

Organic Compounds in the Environment

Soil Sorption of Acidic Pesticides: Modeling pH Effects

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ABSTRACT

A model of acidic pesticide sorption in soils was developed from theoretical modeling and experimental data, which initially considered a combination of a strongly acidic pesticide and a variable-charge soil with high clay content. Contribution of 2,4-D [(2,4-dichlorophenoxy) acetic acid] anionic-form sorption was small when compared with molecular sorption. Dissociation of 2,4-D was not sufficient to explain the variation in K_d as a function of pH. Accessibility of soil organic functional groups able to interact with the pesticide (conformational changes) as a function of organic matter dissociation was proposed to explain the observed differences in sorption. Experimental 2,4-D sorption data and K_{oc} values from literature for flumetsulam [*N*-(2,6-difluorophenyl)-5-methyl [1,2,4] triazolo [1,5-*a*] pyrimidine-2-sulfonamide] and sulfentrazone [*N*-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl] phenyl] methanesulfonamide] in several soils fit the model.

ACIDIC PESTICIDES are sorbed to organic soil colloids and the sorption depends on pH, being greater under acid conditions where the pesticides are sorbed in molecular (neutral) form (Weber, 1972). Grover (1968) found that reducing soil pH from 6.5 to 5.0 reduced the bioactivity of picloram, owing to increased binding of molecular forms by organic matter. The pH-dependence of sorption has been reported for many acidic pesticides, including bentazone (Abernathy and Wax, 1973; Grey et al., 1996), chlorimuron (Goetz et al., 1989), chlorsulfuron (Shea, 1986; Walker et al., 1989), metsulfuron-methyl (Walker et al., 1989), and picloram (Nearpass, 1976).

Abernathy and Wax (1973) concluded that bentazone was mobile if the soil pH was near neutral. The high mobility around neutral pH was attributed to the combined effects of relatively high water solubility and acidic characteristic of the compound. A cation exchange resin retained no bentazone, while the greatest sorption occurred on an anion resin between pH 5 and 7. Bentazone has a pK_a of 3.2; thus, it exists predominantly in anionic form under pH conditions near neutrality. Grey et al. (1996) noted that bentazone sorption decreased as pH increased for U.S. Coastal Plains Ultisols.

Goetz et al. (1989) evaluated chlorimuron sorption and mobility in Ultisols and Inceptisols, with sorption being inversely related to soil pH. Chlorimuron is a weak acid with a pK_a of 4.2; therefore, anionic forms

predominate in solution for most soils. Shea (1986) studied chlorsulfuron dissociation and sorption on selected sorbents and soils, and noted that lowering the pH increased herbicide sorption. However, it was shown that chlorsulfuron, which has a pK_a of 3.8, was not sorbed by technical kaolinite at pH 4.7.

Walker et al. (1989) measured sorption and degradation rates of chlorsulfuron and metsulfuron-methyl in soils taken from different depths. Sorption of both herbicides was inversely correlated with soil pH and positively correlated with organic matter content. It was suggested that soil pH was the dominant factor controlling sorption in most soils. Chlorsulfuron and metsulfuron-methyl have pK_a values of 3.8 and 3.3, respectively; hence, only under very acid conditions will a significant proportion of these herbicides exist in nonionized form.

Nearpass (1976) studied the sorption of picloram by humic acids and humin. The pH-dependent sorption of picloram ($pK_a = 3.4$) agreed with the concept that its sorption is largely that of uncharged molecules. Sorbate-dependent pH effect and sorbent-dependent effects were pointed out. An increase in picloram sorption by humin and humic acids was observed at pH values close to the compound's pK_a (3.4), when a small change in pH with increasing ionic strength would result in a significant increase in the neutral fraction of the herbicide. Higher ionic strengths result in displacement of more hydrogen ions from soil solids, thereby reducing soil solution pH and shifting acidic compounds toward neutral forms.

Bailey et al. (1968) noted early on the difficulty in predicting sorptive behavior for pesticides that dissociate to form an ion. Several factors, such as dissociation, soil solution pH, ionic strength and composition, and surface charge, may have to be considered to successfully predict sorption of acidic compounds by soils. Furthermore, sorption of ionizable organic compounds can occur through various mechanisms (Koskinen and Harper, 1990), such as ion exchange, charge-transfer interaction, hydrogen bonding, and van der Waals forces.

