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Adsorption of Methyl Parathion by Soils

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With the increased use of pesticides, there has been an increasing awareness of the importance of soil colloids in the adsorption, movement, persistence, degradation and bioactivity of pesticides. The fate and behavior of pesticides in soil systems are generally dependent upon the following factors; chemical, photochemical and microbial decomposition, volatilization, movement, plant uptake and adsorption (WRIGHT 1971 and BAILEY et al. 1968). The limited data on insecticides adsorption have dealt primarily with chlorinated hydrocarbons. Very little information is available on the adsorption of organophosphorus insecticides. These chemicals are generally more water soluble, and consequently are more susceptible to leaching than the chlorinated hydrocarbons.

Methyl parathion is one of the widely used insecticides. Its adsorption characteristics on soil colloids would reveal the nature of its persistence, movement, and consequently, its fate in the environment. The present paper deals with the methyl parathion-soil interaction in several types of Egyptian soils differing in their physical and mineralogical composition. The adsorption by the clay fractions separated from these soils were also investigated.

MATERIALS AND METHODS

Pure crystalline methyl parathion, (O,O-dimethyl O-4-nitrophenyl phosphorothioate) was obtained from the Agriculture Division, Monsanto Company, St. Louis, Missouri, USA. Three soils representing the main soil types in Egypt, (Nile alluvium, calcareous deposits, and sandy desert soils), were used. These were Tel El-Kabeer, El-Nahda and Tahreer soils respectively.

Preparation of soils: Soil samples were collected from the top layers (0-30 cm) of the soil profiles. The samples were air-dried and sieved to pass a 2 mm screen. Table 1 lists some physical and chemical properties of these samples according to the methods described by BLACK (1965).

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TABLE 1

Some physical and chemical properties of the soils and their clay fraction.

Soil	Clay (< 2 um) %	$CaCO_3$ %	Organic matter %	CEC me/100 g	Clay fraction	
					$CaCO_3$%	CEC me/100 g
El-Nahda	55.88	32.02	1.72	24.50	19.44	46.70
Tel El-Kabeer	71.92	11.61	0.63	40.00	2.97	59.89
Tahreer	5.07	1.92	0.43	4.25	-	

Preparation of soil clay fraction: Clay fraction in each soil was separated by sedimentation technique, and then saturated with Mg^{2+} using $MgCl_2$. The saturation process was repeated three times, then the excess salt was washed out using distilled water and neutral ethanol. The clays were oven-dried at 60°C for 48 hrs and sieved to pass a 100 mesh screen. No clay was fractionated from Tahreer soil because of its very low clay content.

Determination of methyl parathion: The procedure used depended upon the hydrolysis of methyl parathion in highly alkaline solutions and measuring the released 4-nitrophenol spectrophotometrically (KISHK et al. 1976). A preliminary study indicated that methyl parathion was completely hydrolyzed within two hours when a solution of methyl parathion was added to an equivalent volume of 0.5 N-NaOH at room temperature. After hydrolysis, the 4-nitrophenol released was measured at 420 nm using a Beckman DB Spectrophotometer.

Adsorption experiments: Adsorption of methyl parathion was studied by equilibrating a suitable amount of soil; 0.5 g for Tel El-Kabeer and El-Nahda soils and 1 g for Tahreer soil with methyl parathion in a total volume of 20 ml of acetone-water (15% v/v). The mixtures were placed in 50 ml centrifuge tubes and shaken at a constant temperature for 4 hrs. After equilibrium had been established, the mixtures were centrifuged at 5000 rpm for 15 min. An aliquat of the supernatant was taken for methyl parathion determination. All experiments and methyl parathion determinations were carried out in duplicates. Several concentrations of methyl parathion were used, 50, 100, 150, 200, 250 and 400 µmole/liter. The adsorption isotherms were obtained at laboratory temperature (19 ± 2°C) for the soils and the soil clay fractions.

RESULTS AND DISCUSSION

Adsorption isotherms for the soils and their clay fractions are illustrated in Figure 1. The data were found to conform to the principal isothermal Freundlich relationship written as:

$$x/m = kC^{1/n}$$

where x/m is the amount of methyl parathion (x) adsorbed by a given amount of adsorbent (m). The constants k and n embrace all factors affecting adsorption from solution namely, properties of the adsorbate, adsorbent, and solvent, and the equilibria between the adsorbate-adsorbent, adsorbate-solvent and solvent-adsorbent (BAILEY et al. 1968); C is the equilibrium concentration of the adsorbate in solution.

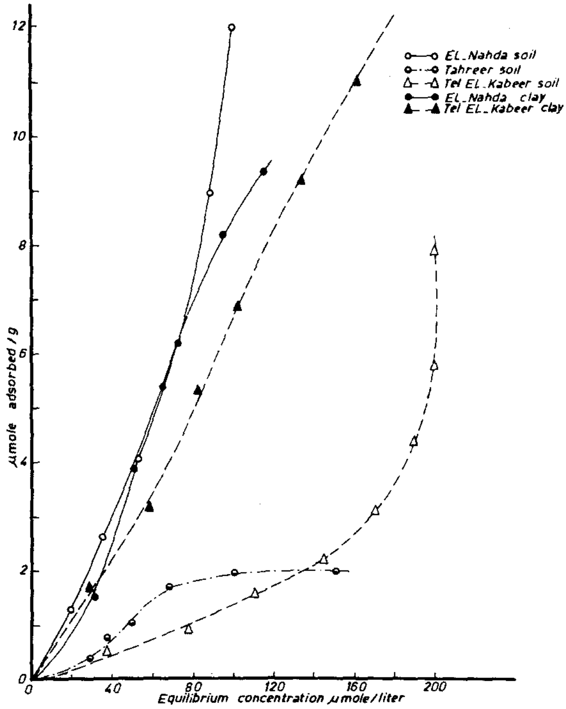

Fig. 1 Adsorption isotherms of methyl parathion on the different types of soils and their clay fractions.

