# Movement of Parathion in Soil Columns

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Parathion movement in soils was studied in laboratory columns by leaching applied parathion with distilled water. Distribution coefficients for the adsorption of parathion by soils were calculated from leaching experiments. The amount of rainfall required to leach parathion to a depth of 60 inches was estimated from leaching experiments. It varied from 230 inches for a Nacogdoches clay subsoil to 1725 inches for a Houston Black clay surface soil. Desorption experiments indicate that parathion is not effectively displaced by inorganic electrolyte salts or by aqueous solutions. However, it readily moves through soil columns when leached with ethanol.

The movement of pesticides in soils is of extreme importance owing to possible eventual contamination of underground water supplies. It is dependent on the amount of water moving through the soil and the degree of adsorption of the pesticide by the soil. Most data on the movement of pesticides in soils have been obtained using herbicides. The limited data on insecticide movement in soils have dealt primarily with chemicals of the chlorinated hydrocarbon type. Very little information is available on the movement of organophosphorus insecticides in soils (Lichtenstein, 1958; Nicholson et al., 1962; Weidhaas et al., 1961). Organophosphorus insecticides generally are more soluble in water than the chlorinated hydrocarbon compounds. This would indicate that they are much more susceptible to leaching than the chlorinated compounds. Reynolds and Metcalf (1962) found that the movement of several systemic organophosphate insecticides was directly related to their water solubility.

Parathion is generally considered not to persist in soils. Carlo et al. (1952) reported that no parathion was detectable in a soil 16 days after application of 2 pounds of parathion per acre. However, Nicholson et al. (1962) found that parathion was still present in Appling and Cecil soils 9 months after the last application. MacPhee et al. (1960) were able to recover 21% of the parathion added to a soil 4½ years previously.

Ahmed and Casida (1958) reported that parathion did not undergo oxidation in soils since they were unable to detect para-oxon, an oxidation product of parathion (Lichtenstein and Schulz, 1964), in parathion-treated soils. However, Lichtenstein and Schulz (1964) found that para-oxon was very rapidly hydrolyzed, in a matter of hours, in a loam soil. They also reported that the major pathway of loss of parathion in soils is by hydrolysis rather than

volatilization, since soils treated with parathion do not give off toxic vapors (Harris and Lichtenstein, 1961).

Although parathion undergoes degradation more readily than the chlorinated hydrocarbons, the possibility of it being leached through soils and into underground water supplies warrants investigation since parathion is extremely toxic. To obtain more information, laboratory experiments were conducted to study the adsorption, desorption, and movement of parathion in soils.

## EXPERIMENTAL

**Materials.** Eight important agricultural soils from various locations in Texas were selected to represent the major soil types in the state. Analytical characterizations are given in Table I. All soils were surface samples except the Nacogdoches soil, which was a subsurface sample from the $B_2$ horizon. Each soil was ground to pass a 30-mesh sieve and stored until needed.

The organophosphate pesticide used was $O,O$-diethyl $o$-$p$-nitrophenyl thiophosphate (parathion). For most experiments, ^{32}P-labeled parathion was used. The purity

**Table I. Composition of Soils Used in Experiments**

| Soil[a] | pH | Clay, % | O.M., % | CEC, Meq./ 100 G. | Predominant Clay |
|---|---|---|---|---|---|
| Norwood si.l. | 8.2 | 17 | ... | ... | Montmorillonite-mica |
| Nacogdoches c. | 5.0 | 44 | 0.4 | 14 | Kaolinite |
| Houston Black c. | 7.8 | 52 | 4.4 | 63 | Montmorillonite |
| Hoban si. c.l. | 7.7 | 33 | 1.3 | 22 | Mica |
| Willacy f.s.l. | 7.6 | 11 | 1.3 | 11 | Montmorillonite-mica |
| Harlingen c. | 8.2 | 72 | ... | ... | Montmorillonite |
| Amarillo f.s.l. | 7.7 | 8 | 0.5 | 8 | Mica-mont-morillonite |
| Katy s.l. | 5.1 | 6 | 1.0 | ... | Kaolinite |

[a] Si.l. = silty loam; c. = clay; si.c.l. = silty clay loam; f.s.l. = fine sandy loam; s.l. = silt loam.

of the material was checked by means of gas chromatography. The only peak that was detectable in an ethanol solution of the ^{32}P-labeled material was that of parathion.

