



Sorption of weak organic acids in soils: clofencet, 2,4-D and salicylic acid

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Abstract

The sorption behaviour of a new wheat hybridising agent (clofencet, 2-4-(chlorophenyl)-3-ethyl-2,5-dihydro-5-oxopyridazine-4-carboxylic acid) was investigated in batch equilibrium experiments and compared to that of two other organic acids (2,4-D and salicylic acid). Sorption coefficients K_d for the three compounds were determined in 18 Cambisols and Ferralsols. K_d values for clofencet were 0.3–9.4 l/kg for Cambisols and 2.1–68 l/kg for Ferralsols. Sorption of clofencet was strongly related statistically to that of salicylic acid. Sorption of clofencet and salicylic acid decreased exponentially with increasing solution pH in Cambisols whereas a bell-shaped curve was obtained for the sorption of salicylic acid in Ferralsols. Sorption of 2,4-D (2,4-dichlorophenoxyacetic acid) was not statistically related to the pH of the different soils. Positively charged oxide surfaces were shown to play a significant role in the sorption of clofencet and salicylic acid. The use of simple correlation and multiple linear regressions suggested that the main sorption mechanisms of clofencet in soils were likely to be ligand exchange on oxide surfaces and, to a lesser extent, cation bridging. Differences in the sorption behaviour of clofencet/salicylic acid and 2,4-D might be attributed to the possibility of the two former compounds forming bidentate complexes with metals. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sorption; Soil; Organic acid; Pesticide; pH

1. Introduction

Sorption is one of the key processes controlling transport, transformation and biological effects of pesticides (Calvet, 1989). Soil organic matter is the most important factor in the retention of non-polar pesticides (Hamaker and Thompson, 1972; Johnson and Sims, 1993). Pesticide sorption may be estimated predictively from the pesticide lipophilicity and the organic matter content of the soil (Briggs, 1981; Green and Karickhoff, 1990). The distribution coefficient K_d is often normalised to organic

matter (K_{om}) or organic carbon (K_{oc}) (Hamaker and Thompson, 1972), which reflects the major role of organic matter in adsorption processes.

Sorption of ionisable pesticides has received less attention than that for neutral compounds. For ionisable pesticides which can have anionic groups such as carboxylate and phenolate, statistically significant relationships between sorption and organic carbon content have rarely been observed (Shimizu et al., 1992; Ukrainczyk and Ajwa, 1996). The use of normalised K_{om} and K_{oc} distribution coefficients may not be appropriate for such compounds (von Oepen et al., 1991). This lack of relationship between sorption of anionic molecules and the organic matter content has been attributed to the repulsion between the negative charge of the molecule and the net negative charge of organic matter and clays (Borggaard and Streibig, 1988). The distribution of the

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ionised and neutral forms of an ionisable compound is regulated by the soil pH in relation to the pK_a of the molecule. A K_d value for an ionisable compound thus reflects a weighted combination of the K_d of the neutral molecule and that of the anion (Fontaine et al., 1991). These different forms are sorbed by different sorption mechanisms (Calvet, 1989).

Clofencet (2-(4-(chlorophenyl)-3-ethyl-2,5-dihydro-5-oxopyridazine-4-carboxylic acid) is a chemical wheat hybridising agent developed by Monsanto, which offers new opportunities for genetic improvement of this cereal. The molecule can be used to produce hybrid wheat seeds by preventing pollen development in wheat without affecting female fertility and by allowing cross-pollination from nearby untreated wheat plants. The compound is applied in strips in a single post-emergence application at the flag leaf stage. Hybrid wheat is likely to benefit the farmer by providing increased resistance to pests, thereby decreasing the pesticide input on the crop, and increased vigour, which makes the hybrid seeds particularly suited for farming management practices based on reduced or minimum tillage.

Clofencet is a carboxylic acid with a pK_a of 2.8 and the molecule will be mostly in anionic form in the pH range of agricultural soils in Europe. Anionic forms of organic acids are generally weakly retained by most soils (Nicholls and Evans, 1991) and weak acids have been detected in ground and surface waters in Europe (Croll, 1991; Barcelo et al., 1996; Heberer et al., 1998) and North America (Caux et al., 1995; Wade et al., 1998). Although the hybridising agent is to be used on a very limited area under controlled conditions, its proposed application rate (up to 5 kg a.s./ha) and its persistence (DT50 values 25–253 days) make it important to carefully assess the risk of leaching of the compound to groundwater.