Jafvert (1990) presented a method to obtain sorption coefficients for organic acid compounds on sediments. Invariant sorption of neutral form with pH and linear pH-dependent sorption of anionic form were assumed. Fontaine et al. (1991) obtained anionic and neutral sorption coefficients using nonlinear optimization of flumetsulam sorption normalized with respect to organic carbon, as a function of pH. Sorption of neutral and anionic forms was assumed to occur only on organic matter.

Lee et al. (1990) showed that equilibrium sorption of pentachlorophenol (PCP) could be predicted from a knowledge of soil solution pH, organic carbon content,

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Published in J. Environ. Qual. 32:949-956 (2003).

and pK_a value of PCP. Regitano et al. (1997) combined the data on imazaquin sorption obtained in their study with a data set from Loux et al. (1989). The model presented by Lee et al. (1990) was fitted to the combined data to optimize for values of organic carbon-normalized coefficients, with sorption of anionic form being much lower than that observed for molecular form.

Sorption coefficients for neutral and anionic forms, based on traditional interpretation of batch equilibrium experiments, are empirically combined to produce an overall sorption coefficient. In this study theoretical modeling is combined with experimentally determined and published sorption coefficient data. It is intended to offer a model based on current understanding of the contribution of nonionic and ionic processes to the sorption of acidic pesticides, with emphasis on weathered, variable-charge soils.

The herbicide 2,4-D was chosen as a model acidic pesticide, which can exist in molecular and anionic forms in soils. Due to its low pK_a value (2.8), 2,4-D appears predominately in anionic form in the pH range common to variable-charge soils. Hence, ionic sorption could also occur on positively charged soil minerals. Hydroxy-iron and -aluminum soil compounds exhibit a high sorption capacity for phenolic acids, such as 2,4-D. This is attributed to the large chemical reactivity of these positively charged minerals toward the negatively charged carboxyl and phenolic hydroxyl groups of the phenolic acid compounds (Huang et al., 1977). Oxisols are highly weathered soils containing kaolinite and iron and aluminum oxides. Weathered soils with variable-charge minerals constitute an important soil category in tropical and subtropical agricultural regions of the world (e.g., Brazil, Australia, India, China, Central Africa, the southeastern region of the USA, and Hawaii).

There have been many research studies of pesticide sorption mechanisms on isolated soil fractions. However, as pointed out by Graham-Bryce (1981), there has been less work on mechanisms of sorption by whole soils. Although highly elegant in many respects, studies of pesticide-clay mineral interactions are largely irrelevant to modeling purposes (Karickhoff, 1984). In such studies, the mineral surfaces are highly prepared while, in natural systems, mineral surfaces are commonly covered with coatings (organic and inorganic polyelectrolytes).

The purpose of the present study was to model the sorption of acidic pesticides in soils, using theoretical modeling and experimental data. Combination of a strongly acidic pesticide and a high-clay-content soil with predominantly variable-charge minerals was ini-

tially chosen as an extreme case study for sorption. Sorption of acidic compounds is mainly driven by their dissociation. In this study it is hypothesized that the sorption (and consequently the transport) of acidic pesticides also depends on soil variable charges and organic matter dissociation.

MATERIALS AND METHODS

Samples of an Oxisol were collected in Ribeirão Preto region, São Paulo State, Brazil, and soil properties were determined according to methods presented by Empresa Brasileira de Pesquisa Agropecuária, Serviço Nacional de Levantamento e Conservação de Solos (1979) and Camargo et al. (1986). Clay content was determined based on a method presented by Bouyoucos (1927). Texture was classified according to the USDA system (USDA Soil Conservation Service, Soil Survey Staff, 1975). Mineralogy description was based on methods presented by Jackson (1969), using X-ray diffraction (XRD) techniques. The point of zero charge (PZC) was determined based on the method of van Raij and Peech (1972). The method used for organic carbon determination was that of Walkley and Black (1934). Soil pH was measured in 1:1 (w/w) soil and 0.01 M calcium chloride ($CaCl_2$) solution mixtures. Soil properties are presented in Table 1. This Oxisol was chosen due to its high clay content and predominance of variable-charge minerals.

