger than that on the clay. It can also be noted that K_d on the HA-clay mixture for every herbicide is smaller than what would be expected by assuming independent sorptive behavior. This suggests that the interaction of HA and clay reduced the availability of adsorptive sites or modified some properties of the adsorbents in such a manner that sorption is reduced. Other investigators have reported similar observations for binary or ternary systems (Pusino, 1992, 1994; Celis, 1997, 1998). For instance, Pusino *et al.* (Pusino, 1992, 1994) showed that K_d of metolachlor or triclopyr on humic acid and Ca^{2+} -clay mixtures was consistently smaller than that estimated from adsorption on separate components. Celis *et al.* (1997, 1998), using model adsorbents, found that adsorption of Thiazafururon, atrazine, or simazine on inter-associations of Ca-clay, ferrihydrite and humic acids was not the simple sum of the sorption on single components. Thus, extrapolation of sorptivity on single components to whole soils is complicated by component interactions. Understanding such interactions, particularly bonding interaction between components, may therefore shed light on the mechanisms of adsorption.

2.2 Adsorption mechanisms

One interesting aspect of the data is that the measured K_f in different soils for the four herbicides invariably followed the order: metolachlor > acetochlor > propachlor > alachlor (Table 2). The same order was also obeyed for the sorption on HA, but deviated slightly on clay, where the order became: metolachlor > acetolachlor > alachlor > propachlor (Table 3). These

Table 2 Freundlich constants (K_f and n_f) and correlation coefficient (r^2) for the four kinds of acetanilide herbicides adsorption on three of soils

Herbicide	K_f	N_f	r^2
Soil A			
Metolachlor	11.77 ± 0.05	0.771 ± 0.011	0.997
Acetochlor	10.83 ± 0.06	0.772 ± 0.015	0.994
Propachlor	7.03 ± 0.05	0.805 ± 0.013	0.996
Alachlor	3.25 ± 0.03	0.838 ± 0.009	0.998
Soil B			
Metolachlor	5.86 ± 0.08	0.812 ± 0.020	0.990
Acetochlor	4.93 ± 0.08	0.842 ± 0.021	0.990
Propachlor	4.10 ± 0.05	0.778 ± 0.014	0.995
Alachlor	1.68 ± 0.07	0.841 ± 0.018	0.992
Soil C			
Metolachlor	2.50 ± 0.05	0.752 ± 0.012	0.996
Acetochlor	1.82 ± 0.06	0.794 ± 0.016	0.994
Propachlor	1.54 ± 0.04	0.806 ± 0.012	0.997
Alachlor	0.895 ± 0.097	0.844 ± 0.028	0.983

Table 3 Distribution coefficient K_d of acetanilide herbicides on Ca^{2+} -clay, HA, and HA-clay mixture ($n = 2$)

Herbicide	Adsorbent	K_d , g/ml
Metolachlor	Ca^{2+} -clay	97.31
	HA	189.16
	HA-clay	92.05 (106.5) **
Acetochlor	mixture*	
	Ca^{2+} -clay	48.22
	HA	103.34
Propachlor	HA-clay mixture	45.78(53.7)
	Ca^{2+} -clay	32.68
	HA	77.42
Alachlor	HA-clay mixture	30.86(37.2)
	Ca^{2+} -clay	34.45
	HA	60.23
	HA-clay mixture	30.18(37.0)

Notes: * Mixture of 10% HA and 90% Ca^{2+} -clay; ** Values in parenthesis are calculated assuming independent adsorption on HA and clay

sorptivity orders cannot be correlated to herbicide solubility, which follows: propachlor (618 mg/L) > metolachlor (530 mg/L > alachlor (242 mg/L) > acetochlor (223 mg/L) (Worthing, 1991). Nor can they be correlated with the K_{ow} value 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).

To understand the mechanisms that define the observed sorptivity order, we obtained differential FT-IR spectra of herbicides sorbed on Ca^{2+} -clay and HA-clay mixture. The self-supporting film technique used for sample preparation gave good adsorbent

uniformity, so differential spectra may be obtained by directly subtracting the spectra of the herbicide-free adsorbents. Similar FT-IR spectra were observed for metolachlor, alachlor, and acetochlor sorbed on clay or HA-clay, which were somewhat different from those for propachlor. The spectra of metolachlor and propachlor are given separately in Figs. 3 and 4.