The first objective of the study was to assess the sorption of clofencet in a large number of soils and to compare it to that of 2,4-D (2,4-dichlorophenoxyacetic acid) and salicylic acid (2-hydroxybenzoic acid). These two organic acids were selected because they exhibit pK_a values similar to that of clofencet (2.6 for 2,4-D, 2.8 for salicylic acid) and a significant amount of literature on their sorption mechanisms was available. The second objective was to identify soil properties that affect sorption of the three compounds. For this purpose, soils were selected for a contrast in their organic matter contents, pH characteristics and presence of oxides.

2. Materials and methods

2.1. Chemicals

Three ^{14}C -labelled molecules (radiochemical purity >99%) were used in this experiment: clofencet, 2,4-D and salicylic acid (Fig. 1). Salicylic acid and 2,4-D were uniformly ^{14}C -labelled on their phenyl ring (specific activity 3.7×10^{11} Bq/mol and 7.4×10^{11} Bq/mol, respectively). ^{14}C -labelling was in the pyridazine ring for clofencet (specific activity 1.2×10^{12} Bq/mol). Radiolabelled and non-radiolabelled clofencet were supplied by Monsanto whereas the two other compounds were purchased from Sigma France. Non-radiolabelled water solutions of the three chemicals were prepared in 0.01 M CaCl_2 and were spiked with ^{14}C -labelled solutions to achieve a concentration of 10 mg/l for all three chemicals ($31.6 \mu\text{mol/l}$ for clofencet, $45.2 \mu\text{mol/l}$ for 2,4-D and $72.4 \mu\text{mol/l}$ for salicylic acid) with a radioactivity of ca. 1.5×10^5 Bq/l. Selected properties for the three compounds are presented in Table 1.

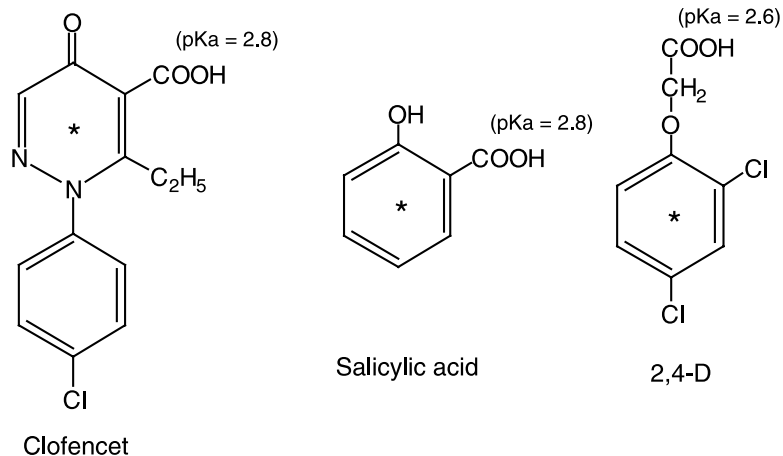


Fig. 1. Chemical structures for clofencet, salicylic acid and 2,4-D. The star indicates the location of the radioactivity within each molecule.

Table 1
Selected chemical properties for the three compounds used

Compound	Solubility in water (mg/l)	$\log K_{ow}^a$	pK_a
Clofencet	552 000	-2.2	2.8
2,4-D	620	2.83	2.6
Salicylic acid	1800	2.26	2.8

^a Octanol/water partition coefficient.

2.2. Soils

Eighteen soil samples from France, Brazil and New Caledonia were selected on the basis of soil pH, organic matter and iron and aluminium oxide contents (Table 2). These were classified into Cambisols and Ferralsols according to the FAO classification (WRB, 1998). Cambisols were sampled from across France and a particular emphasis was put on obtaining a diversity in pedogenesis. Sample 1 (rendzina) was taken under a forest canopy, while samples 2 and 3 (humic Cambisols) were taken from a plot under permanent grass. These three samples had a large organic carbon content ($\geq 5\%$). Samples 4–7 were calcic Cambisols, which are typical of the main areas of cereal cultivation in France. The former two samples were selected on the basis of their high pH. Samples 8, 9 and 10 were dystic, gleyic