Conformity to the Freundlich equation existed for all systems. The calculated values of k and n are listed in Table 2. The results show that in the case of Tahreer soil, the maximum adsorption was attained at x/m = 1.9 μmole methyl parathion/g soil, while in the case of El-Nahda soil, the maximum adsorption was observed at x/m = 9.5 μmole/g soil. In Tel El-Kabeer soil, and despite the higher initial concentration of 400 μM methyl parathion used, no maximum adsorption was observed within the range of concentrations used in the study.

TABLE 2

Values of Freundlich parameters of methyl parathion adsorption on different adsorbents.

Adsorbent	k	1/n
El-Nahda soil	0.0430	1.155
El-Nahda clay	0.0027	1.835
Tel El-Kabeer soil	0.0056	1.225
Tel El-Kabeer clay	0.0310	1.155
Tahreer soil	0.0120	1.150

Both clay fractions of El-Nahda and Tel El-Kabeer soils, showed maximum adsorption within the range of concentrations applied. The results revealed that El-Nahda clay fraction adsorbed 23 μmole methyl parathion/g clay against an equilibrium concentration of 125 μM, while Tel El-Kabeer clay fraction adsorbed 17 μmole of methyl parathion/g clay against an equilibrium concentration of 187.5 μM. Since the values of k shown in Table 2 were found to be very small, the slope 1/n will determine the extent of adsorption in these systems. The results indicated similar slope values for all the adsorbents except for El-Nahda clay fraction which had a higher value (1.835). This might be attributed to the relatively higher adsorption capacity of that particular clay fraction toward methyl parathion.

On examining the minerological composition of the clay fraction of the Tel El-Kabeer and El-Nahda soils, it was found that they contained different proportions of clay minerals, as shown in Table 3. It was expected that Tel El-Kabeer clay fraction would exhibit a higher adsorption capacity for methyl parathion because of its high specific surface area resulting from its higher content of montmorillonite. However, El-Nahda soil exhibited a higher adsorptive capacity for methyl parathion. This is probably due to the higher organic matter content in the soil which is in agreement with the report that soil organic matter adsorbed significantly large amounts of parathion (LEENHEER and AHLRICHS 1971).

TABLE 3

Clay mineral composition of Tel El-Kabeer and El-Nahda soils

	Tel El-Kabeer	El-Nahda
Montmorillonite %	40 - 50	16 - 20
Kaolinite %	20 - 25	20 - 25
Illite %	10 - 15	20 - 25
Attapulgite %	-	20 - 25
Sp. surface (m^2/g)	420	250

The change in the partial molar free energy ($\Delta\bar{G}$) as a result of the adsorption process was calculated from the thermodynamic relationship:

$$\Delta\bar{G} = -RT \ln (C_0/C_e)$$

where C_e is the equilibrium concentration and C_0 is the initial concentration. The value of $\Delta\bar{G}$ may be used as a measure of the extent of the driving force of the reaction. The greater the absolute magnitude of $\Delta\bar{G}$ value, the greater is the extent to which the adsorption reaction may take place. Table 4 shows that the highest value of $\Delta\bar{G}$ was obtained with El-Nahda soil and the least value was obtained with Tahreer sandy soil. The value of Tel El-Kabeer soil was intermediate. In every case, the magnitude of $\Delta\bar{G}$ was higher for the clay over the case of the corresponding soils.

The low capacity for methyl parathion adsorption by Tahreer sandy soil, indicates that the clay content is an important factor in the adsorption process. El-Nahda soil which had a clay content of 55.88%, began to show maximum adsorption at about 95 μmole/g, while Tel El-Kabeer soil, which had the highest clay content (71.9%), showed unlimited capacity for methyl parathion adsorption.

The difference found in the extent of methyl parathion adsorption on the soil clay fractions would be due to variations in the type of clay predominating in both fractions.

TABLE 4

The change in partial molar free energy, $\Delta\bar{G}$ of methyl parathion adsorption on soils and clays.

Adsorbent	Temp. of reaction °C	$\Delta\bar{G}$ cal/mole
El-Nahda soil	21	-649.50
El-Nahda clay	21	-678.79
Tel El-Kabeer soil	19	-387.60
Tel El-Kabeer clay	20	-417.77
Tahreer soil	20	-287.50

It is speculated that in soil-aqueous acetone-methyl parathion systems, the solvent is preferentially, adsorbed, but small amounts of methyl parathion diffuse through the solvent pellicles, and as they approach the colloid surface they are absorbed as has been suggested for parathion adsorption in soil-water-parathion systems (YARON and SALTZMAN 1972).

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