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Effect of Colloidal Soil Components on the Adsorption of Mevinphos

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Even the least persistent pesticides which, intentionally or not, enter into contact with the soil remain for some time in the environment. It is therefore of great interest to gain information concerning the factors that determine the site and duration of their residence. Among the processes affecting the final behaviour of pesticides in soils, adsorption is of paramount importance since this controls the other processes involved.

The adsorption equilibrium of a pesticide is mainly determined by the characteristics and composition of the soil; in this the content and nature of the clay fraction and of organic matter are of special importance in so far that these components are colloidal and have high cation exchange capacities and a high surface area. The chemical structure of the pesticide also affects the adsorption equilibrium by determining its direct affinity for clays or for organic matter.

In the present work we studied the adsorption of mevinphos (0,0 dimethyl 0 (1-methyl 2-carbomethoxyvinyl) phosphate) by 20 soils in an aqueous medium, together with the correlations between adsorption and the characteristics of the soils and also the effect of removing the organic matter on adsorption. Mevinphos is a toxic systemic insecticide widely used in agriculture.

In previous works, the present authors (Sánchez-Martín and Sánchez Camazano, 1980; Sánchez-Camazano and Sánchez-Martin, 1983) studied the interaction mechanism of mevinphos with montmorillonite (a clay mineral belonging to the group of smectites that is common in soils and that has a high adsorption capacity) and demonstrated that the mineral forms stable interlayer complexes of one or two molecular layers with this pesticide, according to the exchange cation of the silicate; the interaction mechanism is essentially ion-dipole.

According to the results offered in the literature on the adsorption of different organophosphorus pesticides by soils, a certain relationship seems to exist between the

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chemical structure of the pesticide and its affinity for the clay or organic matter fractions. The phosphates and phosphonates exhibit a greater affinity for the clay fraction (Grice et al. 1973; Hayes et al. 1972) whereas the thiophosphates and dithiophosphates do so for the organic matter (Baarchers et al. 1983; Felsot and Dahm, 1979). The results of the present authors working on the adsorption of azinphosmethyl (dithiophosphate) by the same soils used in the present study (Sánchez-Camazano and Sánchez-Martín 1984) are also in agreement with such findings.

MATERIALS AND METHODS

The characteristics of the soils used in this study are shown in Table I. The contents in clay and organic matter of the soils ranged between 8.7% to 62% and from 0.03 and 13.10%, respectively. The content in smectite of the soils was determined by X-ray diffraction of the <2 µm fraction. Mevinphos was supplied by the Shell International Chemical Company Limited (England). It is a liquid compound that is miscible in water, alcohols, ketones and aromatic hydrocarbons; it is also slightly soluble in aliphatic hydrocarbons.

Table 1. Characteristics of the soil samples.

Sample N°	pH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Smectite (%)	Clay Mine-neralogy[a]
1	7.8	1.87	56.2	20.1	21.9	2	M,K
2	4.5	0.12	46.3	31.5	21.3	-	M,K
3	7.8	4.03	33.4	25.2	37.7	4	M,K
4	8.1	1.19	38.0	15.0	46.4	5	M,K
5	6.6	5.30	61.2	18.5	12.2	-	M,K
6	6.9	8.77	32.5	34.0	21.5	-	M,V,K
7	6.2	0.81	71.3	17.9	9.7	1	M,K
8	7.8	0.03	62.5	24.3	10.7	4	M,K
9	7.9	0.19	25.5	5.0	33.0	8	M,K
10	7.7	0.77	22.5	12.5	62.0	16	M,K
11	5.2	0.39	52.5	13.0	33.0	12	M,K
12	5.8	5.74	54.0	18.8	19.0	-	M,Cl, K,G
13	5.8	13.10	29.2	34.8	23.2	-	M,V,K,G
14	6.5	0.17	77.0	12.7	9.2	-	M,K,V,G
15	5.5	5.83	63.5	20.0	10.4	-	M,V,G,K
16	5.8	2.31	69.0	18.3	9.5	-	M,V,K,G
17	5.6	1.18	54.5	30.0	13.0	-	M,K,V,G
18	5.5	4.12	73.0	15.4	9.4	-	M,V,G,K
19	5.5	11.00	58.0	17.5	8.7	-	M,K,V,G
20	6.1	1.01	56.5	27.6	13.0	-	V,M,K

[a] Besides smectite (in order of abundance): M, mica; K, kaolinite; V, vermiculite; Cl, chlorite; G, gibbsite.

