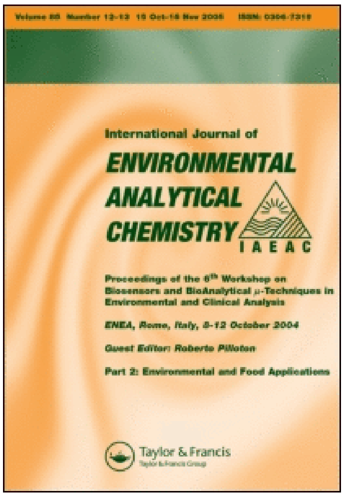

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MOVEMENT OF PHOSPHAMIDON IN SOIL COLUMNS

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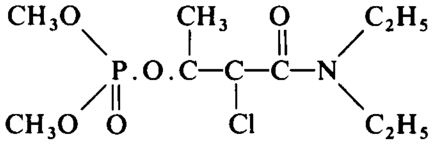
Adsorption and movement of phosphamidon, a systemic non-ionic insecticide, was studied using two different types of Indian soil, clay loam and silt loam, of alluvial origin. Equilibrium adsorption coefficient, K, values determined by batch slurry technique were in the order: clay loam > silt loam. The distribution coefficient, K_d, for both soils in batch adsorption as well as in columns was also calculated. The phosphamidon movement measured in soil columns during water infiltration was in the order: silt loam > clay loam. This order was anticipated from the K and K_d values. A larger amount of water was needed for leaching the phosphamidon to 60 inches in clay loam than in silt loam soil.

INTRODUCTION

The adsorption, movement and leachability of pesticides in soils which are essential in modern agriculture play a vital role in determining their efficacy for crop protection and potential for environmental pollution.[1–3] This has led both agricultural and environmental scientists to become more interested in finding out the fate of pesticides. For the last few years much attention has been focused on this kind of research for pesticide used in crop production.[4,5].

Several workers[6–14] have extensively studied the movement of herbicides and nematicides using soil column techniques and these have shown the probability of ground water being polluted due to transportation of pesticides. Therefore, there is a need to study the movement of pesticides in soils under different conditions.

Phosphamidon (2-chloro-2-diethyl carbomoyl-1-methyl vinyl dimethyl phosphate) having the structure



$$(CH_3O)_2P(=O).O.C(CH_3)\text{—}C(Cl)\text{—}C(=O)\text{—}N(C_2H_5)_2$$

is a non-ionic systemic insecticide used for the control of sucking, mixing and chewing insects, pests and nematodes. The information pertaining to factors affecting the movement of phosphamidon in soils is very scanty. Therefore, in the present study, it was considered desirable to study the movement of phosphamidon in two different types of soil of alluvial origin to a depth of 60 inches with a view to examine the probability of its polluting the ground water during the rainy season.

EXPERIMENTAL

The soil used for our studies was collected (surface samples; 0–30 cm) from the Aligarh Muslim University farm and the village of Bhartari in the Aligarh district. The soils have the following physicochemical properties. Clay loam soil: sand, 39.9%; silt, 29.6%; clay, 30.5%; pH, 7.85; organic matter, 0.30%; CEC, 0.33 meq/g soil, and silt loam soil: sand, 33.3%; silt, 59.10%; clay, 7.60%; pH, 8.33; organic matter, 0.183%; CEC, 0.12 meq/g soil.

Stock solution of phosphamidon (Hindustan Ciba-Geigy, India) were prepared by dissolving 5.00 g of phosphamidon in 1000 ml of distilled water. All laboratory studies were conducted using BDH analytical-grade chemicals.

Time of equilibrium. To study the effect of the time of equilibrium, 5 ml of phosphamidon solution (5000 μg/ml) were taken in different 100 ml glass-stoppered conical flasks and the volume in each flask was made up to 20 ml with distilled water. To these solutions,. 1.00 g clay loam or silt loam soil was added and the flasks were shaken on a mechanical shaker at room temperature. After a certain period of time the suspensions were centrifuged and the amount of phosphamidon left in the supernatants was determined spectrophotometrically[15] at 440 nm against a blank.

Adsorption studies. The adsorption of phosphamidon on soils was studied by taking various amounts (0.5–10 ml) of phosphamidon solution (5000 μg/ml) in a number of 100 ml glass-stoppered conical flasks. The volume of each flask was made up to 25 ml with distilled water and 1.00 g clay loam or silt loam soil was added. The suspensions obtained were shaken on a mechanical shaker for 6 h at room temperature. The mixture was then centrifuged at 3500 rpm for 10 min and phosphamidon in the supernatant liquids was determined spectrophotometrically.[15] The amount of phosphamidon adsorbed was determined as the difference between the amount added and the amount left in the equilibrium suspension.

