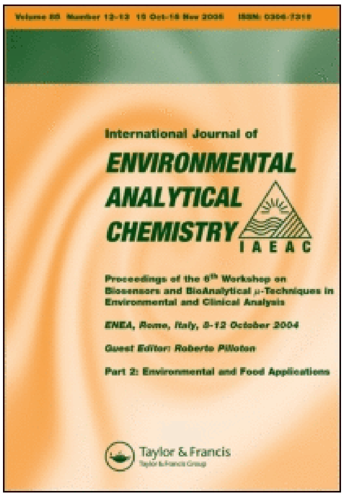

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SOIL TYPE AND HERBICIDES ADSORPTION

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Herbicides behaviour in soils greatly depends on adsorption through its influence on degradation and movement. The adsorption intensity depends on both the chemical structure of pesticides, the nature of soil constituents and soil physico-chemical factors such as the pH. In this paper, the role played by these factors is analysed and used to evaluate the possible use of soil surveys for assessing adsorption behaviour of pesticides in soils. The analysis is based on adsorption measurements of three herbicides (atrazine, terbutryn and 2,4-D) by several soils differing in their mineralogical composition, organic matter content and pH. Using statistical analysis, it is shown that some relations can be defined between soil types and adsorption behaviour. These relations are strongly dependent on the electrical state of the herbicide molecule (cationic, anionic and neutral).

KEY WORDS: Herbicides, soil, adsorption, desorption, atrazine, terbutryn, 2,4-D.

INTRODUCTION

The fate of herbicides in soil plays a central part in their behaviour in natural media, more especially as regards the hazard of underground water pollution. Thus, predicting this fate is an important goal because it can provide a way to improve the chemical quality of natural waters.

Adsorption of herbicides by soils and soil constituents has been extensively studied and numerous reports are found in the literature[1–3].

Molecular mechanisms have been described in terms of ionic, polar or hydrophobic interactions. Their description is not yet complete owing to the complex nature of soil constituents and to the great variety of pesticide molecules. Nevertheless, our purpose was not to discuss the validity of these mechanisms, but to use descriptions which are generally accepted for them.

This paper aimed to determine whether information from soil surveys is useful for predicting the pesticide behaviour in soils. Limiting this question to adsorption phenomena, we tried to look for some general relationship between adsorption characteristics and soil types. This would have required the determination of adsorption and desorption isotherms for a rather large number of soils and led to an unrealistic number of measurements. Thus, a selected collection of soils was used to reduce the number of determinations.

The study has been done with 58 soils and three herbicide molecules whose distribution coefficients were determined. These coefficients were discussed in relation to soil and molecular properties and analysed by a statistical method: principal components analysis (STAT-ITCF Software[4]). This analysis was used to select soils for more detailed studies based on adsorption and desorption isotherms.

MATERIALS AND METHODS

Soils

A great variety of soil types from various origins was used covering a wide range of pH values, organic carbon contents and mineralogical compositions. Some of these properties are given in Table 1.

Chemicals

Three herbicides were used: atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), terbutryn (2-ter-butylamino-4-ethylamino-6-methylthio-1,3,5-triazine) and 2,4-D ((2,4-dichlorophenoxy)acetic acid). These well known chemicals were chosen as models to provide neutral, cationic or anionic molecules. For the range of soil pH encountered, atrazine (pKa = 1.7) was always in a neutral form, 2,4-D (pKa = 2.6) in an anionic form and terbutryn (pKa = 4.4) in either neutral or cationic forms.

Table 1 Soil properties.