To obtain the adsorption isotherms of mevinphos for natural soils and for soils from which the organic matter had previously been removed (oxidized soils), 500 mg of soil sample were treated with 10 ml of an aqueous solution containing 20, 30, 40 or 50 µg/ml of mevinphos. The suspensions were kept for 48 h in a thermostatted chamber at 20°C with intermittent shaking. Previous studies had shown that equilibrium is reached after 18 h. The suspensions were centrifuged and the equilibrium concentration was determined in the supernatant fluid by UV spectroscopy (absorption maximum 220 nm). All determinations were carried out in duplicate.

The organic matter of the soils was removed by oxidation under heating with 6% hydrogen peroxide. After repeated treatments the organic matter was practically eliminated in all the samples except those with a high content in this fraction (samples 6, 13 and 19). The organic matter was determined in natural and oxidized soils by the modified Walkley and Blank method (Prat and Sánchez, 1973).

RESULTS AND DICUSSION

Adsorption isotherms were obtained for all the soils studied. Figure 1 shows those corresponding to four soil samples. The isotherms show the amount adsorbed in µg/g (Cs) against the equilibrium concentration in µg/l (Ce). Sample 2 corresponds to a soil with a very low content in organic matter and an intermediate clay content (without montmorillonite or vermiculite). Sample 4 is a soil with an intermediate content in organic matter and a high clay content (with montmorillonite). Sample 5 has a high content in organic matter and a low clay content (without montmorillonite and vermiculite); sample 7 has low contents in both organic matter and clay (with montmorillonite).

In all cases the isotherms fit the Freundlich adsorption equation ($\log Cs= \log K + 1/n \log Ce$). From this equation the values of the constants K and n for each soil sample were obtained; these are characteristic parameters of their adsorption capacity for the pesticide. K is the amount adsorbed for an equilibrium concentration of 1 µg/ml and hence represents adsorption at low adsorbate concentrations; n reflects the degree to which adsorption is a function of concentration. We also calculated the distribution coefficient K_d, which measures the relationship between the concentration of pesticide in the soil and in the solution for a given equilibrium concentration (C_e= 15 µg/ml).

The values of K, n, and K_d were found to vary considerably with the characteristics of the adsorbent (Table 2). The highest values of K correspond to two samples with high clay contents: sample 3 with 37.7% clay and sample 10, with 62% clay. Other high K values, higher than 13, correspond to samples with a high clay content, such as sample 4, or to those with a high content in organic matter (samples, 6 and 13) but also with a clay content higher than 20%. The remaining samples with a high (sample 19) or

