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STUDY OF SORPTION PROCESSES OF SELECTED PESTICIDES ON SOILS AND CERAMIC POROUS CUPS USED FOR SOIL SOLUTION SAMPLING

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Soil sorption constants of four organochlorine (lindane, dicofol, chlorfenson and tetradifon) and three organophosphorus pesticides (dimethoate, fenitrothion and methidathion) were measured using two different soils at six concentrations.

Soil samples were collected at depths of 0–20 cm and around 100 cm from an experimental citrus crop field. Effects of soil properties (organic matter, moisture content, pH and texture) on the sorption processes were also investigated.

Partitioning of pesticides between soil and solution was investigated after batch equilibration, using pesticide concentrations ranging from 10 to 200 $\mu\text{g l}^{-1}$. The equilibration time was estimated in 2 h for organochlorine, and 72 h for organophosphorus pesticides. Data fitted to Freundlich types adsorption isotherms.

Analytical determinations were carried out by gas chromatography with ECD and NPD detectors, after liquid-liquid extraction with dichloromethane of the water supernatant.

Moreover, a validation of the use of suction samplers used to collect soil solution samples from the vadose zone, based on a short term study in the laboratory was determined.

KEY WORDS: Organochlorine and organophosphorus pesticides, soils, sorption isotherms.

INTRODUCTION

Contamination of soil by pesticides may occur when a compound is applied for the control of insect pests that inhabit the soil or for systemic movement into plants and later consumption of the leaves by parasites. Foliar application also provides potential for contamination of soil by pesticides as a result of the washoff of sprays or as result of shredding and cultivation of treated foliage. Accidental exposures may occur when the pesticide moves in the air or in water from the site of application to other areas. Accordingly, the soil constitutes a reservoir for such chemicals, and the factors affecting their later behaviour and fate are many and varied.

From an environmental point of view, it is of great importance to know about the sorption of pesticides by soil because these phenomena affect other processes that determine the compounds final fate, such as chemical, photochemical and microbiological decomposition, volatilization, uptake by higher plants and diffusion, as well as leaching and groundwater pollution.

The chemical nature of the pesticide and the soil characteristics are the factors affecting the adsorption equilibrium to the greatest extent. The best correlation is usually with soil organic matter content. Since the organic matter in soil has a very large surface area it is to be expected that it will adsorb pesticides to a considerable extent, but it might equally be expected that the enormous surface area of the clay minerals in soils would contribute substantially to the observed adsorption¹⁻⁵.

The adsorption of a pesticide on a soil is usually determined by shaking an aqueous solution of the pesticide of known concentration with a known mass of soil until equilibrium is reached. The distribution of a pesticide between soil and water can then be described by the expression:

$$K_d = \frac{\mu\text{g pesticide} / \text{g soil}}{\mu\text{g pesticide} / \text{g water}}$$

where K_d is the soil sorption coefficient (distribution coefficient). In general, the K_d values vary considerably according to the properties of the soils tested. Therefore, the sorption characteristics of a pesticide can be normalized to obtain a general soil sorption constant (K_{oc}) based on the organic carbon content; K_{oc} is applicable to all soil types:

$$K_{oc} = \frac{K_d \times 100}{\text{organic carbon in soil (\%)}}$$

Adsorption of pesticides in soil is best shown by adsorption isotherm patterns, which may be obtained by measuring adsorption at a number of different concentrations^{1,4-7}. Frequently, such isotherms are non linear and it is found that they may be best described by the empirical Freundlich equation:

$$C_s = KC_w^n$$

$$\ln C_s = \ln K + n \cdot \ln C_w$$

where C_s is the amount of adsorbed pesticide ($\mu\text{g/g}$ soil), C_w is the concentration of the pesticide in the solution at equilibrium ($\mu\text{g/ml}$ solution), K and n are constants.

Environmental investigations of natural soil processes often require sampling of soil solutions. Obviously, the chemical composition of the sample reliably should reflect the composition of the soil solution if misleading conclusions are to be avoided. This requires that the soil water solution must not be changed by leaching or retention of elements by the sampler itself during sampling.

Essentially, environmental vadose zone studies include surface liquid and soil sampling,

vadose zone monitoring, and groundwater monitoring. The standard method for sampling pore fluids in the vadose zone is core sampling of vadose zone solids, followed by extraction of pore fluids. Porous suction samplers are an alternative approach for soil solution sampling from the vadose zone. Among these, porous cups made of ceramic materials are widely used⁸⁻¹².

Assessments of the validity of the soil solution samplers are usually based on short term studies in the laboratory, and the influence of the samplers is evaluated by sampling solutions of well known concentrations of compounds followed by comparison of the solute concentrations before and after passing the ceramic cup. Most of these studies deal with inorganic ions behaviour, mainly nitrate, ammonium and phosphate¹¹⁻¹².

This paper forms a part of a wider study on fate of selected organochlorine and organophosphorus pesticides in the vadose zone of an experimental citrus crop field sited in Castellón (Spain). This study involves the development of analytical procedures for the analysis of those pesticides in soil and interstitial water samples, and sampling of soil solution at different depths in order to determine the movement of pesticides along the vadose zone¹³⁻¹⁶. In order to have a better knowledge of the processes involved it is necessary to know the sorption characteristics of the selected pesticides in the related soils. As porous suction samplers were used to collect soil solution samples, the validity of such devices has to be determined too.

Pesticides selected in this paper include four organochlorine (lindane, dicofol, chlorfen-son and tetradifon) and three organophosphorus pesticides (dimethoate, fenitrothion and methidathion) which are widely applied in the studied area. Chemical structures are shown in Figure 1.

EXPERIMENTAL

Soil samples were obtained from the 0–20 (soil 1) and 100–115 cm (soil 2) horizons in an experimental field located in a citrus grove, dried in ambient air and passed through a 2 mm opening sieve, then sealed in a bottle until used. Their properties are listed in Table 1 and were determined according to literature¹⁷.

