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Specific Surface Area Effect on Adsorption of Chlorpyrifos and TCP by Soils and Modelling

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The adsorption of chlorpyrifos and TCP (3,5,6, trichloro-2-pyridinol) was determined in four soils (Mollisol, Inceptisol, Entisol, Alfisol) having different specific surface areas (19–84 m^2 g^{-1}) but rather similar organic matter content (2.4–3.5%). Adsorption isotherms were derived from batch equilibration experiments at 25°C. After liquid-liquid extraction, the chlorpyrifos and TCP concentrations in the solution phase were determined by gas chromatography with an electron capture detector. Adsorption coefficients were calculated using the Freundlich adsorption equation. High K_F coefficients for chlorpyrifos (15.78) and TCP (6.54) were determined for the Entisol soil, while low K_F coefficients for chlorpyrifos (5.32) and TCP (3.93) were observed in the Alfisol soil. In all four soils, adsorption of chlorpyrifos was higher than that of TCP. A surface complexation model, the constant capacitance model, was well able to fit the adsorption isotherms of both chlorpyrifos and TCP on all four soils. The results showed that specific surface area affected adsorption of both chlorpyrifos and TCP. Among the soil properties, specific surface area could be a better indicator than organic matter content alone for adsorption of chlorpyrifos and TCP by soils that contained low organic matter.

Keywords Chlorpyrifos, TCP, soil types, Freundlich equation, surface complexation model

Introduction

Organophosphates generally break down in the environment relatively quickly (two weeks to one year), but one of the potential problems is that they are extremely toxic to humans and wildlife (Merrington *et al*., 2002).

For one of the organophosphate pesticides, chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate), usage has been vastly restricted for domestic use in the US and some European countries, even for agricultural purposes. However, it is still a widely used pesticide in developing countries (Bhagobaty *et al*., 2007). Typical half-lifes for chlorpyrifos ranges from a few days to four years, depending on the environmental characteristics (Racke *et al*., 1993). It has been shown that, in some soils, chlorpyrifos rapidly hydrolyzes to its primary metabolite, TCP (Racke *et al*., 1996). The chemical structure of

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the metabolite differs from the parent material and thus each behaves differently. TCP has greater water solubility than chlorpyrifos and causes widespread contamination in soils and in the aquatic environment (Racke *et al.*, 1988). Chlorpyrifos has been detected in natural sources and human dietary samples, although its water solubility is low (2 $\mathrm{mgL^{-1}}$) and its hydrophobicity high (log k_{ow}: 5.2) (Claver *et al.*, 2006; Gebremariam *et al.*, 2012a).

Chlorpyrifos is used for crops such as corn, sugarbeet, sunflower, pistachio, and turfgrass (Racke *et al.*, 1993; U.S. Department of Health and Human Services, 1997). Racke *et al.* (1993) reported that chlorpyrifos, applied as a pre-plant soil incorporation, exhibited slightly greater persistence than when used as a foliar/soil spray, while the application of chlorpyrifos as a barrier for termites resulted in residues with very high concentrations in the soil.

Chlorpyrifos is adsorbed by soils, clays, sediments, and humic acids (van Emmerik *et al.*, 2007; Gebremariam, 2011). Soil properties such as organic matter, pH, and clay content affect chlorpyrifos adsorption (Gold *et al.*, 1996; Gennari *et al.*, 2007; Gebremariam *et al.*, 2012b). On the other hand, in their review on chlorpyrifos, they stated that soil organic matter cannot be considered as the sole factor responsible for the sorptive interaction of chlorpyrifos in soil (Gebramariam *et al.*, 2012b). Clausen *et al.* (2001) found that specific surface area and mineral surface charge are important for the adsorption of some pesticides. Some reviews on chlorpyrifos and pesticide adsorption indicated that the effects of other soil properties or soil components on pesticide adsorption are still unclear, and there is a need to study these effects (Wauchope *et al.*, 2002; Gebremariam *et al.*, 2012b).