Three possible types of binding are visible by examining the FT-IR spectra. (1) H-bonding between the carbonyl oxygen of herbicides and hydroxyl group on clay or hydroxyl and carboxyl groups of HA. This is indicated by the shift of carbonyl absorption band at 1670 cm^{-1} of the pure metolachlor to 1629 after interaction with Ca^{2+} -clay or HA-clay (Fig. 3). A similar shift was also observed with propachlor, where the $\text{C}=\text{O}$ absorption band at 1668 cm^{-1} moved to about 1620 cm^{-1} after reaction with clay or HA-clay (Fig. 4). H-bonding has been frequently observed in the interaction of pesticides with humic or clay substances. H-bonding was suggested to play an important role in the adsorption of alachlor (Senesi, 1992) and metolachlor (Kozak, 1983), as

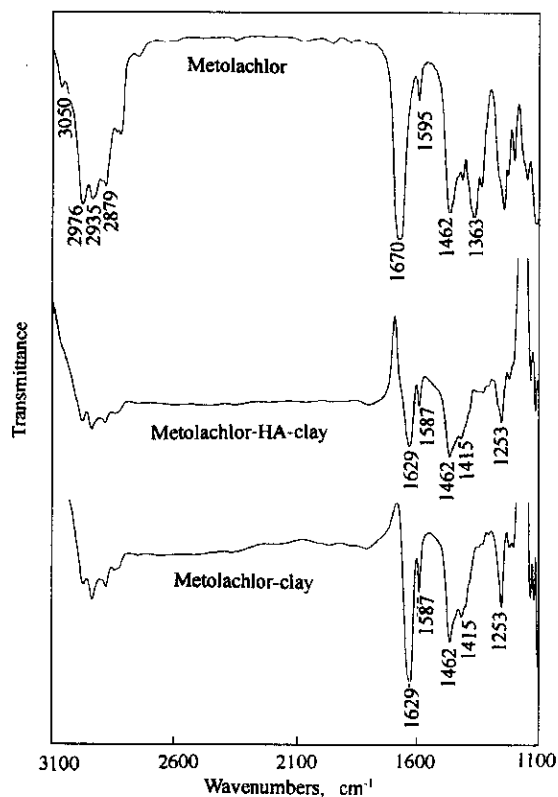


Fig.3 FT - IR spectra of metolachlor on soil model components (a) metolachlor; (b) metolachlor sorbed on humic acid (10%) and Ca^{2+} -montmorillonite (90%); and (c) metolachlor sorbed on Ca^{2+} -montmorillonite

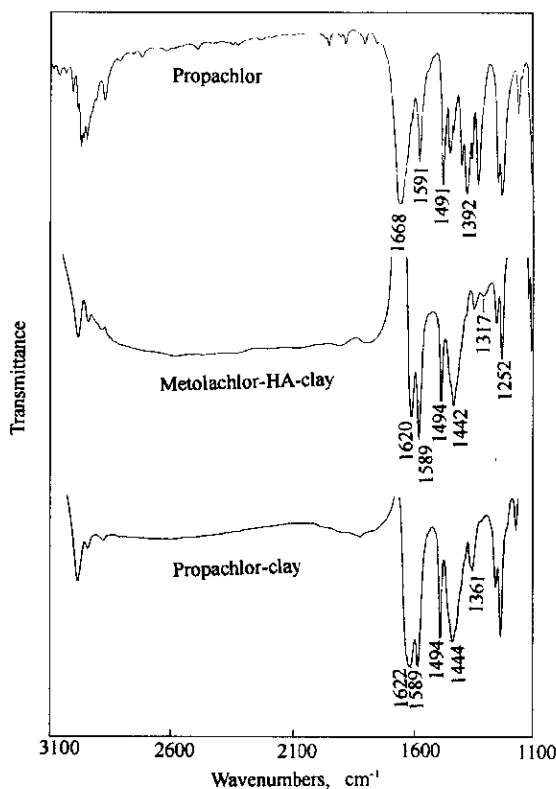


Fig.4 FT - IR spectra of propachlor on soil model components (a) propachlor; (b) propachlor sorbed on humic acid (10%) and Ca^{2+} -montmorillonite (90%); and (c) propachlor sorbed on Ca^{2+} -montmorillonite