The distribution coefficient, K_d, for each soil was calculated from

$$K_d = \frac{\sum\left(\frac{x}{m}\cdot C_e\right)}{\sum(C_e)^2} \qquad (1)$$

where C_e is the μg of phosphamidon/ml in the equilibrium suspension, and x/m the amount of phosphamidon adsorbed in μg/g soil and $\sum$ indicates the summation of the values.

The adsorption data of both soils were fitted to a Freundlich equation

$$\frac{x}{m} = KC_e^N \qquad (2)$$

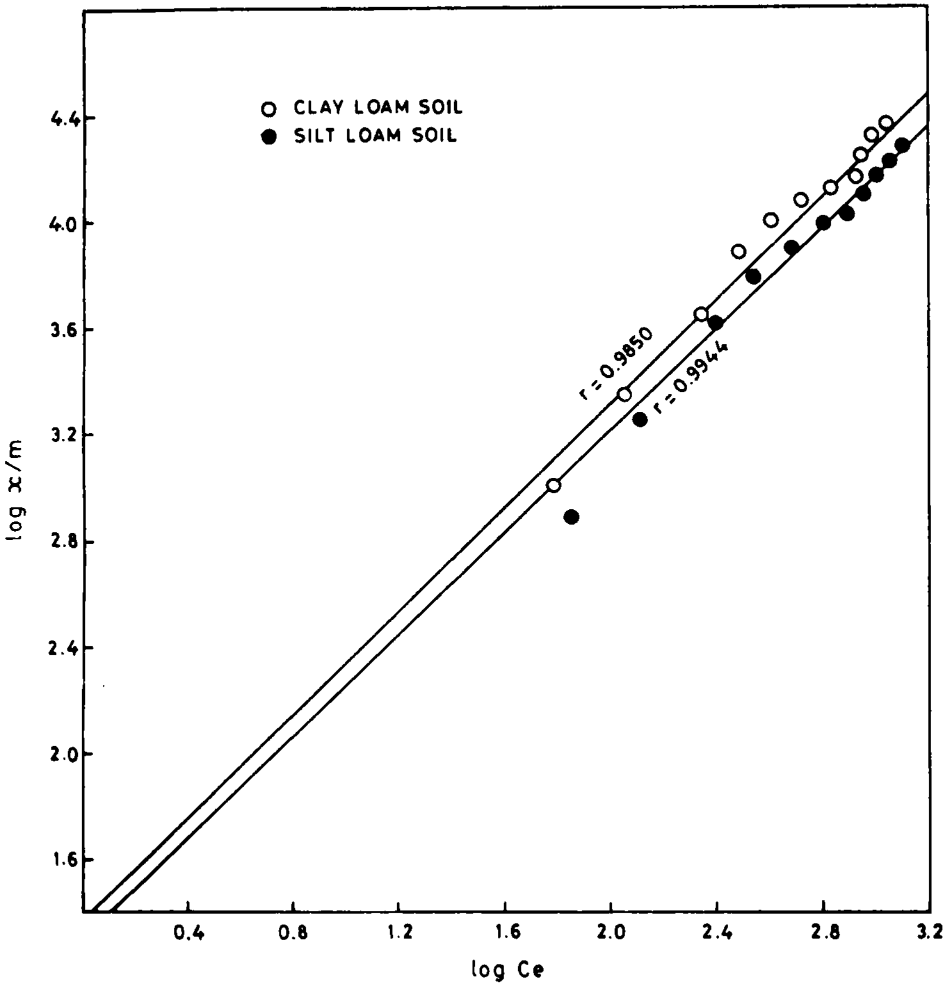


Figure 1 Freundlich isotherms of phosphamidon on soils at 25 °C.

where K and N are empirical adsorption constants specific to each soil-phosphamidon being considered and x/m and C_e are the adsorbed (μg phosphamidon/ml) and solution phase (μg phosphamidon/ml) concentrations, respectively (Figure 1). The adsorption coefficient, K, has the dimension $\mu g^{1-N} ml^N g^{-1}$; N is dimensionless. The values of K and N were determined by linear regression of the log-transformed data.