In this study, we aim to investigate the effects of organic matter content and surface area on adsorption of chlorpyrifos and TCP by soils and to compare the adsorption characteristics of both chemicals. A surface complexation model, the constant capacitance model, was evaluated for its ability to fit the adsorption isotherm data for both chlorpyrifos and TCP by the soils. Surface complexation models have been applied extensively to describe inorganic ion adsorption on mineral surfaces (Goldberg, 1992). However, the extension of these models to describe pesticide adsorption by soils remains to be investigated. Our study represents the first application of the constant capacitance surface complexation model to describe chlorpyrifos and TCP adsorption by soils.

Materials and Methods

Chlorpyrifos and TCP

Analytical-grade chlorpyrifos, with the IUPAC name *O,O*-diethyl *O*-(3,5,6-trichloropyrid-2-yl) phosphorothioate and molecular formula $C_9H_{11}C_{13}NO_3PS$ (purity > 99%), was used (Bayer Co). The chemical has a molecular weight of 350.6, and solubility (25°C) 2 mg L^{-1} (water). Analytical-grade TCP (3,5,6, trichloro- 2- pyridinol), the primary metabolite of chlorpyrifos (purity > 99%), was supplied by Chem Service. The solubility of TCP in water is 117 mg L^{-1}.

Soils

Four soil samples belonging to different soil orders (Mollisol-Lithic Hapludoll, Alfisol-Typic Hapludalf, Inceptisol-Calcixerollic Xerochrept, and Entisol-Aquic Ustifluvent) (Soil Survey Staff, 1999) were used.

Soils were air-dried and sieved to < 2 mm. Soil texture, pH, electrical conductivity (EC), cation exchange capacity (CEC), organic matter, and calcium carbonate were determined (Page, 1982). The specific surface area and micro pore volume in the soil samples was determined by application of the Brunauer–Emmett–Teller (BET) equation to sorption–desorption of N_2 (99.9% pure) at 120°C using Quantachrome Nova 2200 equipment single-point measurements (Brunauer *et al.*, 1938). This method gives the external surface area. Clay minerals were determined by XRD on soil (< 2 μm) samples in oriented slides treated with ethylene glycol and heated at 300°C and 550°C by XRD. Clay, silt, and sand (%) fractions was determined according to the hydrometer method (Bouyoucous, 1951).

Adsorption Analysis

Adsorption of chlorpyrifos and TCP was studied following the method of Reichenberger *et al.* (2002). Recovery test results of chlorpyrifos and TCP in dichloromethane were 86.24 ± 3.27% and 110.0 ± 1.5%, respectively. Stock solutions of chlorpyrifos and TCP were prepared in methanol. The concentration of working solutions for each chemical varied between 0, 0.5, 1.0, 1.5 and 2 mg L^{-1} in water. For each soil sample, adsorption isotherms were determined on air-dried samples by the batch equilibrium technique. The ratio of soil/water was 1 g of soil to 10 ml working solution. Samples were equilibrated at 25°C for 24 hours with continuous shaking. Two replicates were used for each treatment. The soil suspensions were centrifuged. Chlorpyrifos and TCP in 2 ml aliquot were extracted three times with 2 mL dichloromethane by shaking for 30 minutes. The dichloromethane was dried under nitrogen (Reichenberger *et al.*, 2002). Chlorpyrifos was resolved in 0.25 mL hexane, while the solvent for TCP was 0.25 mL cyclohexane.

The chlorpyrifos and TCP concentrations were determined by using a Shımadzu GC14B gas chromatograph equipped with the detector/column configurations: Electron Capture Detector (ECD), TC1 (60 m × 0.32 mm × 0.25 μm) capillary column. The detector operating temperature was 300°C, injector 275°C, oven temperature was maintained at 100°C for 5 min, and then increased by 10°C per min to 180°C and maintained for 2 min. Finally, the temperature was increased by 10°C per min to 250°C and maintained for 8 min. Under these conditions, the retention times of TCP and chlorpyrifos were determined as 11 and 20 minutes, respectively.

Calculation

Adsorption isotherms of the chemicals were derived using the Freundlich equation:

$$x/m = K_F C^{1/n} \tag{1}$$

where x/m is the amount of chemical adsorbed μmol per kg soil, C is equal to the equilibrium solution concentration, and K_F and 1/n are constants. The K_F value indicates the extent of adsorption while the 1/n value shows the degree of nonlinearity between adsorption and solution concentration.