Standard pesticides were purchased from Riedel de Haen (Scharlau) and used without purification. 500 $\mu\text{g}\cdot\text{ml}^{-1}$ acetone stock solutions of these pesticides were prepared and used as the analytical standards by diluting them to the appropriate concentrations with acetone or hexane.

Table 1 Soil properties.

	<i>Soil 1</i>	<i>Soil 2</i>
Depth (cm)	20	100
pH	7.62	7.45
% organic matter	2.21	0.40
% sand	21.1	31.8
% clay	40.2	41.5
% silt	38.7	26.7
% moisture	1.45	1.25

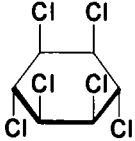
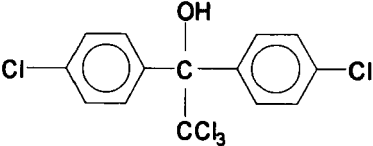
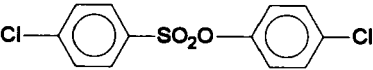
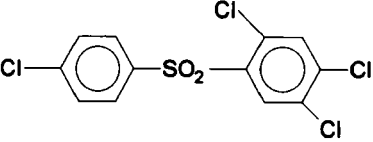
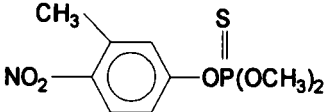
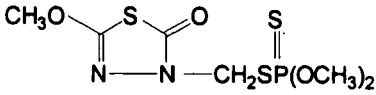
Pesticide	Chemical structure
Lindane	
Dicofol	
Chlorfenson	
Tetradifon	
Dimethoate	$\text{CH}_3\text{NHC}(\text{O})\text{CH}_2\text{S}(\text{O})\text{P}(\text{O})(\text{OCH}_3)_2$
Fenitrothion	
Methidathion	

Figure 1 Chemical structures of selected pesticides.

Batch-type adsorption experiments were used to generate adsorption data. Thus, 20 g of the soil sample were treated with 50 ml of an aqueous solution containing different concentrations of the pesticide mixture, shaken mechanically until equilibration and then centrifuged at 2000 r.p.m. during 15 min. The aqueous phase was separated and extracted by liquid-liquid extraction with dichloromethane, and the extracts were analyzed by GC-ECD/NPD on a Ultra 2 capillary column (30 m 0.25 mm id., 0.33 μm film thickness)¹³.

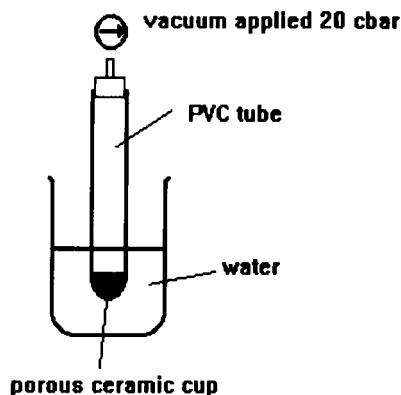


Figure 2 Experimental design of adsorption study on porous ceramic cups.

In order to validate the use of porous ceramic cups for soil solution sampling, additional laboratory experiments were carried out submerging a porous suction sampler in a beaker containing groundwater spiked at $10 \mu\text{g}\cdot\text{l}^{-1}$ pesticide level, as shown in Figure 2. After 24 hours of suction (20 cbar), water inside the sampler was collected, the volume measured and analysed as well as the water remaining in the beaker. The experiment was made in triplicate.

RESULTS AND DISCUSSION

Firstly, equilibrium times for each pesticide were obtained by shaking the samples and analyzing the aqueous phase after 2, 6, 12, 24 and 72 hours, with the two types of soil. Results obtained are shown in Figure 3 (organochlorine pesticides) and 4 (organophosphorus pesticides).

As it can be seen, organochlorine pesticides reach equilibrium after only two hours. The remaining concentration in the solution was higher when using the soil 2 which could be due to its lower organic matter content. Organophosphorus pesticides reached the equilibrium at longer times. Thus, the equilibrium time selected in order to determine the isotherms, was 72 hours.

Isotherms corresponding to each pesticide and type of soil were obtained. Initial concentrations used were 10, 50, 75, 100, 150 y $200 \mu\text{g}\cdot\text{l}^{-1}$ of each pesticide.

In Table 2 are shown the distribution coefficients K_d (mean value and standard deviation for the concentrations listed above) and sorption constants K_{oc} obtained using the equations listed in the Introduction section.

Moreover, adsorption blanks were made, the results showing that is not necessary any correction for glass adsorption as recoveries obtained for 5 blank replicates ($50 \mu\text{g}\cdot\text{l}^{-1}$) ranged from $86 \pm 6\%$ for chlorfenson to $97 \pm 6\%$ for fenitrothion.

As it can be seen (Table 2), the K_d values obtained with the soil 1 are quite higher than

(a)