Soils[*]	*Origin*	*Vegetation*	*Samples*
Rendzina	Lorraine	Forest	1
Humic Cambisols[†]	Jura	Grassland	6
Mollic Cambisols[†]	Jura	Grassland	5
Calcic Cambisols[‡]	Ile de France	Maize	9
Dystric Cambisols	Lorraine/Jura	Maize/Wheat	4
Gleyc Cambisols	Lorraine	Maise/Wheat	1
Vertisols	Martinique	Sugar-cane	6
Ferralsols[¶]	Brazil	Wheat/Soja/Sugar-cane	20
Andosols	Martinique	Sugar-cane	2

Soils[*]	*Carbon content (%)*	*pH ($0.01\ M\ CaCl_2$)*	*C.E.C. (meq 100 g^{-1})*	*Clays (%)*
Rendzina	6.8–9.5	7.0	50	30
Humic Cambisols	10.0–14.1	6.5–7.0	45	20–40
Mollic Cambisols	4.5–9.2	6.8–7.8	35	20–50
Calcic Cambisols	0.9–1.4	7.0–7.5	15	25
Dystric Cambisols	1.4–2.6	4.5–5.4	15	15–30
Gleyc Cambisols	1.3–1.5	6.2–6.5	20	50
Vertisols	2.0–2.9	5.9–6.3	40	40–60
Ferralsols	1.2–4.7	4.2–5.5	2–13	30–50
Andosols	9.2–10.7	4.3–4.4	100	—

[*] F.A.O. Classification, [†] Blondé *et al.*[5], [‡] Morel *et al.*[6], [¶] Cerri *et al.*[7]

Determination of distribution coefficients

All measurements were made in duplicate. Five grams of air-dried soil were mixed with 20 ml of a herbicide-0.01 M $CaCl_2$ solution in stoppered centrifuge tubes. The herbicide concentration was (10 ± 0.5) $mg{\cdot}l^{-1}$ for all the herbicide-soil systems. The suspensions were shaken for 24 hours in a thermostated box at (25 ± 1)°C with an end-over-head agitator. Preliminary experiments had shown that equilibrium was reached within this time. After agitation, the mixtures were centrifuged at 48 000 g for 15 min and the supernatant solutions analysed by HPLC for herbicide concentrations on a NovaPak-C18 (15 cm × 3.9 mm) column and a Waters appliance with UV detector. The mobile phases used were methanol–water mixtures for all three herbicides: 70/30 (v/v) for atrazine, 80/20 (v/v) for terbutryn and 70/30 (v/v) plus 0.01 M tetrabutylammonium chloride for 2,4-D. The operating wavelengths were 222, 224 and 228 nm for atrazine, terbutryn and 2,4-D, respectively.

Amounts of adsorbed herbicide were calculated as the difference between the initial herbicide concentration and the equilibrium concentration. The Kd distribution coefficients were calculated as the ratio of the amount of adsorbed herbicide (mg) per unit mass of soil (kg) to the equilibrium concentration ($mg{\cdot}l^{-1}$). The distribution coefficients relative to the soil organic carbon (KOC) were obtained by dividing the Kd values by the organic carbon content.

Adsorbed amounts–pH relationships were determined by varying the soil suspension pH with $Ca(OH)_2$ or HCl.

Adsorption and desorption isotherms

Adsorption and desorption isotherms were obtained with the soils selected by the statistical analysis. For adsorption isotherms the above procedure was followed for five different initial herbicide concentrations and each measurement was made in duplicate. To obtain desorption isotherms, the equilibrated solutions wer diluted after adsorption with a 0.01 M $CaCl_2$ herbicide-free solution, the total volume of the suspension (20 ml) being constant. The mixtures were shaken to disperse the soil pellet remaining at the bottom of the centrifuge tube and the suspensions were shaken again at (25 ± 1)°C for 24 h to reach a new equilibrium. The mixtures were then centrifuged and the supernatant solution analysed for herbicide concentrations in order to calculate the remaining adsorbed quantities. The process was repeated either four or five times until it was not possible to detect the herbicide in solution.

RESULTS AND DISCUSSION

Distribution coefficients

Measurements made in this study led to low equilibrium concentrations which allowed distribution coefficients to be used for describing adsorption phenomena. This is because adsorption isotherms can be approximately represented by linear relations under this condition.