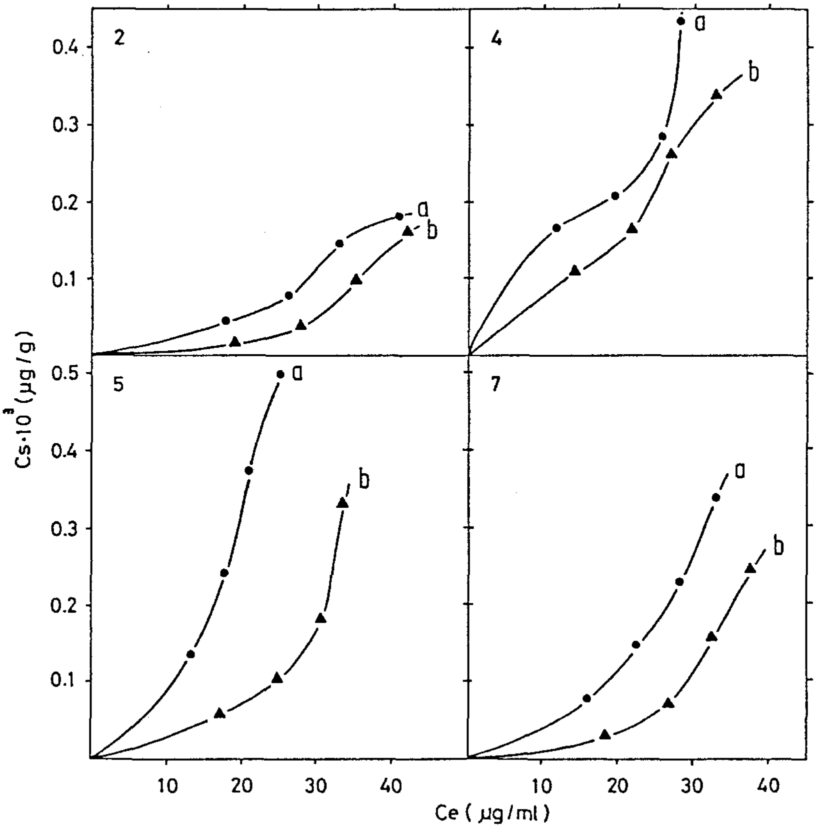

Figure 1. Adsorption isotherms of mevinphos by natural (a) and oxidized (b) soils 2, 4, 5 and 7.

intermediate (samples 5, 12, 15 and 18) content in organic matter but with low or very low clay levels afforded K values lower than 3.

In principle it is possible to observe a high affinity of the clay fraction for mevinphos at low concentrations of the pesticide; however, at the same time the amount of organic matter present in the samples is seen to affect adsorption strongly.

The values of n range between 0.37 and 1.40. According to the meaning of this constant, when n is greater than 1, K is greater than K_d, and when n is less than 1 the opposite occurs. The highest values of n correspond to the samples with the highest K values (samples 3 and 10). The great affinity of these samples for mevinphos owing to their high clay contents means that the active sites are saturated or almost saturated at low concentrations of the pesticide. The opposite is the case of the samples with a lower affinity for the compound, with a high content in organic matter and low clay levels (samples 5, 12 , 18 and 19), where the value of K is lower than that of K_d, indicating that the affinity of the organic matter for the pesticide increases with concentration. This can be seen in the statistical study of the correlations between the values of K and K_d and the characteristics of the soils.

Table 2. Freundlich constants (K and n) and distribution coefficients (Kd) for the adsorption of mevinphos by natural and oxidized soils.

Sample	Natural soils			Oxidized soils		
N°	n	K	Kd[a]	n	K	Kd[a]
1	0.82	5.93	10.94	0.46	0.12	2.81
2	0.57	0.27	2.19	0.30	0.01	0.40
3	1.32	55.81	29.07	0.53	0.53	5.68
4	1.05	14.73	13.02	0.75	3.01	7.65
5	0.50	0.77	12.11	0.42	0.07	2.64
6	1.08	13.49	11.03	1.43	50.57	22.66
7	0.50	0.28	4.44	0.32	0.01	0.87
8	0.50	0.81	9.58	0.39	0.03	1.96
9	0.60	0.77	4.74	0.27	0.01	0.46
10	1.40	39.99	18.66	0.80	4.11	8.20
11	0.50	0.22	3.46	0.53	0.18	2.02
12	0.53	0.80	8.94	0.52	0.54	6.27
13	1.03	26.35	24.38	1.47	58.94	24.99
14	0.50	0.10	1.48	0.36	0.01	1.03
15	0.69	1.50	5.06	0.37	0.02	2.15
16	0.39	0.02	1.37	0.66	1.15	4.76
17	0.43	0.05	1.57	0.52	0.17	2.21
18	0.50	0.15	2.32	0.47	0.13	2.86
19	0.63	2.65	13.33	0.80	2.21	4.38
20	0.34	0.01	0.81	0.38	0.01	1.07

[a] Ce= 15 µg/ml.