In a subsample, soil pH changes were promoted by addition of 1 M hydrochloric acid, HCl, or 1 M calcium hydroxide, $Ca(OH)_2$, to produce values either below or above its natural pH level. Soil samples were moistened to field capacity and allowed to equilibrate for 6 wk. Each soil sample was remoistened to field capacity every 2 d. Another set of soil subsamples was used to study the effects of organic matter reduction from the soil on sorption, at different pH levels. Soil was treated with hydrogen peroxide (H_2O_2) based on methods presented by Jackson (1958) and Black (1965). The residual organic carbon content was measured, and then pH changes were also performed as described above.

Sorption coefficients were determined with a standard batch equilibrium method, with 10 mg of analytical 2,4-D per liter of a 0.01 M $CaCl_2$ solution being used. A 10.00-mL aliquot of the solution was added to 5.00 g of soil in a centrifuge tube, and it was shaken in an agitator for 24 h at about 25°C. Preliminary studies have shown that more than 90% of the 2,4-D sorption occurs within 2 h, and microbial degradation was considered negligible. Hornsby et al. (1996), considering many references, selected 10 d as half-life value for 2,4-D. Assuming first-order degradation rate, it indicates that more than 93% of 2,4-D would remain after 24 h. In addition, several researchers also have noted that sorption processes tend to limit the biodegradation rate of pesticides. Ogram et al. (1985) suggested that microbial degradation of 2,4-D occurred only in the solution phase, and not when the pesticide was sorbed.

At the end of the equilibrium period, the suspensions were

Table 1. Properties of the soil† used in the 2,4-D sorption experiment.

Clay content	Organic carbon	CEC‡	pH ($CaCl_2$)	PZC§	Mineralogy
%	g/kg	cmol/kg			
64	16	10.3	4.9	4.1	K > Gi >> H ≈ Go

† Typic Haplorthox (USDA Soil Conservation Service, Soil Survey Staff, 1975), Rhodic Ferralsol (Food and Agricultural Organization of the United Nations/United Nations Educational, Scientific and Cultural Organization, 1971), Latossolo Roxo (Empresa Brasileira de Pesquisa Agropecuária, Serviço Nacional de Levantamento e Conservação de Solos, 1988).

‡ Cation exchange capacity at pH 7.

§ Point of zero net charge.

|| K, kaolinite; Gi, gibbsite; H, hematite; Go, goethite.

centrifuged for 20 min at 10 000 rpm, and the supernatant filtered through a 0.45- μm filter. The amount of pesticide in the supernatant was determined by high performance liquid chromatography (HPLC) analysis (3.9- by 150-mm C_{18} column, 5- μm particle diameter; Waters, Milford, MA), with duplicate injections of supernatant and standard solutions being made. The mobile phase was methanol and water (70:30 v/v) and 0.01 M tetrabutyl-ammonium chloride, with detection being performed at 228 nm. Supernatant pH values were read on a pH meter, and changes in pesticide sorption with pH were studied.

Sorption at equilibrium was calculated as the difference in concentration between the initial solution and solution at equilibrium with the soil, at a single solution concentration for each pH level, and an apparent K_d value was estimated. The overall sorption coefficient (K_d) was calculated as $K_d = S/C$, where S is the mass of sorbed herbicide per mass of soil (g/kg) and C is the herbicide concentration of the supernatant solution at equilibrium (g/L).

In addition, soil sorption data for two other acidic pesticides, covering a large range of pK_a values, were obtained from the literature. The fit of the theoretical model to the measured and literature sorption data sets was evaluated with the SAS/STAT program (SAS Institute, 1989). The NLIN procedure in SAS fits nonlinear regression models using a least squares method. A Gauss-Newton procedure was used for finding the least squares estimator (Bard, 1974; Kennedy and Gentle, 1980; Draper and Smith, 1981). Based on Myers (1986), an F test was applied and the coefficient of determination (R^2) was calculated for a given nonlinear model.

The overall sorption coefficient (K_d) of acidic pesticides in soils with variable-charge minerals can be expressed as:

$$K_d = (K_m' \times \phi_m) + (K_a' \times \phi_a) \quad [1]$$

where $K_m' \times \phi_m$ represents the sorption coefficient of pesticide in molecular form (K_m), and $K_a' \times \phi_a$ is the sorption coefficient

of pesticide anionic form (K_a) on positively charged soil particles. The term ϕ_m is the fraction of pesticide in molecular form, and ϕ_a is the fraction of pesticide in anionic form.