**Apparatus.** A Packard 3214 Tri-Carb liquid scintillation spectrometer was used for counting phosphorus-32 activity. The scintillation liquid consisted of 50 grams of naphthalene, 7 grams of PPO (2,5-diphenyloxazole), and 0.05 gram of POPOP [2,2-p-phenylenebis (5-phenyloxazole)] diluted to 1 liter with dioxane. Nonlabeled parathion was determined using a 5360 Barber-Colman pesticide analyzer gas chromatograph equipped with a sodium thermionic flame detector. A 6-foot column with 10% DC-200 on Anakrom ABS was used in the chromatograph. The injector, column, and detector temperatures were maintained at 230°, 200°, and 210° C., respectively. Helium, with a flow rate of 180 cc. per minute, was used as the carrier gas.

For column experiments, chromatographic columns of several dimensions were used as required by the experiment. A Warner-Chilcott automatic fraction collector was used to collect effluent samples from the column experiments.

**Procedure.** The equilibrium adsorptive properties of the soils were studied using batch equilibrium experiments. Soil samples weighing 2 grams were equilibrated for 2 hours with 10 ml. of various concentrations of ^{32}P parathion in water. Four concentrations ranging from 4.1 to 16.5 p.p.m. were used. After equilibration, the suspensions were filtered and the amount of ^{32}P parathion remaining in solution was determined. The amount adsorbed by the soils was determined by difference. Distribution coefficients, $k_d$, were calculated as the ratio of parathion adsorbed (micrograms per gram) to the concentration of parathion in solution (micrograms per milliliter).

To study the mechanism of parathion adsorption, three columns (27 mm. in diameter) were prepared by mixing 30 grams of a Katy soil with 10 grams of Whatman cellulose powder (filter paper pulp) which was added to obtain suitable flow rates. Preliminary experiments showed that cellulose powder does not adsorb parathion. The columns were saturated with water and 1 ml. of a ^{32}P parathion solution was added to the surface of the columns. The soils were then leached with ethanol, distilled water, and aqueous 0.01$N$ $CaCl_2$. The effluents were collected in 5-ml. fractions and the ^{32}P activity counted in each fraction. The procedure was repeated using nonlabled parathion, smaller columns, and 0.1$N$ HCl, ethanol, and water as the leaching solvents. Gas chromatography was used to determine parathion concentrations and to verify that no parathion decomposed during the leaching.

The movement of parathion in soils was studied by packing chromatographic columns with a mixture of 50 grams of soil and 12.5 grams of Whatman cellulose powder and placing them in chromatographic columns (27 mm. in diameter) equipped with fritted glass filters. The columns were weighed and then slowly saturated with distilled water from bottom to top to remove entrapped air.

After saturation the columns were reweighed to determine the volume of water (void volume) present. One milliliter of a dilute ethanol solution containing 0.2 mg. of ^{32}P-tagged parathion was then added to the surface of the columns. After the parathion solution had entered into

the surface of the soil, the columns were slowly leached with 100 ml. (17.5 cm.) of distilled water at a rate of about 1 ml. per minute. After the water had passed through the soils the soil-cellulose mixtures were removed from the columns, divided into 1-cm. sections, and dried at 40° C. Two grams of the mixture from each section were then extracted by shaking with 25 ml. of acetonitrile for 2 hours. The suspension was then filtered and a 1-ml. aliquot of the filtrate taken for ^{32}P determination.

For determination of distribution coefficients, $k_d$, soil columns were prepared as above except that 30 grams of soil and 10 grams of cellulose powder were used. The effluents were collected in 5-ml. fractions and ^{32}P activity was counted.

Distribution coefficients, $k_d$, were calculated using the expression first described by Ketelle and Boyd (1947).

$$k_d = \left[ \frac{Vp}{Vc} - 1 \right] \frac{Vc}{W} \tag{1}$$

where

$Vp$ = volume of effluent to leach one-half of the solute through the column
$Vc$ = void volume in the column
$W$ = weight of adsorbent in column

Distribution coefficients measure the ability of soils to absorb parathion. If a soil does not adsorb parathion, $k_d$ will equal zero.