and vertic Cambisols, respectively, and were all used for wheat or maize cultivation. Ferralsols were selected for this study on the basis of their oxide contents. Samples 11 and 12 originated from Brazil and have already been used to study the fate of ionic herbicides (Barriuso et al., 1992). Samples 13–18 from New Caledonia (South Pacific) were particularly rich in aluminium and iron oxides. Samples 16–18 were taken from the same soil profile under bushfallow on the Maré island (Duwig et al., 1998) and mainly differed from samples 13–15 sampled on the “Grande Terre” by their larger organic carbon contents and pH values. Soil samples were air-dried, passed through a 2-mm sieve and stored at room temperature. Selected physical and chemical properties are presented in Table 2. Selective dissolution of Al and Fe compounds was carried out using extractions with oxalate (McKeague and Day, 1966) and dithionite–citrate–bicarbonate (Mehra and Jackson, 1960).

2.3. Batch equilibrium sorption

Chemical solutions (10 ml) were added to two replicates of 5 g air-dried soil in 25-ml glass centrifuge tubes fitted with Teflon caps. Tubes were equilibrated for 24 h by shaking in an end-over-end shaker (70 rpm) at $25 \pm 1^\circ\text{C}$ in the dark. Equilibrium was assumed to be reached within the 24-h period. At the end of the

Table 2
Selected characteristics of the 18 soils used

Soil no.	Clay (%)	Silt (%)	OC (%) ^a	pH _{H₂O}	CEC (cmol/kg) ^b	Oxalate		DCB ^c	
						Al (%)	Fe (%)	Al (%)	Fe (%)
<i>Cambisols</i>									
1	33.3	36.1	10.4	7.5	38.5	0.26	0.17	0.29	2.00
2	67.1	26.4	7.0	6.3	43.2	0.43	0.48	0.44	2.25
3	57.1	36.7	5.0	6.3	51.1	0.41	0.60	0.69	3.98
4	25.0	53.8	1.6	8.3	14.4	0.10	0.15	0.12	0.90
5	28.6	56.6	1.8	7.8	16.5	0.11	0.17	0.13	1.23
6	23.7	62.2	1.7	7.0	13.1	0.07	0.24	0.11	0.91
7	35.7	56.5	1.4	6.6	21.1	0.12	0.18	0.18	1.17
8	32.5	64.7	1.1	6.2	13.0	0.15	0.30	0.36	2.24
9	22.9	40.0	1.3	6.6	12.3	0.06	0.27	0.19	2.23
10	53.9	42.4	1.9	7.6	23.7	0.12	0.56	0.21	2.49
<i>Ferralsols</i>									
11	63.9	29.6	3.9	4.6	14.3	0.43	0.25	1.93	7.95
12	54.2	20.2	1.5	4.8	6.6	0.21	0.17	0.93	7.76
13	28.3	28.0	3.6	5.2	6.6	0.10	0.22	2.09	21.74
14	31.4	16.6	0.3	5.1	0.9	0.17	0.15	2.06	19.66
15	30.5	63.6	1.2	5.6	3.3	0.10	0.19	1.35	22.89
16	25.9	52.4	9.3	7.2	48.8	1.42	0.48	3.38	9.78
17	19.9	48.8	5.1	6.9	21.9	1.52	0.52	2.80	8.35
18	21.5	41.3	2.7	6.6	11.6	1.13	0.51	2.92	9.32

^a Organic carbon content.

^b Cation exchange capacity.

^c Dithionite–citrate–bicarbonate.

equilibration, the suspension was centrifuged at 5000g for 15 min (Sorvall RC5B). Aliquots (1 ml) of the supernatant were taken for measurement of the radioactivity content by liquid scintillation counting (Kontron Betamatic V) after addition of 10 ml of scintillation cocktail (Pico-Fluor 40, Packard). The pH of the remaining supernatant was measured (Metrohm 682 Titrprocessor). Concentrations of chemicals in solution were calculated from radioactivity content and the amount of chemical sorbed to soil was calculated as the difference between concentrations in the initial solution and in the supernatant.