Surface complexation theory describes adsorption phenomena in terms of chemical reactions between surface functional groups and dissolved chemical species. One such model, the constant capacitance model (Stumm *et al.*, 1980), considers adsorbed species to form inner-sphere complexes located in a surface plane associated with a solid. The surface functional group, SOH, is considered as an average reactive surface hydroxyl ion bound to a metal ion at soil particle edges. The constant capacitance model was used to describe the adsorption of chlorpyrifos and TCP onto the four soils. The constant capacitance model was chosen because it is the simplest of the surface complexation models and has by far the least number of adjustable parameters. Since the adsorption mechanisms of chlorpyrifos and TCP have not yet been established, it is most appropriate to investigate the application of the simplest surface complexation model containing the least number of adjustable parameters. The constant capacitance model has been applied previously to organic materials acting both as the adsorbent and (the study of Goldberg and Grieve, 2003, on boron adsorption by maize cell walls) as the adsorbate (the study of Mitchell *et al.*, 2011, on organic arsenical adsorption by iron oxides). In the model application, the following surface complexation reactions were used:

$$SOH + H^+ \leftrightarrow SOH_2^+ \tag{2}$$

$$SOH \leftrightarrow SO^- + H^+ \tag{3}$$

$$SOH + C_9H_{11}Cl_3NO_3PS \leftrightarrow SC_9H_{10}Cl_3NO_3PS + H_2O \text{for chlorpyrifos} \tag{4}$$

$$SOH + C_5H_2Cl_3NO \leftrightarrow SC_5HCl_3NO + H_2O \text{for TCP} \tag{5}$$

Chlorpyrifos contains no readily dissociable functional group. Therefore, it is possible that chlorpyrifos does not adsorb onto soil surfaces by ligand exchange and the constant capacitance model description might be empirical. However, TCP undergoes aqueous dissociation, pKa = 4.55 (APVMA, 2000), and ligand exchange would be expected to be the appropriate adsorption mechanism. Therefore, using the constant capacitance model to fit TCP adsorption provides a description that is in agreement with its anticipated mechanistic behavior. The aqueous dissociation reaction of TCP is included in the model application:

$$C_5H_2Cl_3NO \leftrightarrow SC_5HCl_3NO^- + H^+ \tag{6}$$

Equilibrium constant expressions for the surface complexation reactions are:

$$K_+(\text{int}) = \frac{[SOH_2^+]}{[SOH][H^+]} \exp(F\psi/RT) \tag{7}$$

$$K_-(\text{int}) = \frac{[SO^-][H^+]}{[SOH]} \exp(-F\psi/RT) \tag{8}$$

$$K_{CP}(\text{int}) = \frac{[SC_9H_{10}Cl_3NO_3PS]}{[SOH][C_9H_{11}Cl_3NO_3PS]} \tag{9}$$

$$K_{TCP}(\text{int}) = \frac{[SC_5HCl_3NO]}{[SOH][C_5H_2Cl_3NO]} \tag{10}$$

where CP stands for chlorpyrifos, F is the Faraday constant (C/mol$_c$), ψ is the surface potential (V), R is the molar gas constant (J/mol/K), T is the absolute temperature (K), and square brackets indicate concentrations (mol L^{-1}). The exponential terms can be considered as solid phase activity coefficients that correct for the charges on the surface functional groups.

The mass balance expression for the reactive surface functional group is:

$$SOH_T = [SOH] + [SOH_2^+] + [SO^-] + [SC_9H_{10}Cl_3NO_3PS] or [SC_5HCl_3NO] \tag{11}$$

Table 1
Some characteristics of soil samples

Soils	pH*	EC (dSm^{-1})	$CaCO_3$ (%)	Org mat. (%)	CEC (cmol kg^{-1})	Clay (%)	Silt (%)	Sand (%)	Surface area (m^2g^{-1})	Micro pore volume (cm^3g^{-1})
Alfisol	6.42	0.33	0.33	2.49	27.0	30.6	18.9	50.5	18.7	0.0026
Mollisol	6.52	0.30	0.26	3.45	58.3	14.2	17.3	68.5	30.4	0.0041
Inceptisol	7.67	0.33	17.0	2.42	24.5	28.5	35.7	35.8	60.6	0.0158
Entisol	7.97	0.73	11.3	3.45	43.9	63.0	30.3	6.76	83.5	0.0163