Data analysis Figure 1 shows the results of the principal component analysis for distribution coefficients. The two axes on the graph correspond to the two principal components which explain 84% of the total variation. This graph shows that the various soil types are distinguished quite well. Soil types such as Mollic Cambisol, Humic Cambisol and Vertisol adsorbed efficiently atrazine and terbutryn whereas Ferralsols and Andosols adsorbed 2,4-D more efficiently.

The vectors of the barycentre of the points corresponding to organic carbon contents, pH values and Kd values show that:

- atrazine's Kd is strongly correlated with the organic carbon content, consistently with published results[8], but not correlated with the soil pH.
- terbutryn's Kd is less correlated with the organic carbon content and shows some correlation with the soil pH.
- 2,4-D's Kd is inversely correlated with the soil pH in agreement with the literature[9,12] but it is not correlated with the organic carbon content.
- atrazine adsorption presents some correlation with that of terbutryn; adsorption of these two triazine herbicides, however, does not show any correlation with that of 2,4-D.

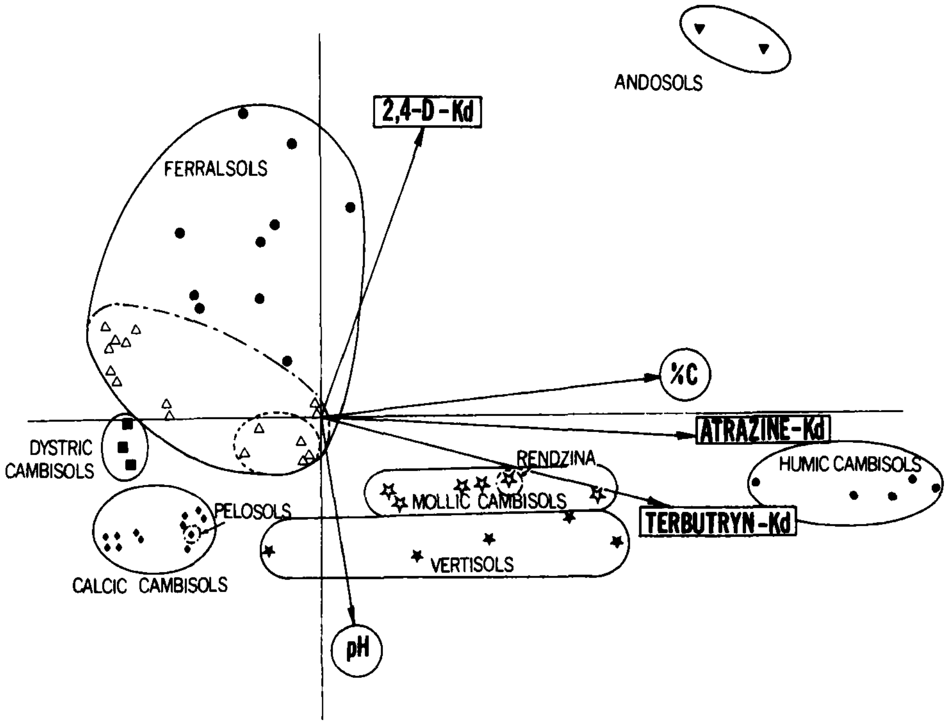

Figure 1 Results of the principal components analysis.

Influence of organic carbon content Published results on pesticide adsorption frequently report some correlation between distribution coefficient values and soil organic carbon content or organic matter content[1,13]. This correlation more or less depends on the nature of both the herbicide molecule and the soil[2]. In fact, the plot of Kd values against the organic carbon contents for atrazine and terbutryn (Figure 2) shows a good linear relation Kd = f(%OC) for atrazine (Kd = $-0.26 + 0.88(\%OC)$, $r = 0.90$) and a less good one for terbutryn (Kd = $2.54 + 6.74(\%OC)$, $r = 0.60$). This can be explained on the basis of adsorption mechanisms. Atrazine is mainly adsorbed by the soil organic matter in non-ionized form through hydrogen bonds and hydrophobic interactions[14,15] and also probably through charge transfer bonds[16]. Thus, the amount of organic matter is probably the main factor in atrazine adsorption whereas its nature and composition is probably less important. On the contrary, terbutryn is adsorbed in neutral or cationic forms according to the soil pH so that other factors than the organic matter content have to be taken into account[17]. This is also true for 2,4-D for which adsorption is not correlated with the organic carbon content. Because they are all in an anionic form, 2,4-D molecules are mainly adsorbed by Ferralsols and Andosols through ionic interactions.