3. Results and discussion

3.1. Sorption in relation to soil properties

Distribution coefficients K_d for clofencet, salicylic acid and 2,4-D ranged from 0.3 to 67.9, 3.6 to 397 and 0.3 to 9.5 l/kg, respectively (Table 3). K_d for the Cambisols were ranked as follows: salicylic acid > clofencet > 2,4-D except for Soil 6, for which sorption of clofencet and 2,4-D was similar ($P < 0.05$) and for Soils 1, 4 and 5, for which clofencet was the least sorbed chemical ($P < 0.05$). These three latter soils were all characterised by the presence of carbonates (251, 58 and

14 g CaCO₃/kg, respectively). K_d values for the Ferralsols which have large contents of oxides were larger than those for Cambisols (Table 3). This is a general trend for anionic compounds (Baskaran et al., 1996). The largest K_d (397 l/kg) reported for the sorption of salicylic acid in Soil 15 was equivalent to a sorption of 99.5% of the salicylic acid applied. In Ferralsols samples 16, 17 and 18, which originated from the same soil profile, sorption of clofencet and salicylic acid increased with depth. This might be explained by a coating of the mineral surfaces by the soil organic matter and the blocking of specific sorption sites on oxide surfaces. Also, a decrease in organic matter content is likely to reduce repulsion between its dissociated acid functional groups and the chemicals in their anionic forms. The negative relationship between sorption and organic matter content observed for this profile clearly demonstrates that sorption mechanisms for the two chemicals in these soils are different from those involved in the sorption of non-ionisable compounds (Hamaker and Thompson, 1972).

In contrast to clofencet and salicylic acid, sorption of 2,4-D decreased with depth in the profile. Hence, there may be different processes involved in the sorption of clofencet/salicylic acid and 2,4-D, although all three organic acids have very similar pK_a values. A possible explanation for this discrepancy between compounds is that the chemical structures of both clofencet and salicylic acid allow the formation of bidentate surface complexes with metals (Kummert and Stumm, 1980), while this is not the case for 2,4-D. Gennari et al. (1998) also reported clusters in sorption magnitude and mechanisms for three imidazolinone molecules having similar pK_a values. Sorption of clofencet was clearly related to that of salicylic acid for cambisols (Pearson correlation coefficient $r = 0.98$), which may suggest that clofencet and salicylic acid are sorbed by similar dominant mechanisms in cambisols. No such significant relationship was noted for the sorption of salicylic acid and 2,4-D or for that of 2,4-D and clofencet.

Relationships between sorption of the three molecules and soil properties were investigated using simple correlation and stepwise multiple linear regression analyses for the two different groups of soils (Table 4). Sorption of clofencet and salicylic acid was correlated to the pH for cambisols ($r = -0.85$ and $r = -0.87$, respectively). K_d values for the three molecules were plotted against pH measured in the batch equilibrium supernatant (Fig. 2). For cambisols, sorption of clofencet and salicylic acid increased sharply with decreasing pH and the datapoints were well matched by an exponential fitting ($r^2 = 0.98$ and $r^2 = 0.97$, respectively). An increase in sorption with decreasing pH has been noted in a large number of studies investigating the sorption of weak acids (Shimizu et al., 1992; Baskaran et al., 1996; Hamaker et al., 1966; Ukrainczyk and Ajwa, 1996). The high r^2 value obtained for clofencet makes it possible to

Table 3
Distribution coefficients K_d (l/kg) for clofencet, salicylic acid and 2,4-D for 18 soils^a

Soil	Distribution coefficient K_d		
	Clofencet	Salicylic acid	2,4-D
<i>Cambisols</i>			
1	1.13 (e)	3.59 (g)	1.83 (c)
2	6.79 (b)	12.34 (c)	2.60 (a)
3	6.88 (b)	14.71 (b)	1.96 (b)
4	0.28 (f)	4.17 (fg)	0.31 (h)
5	0.30 (f)	3.71 (g)	0.44 (g)
6	0.56 (ef)	4.33 (fg)	0.53 (f)
7	4.99 (c)	9.61 (d)	0.72 (d)
8	9.35 (a)	16.50 (a)	0.59 (ef)
9	2.32 (d)	8.65 (e)	0.40 (gh)
10	0.95 (e)	4.59 (f)	0.64 (de)
<i>Ferralsols</i>			
11	67.87 (a)	31.33 (c)	3.14 (d)
12	40.77 (b)	26.04 (c)	9.53 (a)
13	29.48 (c)	270.54 (b)	6.81 (b)
14	13.08 (d)	384.26 (a)	0.93 (f)
15	11.19 (e)	397.34 (a)	1.94 (e)
16	2.11 (g)	7.94 (c)	4.27 (c)
17	2.68 (g)	64.58 (c)	4.30 (c)
18	4.40 (f)	302.32 (b)	3.53 (d)

^a For each group of soils and compound, values having the same letter are not statistically different at a probability level of 0.05.