Column studies. The movement of phosphamidon in soils was studied by preparing a column of polythene tubing having an 1.7 cm internal diameter, fixed in a stop-cork-containing glass tube of appropriate length (Figure 2). The column was packed with 50 g clay loam or silt loam soil by constant tapping in order to pack the soil into a constant volume. The column was weighed and then slowly

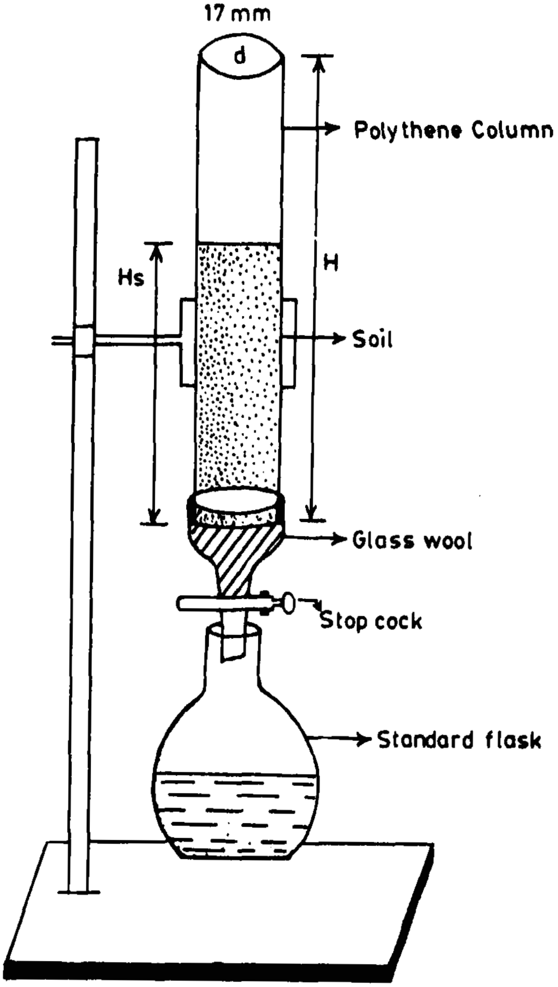


Figure 2 Movement of phosphamidon in soil column.

saturated with distilled water from bottom to top to remove entrapped air. After saturation the column was reweighed to determine the volume of water (void volume) present. Phosphamidon movement in both soils was calculated by dispensing 5 ml of a phosphamidon (5000 μg/ml) solution from a burette on to the surface of the soil in the column. The column was then drenched with 100 ml (44.04 cm) of distilled water and the effluent was collected. After the water had passed through the soil, the soil column was divided into seven equal parts and dried at room temperature. 5 g of soil from each section were then treated with 15 ml of distilled water and shaken on a mechanical shaker for 3 h and then centrifuged. The supernatant thus obtained and the effluent collected earlier were used for phosphamidon determination. The percentages of phosphamidon present in the effluent and in different soil sections were calculated.

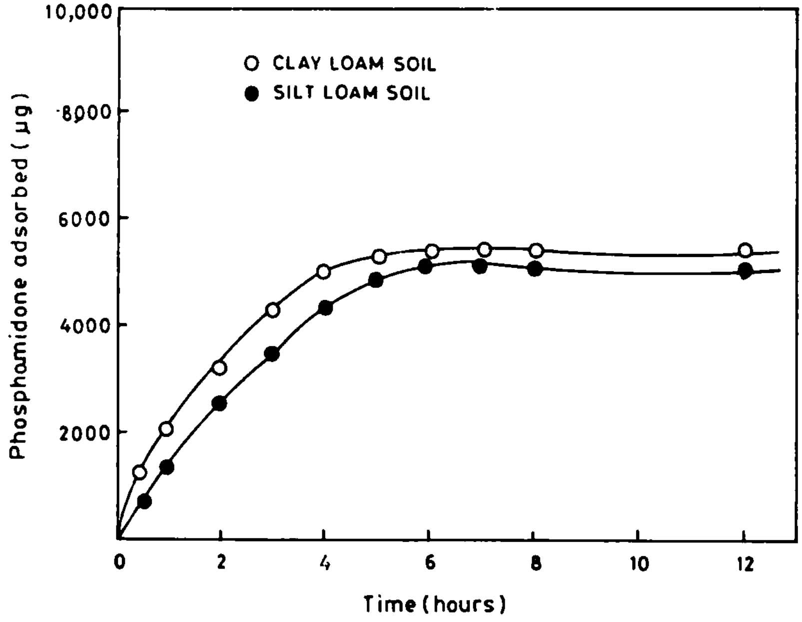


Figure 3 Phosphamidon adsorption on soils as a function of time.