Influence of the soil pH Variations of Koc values against soil pH are presented in Figures 3 and 4 for terbutryn and 2,4-D respectively. If adsorption of these two herbicides was determined only by the amount of organic matter, Koc values should be identical irrespective of the soil type. This is not what is observed.

Studies on the influence of soil pH have shown that adsorption of terbutryn by Ferralsols presented a maximum in the 4.4–5.5 pH range[18]. The curve in Figure 3

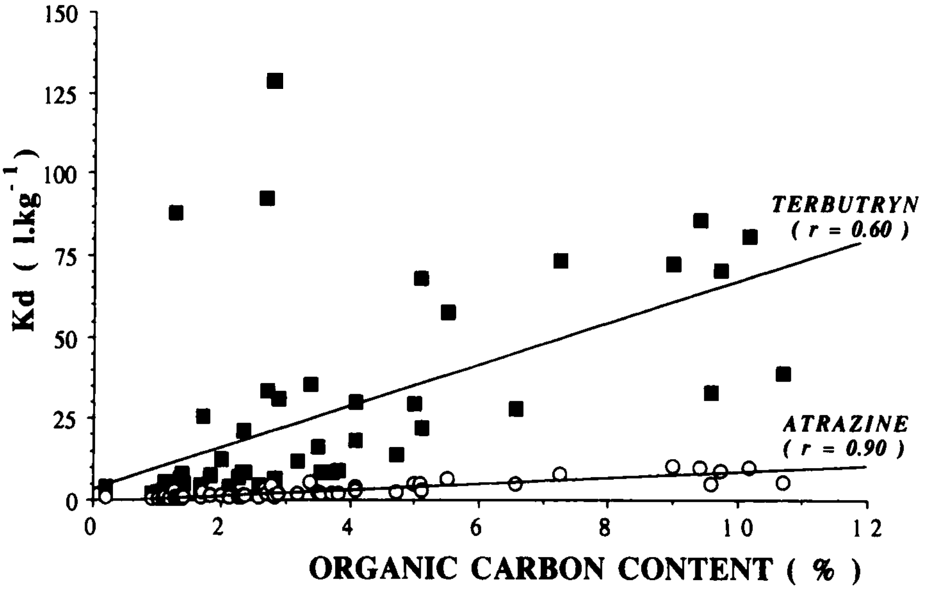

Figure 2 Plot of distribution coefficient values against organic carbon content.

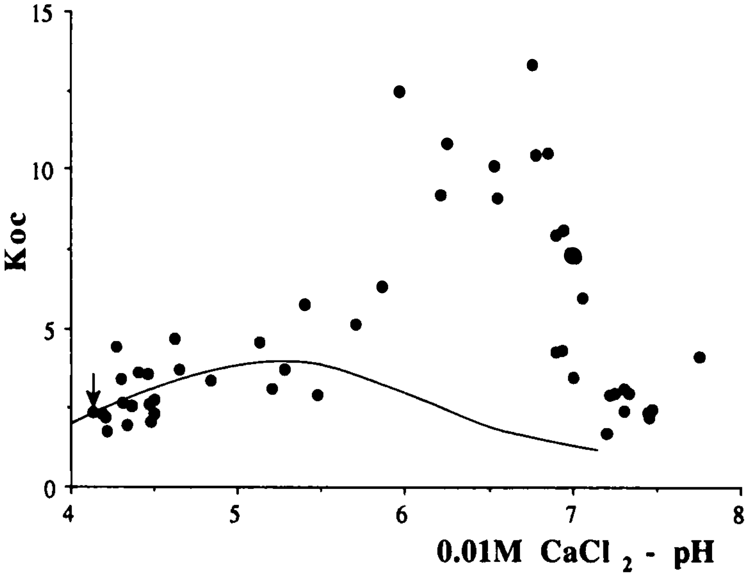

Figure 3 Effect of soil pH on the Koc value for terbutryn. The curve represents the variation of Koc with pH obtained for the soil indicated by the arrow.