*(1:2.5 water/soil suspension).

where SOH_T is related to the surface site density, N_s in units of sites/nm^2, by the expression:

$$SOH_T = \frac{S_A C_p 10^{18}}{N_A} N_s \tag{12}$$

where S_A is the surface area (m^2g^{-1}), C_p is the particle concentration (gL^{-1}), N_A is Avogadro's number.

The charge balance expression for the reactive surface functional group is:

$$\sigma = [SOH_2^+] - [SO^-] \tag{13}$$

where σ is the surface charge (mol_cL^{-1}). The relationship between surface charge and surface potential is defined as:

$$\sigma = \frac{CS_A C_p}{F} \psi \tag{14}$$

where C is the capacitance (F/m^2).

The computer program FITEQL 4.0 (Herbelin and Westall, 1999) was used to fit surface complexation constants to the experimental chlorpyrifos and TCP adsorption data. The FITEQL code uses a nonlinear least-squares optimization routine to fit surface complexation constants to experimental data and contains the constant capacitance model of adsorption. The program tests the overall variance, V, in Y as the goodness-of-fit criterion:

$$V_Y = \frac{SOS}{DF} \tag{15}$$

where SOS is the weighted sum of squares of the residuals and DF is the degrees of freedom. In our application of the constant capacitance model, the surface site density was set at 2.31 sites/nm^2, as had been recommended for natural materials (Davis and Kent, 1990). Other parameter input values for the model were: capacitance, $C = 1.06$ F/m^2 considered optimum for aluminum oxide by Westall and Hohl (1980) and protonation and dissociation constants: $\log K_+(\text{int}) = 7.35$, $\log K_-(\text{int}) = -8.95$ obtained from a literature compilation of experimental values for iron and aluminum oxides and recommended for soils by Goldberg and Sposito (1984).

Table 2
Clay minerals in soil samples

Soil orders	Clay minerals			
Mollisol	Smectite +++*	Smectite-chlorite +	Illite +	Zeolite+
Alfisol	Smectite +++			
Inceptisol	Illite +++	Chlorite ++	Smectite ++	Kaolinite ++
Entisol	Smectite +++	Smectite-chlorite +++		Kaolinite

*+ refers to dominancy.

Results and Discussion

Soil characteristics are presented in Table 1. Soil pH values changed between 6.42 to 7.97. Organic matter content of the soil samples was somewhat similar (2.4–3.5%).

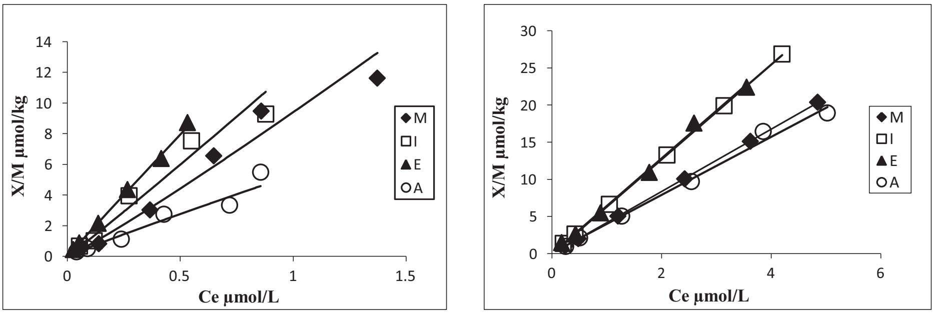
Surface area ranged between 19 and 84 m^2g^{-1}. The Inceptisol and the Entisol contained a much higher percentage of $CaCO_3$ compared to the other two soils. Clay minerals in soils are given in Table 2, smectite was the dominant clay mineral, except for the Inceptisol, where it was illite.