Table 4
Relationship between sorption coefficients and soil properties as determined from stepwise multiple linear regressions^a

Compound	Relationship	r^2
<i>Cambisols</i>		
Clofencet	$K_d = 30.57 - 3.88 \times \text{pH}^{**} + \varepsilon$	0.72
Salicylic acid	$K_d = 48.74 - 5.77 \times \text{pH}^{**} + \varepsilon$	0.75
2,4-D	$K_d = -0.06 + 4.48 \times \text{Al}_{\text{oxalate}}^{***} + 0.01 \times \text{OC}^* + \varepsilon$	0.96
<i>Ferralsols</i>		
Clofencet	$K_d = -14.18 + 0.08 \times \text{clay}^* + 0.22 \times \text{Mn}^* + \varepsilon$	0.92
Salicylic acid	$K_d = -79.35 + 20.19 \times \text{Fe}_{\text{DCB}}^* + \varepsilon$	0.66
2,4-D	No significant relationship at $P = 0.05$	–
<i>All soils together</i>		
Clofencet	$K_d = 64.52 - 9.09 \times \text{pH}^{***} + 0.22 \times \text{Mn}^{**} + \varepsilon$	0.80
Salicylic acid	$K_d = -1.86 + 16.54 \times \text{Fe}_{\text{DCB}}^{***} - 0.83 \times \text{CEC}^* + \varepsilon$	0.83
2,4-D	$K_d = -1.82 + 2.35 \times \text{Al}_{\text{DCB}}^{***} + 0.01 \times \text{clay}^* + \varepsilon$	0.62

^a Abbreviations are similar to those of Table 2 except for Mn, which stands for manganese.

* Denotes significance at 0.05 level.

** Denotes significance at 0.01 level.

*** Denotes significance at 0.001 level.

use the relationship as a predictive tool for estimating sorption of this new compound in Cambisols. Sorption of 2,4-D was not significantly related to pH ($r = -0.42$, $P > 0.05$; Fig. 2) even though a significant negative relationship has been noted on numerous occasions (Hermosin and Cornejo, 1991; Barriuso and Calvet, 1992; Barriuso et al., 1992; Baskaran et al., 1996). Such contrasting observations with regard to the influence of pH have been noted elsewhere (Gan et al., 1994; Pusino et al., 1997). Sorption of 2,4-D in Cambisols was positively related to the aluminium extracted by oxalate, and, to a lesser extent, to organic matter (Table 4). These soil components were also found to have a large influence on sorption by Huang et al. (1977) and Reddy and Gambrell (1987).

In Ferralsols, K_d of clofencet was related to clay content and manganese content, while K_d of salicylic acid was positively related to iron extracted by dithionite–citrate–bicarbonate (Table 4). The influence of the clay content on the sorption of clofencet in Ferralsols could be considered as a reflection of the abundance of fine discrete oxide particles (Gallez et al., 1976) as there are no phyllosilicates in most of the soils considered (Latham, 1980). The presence of the manganese content in the multiple linear regressions may be associated with a relative dominance of cation-bridging sorption mech-