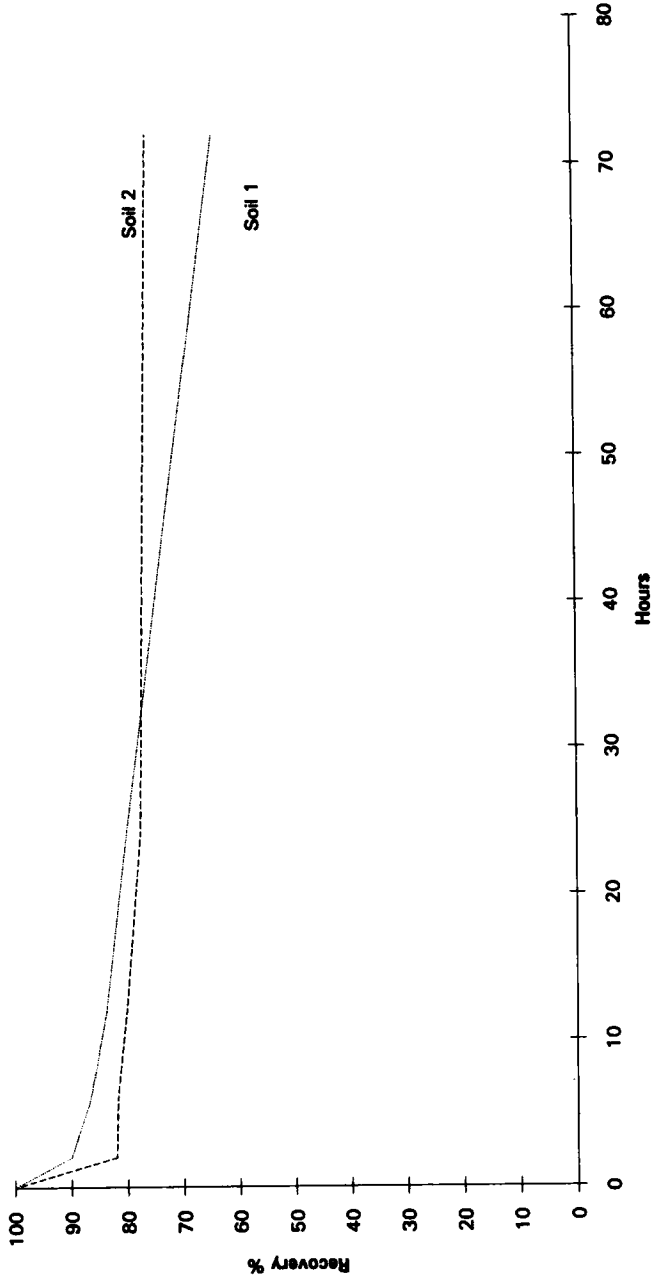


Figure 3 Adsorption rates of organophosphorus pesticides in two soils. Initial pesticide concentration $50 \mu\text{g}\cdot\text{l}^{-1}$. (a) dimethoate, (b) fenitrothion and (c) methidathion. Soil 1 (20 cm) soil 2 (100 cm).

(b)

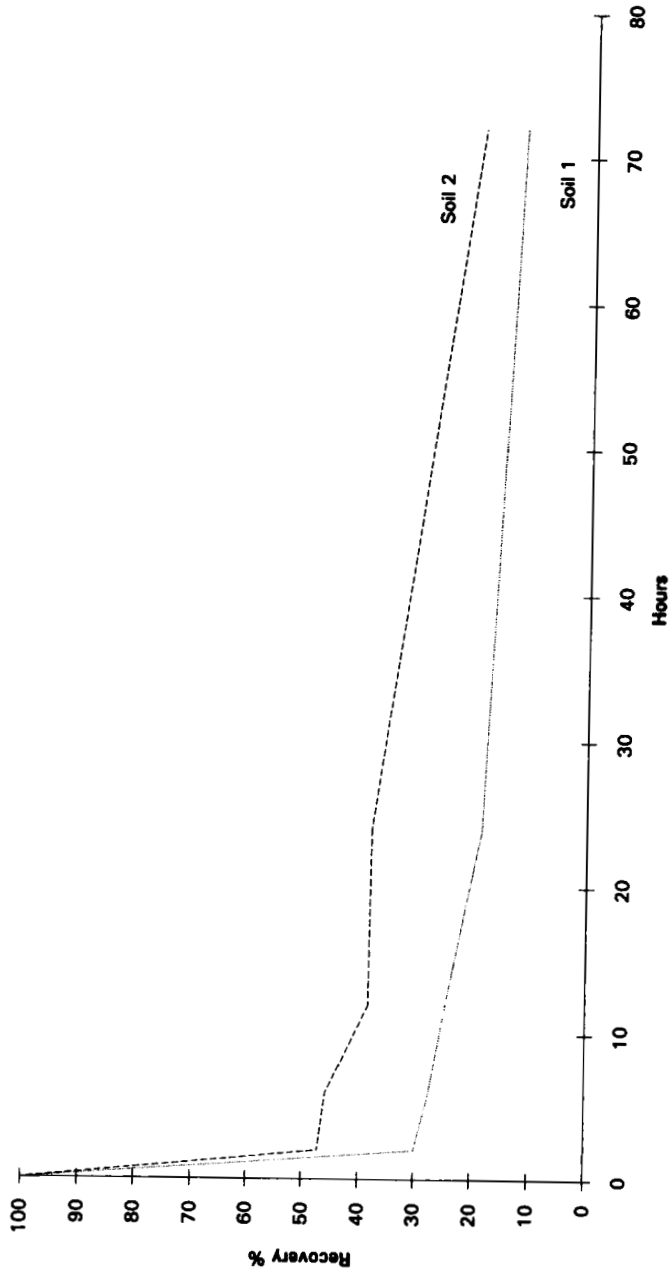


Figure 3 Adsorption rates of organophosphorus pesticides in two soils. Initial pesticide concentration $50 \mu\text{g l}^{-1}$. (a) dimethoate, (b) fenitrothion and (c) methidathion. Soil 1 (20 cm) soil 2 (100 cm).