Sorption isotherms were fitted to the Freundlich equation and sorption coefficients K_F and 1/n were calculated (Table 3). K_F values for adsorption ranged from 5.32 to 15.78 for chlorpyrifos and from 3.93 to 6.54 for TCP. Similar observations have been reported in studies involving chlorpyrifos soprtion in soils (El-Nahhal, 2002; Li *et al.*, 2005). The results showed that chlorpyrifos bound more strongly to soils than its metabolite TCP. This can be attributed to the lower polarity and lower solubility of chlorpyrifos than that of TCP. These observations are consistent with the findings of Baskaran *et al.* (2003) for soils. Adsorption coefficients of soils were in accordance with the K_F value of TCP calculated by Racke and Robbins (1991). According to K_F values, adsorption by the soil samples followed the same order; i.e., Entisol > Inceptisol > Mollisol > Alfisol soil orders for both chemicals: chlorpyrifos and TCP.

In the present study, if organic materials were a dominant factor in the adsorption of chlorpyrifos and TCP, as reported by several researchers, (Alvarez *et al.*, 2013; Gebremariam, 2011), then adsorption would have been high only in the Mollisol and the Entisol and would have been similar for the Alfisol and the Inceptisol. On the other hand, the Entisol and the Inceptisol soils showed high adsorption capacity for both chemicals. Thus, soil

Table 3
Freundlich adsorption coefficients for chlorpyrifos and TCP

	Chlorpyrifos				TCP			
Soil	K_F	1/n	R^2	Adsorption type	K_F	1/n	R^2	Adsorption type
Alfisol	5.32	0.94	0.98	L	3.93	1.00	1.00	C
Mollisol	9.40	1.09	0.98	S	4.16	1.00	1.00	C
Inceptisol	12.72	1.05	0.98	S	6.29	1.00	1.00	C
Entisol	15.78	0.99	1.00	L	6.54	0.95	0.99	L



a) b)

Figure 1. (a) Chlorpyrifos adsorption isotherms; (b) TCP adsorption isotherms.

organic matter content was not the sole factor affecting the adsorption of these chemicals by the soils in this study. This may arise from the percentage amount of the organic matter in the soils. Đurović *et al.* (2009) reported that if soil organic matter content was higher than 5%, adsorption was strongly related to soil organic matter content of the soil. In soils low in organic matter content, the soil mineral fraction, either alone or together with the soil organic matter fraction,would be responsible for the adsorption process. Also, Laabs and Amelung (2005) reported that chloropyrifos adsorption was greater in soils with higher organic matter content and higher clay content. Since organic matter content of the study