The prime sorption coefficient of pesticide in molecular form (K_m') is, in fact, a composite coefficient and depends on effects of organic matter dissociation on the accessibility of humin. In turn, values for the prime sorption coefficient of a pesticide in anionic form (K_a') are a function of positive charges on soil minerals (or a function of soil positive net charge). The soil net charge can be estimated using equations presented by van Raij and Peech (1972), and by introducing reasonable values for required parameters, which can be adjusted according to experimental observations. It should be possible to calculate the double layer potential at any pH value, as the point of zero net charge is known.

Equation [1] can be rewritten as:

$$K_d = (K_{oc,m}' \times F_{oc} \times \phi_m) + (K_{min,a}' \times F_{min} \times \phi_a) \quad [2]$$

where $K_{oc,m}'$ is the organic carbon-normalized prime sorption coefficient of molecular form, F_{oc} is the soil organic carbon fraction, $K_{min,a}'$ is the mineral-normalized prime sorption coefficient of anionic form, and F_{min} is the soil mineral fraction.

RESULTS AND DISCUSSION

Changes in sorption coefficient values measured for whole soil (i.e., without treatment with hydrogen peroxide) were developed as a function of pH and can be seen in Fig. 1. At low pH, where acidic pesticides exist largely in neutral form, the soil sorbs much more 2,4-D as compared with sorption at high pH, where the pesticide is mostly in anionic form. This suggests that the anionic form of 2,4-D has a much lower sorption coefficient than the neutral form. Ionic interactions may contribute, to some degree, to anionic pesticide sorption

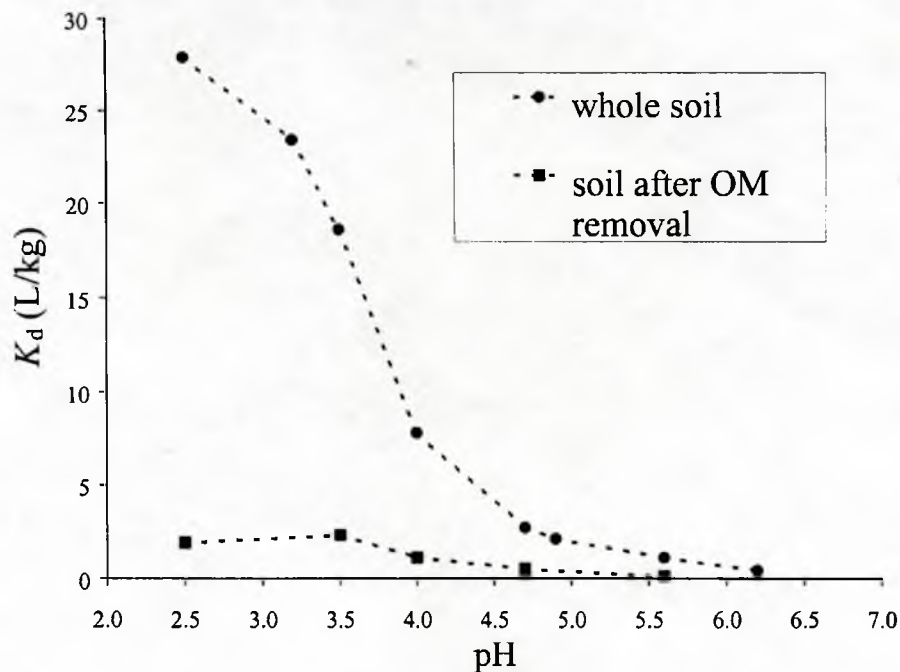


Fig. 1. Sorption coefficients of 2,4-D measured for whole soil (Typic Haplorthox) with 16 g/kg organic C and when organic matter was largely reduced (1 g/kg organic C), as a function of pH.

under some conditions. This is more apparent in soils with low organic carbon content and high clay content. Based on the hypothesis of mineral blockage by organic matter, mineral contribution is expected to be at a maximum when the ratio of mineral to organic carbon fractions is more than 30, regardless of the mineral content (Karickhoff, 1984).

Changes in sorption coefficients measured when organic matter was reduced can also be seen as a function of pH in Fig. 1. The curve for the whole soil refers to the overall sorption coefficient (K_d), and the premise is that the curve for the soil with organic matter removed could be related approximately to the anionic sorption coefficient (K_a). However, removal of soil organic matter by H_2O_2 treatment was not complete and in this study the organic carbon content was reduced to 1 g/kg after treatment. Therefore, some residual organic matter content remained in the soil, partially covering mineral surfaces, and contributing to (or controlling) pesticide sorption. Many researchers have recognized that, at organic carbon levels below 1 g/kg, interactions of nonionic organic compounds with mineral surfaces may be more important (Pignatello, 1989). However, that would be an unrealistically low organic matter content for Oxisols, such as that used in the present study under natural conditions, even in the Bw horizon.