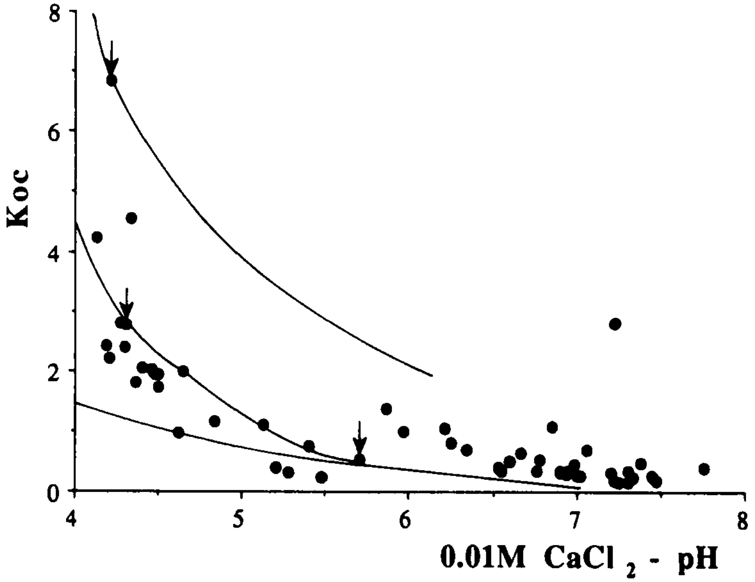

Figure 4 Effect of soil pH on the Koc value for 2,4-D. The curves represent the variations of Koc with pH obtained for the soils indicated by the arrows.

shows the variation of Koc with varying pH for a Ferralsol. Below pH = 5.5, the scattering of experimental points does not allow any observation about the influence of the pH to be made. Above pH = 5.5, terbutryn molecules are non-ionized and the observed variations of Koc values can only be explained in terms of variations in the soil organic matter properties.

The 2,4-D adsorption-soil pH relation displays a more simple behaviour. The curves represent the variations of Koc with the pH for three Ferralsols. This shows that the soil pH is effectively the main factor that influences the adsorption of 2,4-D through ionization of surface sites leading to the appearance or the disappearance of positive electrical charges[11,19].

Adsorption isotherms

As mentioned in the Introduction section, adsorption isotherms were only determined for a limited number of soils. These soils were chosen from the results of the data analysis. In Figure 1, soils of the same type are grouped into more or less extended clouds. Representative soils were chosen by taking for each groups the soil whose corresponding point was closest to the barycentre of the cloud. Adsorption isotherms were determined with these representative soils and also with some other soils such as Pelosol and Rendzina. No adsorption isotherms were determined for atrazine. Adsorption isotherms for terbutryn are represented in Figure 5, and they can be