The distribution coefficient, K_d, in the soil column was calculated for both soils according to the expression initially described by Ketelle and Boyd[16] and used by Swoboda and Thomas[17] and Kumari *et al.*[14]

$$K_d=\left(\frac{V_p}{V_v}-1\right)\frac{V_v}{W} \tag{3}$$

where V_p stands for the volume of effluent to elute one-half of the phosphamidon from the column, V_v is the void volume and W is the weight of the soil in the column.

RESULTS AND DISCUSSION

It is evident from Figure 3 that the adsorption of phosphamidon on soils increases with an increase of time up to 6 h, afterwards becoming constant. Hence, this period was chosen for further adsorption studies of phosphamidon on soils.

The values of the adsorption and distribution coefficients and Freundlich adsorption constants, K and N, for the soil-phosphamidon combinations studied are summarized in Table 1. Comparing the adsorption data for both soils it is clear that the adsorption of phosphamidon is higher in clay loam soil than silt loam soil, probably due to differences in organic matter, clay content and cation-exchange capacity of the soils, the values being higher in the former case. The higher K_d value (Table 2) obtained for clay loam soil than silt loam soil also

Table 1 Adsorption data and distribution coefficient of phosphamidon on clay loam soil at room temperature

Sample no.	*Phosphamidon added* (*μg*)	*Phosphamidon in total 25ml suspension* (*μg*)	*Amount of phosphamidon in equilibrium suspension* (*μg/ml*; C_e)	*Amount of phosphamidon adsorbed* (*μg/g*; x/m)	*log* C_e	*log* x/m	$\sum C_e . x/m$	$\sum C_e . C_e$	*% adsorbed*	K_d
1	2 500	1 500	60	1 000	1.778	3.000	60 000	3 600	40.0	20.37
2	5 000	2 800	112	2 200	2.049	3.342	246 400	12 544	44.0	
3	10 000	5 500	220	4 500	2.342	3.653	990 000	48 400	45.0	
4	15 000	7 500	300	7 500	2.477	3.875	2 250 000	90 000	50.0	
5	20 000	10 000	400	10 000	2.602	4.000	4 000 000	160 000	50.0	
6	25 000	13 250	530	11 750	2.724	4.070	6 227 500	280 900	47.0	
7	30 000	17 000	680	13 000	2.832	4.113	8 840 000	462 400	43.3	
8	35 000	20 750	830	14 250	2.919	4.153	11 827 500	688 900	40.7	
9	40 000	22 250	890	17 750	2.949	4.249	15 797 500	792 100	44.3	
10	45 000	24 000	960	21 000	2.982	4.322	20 160 000	921 600	46.6	
11	50 000	27 500	1 100	22 500	3.041	4.352	24 750 000	1 210 000	45.0	
							95 148 900	4 670 444		

Table 2 Adsorption data and distribution coefficient of phosphamidon on silt loam soil at room temperature

Sample no.	*Phosphamidon added (μg)*	*Phosphamidon in total 25ml suspension (μg)*	*Amount of phosphamidon in equilibrium suspension (μg/ml; C_e)*	*Amount of phosphamidon adsorbed (μg/g; x/m)*	*log C_e*	*log x/m*	$\sum C_e . x/m$	$\sum C_e . C_e$	*% adsorbed*	K_d
1	2 500	1 750	70	750	1.845	2.875	52 500	4 900	30.0	15.11
2	5 000	3 250	130	1 750	2.113	3.243	227 500	16 900	35.0	
3	10 000	6 000	240	4 000	2.380	3.602	960 000	57 600	40.0	
4	15 000	8 500	340	6 500	2.531	3.812	2 210 000	115 600	43.3	
5	20 000	12 000	480	8 000	2.681	3.903	3 840 000	230 400	40.0	
6	25 000	15 500	620	9 500	2.792	3.977	5 890 000	384 400	38.0	
7	30 000	19 250	770	10 750	2.886	4.031	8 277 500	592 900	35.8	
8	35 000	22 250	890	12 750	2.949	4.105	11 347 500	792 100	36.4	
9	40 000	25 250	1 010	14 750	3.004	4.168	14 307 500	940 900	36.8	
10	45 000	28 250	1 130	16 750	3.053	4.224	18 425 000	1 210 000	37.2	
11	50 000	31 000	1 240	19 000	3.093	4.278	23 750 000	1 562 500	38.0	
							89 287 500	5 908 200		

Table 3 Relevant parameters for phosphamidon in clay and silt loam soils

Soil	*K* ($\mu g^{1-N} ml^N g^{-1}$)	*N*	*Correlation coefficient* (*r*)	*Regression equation*[a]
Clay loam	23.90	0.967	0.9850	$x/m = 23.9 + 0.967\,C_e$
Silt loam	19.90	0.953	0.9944	$x/m = 19.9 + 0.953\,C_e$

[a] x/m = amount of phosphamidon adsorbed (μg/g soil); C_e = amount of phosphamidon in equilibrium suspension (μg/ml).