Clay and organic matter function more as a unit than as separate entities, and the relative contributions of organic and inorganic surfaces to sorption depend on the extent to which the clay is coated with organic substances (Stevenson, 1982). The whole soil used here had a mineral to organic carbon ratio of 40. When about 94% of the organic matter was removed that ratio increased drastically and, consequently, the soil point of zero net charge was assumed to rise. Therefore, the maximum contribution of mineral ionic sorption was expected after organic matter reduction.

However, when organic matter was largely reduced, the sorption of 2,4-D diminished markedly (Fig. 1). As a consequence of organic matter reduction, sorption at different pH levels was about 10-fold smaller than sorption for the whole soil. This approximately parallels the decrease in soil organic carbon content. Therefore, interaction of organic matter with minerals may provide an organic surface for sorption, and mechanisms other than molecular interaction with organic matter are weaker.

It appears that the anionic form of the pesticide, owing to its relative larger size and lower concentration, is not able to compete effectively for anion exchange sites with other anions present in the soil solution. On the other hand, ion pairing between the pesticide's anionic form and cations in the soil solution could occur, and sorption of neutral ion pairs would be possible. However, this process depends on cation (complementary ion) availability in solution, either due to high salt concentrations (Westall et al., 1985) or near negatively charged colloidal surfaces.

It is known that sorption of 2,4-D is mainly driven by its dissociation; however, 2,4-D dissociation is not enough to explain the variation in K_d as a function of pH. Assuming that the overall K_d is dominated by sorption of

the molecular form, the prime sorption coefficient of the pesticide, estimated by the expression $K_m' = K_d/\phi_m$, increases when pH values rise.

Organic matter becomes more accessible for solute sorption at high pH due to conformational changes. Therefore, accessibility of organic matter functional groups able to interact with the pesticide may explain some of the differences observed in sorption coefficient values. Furthermore, hydrophobicity of the neutral form of the pesticide, expressed as K_m' , does not appear to vary substantially at low pH levels.

Previous efforts to model sorption of acidic organic compounds have, in general, overvalued anionic-form sorption. On the other hand, the overall effect of organic matter dissociation owing to pH changes has been overlooked. Jafvert (1990), Lee et al. (1990), and Fontaine et al. (1991) tried to explain greater sorption than would be expected for acidic compounds, particularly at high pH levels.

Jafvert (1990) presented a model assuming invariant sorption of the neutral form with pH and linear pH-dependent sorption of the anionic form. Anionic-form sorption was considered to occur mainly at high pH. However, based on current knowledge, sorption of anionic form would not be expected, owing to the predominant negative surface charge in soils at high pH levels. His modeling work was made considering sediment with 49.4% clay content and 15 g/kg organic carbon; therefore, most of the mineral surfaces were expected to be covered by organic matter.

Fontaine et al. (1991) obtained anionic and neutral sorption coefficients using nonlinear optimization of sorption normalized by organic carbon as a function of soil pH. Sorption of neutral and anionic forms was assumed to be occurring only on organic matter. However, anionic-form sorption is not expected on organic matter, except at very low pH levels, when some functional groups become positively charged (e.g., amines). Bohn et al. (1985) have shown that soil organic matter possessing a net positive charge has not been found at normal soil pH values. Protonated amide groups may yield positive charge mostly at very low pH levels; in spite of this, the overall charge on organic matter remains negative.

Lee et al. (1990) showed that equilibrium sorption could be predicted using a weighted combination of sorption coefficients for the neutral molecule and organic anion, normalized to soil organic carbon content. The assumption was made that sorption of the ionized form may occur on formation of a neutral ion pair. It was also suggested that the hydrophobic part of the organic anion might sorb to a hydrophobic surface, with its polar end oriented toward the more polar aqueous phase. However, if these processes truly occur, they might not be relevant because it has been shown that overall sorption of acidic compounds decreases markedly with pH when the anionic form is dominant.