(c)

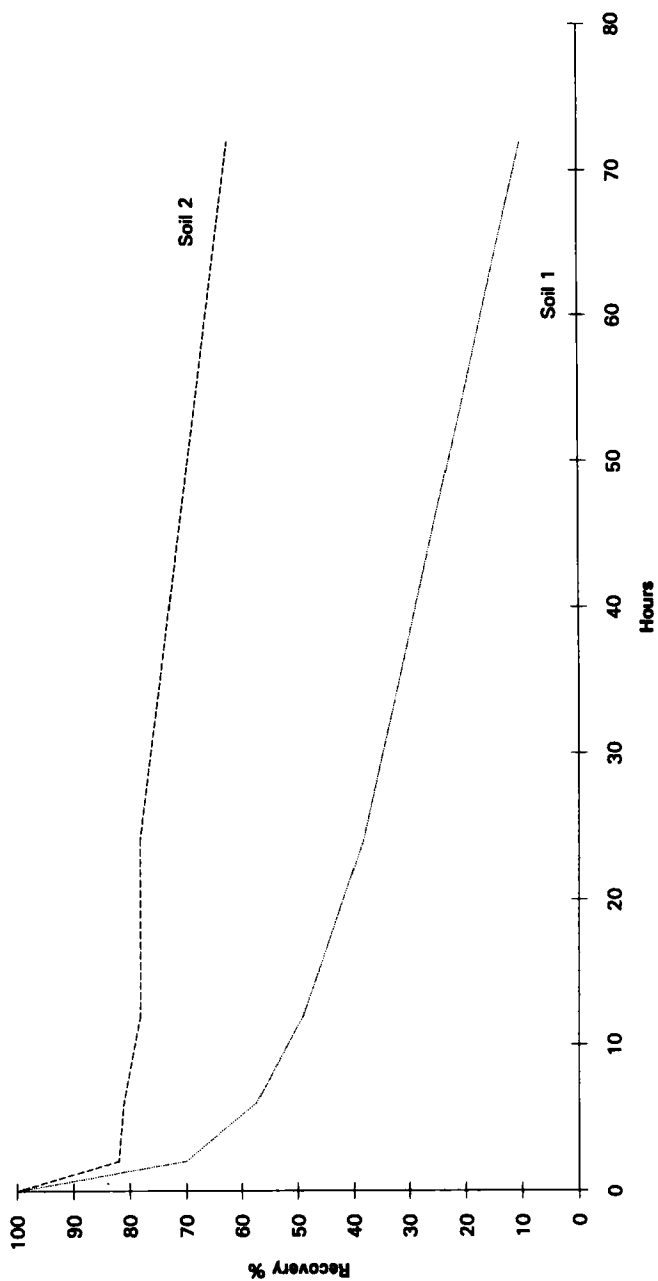


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(a)

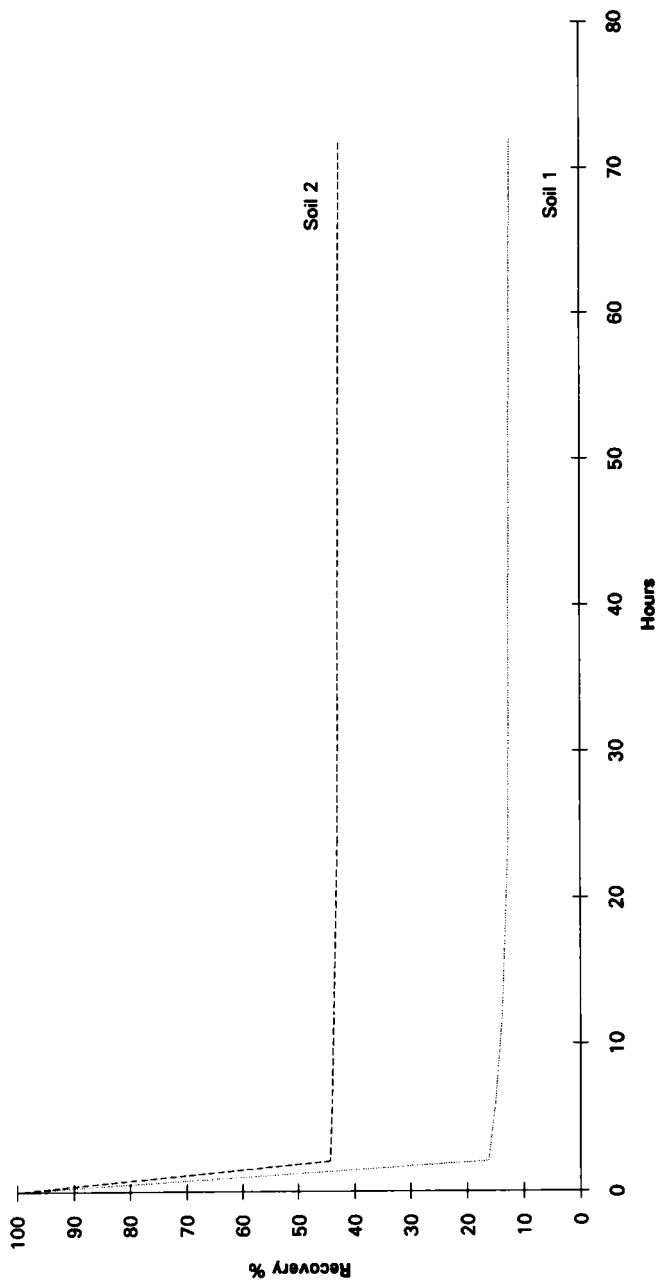


Figure 4 Adsorption rates of organochlorine pesticides in two soils. Initial pesticide concentration $50 \mu\text{g l}^{-1}$. (a) lindane, (b) dicofol and (c) chlorfenson and (d) tetradifon. Soil 1 (20 cm) soil 2 (100 cm).

(b)