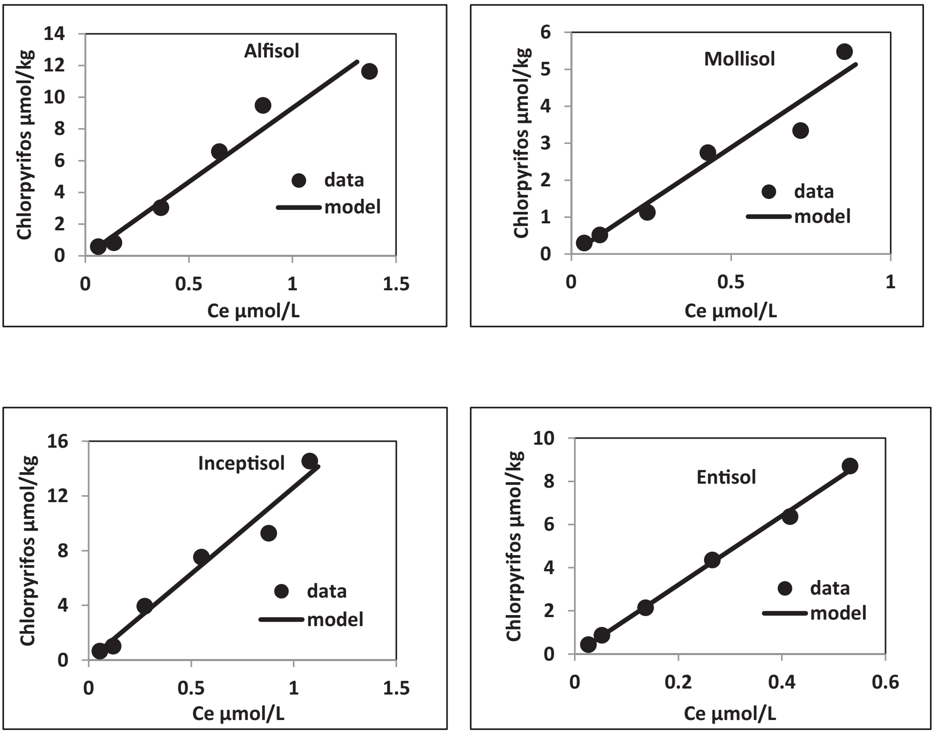


Figure 2. Fit of the constant capacitance model to chlorpyrifos adsorption isotherms.

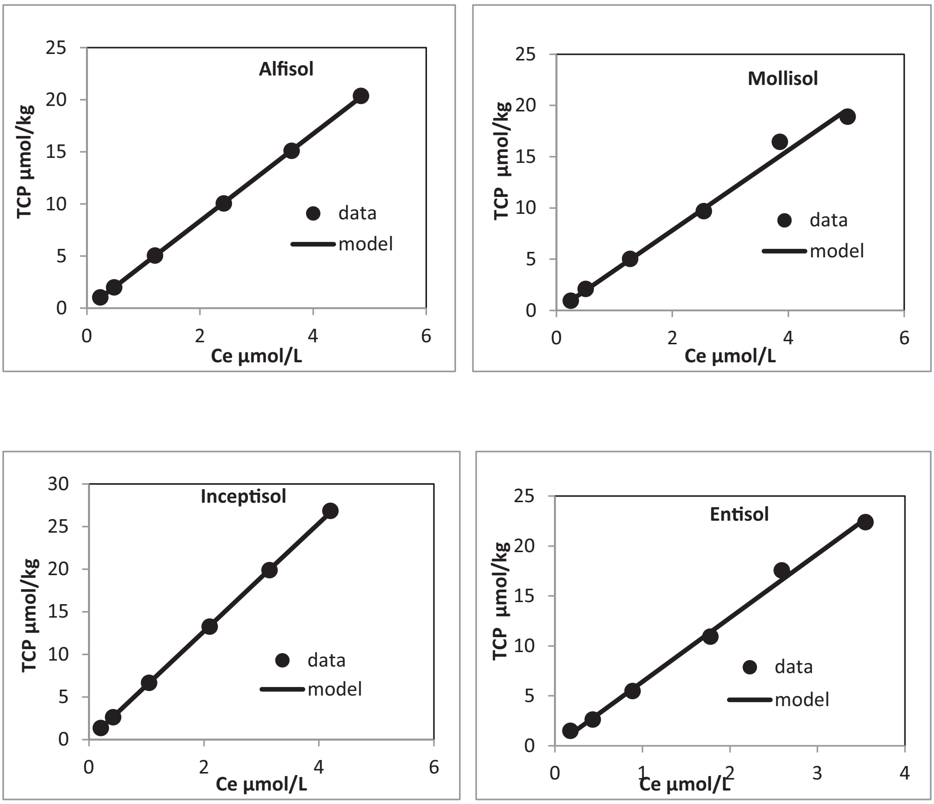


Figure 3. Fit of the constant capacitance model to TCP adsorption isotherms.

soils was lower than 5%, other factors would be considered. This study showed that soil organic matter is not always the sole factor affecting sorption. This finding is consistent with the review of Wauchope *et al.* (2002). Kaiser and Guggenberger (2003) found that organic matter is involved in adsorption by covering the mineral surfaces. They stated that specific surface area is decreased with increasing loading of organic matter, either covering or clogging micropores, which are the preferred sorption sites.