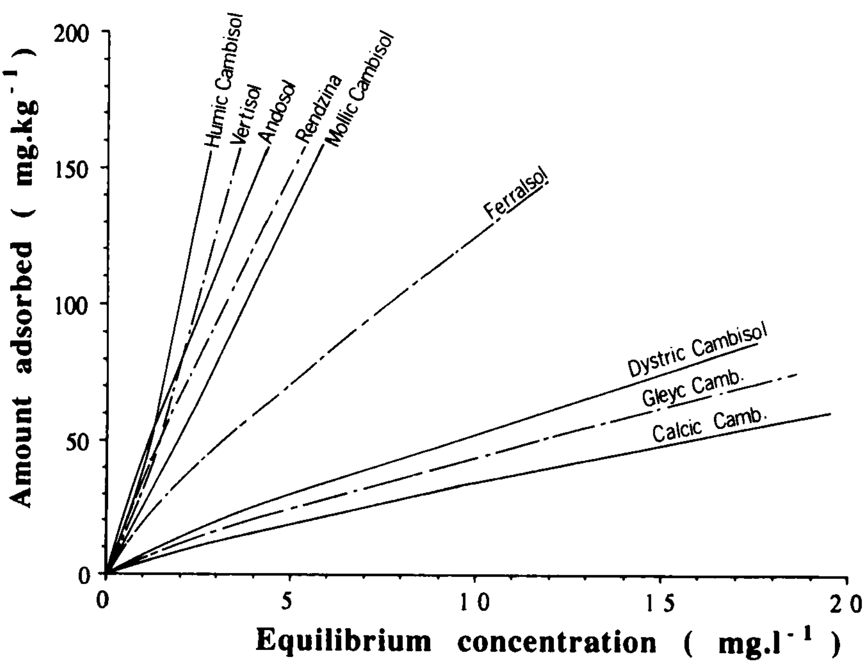

Figure 5 Adsorption isotherms for terbutryn.

numerically described by the Freundlich's equation:

$$q = \mathrm{Kf{\cdot}Ce^{nf}}$$

where, q is the adsorbed amount per unit mass of adsorbent ($\mathrm{mg \cdot kg^{-1}}$), Ce is the equilibrium concentration ($\mathrm{mg \cdot l^{-1}}$), and Kf and nf are two constants for a given herbicide-soil system.

For terbutryn, values of Kf and nf are given in Table 2 along with average values of Kd for each soil type.

Three groups of adsorption isotherms appear in Figure 5:

i) soils with high adsorption capacity (Kf > 25) which have a high organic matter content alone (Humic, Mollic Cambisol) or accompanied either by a high content of aluminum (Andosols) or a high content in smectite-type clay (Vertisol). This can be explained by the possible presence of a great number of adsorption sites bearing negative electrical charges. For Andosols, the high adsorption capacity is probably due to both a high organic matter content and adsorption through coordination bonds with aluminium[20].

ii) Ferralsols (Kf = 25) for which adsorption can be also due to coordination bonds with iron[21].

iii) soils with low organic matter content (Kf < 10).

Kf values reported in Table 2 show that adsorption isotherms obtained with a limited number of selected soils led to the same classification of soil adsorption capacity as the Kd values obtained with all soils.

For 2,4-D, adsorption isotherms are represented in Figure 6 and Freundlich's parameters are given in Table 3 together with average values of Kd.

Here again, adsorption isotherms and distribution coefficients led to the same order of adsorption capacity. Three groups of soils can be identified:

i) soils (Kf > 15) with a high metallic oxide and hydroxide contents which are known to adsorb anionic molecules[11,19];

ii) soils (Kf = 2–5) with such organic matter content that adsorption can be assumed to result from competition between hydrophobic interactions and repulsion due to ionized carboxylic groups;

Table 2 Adsorption characteristics for terbutryn.

Soils	*Kf*	*nf*	r^2	*Kd*
Rendzina	36.86 ± 0.03	0.87 ± 0.02	0.990	28.3
Humic Cambisols	39.80 ± 0.08	1.34 ± 0.10	0.989	77 ± 6
Mollic Cambisols	25.08 ± 0.05	1.06 ± 0.04	0.997	35 ± 13
Calcic Cambisols	5.00 ± 0.06	0.84 ± 0.03	0.995	3.2 ± 0.8
Dystric Cambisols	8.22 ± 0.09	0.82 ± 0.04	0.986	7.2 ± 1.4
Gleyc Cambisols	6.77 ± 0.05	0.83 ± 0.03	0.996	4.3
Vertisols	32.94 ± 0.06	1.24 ± 0.07	0.980	80 ± 38
Ferralsols	27.12 ± 0.01	0.76 ± 0.01	0.998	9 ± 4
Andosols	44.53 ± 0.06	0.87 ± 0.03	0.987	36 ± 4