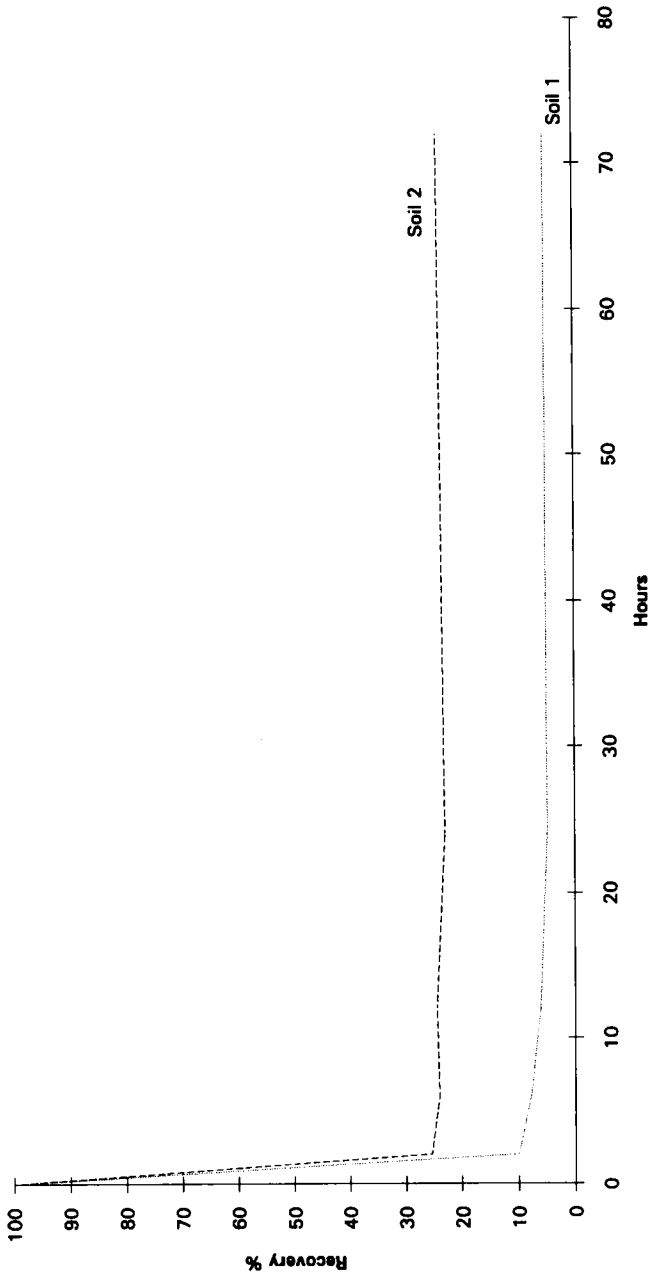


Figure 4 Adsorption rates of organochlorine pesticides in two soils. Initial pesticide concentration $50 \mu\text{g}\cdot\text{l}^{-1}$. (a) lindane, (b) dicofol and (c) chlorfenson and (d) tetradifon. Soil 1 (20 cm) soil 2 (100 cm).

(c)

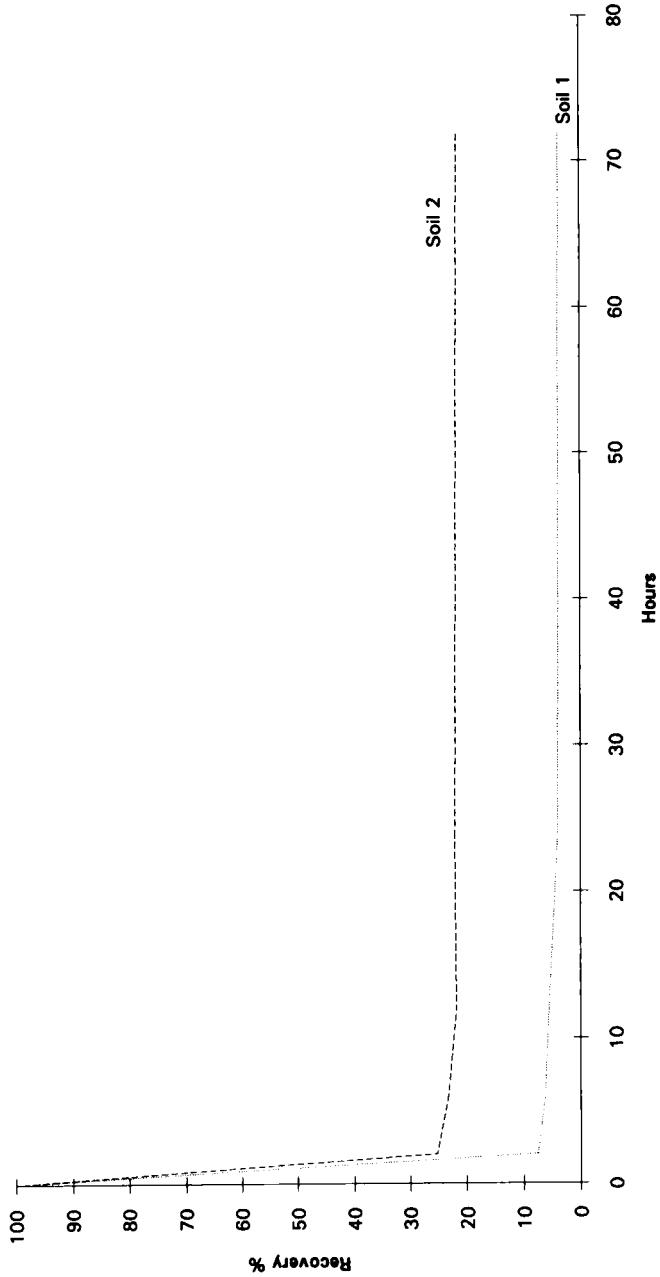


Figure 4 Adsorption rates of organochlorine pesticides in two soils. Initial pesticide concentration $50 \mu\text{g}\cdot\text{l}^{-1}$. (a) lindane, (b) dicofol and (c) chlorfenson and (d) tetradifon. Soil 1 (20 cm) soil 2 (100 cm).