Table 3 shows the simple correlation coefficients between K and K_d and the parameters of the soils. A highly significant correlation can be seen between the values of K and the content in clay. This correlation coefficient is higher when one considers silt plus clay or organic matter plus clay. There is no correlation between K and the content in organic matter. However, the correlation between K_d and the content of organic matter is significant. This agrees with what has been mentioned above to the effect that the affinity of the pesticide for organic matter increases at higher concentrations.

The multiple correlations between K and K_d with the soil variables were also calculated

Table 3. Simple correlation coefficients (r) between K (Freundlich constant) and K_d (distribution coefficient) and soil characteristics

	OM	Clay	Silt	Silt plus clay	OM plus clay	Sand	pH
K	0.21	0.69[c]	0.16	0.76[c]	0.75[c]	-0.66[b]	0.46[a]
K_d	0.50[a]	0.52[a]	0.21	0.62[b]	0.66[b]	-0.61[b]	0.46[a]

OM, Organic matter

[a]Significant at 0.05 to 0.01 level

[b]Significant at 0.01 to 0.001 level

[c]Significant at < 0.001 level

to determine the relative importance of these parameters when they vary simultaneously. The corresponding coefficients of determination are shown in Table 4. According to the values of these coefficients, when the constant K is considered, organic matter and clay account for 59% of the variability in adsorption, slightly higher than the simple correlations between K and the sum of organic matter and clay (r^2=56). The value of the determination coefficient increases progressively when the variables organic matter and silt + clay, organic matter, silt and clay and organic matter, silt, clay and pH are considered. The multiple correlations between K_d and the same groups of variables afford higher determination coefficients, probably due, as has been indicated, to the increase in the affinity of organic matter for mevinphos at higher concentrations. The highest explanation of variability in adsorption (78%) is obtained when organic matter, silt, clay and pH are considered, the equation relating these parameters being as follows:

$$K_d = -24.48 + 1.26\,(OM) + 0.25\,(clay) + 3.06\,(pH) + 0.20\,(silt)$$

Table 4. Determination coefficients (R^2) of the multiple correlations between K (Freundlich constant) and K_d (distribution coefficient) and different soil parameters.

	OM clay	OM, silt plus clay	OM, silt, clay	OM, silt clay, pH
K	0.59[a]	0.62[a]	0.64[a]	0.69[a]
K_d	0.64[a]	0.62[a]	0.66[a]	0.78[a]

OM, Organic matter

[a] Significant at < 0.001 level.

To experimentally check the effect of organic matter on the adsorption of mevinphos by soils, the adsorption isotherms of oxidized soils were obtained, with the exception of samples 6, 13 and 19, with a high content in organic matter in which elimination of this was not total after repeated treatments with hydrogen peroxide.

Figure 1 shows the isotherms corresponding to four soil samples and Table 2 the values of K and K_d determined from the Freundlich equations of the corresponding isotherms. In general, the adsorption of mevinphos is greater in the case of natural soils than in the oxidized soils, despite the fact that the content and composition of the clay is the same in both cases and that adsorption is essentially related to the clay content.

This seems to point to the possible effect of the clay-organic matter complexes on adsorption, especially in soils with swelling minerals in their clay fraction. Such an idea is in agreement with the results obtained by Mortland (1968) concerning the adsorption of EPTC (a carbamate pesticide) by montmorillonite - pyridinium and by Khan (1973) on the adsorption of diquat and paraquat by the montmorillonite- fulvic acid complex. In those studies, the authors indicate that the clay-organic matter associations facilitate the adsorption and complexing of montmorillonite with the pesticides.

Finally, the simple correlations between the values of K and K_d of the oxidized soils and the clay content were determined, obtaining correlation coefficients of 0.79 (significant at a level of < 0.001) and 0.65 (significant at a level between 0.01 and 0.001), respectively. These correlation coefficients are higher than those obtained in the correlations between K and K_d and clay content for natural soils (Table 3).

It may be concluded that the most important parameter in the adsorption of mevinphos by soils is the clay content, adsorption being facilitated by the clay-organic matter complexes.

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