Further work to model ionic interactions, as a function of pH, was not pursued in this study due to the small contribution of anionic sorption when compared with overall sorption (Fig. 1). This was even true in this

specific case, which involves a combination of an acidic pesticide with low pK_a (strong acid) and a soil with high clay content and predominantly variable-charge minerals (kaolinite, gibbsite, hematite, and goethite).

The organic carbon-normalized prime sorption coefficient of molecular form ($K_{oc,m}'$) can be expressed as:

$$K_{oc,m}' = (\kappa'oc^d \times f^d) + (\kappa'oc^n \times f^n) \quad [3]$$

Therefore, Eq. [2] can be written as:

$$K_d = [(\kappa'oc^d \times f^d) + (\kappa'oc^n \times f^n)] \times F_{oc} \times \phi_m \quad [4]$$

or

$$K_{oc} = [(\kappa'oc^d \times f^d) + (\kappa'oc^n \times f^n)] \times \phi_m \quad [5]$$

where ϕ_m represents the fraction of molecular (neutral) form of the pesticide, f^d and f^n are related to the dissociated and nondissociated organic matter, and can be respectively estimated as:

$$\phi_m = (1 + 10^{pH - pK_a})^{-1} \quad [6]$$

$$f^d = \frac{10^{\frac{1}{\eta}(pH - pK_{om})}}{1 + 10^{\frac{1}{\eta}(pH - pK_{om})}} \quad [7]$$

$$f^n = 1 - f^d \quad [8]$$

The values of the empirical constant, η , and the apparent dissociation constant for organic matter, pK_{om} , used in this study were in accordance with expected values of $\eta = 2$ (McBride, 1994) and $pK_{om} = 5$ (Bohn et al., 1985; Sparks, 1995). The coefficients $\kappa'oc^d$ and $\kappa'oc^n$ are reference values for the magnitude of sorption, while the estimates of the accessibility of humin in dissociated and nondissociated organic matter (f^d and f^n) are expected to change with pH. They, along with ϕ_m , will define the shape of the K_d vs. pH curve.

The fit of the theoretical model in Eq. [5] to the measured 2,4-D sorption data set for the whole soil was evaluated. The measured data and fitted curve using the NLIN procedure of the SAS/STAT program (SAS Institute, 1989) are presented in Fig. 2. The analysis made here should be applicable for other compounds as well, for verifying if the model represents good fit to the response of sorption as a function of pH. Searching for expressions of Eq. [5] for other acidic pesticides, K_d data from the literature were obtained and curves were fitted following the same methodology. The contribution of ionic interactions to sorption of 2,4-D was shown to be much smaller than nonionic contributions. Henceforth, the data sets presented in this study will not be restricted to variable-charge soils.

Fontaine et al. (1991) reported K_{oc} data for flumetsulam in four soils adjusted to different pH levels. Flumetsulam (a sulfonamide herbicide) is weakly acidic, with a pK_a of 4.6. The measured data and fitted curves according to Eq. [5] are presented in Fig. 3. Though fit for the individual soils was excellent, an overall curve, resulting from fitting all original K_{oc} values for several pH levels in all soils, was less satisfactory but still highly significant.

Grey et al. (1997) reported K_d values for sulfentrazone for four soils with different amended pH values. The clay fraction was determined to be predominantly comprised of kaolinite for Soil 1 (Typic Unifluent) and Soil 2 (Rhodic Paleudult). Equal amounts of kaolinite and smectite were found in Soil 3 (Aeric Ochraqualf). Soil 4 (Typic Rhodudult) contained a combination of kaolinite and iron and aluminum oxyhydroxides of hematite and gibbsite. Sulfentrazone (phenyl-triazolinone herbicide) is a weak acid with a pK_a of 6.6. The calculated K_{oc} values and fitted curves using Eq. [5] for sulfen-