(d)

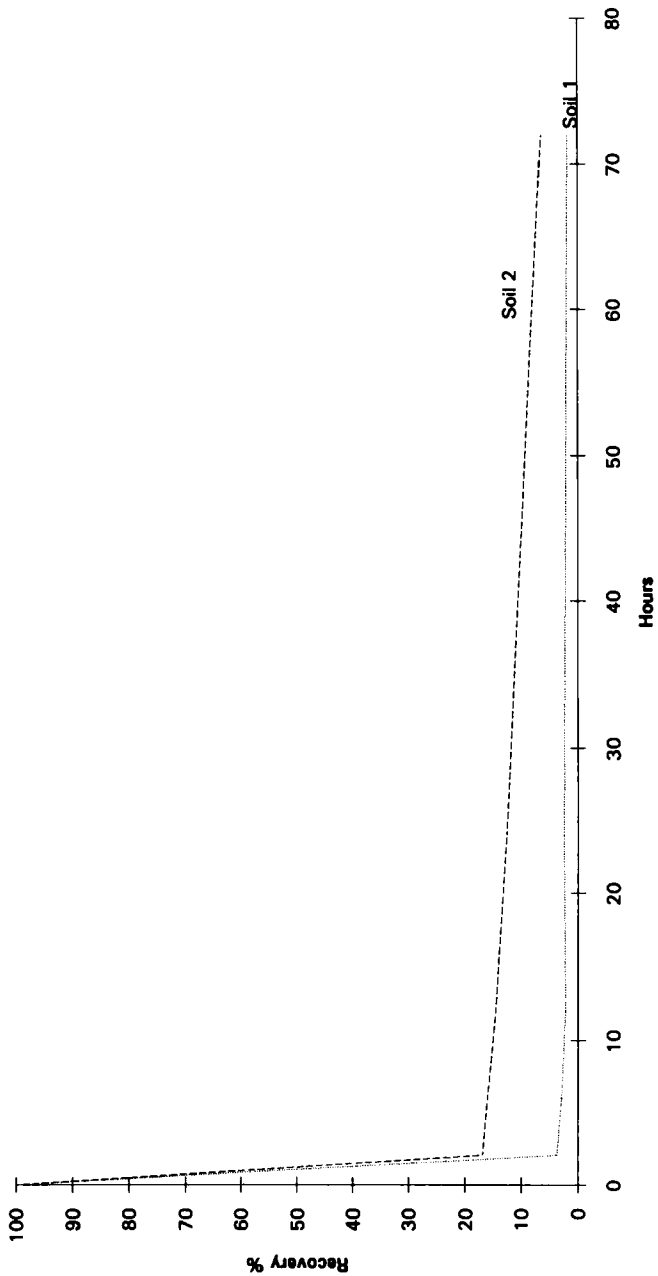


Figure 4 Adsorption rates of organochlorine pesticides in two soils. Initial pesticide concentration $50 \mu\text{g l}^{-1}$. (a) lindane, (b) dicofol and (c) chlorfenson and (d) tetradifon. Soil 1 (20 cm) soil 2 (100 cm).

Table 2 Soil sorption coefficients (Kd) and soil sorption constants (Koc) of pesticides tested in two soils.

	<i>K_d</i>				<i>K_{oc}</i>	
	<i>Soil 1</i>		<i>Soil 2</i>		<i>Soil 1</i>	<i>Soil 2</i>
	<i>Mean</i>	<i>STDV</i>	<i>Mean</i>	<i>STDV</i>	<i>Mean</i>	<i>Mean</i>
Dimethoate	1.10	0.18	0.77	0.13	50	192
Lindane	21.59	2.01	2.94	0.67	977	736
Fenitrothion	25.95	10.86	4.28	0.73	1174	1069
Dicofol	53.46	7.40	5.94	0.61	2419	1485
Methidathion	16.82	7.55	1.24	0.21	761	311
Chlorfenson	53.01	9.99	5.84	0.75	2399	1460
Tetradifon	94.05	19.22	7.21	1.43	4256	1801

those obtained for the soil 2 (5 to 10 times higher), except for dimethoate, which present similar K_d values for both soils (1.1 and 0.77). Moreover, its K_d values were the lowest showing that this pesticide is weakly adsorbed by soil, and seems not to be affected by the organic matter content, which could be explained by both its higher polarity and water solubility.

However, the K_{oc} values are more similar for both soils, being slightly higher for the surface soil with the exception of dimethoate. Thus, the use of the K_{oc} constant is better to describe the adsorption of a pesticide in different types of soil, establishing a good accordance between adsorption and organic matter content.

Pesticides studied in this paper can be sorted based on the K_d (or K_{oc}) values. In this way, the most strongly adsorbed pesticide is tetradifon, followed in decreasing order by dicofol, chlorfenson, fenitrothion, lindane, methidathion and dimethoate. This order agrees with that reported by Kanazawa⁵ for dimethoate, lindane and fenitrothion.

Some authors indicate that adsorption processes can be better described by the Freundlich isotherm equation^{1,4-7}. Values for constants K and n are given in Table 3. The adsorption

Table 3 K and n values for pesticides tested in the Freundlich adsorption equation.

<i>Pesticide</i>	<i>Soil</i>	<i>ln K</i>	<i>n</i>	<i>r</i>	<i>K</i>
Dimethoate	1	0.5414	0.8818	0.9961	1.7
	2	0.0068	0.9287	0.9896	1.0
Lindane	1	2.9630	1.0534	0.9974	19.4
	2	1.6462	0.8297	0.9888	5.2
Fenitrothion	1	3.0627	1.1838	0.9613	21.4
	2	1.8676	0.8688	0.9980	6.5
Dicofol	1	4.3552	0.8523	0.9912	77.9
	2	1.7263	1.0170	0.9956	5.6
Methidathion	1	3.7959	0.6059	0.9919	44.5
	2	0.6385	0.8879	0.9948	1.9
Chlorfenson	1	3.7096	1.2098	0.9940	40.8
	2	2.0017	0.9199	0.9965	7.4
Tetradifon	1	4.3897	1.2191	0.9916	80.6
	2	1.5184	1.1518	0.9914	4.6

Soil 1. 20 cm: % O.M. = 2.21

Soil 2. 100 cm % O.M. = 0.40

(a)