anisms for particular soil conditions. As for Cambisols, the relationships derived for ferralsols are consistent between clofencet and salicylic acid. This reinforces the hypothesis of similar dominant sorption mechanisms for the two molecules suggested previously for Cambisols. Soil pH was not one of the variables appearing in the multiple linear regressions for Ferralsols, but variations of K_d values against pH for each compound were plotted in Fig. 2 nevertheless. The shape of K_d values for clofencet against pH was broadly similar to that observed for Cambisols (i.e., exponential relationship). For salicylic acid, K_d values were distributed according to a bell curve, i.e. small sorption coefficients for low and high pH, maximum of sorption between pH = 5 and pH = 6. To our best knowledge, such a shape when plotting sorption as a function of pH for different soils has never been reported for weak acids, although such behaviour has been observed when modifying the pH artificially for individual soils (Watson et al., 1973; Stumm et al., 1980; Dur et al., 1990; Nicholls and Evans, 1991). Again, as for Cambisols, no clear pattern could be identified for 2,4-D in Ferralsols. The interpretation of results when considering all soils together is more complex. Increasing pH had an inverse effect on sorption and that greater sorption correlated with larger dithionite–citrate–bicarbonate extracts.

3.2. Implications for sorption mechanisms of clofencet

Clofencet and salicylic acid have a pK_a of 2.8 and will be mainly found in their anionic form in soils. However, a proportion of the neutral form may be present in the most acid soils. Sorption mechanisms of weak acids in soils may include non-specific or specific mechanisms (Calvet, 1989). Non-specific interactions (London–van der Waals forces, dipole–dipole interactions or charge transfer) are weak in comparison to specific sorption interactions and are therefore likely to contribute to a limited extent to the sorption of organic acids in most soils. Sorption of the neutral form of the molecules is likely to mainly involve non-specific interactions coupled to hydrophobic interactions and hydrogen bonds (Hamaker and Thompson, 1972). Sorption of the anionic form of the chemicals considered is likely to be weaker than the neutral form in cambisols because of repulsion between electronegative charges of soil constituents and those of the ionised molecules. Nevertheless, sorption mechanisms can involve bridging with a bivalent cation between the ionised molecule and negatively charged surfaces such as phyllosilicates or organic matter. It is unlikely that direct sorption involving the few positive charges at the edge of sheets in clays or protonated amine groups within the organic matter (Stevenson, 1982) is a significant mechanism for weak acids.