On the other hand, if clay percentage were a dominant factor, as in the case of the Entisol, then adsorption would only be higher in this soil and not in the others. K_F coefficient exhibited increasing trends similar to those for surface area. With respect to clay types, smectite was the dominant clay mineral in all of the soils, except for the Inceptisol, which contained illite as the dominant clay mineral. Olmesek (1998) concluded that organic phosphorus compounds were bound to illite clay by weak van der Waals forces. The relationship between K_F values and soil surface area follows the trend: Entisol > Inceptisol >Mollisol >Alfisol. This sequence of large to small was in the same order for the surface area. Micropore surface area increases with increasing specific surface area. Micropores may play a role in the adsorption of these chemicals (Kaiser and Guggenberger, 2003). van Emmerik *et al.* (2007) found that chlorpyrifos adsorption was higher on montmorillonite than kaolinite and gibsite. In their study, the humic acid addition to montmorillonite reduced chlorpyrifos adsorption, while its accumulation was increased because of the coating of humic acid on montmorillonite.

Table 4
Constant capacitance model constants

Solid	$\log K_{CP}$(int)	V_Y	$\log K_{TCP}$(int)	V_Y
Alfisol	2.061	0.002	3.688	0.00002
Mollisol	2.069	0.0007	3.775	0.007
Inceptisol	1.858	0.001	4.680	0.00003
Entisol	1.819	0.00003	4.841	0.0009

It has been known that adsorption of the organic chemicals is affected not only by the soil characteristics, but also by their chemical characteristics. Pesticides with high solubility in water are more easily adsorbed by soils (Sharom *et al.*, 1980; Racke, 1993). The results showed that the binding affinities of chlopyrifos and TCP to soils were different. This can be attributed to the lower polarity and lower solubility of chlorpyrifos than that of TCP.

Types of adsorption isotherms of chlorpyrifos and TCP were evaluated according to 1/n values, which are a function of the strength of adsorption. Values of 1/n less than 1 indicate L-type, greater than 1 indicate S (sigmoidal)-type, and values equal to 1 indicate C-type (linear) (Giles *et al.*, 1960) isotherms. For the Entisol and the Alfisol, L-type adsorption isotherms were obtained for chlorpyrifos (Table 3 and Figure 1a).

This type of isotherm corresponds to decreasing site availability as the solution concentration increases (Calvet, 1989). For the Inceptisol and the Mollisol, S-type adsorption isotherms were obtained for chlorpyrifos, implying that adsorption becomes easier as the concentration in the liquid phase increases (Calvet, 1989). The Mollisol, Alfisol, and Inceptisol soils had C-type adsorption isotherms, while the Entisol showed the L-type for TCP adsorption (Table 2 and Figure 1b). The C-type isotherm corresponds to constant partitioning of the solute between the bulk solution and the adsorbent.

The constant capacitance model was fitted to the chlorpyrifos and TCP adsorption isotherms of all four soils. The model description for the adsorption data of both chemical species was excellent on all four soils (Figures 2 and 3). The constant capacitance surface complexation model fit using only one adjustable parameter is equal in quality to that obtained using the empirical Freundlich adsorption isotherm equation, which contains two adjustable parameters.

It is very encouraging that a model containing chemical parameters and the ability to describe adsorption as a function of changing solution species concentration and solution pH can provide an excellent description of adsorption data using only one adjustable parameter.

Values for the surface complexation constants and goodness-of-fit criteria are provided in Table 4. The high quality of the fit is evident from the very small magnitude of the overall variance values, V_Y.

Conclusion

In all four soils studied, chlorpyrifos and TCP adsorption increased with increasing concentrations of these chemicals. Freundlich adsorption isotherm coefficients (K_F) indicated greater affinity of chlorpyrifos than of TCP for soil sorption sites. A surface complexation model, the constant capacitance model, was able to fit the adsorption isotherms of both chlorpyrifos and TCP on all four soils. In this study, we found that sorption was more dependent on soil BET surface area than on organic matter content and clay type. Therefore, instead of specifying a single soil property as being responsible for the effect on sorption, it would be more accurate to evaluate the effect of soil surface area in soils having lower organic matter content. It can be concluded that, in contrast to most other studies, surface area would be a better determining factor than organic matter and clay content for adsorption of chlorpyrifos and TCP. During application of chlorpyrifos and TCP, soil surface area could be considered for the environmental concern. In addition, further studies should be done to evaluate the effects of mineral components of soils and to determine the mechanisms of chlorpyrifos and TCP adsorption in the case of low organic matter content.

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