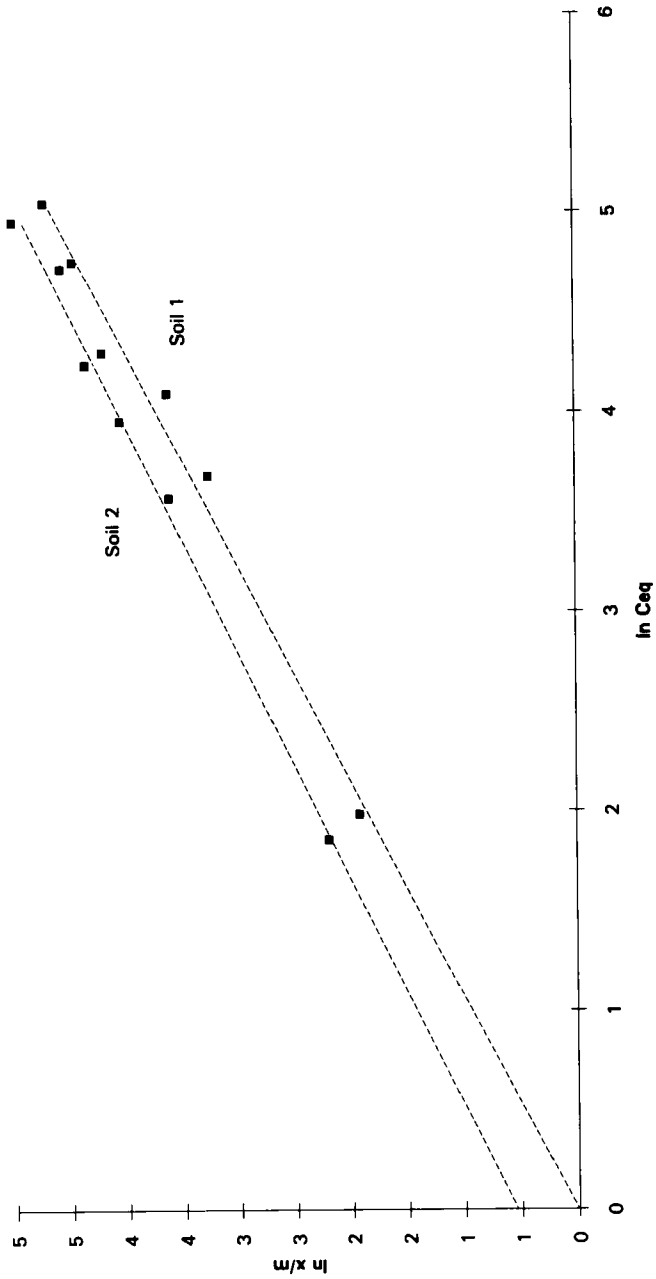


Figure 5 Adsorption isotherms for (a) dimethoate and (b) methidathion in two soils. x/m : adsorbed ammounts ($\mu\text{g}\cdot\text{g}^{-1}$). C_{eq} : equilibrium solution concentration ($\text{ng}\cdot\text{ml}^{-1}$)

(b)

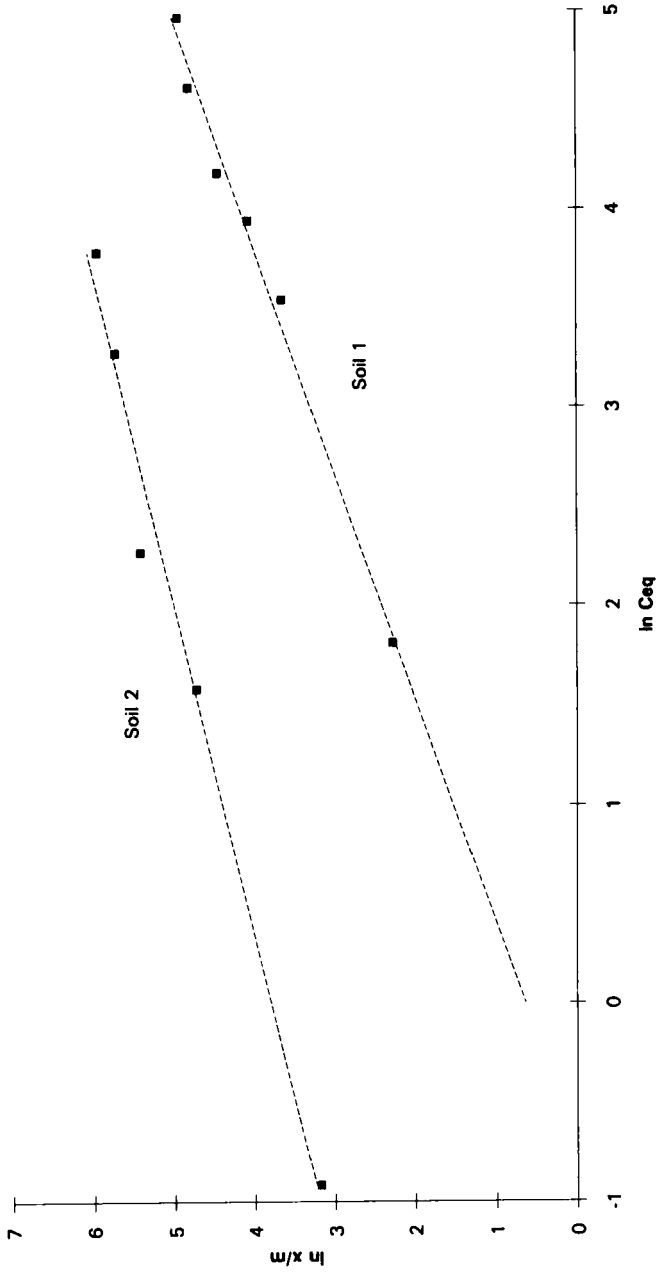


Figure 5 Adsorption isotherms for (a) dimethoate and (b) methidathion in two soils. x/m : adsorbed amounts ($\mu\text{g}\cdot\text{g}^{-1}$). C_{eq} : equilibrium solution concentration ($\text{ng}\cdot\text{ml}^{-1}$)

data plotted using the Freundlich isotherm ($\mu\text{g/g}$ and $\mu\text{g/ml}$) for dimethoate and methidathion are shown in Figure 5. When the n value is around 1, the adsorption is linearly proportional to the solution concentration. The n values obtained in the present paper, ranged from 0.85 (dicofol) to 1.22 (tetradifon). The only exception being methidathion, with $n = 0.61$ for the soil 1.