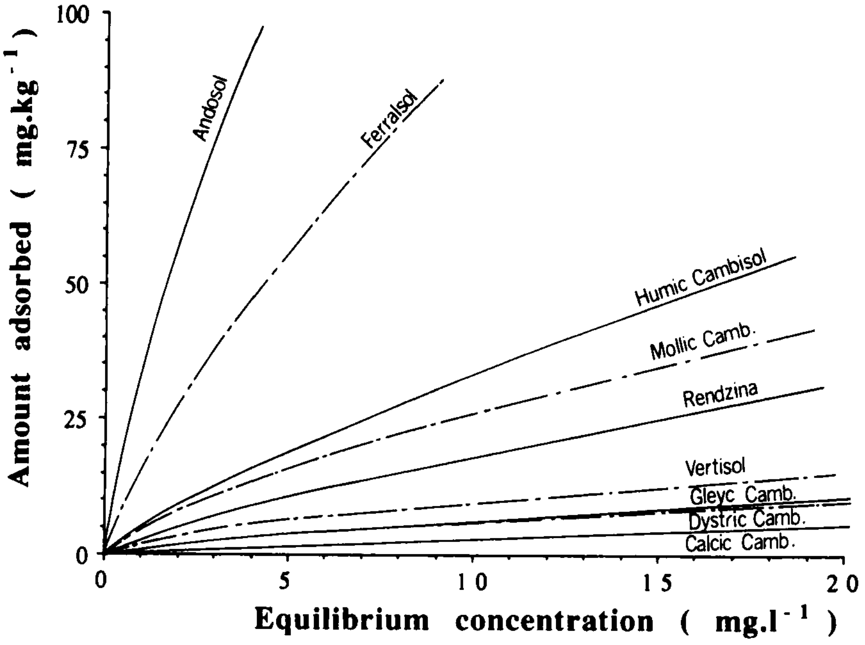

Figure 6 Adsorption isotherms for 2,4-D.

iii) soils (Kf < 2) with either low organic matter content or high clay content; the low adsorption capacity is attributable to either a small number of adsorption sites or to repulsion in the case of the Vertisol.

Desorption isotherms

The examples of desorption isotherms given in Figures 7 and 8 show a slight hysteresis which does not appear to be related to the soil type. It would however be useful to discuss these isotherms on the basis of the partition of adsorbed molecules between two compartments characterized by different surface-molecule binding energies[22].

Table 3 Adsorption characteristics for 2,4-D.

Soils	*Kf*	*nf*	r^2	*Kd*
Rendzina	3.09 ± 0.10	0.78 ± 0.03	0.995	2.5
Humic Cambisols	5.30 ± 0.03	0.80 ± 0.01	0.996	3.1 ± 0.3
Mollic Cambisols	4.99 ± 0.05	0.72 ± 0.02	0.999	2.7 ± 0.9
Calcic Cambisols	0.54 ± 0.19	0.78 ± 0.06	0.989	0.3 ± 0.1
Dystric Cambisols	1.19 ± 0.13	0.73 ± 0.04	0.997	0.8 ± 0.2
Gleyc Cambisols	1.27 ± 0.03	0.68 ± 0.01	0.991	0.8
Vertisols	2.44 ± 0.13	0.61 ± 0.04	0.971	1.3 ± 0.5
Ferralsols	16.81 ± 0.04	0.75 ± 0.01	0.989	9.2 ± 4.3
Andosols	32.55 ± 0.03	0.80 ± 0.01	0.998	26.6 ± 0.8