well as between $-\text{C}=\text{O}$ groups of HA and secondary amino-groups of the *s*-triazines (Senesi, 1982; 1987). H-bonding was also assumed to occur between the water molecules surrounding interlayer clay cations and the carbonyl oxygen of diclofop-methyl (Pusino, 1989) and fluzafop-butyl (Gessa, 1987), or the $-\text{NH}$ group of thiazafluron (Cox, 1995). (2) Ligand exchange between the electron-rich nitrogen of herbicides and electron-deficient atoms of clay (e.g., Ca^{2+}) or HA (e.g., chelated cations), and charge transfer between the electron-rich nitrogen of herbicides and (bonds and/or electron withdrawing groups of HA. Absorption of $-\text{N}-\text{C}$ stretching centered at 1363 cm^{-1} for pure metolachlor, and at 1392 cm^{-1} for pure propachlor. These absorption bands, however, largely disappeared after interaction with Ca^{2+} -clay or HA-clay (Figs. 3 and 4), indicating the involvement of the nitrogen in the bonding process. Ligand exchange was proposed as a possible binding mechanism for substituted ureas, aminotriazoles, and EPTC (Calvet, 1980). Charge transfer between electron donors and acceptors was proposed for adsorption on humic acids of several *s*-triazine herbicides, in which electron-deficient, quinone-like structures in HA remove electrons from the electron-rich donating amine and/or heterocyclic nitrogen atoms of the *s*-triazine molecule via single-electron donor-acceptor processes (Senesi, 1982; Senesi, 1987). There is also spectroscopic evidence for charge transfer complexes between paraquat and diquat with montmorillonite and humic acid (Khan, 1980). (3). π - π charge transfer between the aromatic nuclei of herbicides and aromatic rings of HA. This is evident especially for propachlor, where an increase of the relative strength of absorption around 1591 cm^{-1} (representing $-\text{C}=\text{C}-$ vibration) was found after interacting with HA-clay (Fig. 4). π - π charge transfer was postulated as one of the

bonding possibilities between the electron-donating pyridine ring and/or imidazolinone ring of imazethapyr and electron-acceptor structural units of HA macromolecules, such as quinones (Senesi, 1997).

On clay, only (1) and (2) would occur. The moieties attached to the nitrogen can affect both the ability of nitrogen to interact with electron-acceptors of clay and the H-bonding ability of oxygen with clay hydroxyl group. The bonding ability of nitrogen depends on its ability to donate electrons. Thus, the surrounding environment that enhances the electron-negativity of nitrogen should therefore promote the bonding. Methoxy or ethoxy groups are more electron-repulsive than alkyl groups. From this aspect, the ability for nitrogen to bond with electron-acceptors should follow the order of metolachlor > acetochlor \approx alachlor > propachlor. Similar structural effects should be also valid for the oxygen of the -C=O group, because oxygen and nitrogen are in a conjugation mode because of the double bond, the lone electron pair, and the benzene ring. This order of activity may therefore support the observed order of herbicide sorptivity on Ca^{2+} -clay, which is metolachlor > acetochlor > alachlor > propachlor.

In soil or HA, in addition to the above mechanisms, (3) would also occur. π - π charge transfer between the benzene ring of the herbicide and the aromatic rings of HA should be most significant for propachlor, because it has the least steric hindrance due to its lack of alkyl substitution on the ring. This may explain the switch of order between propachlor and alachlor for their adsorption on soils and HA, where the overall order is: metolachlor > acetochlor > propachlor > alachlor.

3 Conclusions

Chloroacetanilide herbicides are among the most widely used pesticides today, and understanding their impact on the environment is of great importance. This study showed that under the same conditions, adsorption of these herbicides on soil follows a specific order. The order of sorptivity cannot be correlated with the solubility or the n -octanol-water partition coefficient of herbicides, but has been adequately explained with an examination of the potential influence of molecular structure of herbicides on their probable bonding interactions with soil colloidal components.

Adsorption on soil has been long recognized as one of the most important processes governing a pesticide's bioavailability and fate in the environment. Understanding the mechanisms of pesticide adsorption however, is greatly hampered by the complex and unstable nature of soil organic matter and its clay associations, and further by the high diversity of pesticides. As illustrated in this study, a better understanding of pesticide adsorption may be obtained by examining pesticides within their analogous groups. The structural differences among pesticides from the same class are more gradual and quantifiable. These definite differences may be expected to correlate better with pesticide sorptivity. This hypothesis is worthy to be further tested using representative pesticides from other families.

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