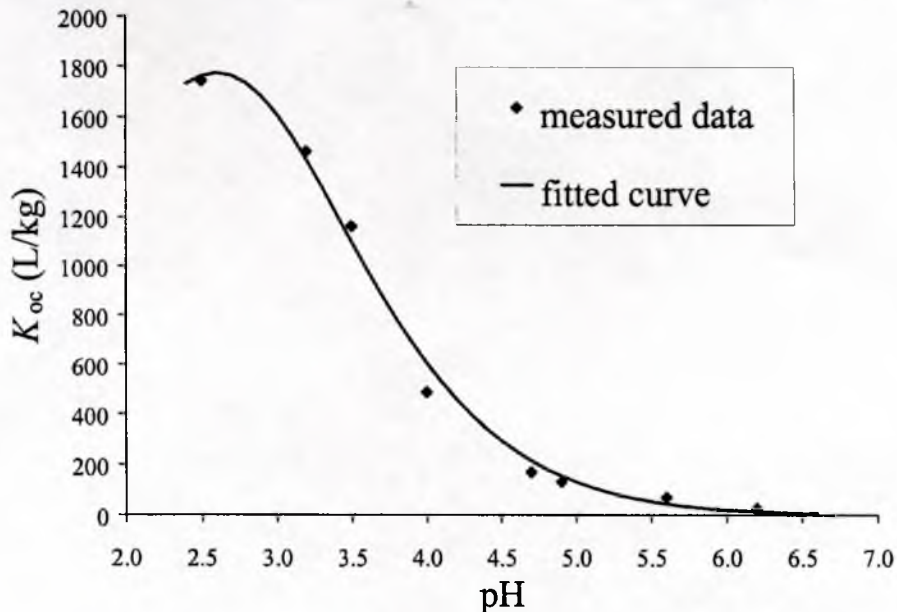


Fig. 2. Measured data and fitted curve when using Eq. [5] for pH dependence of 2,4-D sorption (pK_a , 2.8), expressed by K_{oc} for whole soil (Typic Haplorthox). $K_{oc} = [(41 \times 10^3 \times f^d) + (490 \times f^n)] \times \phi_m$; $R^2 = 0.993$, significant at the 0.001 probability level.

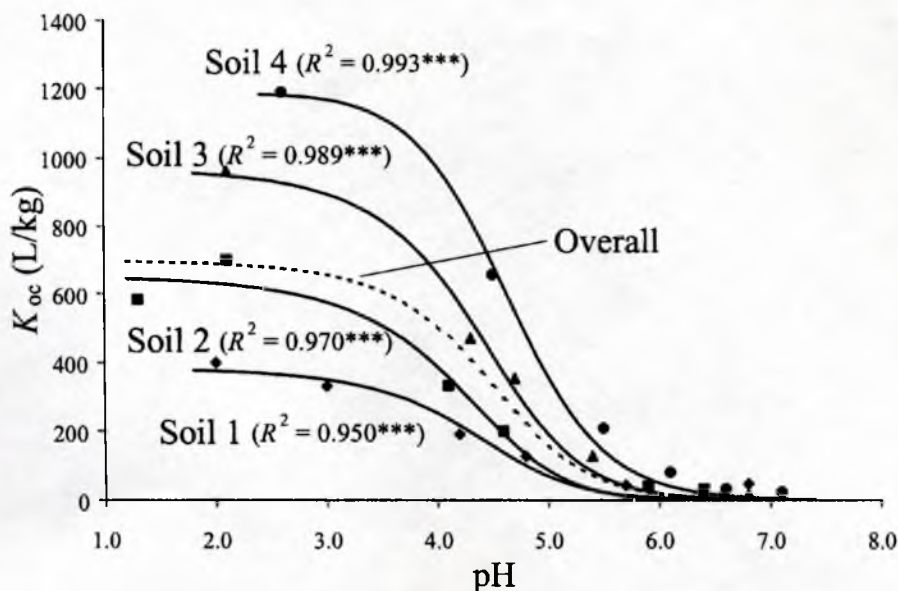


Fig. 3. Measured K_{oc} data set for several pH levels from Fontaine et al. (1991) [with permission], and fitted curves when using Eq. [5] for flumetsulam ($pK_a = 4.6$) in four different soils. Soil 1: Typic Argiudoll (initial pH = 5.9; 22 g/kg organic C). Soil 2: Typic Hapludult (initial pH = 6.4; 6 g/kg organic C). Soil 3: Udic Haploboroll (initial pH = 6.8; 31 g/kg organic C). Soil 4: Typic Haplaquoll (initial pH = 7.1; 42 g/kg organic C). Overall $K_{oc} = [(430 \times f^4) + (700 \times f^3)] \times \phi_{oc}$; $R^2 = 0.660$, significant at the 0.001 probability level.

trazone are shown in Fig. 4. Use of the entire data set to fit an overall curve still produced a highly significant coefficient of determination.