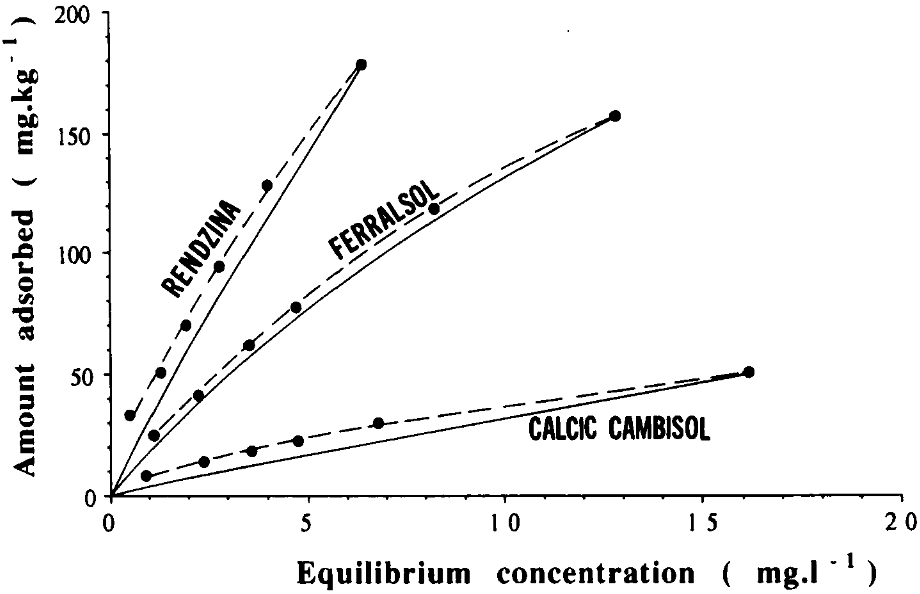

Figure 7 Examples of desorption isotherms for terbutryn (dotted curves).

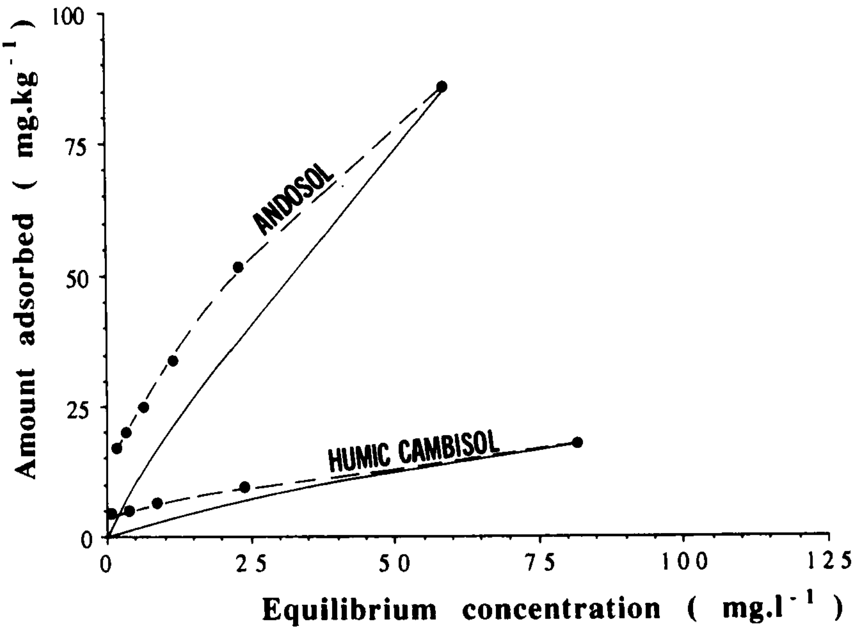

Figure 8 Examples of desorption isotherms of 2,4-D (dotted curves).

Nevertheless, at the present stage of this study, the type of soil seems to have no marked effect on the desorption characteristics of the herbicides investigated.

CONCLUSION

A relationship between soil types and adsorption behaviour of herbicide molecules has been clearly shown. This relationship varies with the form in which the molecules are, i.e. non-ionized, cationic or anionic. Soils can be classified according to their adsorption properties, using distribution coefficients if, and only if, measurements are made under conditions that lead to low equilibrium concentrations.

The organic matter content appears to be a key parameter but its relationship with the distribution coefficient values is only clear with non-ionized molecules. For ionized molecules, the mineralogical composition and the soil pH have to be taken into account, especially for anionic molecules. Thus, information from soil surveys is likely to be used for assessing general features of pesticide adsorption in soils. Further work in this field should be directed towards a more detailed description of the desorption process and towards the establishment of general relationships between Kd values and soil properties for other chemicals than triazines and phenoxy acids.

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