Table 4 Per cent recovery of phosphamidon in different sections of soil column

Clay loam soil			*Silt loam soil*		
Depth (cm)	*μg phosphamidon recovery/ g soil*	*% phosphamidon recovery*	*Depth (cm)*	*μg phosphamidon recovery/ g soil*	*% phosphamidon recovery*
0–2	59	1.7	0–2	46	1.3
2–4	109	3.1	2–4	96	2.7
4–6	129	3.7	4–6	122	3.5
6–8	109	3.1	6–8	96	2.7
8–10	75	2.1	8–10	63	1.8
10–12	55	1.6	10–12	36	1.0
12–13.5	55	1.2	12–14	36	1.0
		16.5			14.0

confirms that clay loam soil displays higher adsorption. The higher values of *K* and the lower values of *N* (Table 3) for clay loam soil again confirms the greater adsorption of phosphamidon to clay loam soil.

The results of the leaching studies where the soil column was leached with 100 ml (44.04 cm) distilled water, are summarized in Table 4. The percentage of phosphamidon in effluents of clay loam and silt loam soil was 34% and 51%, respectively. The slower movement of phosphamidon in clay loam soil compared to silt loam soil again confirms that higher adsorption occurs in clay loam soil. On examination of Table 4, the concentration of phosphamidon is seen to increase with increasing depth up to 6 cm followed by a decrease at greater depth in both soils. The smaller percentage of phosphamidon recovered in silt loam soil compared to clay loam soil again confirming the higher adsorption in clay loam soil.

The distribution coefficients of phosphamidon in the columns calculated by means of Eq. (3) are 2.64 and 1.70 for clay loam and silt loam soil, respectively. The larger K_d value obtained for clay loam soil also indicates that a greater amount of water is required to leach phosphamidon through this soil. The K_d values obtained in the batch and column experiments are not in close agreement, but the trend is the same.

The K_d values are also extremely dependent on the concentration of phosphamidon and that of the solution passing through the column, which are continuously changing.[18] Equation (3) can be rearranged to give

$$K_dW=(V_p-V_v) \tag{4}$$

Since the bulk density, ρ, of a soil is its weight divided by the volume it occupies, V, one then finds

$$K_d\rho=\left(\frac{V_p}{V}-\frac{V_v}{V}\right) \tag{5}$$

where V_p/V is the number of column volumes of leachate required to displace half of the phosphamidon and V_v/V is the porosity of the soils. The term V_p/V is equivalent to the linear ratio R/L, where R is the amount of rainfall required to leach phosphamidon to a depth L. In other words

$$R=L\left(K_d\rho+\frac{V_v}{v}\right) \tag{6}$$

Here the values of the bulk density and porosity for clay loam and silt loam soils are 1.63 and 1.54 g/cm^3, and 0.49 and 0.41, respectively. The amount of infiltrating rainfall required to leach phosphamidon to a depth of 60 inches can be calculated to be 287 and 185 inches for clay loam and silt loam soil, respectively.

Applying the above data to the amount of rainfall/irrigation necessary to move phosphamidon to a depth, L can be calculated via

$$R=\frac{H\rho L}{d\theta} \tag{7}$$

where H is the height of the water column used to displace phosphamidon to a depth, d in the laboratory column and θ and ρ are the bulk densities of the soil in the field and laboratory column, respectively. The bulk density of field soil can be assumed to be 1.5 g/cm^3. The calculated amount of rainfall necessary to leach phosphamidon through 60 inches of field soil becomes 480 inches for clay loam and 460 inches for silt loam soil. Thus, slightly more water is required for leaching phosphamidon for clay loam soil. The 60 inches depth used was chosen for the calculation because most soils have a soil profile at least up to 60 inches.

The R values obtained from Eqs. (6) and (7) for clay and silt loam soil further confirm the adsorption, Freundlich constant and K_d data discussed above.

Acknowledgement

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