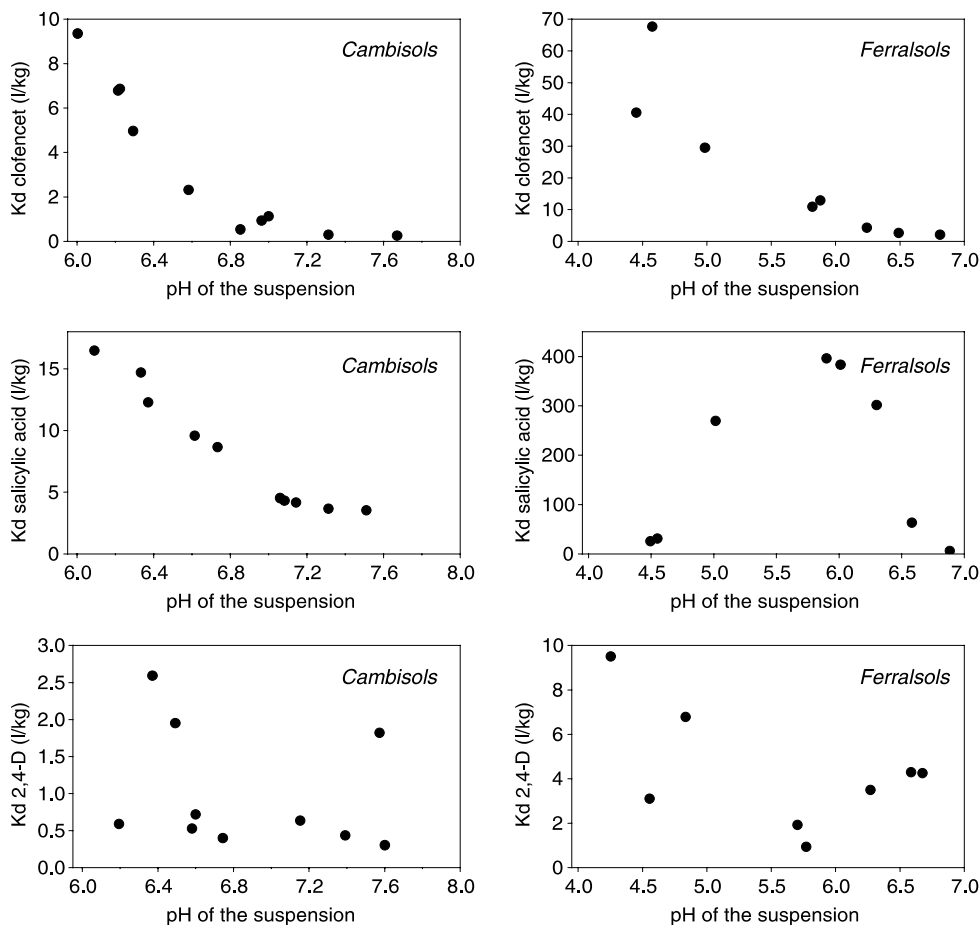


Fig. 2. Sorption distribution coefficients as a function of pH of the solid/liquid suspension for clofencet, salicylic acid and 2,4-D for Cambisols and Ferralsols. Each dot represents the value obtained for an individual soil.

The main sources of positively charged adsorption surfaces in soil are aluminium and iron oxides of various crystallinity and association with organic matter. The net charge of these surfaces varies with pH, becoming more positive at lower pH. These soil components result from a weathering process. They are traditionally found in large quantities in tropical soils (Baskaran et al., 1996), but are also present in smaller quantities in soils from higher latitudes. They are intimately associated with organic matter in soils (Gallez et al., 1976). Their effect on soil chemistry and chemical sorption can be much greater than would be supposed from their small quantities in most soils (Huang and Violante, 1986) and it has been suggested that their contribution to sorption of ionised pesticides has been overlooked (Gennari et al., 1998). The degree of association of the clay-size soil components was shown to determine the adsorption mechanisms of the organic acid 2,4-D (Celis et al., 1999). Sorption of organic acids onto oxide surfaces is achieved

through ligand exchange with OH or OH₂ groups from the oxide surface (Kung and McBride, 1989; Stumm and Morgan, 1996). This sorption mechanism has been demonstrated for numerous inorganic acids (e.g., phosphate, molybdate, fluoride) and has been postulated for the binding of *s*-triazines, bipyridines, organophosphates and glyphosate to soils (von Oepen et al., 1991; Piccolo et al., 1992).

Salicylic acid is known to be adsorbed preferentially in soils by ligand exchange with hydroxyl groups of oxide surfaces (Sigg and Stumm, 1981; Benoit et al., 1993). The sorption of clofencet has been shown to be closely related to that of salicylic acid and largely influenced by pH variation in cambisols. Both molecules have –COOH and =O/OH groups close to one another in the chemical structure and the formation of surface bidentate complexes with metals is possible. It is thus reasonable to assume that sorption to oxides plays a significant role for clofencet in cambisols although the

rest of the chemical structure will allow for other adsorption processes to take place. The large influence of this mechanism has also been demonstrated in ferralsols through a significant relationship between sorption and clay content which reflects small-sized oxide particles. The positive influence of manganese content on sorption of clofencet may reflect the existence of cation bridging as a secondary sorption mechanism for this molecule. Hydrophobic interactions, ligand exchange, cation bridging and other specific and non-specific sorption mechanisms are all likely to participate in the sorption of clofencet in soil. The relative importance of one mechanism over another will be dependent on the soil constituents, the molecule and the chemical environment of the soil.

4. Conclusions

Sorption of clofencet and salicylic acid was largely influenced by variations in pH, although this was not the case for 2,4-D. Sorption of the two former compounds was found to increase with depth in a soil profile where organic matter decreased. In contrast to non-ionic molecules, organic matter did not have a positive effect on sorption of these two compounds. Positively charged oxide surfaces were found to be involved in their sorption, especially in Ferralsols. K_d values for clofencet and salicylic acid were statistically related in Cambisols and they might therefore be sorbed to soil by similar sorption mechanisms (ligand exchange and, to a lesser extent, cation bridging). Similarities in the sorption of clofencet and salicylic acid when compared to that of 2,4-D may be attributed to the possibility for these two former compounds to form bidentate complexes with metals. A statistically significant exponential relationship was found between sorption of clofencet and the pH of a suspension of the compound. This provides a time- and cost-effective way to estimate K_d values for sites most susceptible to leaching where the compound is to be used. This is particularly relevant for clofencet, which is to be used on a limited area and would allow identification of the sites where management with respect to leaching is required.

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