The Freundlich K values represent the degree or strength of adsorption. As it can be seen, there is a great similarity between the Freundlich K (Table 3) and the distribution coefficients K_d (Table 2) for the related pesticides, similarly as reported by other authors^{3,5}, with the exception of methidathion whose K_d and K values for the soil 1 are 16.8 and 44.5 respectively. This difference could be due to the low value of n (0.61), which indicates a non linear proportionality between the adsorption and the solution concentration.

Previous experiments to determine the stability of these pesticides in aqueous solution showed that the decrease in pesticide concentration was not important during the first two weeks, being negligible during the time of the batch experiments (72 hours)¹⁴. Therefore, the concentration decrease observed must be due mainly to adsorption or transformation processes in the soil.

In order to complete the sorption studies related with the fate of pesticides in the vadose zone, and because of the increasing use of porous cup samplers in soil solution sampling, the adsorption of these pesticides on the ceramic cup was checked. Spiked water was passed through the porous ceramic with a 20 cbar vacuum during 24 hours, which led to volumes inside the sampler of 100–180 ml. After this time, water inside the sampler and remaining water in the beaker were analyzed by liquid–liquid extraction and GC-ECD/NPD. Mean recoveries and relative standard deviations obtained for spiked water samples at $10 \mu\text{g}\cdot\text{l}^{-1}$ are shown in Table 4. It can be inferred an important change in the concentration of several pesticides when passing through the porous cup. Thus, the organochlorine pesticides studied here showed a decrease in their concentration when passed through the cup, with recovery values of 48 (lindane), 32 (dicofol), 29 (chlorfenson) and 13% (tetradifon) of initial concentration, which should be imputed to the adsorption on the ceramic material. However, the organophosphorus pesticides did not show significant decrease in their concentrations, only noticeable for fenitrothion with a mean recovery of 72%. This fact constitutes a limitation in the use of ceramic porous cups for soil solution sampling in environmental studies related with the fate of organochlorine pesticides in the vadose zone, as they become strongly adsorbed by the ceramic material. This, together with the fact that organochlorine

Table 4 Recoveries of selected pesticides when sampled with a ceramic porous cup under vacuum using spiked water at $10 \mu\text{g}\cdot\text{l}^{-1}$.

	INSIDE		OUTSIDE	
	Mean	St Dev(%)	Mean	St Dev(%)
Dimethoate	88.9	14.0	100.1	11.3
Lindane	47.9	9.7	77.8	25.6
Fenitrothion	72.3	18.7	92.1	12.3
Dicofol	32.0	13.2	80.6	15.1
Methidathion	93.0	12.1	107.2	7.6
Chlorfenson	29.4	32.4	92.7	5.1
Tetradifon	13.4	36.7	98.1	2.9

pesticides are strongly adsorbed on the soil and their low water solubility, could explain the very low concentrations of dicofol and tetradifon reported in our previous studies on the movement of pesticides along the vadose zone¹⁴. This effect is negligible for organophosphorus pesticides, which could be adequately sampled without significant decrease in their concentration. In any case, the behaviour of selected pesticides on the ceramic cups of suction samplers should be taken into account to properly interpret results obtained in the analysis of soil solution samples from the vadose zone.

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References

1. P. Lafrance, L. Ait-ssi, O. Banton, P.G.C. Campbell and J.P. Villeneuve, *Water Poll. Res. J. Canada*, **23**, 253–269 (1988).
2. W. Mersie and C.L. Foy, *Weed Science*, **33**, 564–568 (1985).
3. K.S. Reddy and R.P. Gambrell, *Agriculture, Ecosystems and Environment*, **18**, 231–241 (1987).
4. M.D. Santos-Buelga, M.J. Sanchez-Martin and M. Sanchez-Camazano, *Chemosphere*, **25**, 727–734 (1992).
5. J. Kanazawa, *Environ. Toxicol. Chem.*, **8**, 477–484 (1989).
6. M. Sanchez-Camazano and M.J. Sanchez-Martin, *Environ. Toxicol. Chem.*, **7**, 559–564 (1988).
7. M.C. Hermosin and J. Cornejo, *Soil Science*, **144**, 453–456 (1987).
8. L.G. Wilson, (D.M. Nielsen and A.I. Johnson Ed., ASTM, Philadelphia 1990) pp. 7–23.
9. C. Beier, K. Hansen, P. Gundersen and B.R. Andersen, *Environ. Sci. Technol.*, **26**, 2005–2011 (1992).
10. C. Bernhard, C. Schenck, *Bulletin du G.F.H.N.*, **20**, 78–85 (1986).
11. C. Cheverry, *Bulletin du G.F.H.N.*, **14**, 47–71 (1983).
12. E.A. Hansen and A.R. Harris, *Soil Sci. Soc. Amer. Proc.*, **39**, 528–536 (1975).
13. F. Hernandez, J. Beltran and J.V. Sancho, *Sci. Total Environ.*, **132**, 297–312 (1993).
14. J. Beltran, F. Hernández Hernández, I. Morell, P. Navarrete and E. Aroca, *Sci. Total Environ.*, **132**, 243–257 (1993).
15. J. Beltran, F.J. López and F. Hernández, *Anal. Chim. Acta*, **283**, 297–303 (1993).
16. J. Beltran, F.J. Lopez and F. Hernandez, (4th Workshop on Chemistry and Fate of Modern Pesticides and Related Pollutants. Prague, 1993).
17. Química Agrícola I. Suelos y fertilizantes. (E. Primo-Yufera, J.M. Carrasco Dorrien, Ed. Alhambra, Madrid, 1987).