It is apparent from Fig. 3 and 4 that variability of the measured K_{oc} data between different soils increases when pH decreases, especially for pH levels below the pesticide pK_a values. The highly scattered points in K_{oc} values could be attributed to the fact that the soil organic matter is mostly in nondissociated form at low pH levels. In other words, at low pH values, organic matter is in

flocculated form and, therefore, the pesticide has to diffuse to sorption sites through organic matter strands (Brusseau and Rao, 1989). The humin fraction of soil organic matter seems to offer a stronger sorptive site for nonionized molecules than humic and fulvic acids. Humin can be considered the foundation material to which humic and fulvic acids are bonded (Nearpass, 1976).

Differences in structure and composition of soil organic matter may arise as a function of local conditions

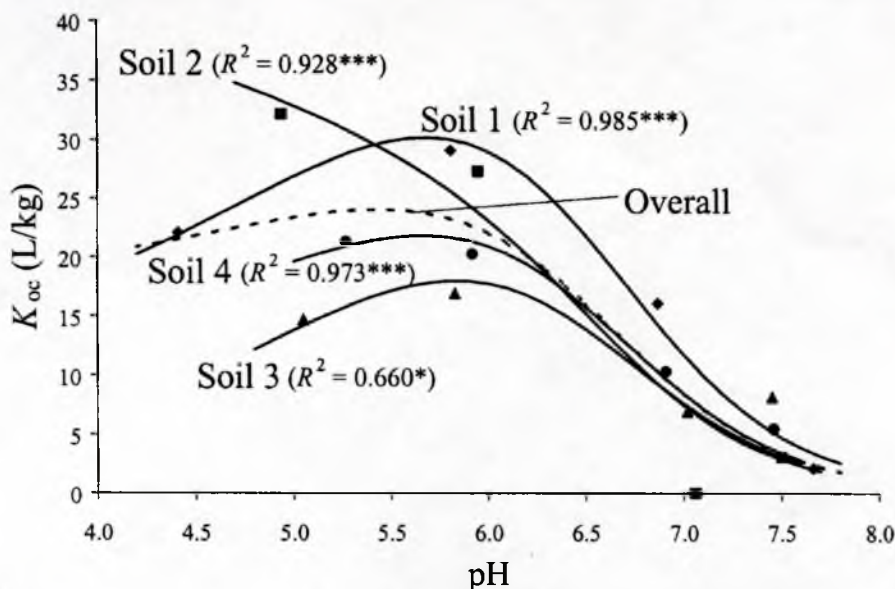


Fig. 4. Calculated K_{oc} data set for several pH levels from Grey et al. (1997) [with permission], and fitted curves when using Eq. [5] for sulfentrazone ($pK_a = 6.6$) in four different soils. Overall $K_{oc} = [(30 \times f^4) + (20 \times f^3)] \times \phi_{oc}$; $R^2 = 0.748$, significant at the 0.001 probability level.

(Stevenson, 1982; Haider, 1992). Thus, hydrophobic sorption depends on the variable physical structure and composition of the solid-phase organic matter, especially at low pH levels. It is difficult to distinguish between two-dimensional sorption onto the soil organic matter surface and sorption within the actual three-dimensional polymeric structure of organic matter (Graham-Bryce, 1981). General (nonspecific) processes can explain apparent pesticide affinity for organic matter. However, as noted by Graham-Bryce (1981), it should be emphasized that, for the system being considered, there are three main components: water, pesticide, and surface. The relative strengths of attractions of these different components for themselves and for each other determine the resultant equilibrium distribution.

CONCLUSIONS

Dissociation of 2,4-D was not enough to explain the variation in K_d as a function of pH. Accessibility of soil organic functional groups able to interact with the pesticide as a function of organic matter dissociation (conformational changes) was proposed to explain the observed differences in sorption. Experimental 2,4-D sorption data fit the model presented. Data on K_{oc} values from literature for flumetsulam and sulfentrazone in several soils also fit the model. This research shows that conformational changes in organic matter caused by changes in pH are key to modeling sorption of acidic pesticides in soils such as those used in this study.

ACKNOWLEDGMENTS

The authors would like to thank Dr. P.S.C. Rao, Dr. Brian L. McNeal, Dr. R. Dean Rhue, Dr. Ron E. Jessup, Dr. Kenneth L. Campbell, and Dr. Loukas G. Arvanitis at the University of Florida, as well as the JEQ reviewers and editors for their insightful comments and recommendations.

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