RESULTS AND DISCUSSION

**Adsorption of Parathion by Soils.** Adsorption isotherms determined by batch techniques for Harlingen, Hoban, and Nacogdoches soils are shown in Figure 1. The highest initial parathion concentration was 16.5 p.p.m. which is below the reported solubility of parathion in water, 24 p.p.m. (Williams, 1951). All three soils exhibited linear adsorptive capacities over the range of concentrations studied. The adsorption isotherms for Harlingen and Hoban soils were very similar over the entire concentration range. Harlingen and Hoban soils adsorbed 59.8 and 58.0 $\mu$g. per gram, respectively, when 2 grams of soil were equilibrated with 10 ml. of solution with
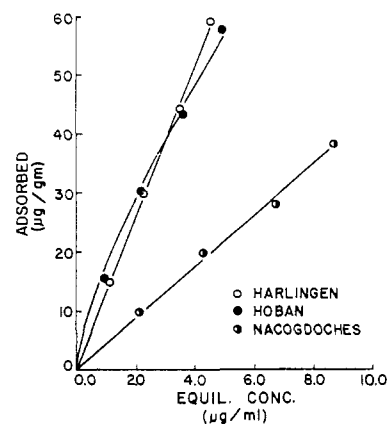


Figure 1. Adsorption isotherms for parathion adsorption on Harlingen, Hoban, and Nacogdoches soils

an initial concentration of 16.5 p.p.m. and an equilibrium concentration of about 4.6 p.p.m. Nacogdoches soil adsorbed only 38.6 $\mu$g. per gram at the same initial concentration. These soils all have a high adsorptive affinity and capacity for parathion. The Harlingen and Hoban soils adsorbed 73% of the parathion in the aqueous solution. The Nacogdoches soil adsorbed only 48% of the parathion at all concentrations studied. In no instance was the maximum adsorptive capacity approached. Distribution coefficients for the three soils at the high concentrations were 11.9 ml. per gram for Hoban, 13.2 ml. per gram for Harlingen, and 4.4 ml. per gram for Nacogdoches. The values for the individual soils were relatively constant at all concentrations except for the Hoban soil in which the $k_d$ values decreased with increasing concentrations.

In an attempt to study the parathion adsorption mechanism in soils several leaching experiments were designed. Columns of Katy silt loam to which $^{32}$P parathion was added on the surface were leached with distilled water, 0.01$N$ CaCl$_2$, 0.1$N$ HCl, and 95% ethanol. The electrolyte solutions were used to determine whether adsorption is associated with the ion adsorption capacity of the soil. Alcohol and distilled water were used to determine whether parathion is adsorbed in a water-soluble state or as a water-insoluble organic constituent of the soil. If it is adsorbed as a water-insoluble organic fraction, the alcohol leaching should readily remove the parathion from the soil. The concentrations of $^{32}$P parathion in the effluent from the columns leached with distilled water, 0.01$N$ CaCl$_2$, and ethanol are shown in Figure 2. The amount of distilled water which was in the columns before leaching was started (void volume of columns) was 36.4 ml. for the columns leached with water and 0.01$N$ CaCl$_2$ and 29.3 ml. for the column leached with ethanol. The peak concentration of parathion in the effluent from the column leached with ethanol occurred after only 31 ml. had passed through the column and after 210 ml. of water had passed through the column leached with water. It is apparent that parathion is not readily
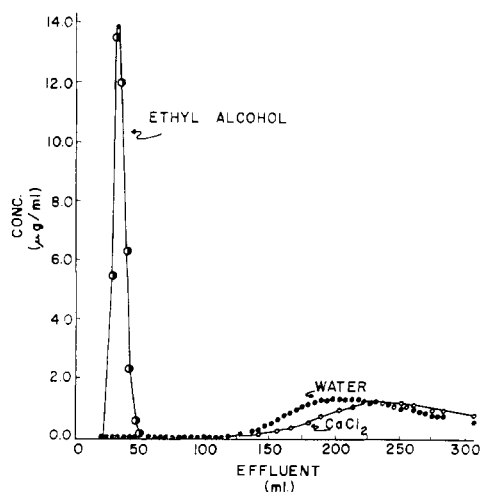
extractable with distilled water or aqueous electrolyte solutions. The effluent concentration curve from the column leached with 0.1$N$ HCl was very similar to the curve from the column leached with distilled water. The differences in the effluent curves of the water and CaCl$_2$-leached columns are believed due to the flow characteristics of the individual columns rather than the elution capabilities of the two solutions. The effluent from parathion-treated columns leached with ethanol, water, and 0.1$N$ HCl were analyzed by gas chromatography to determine if any alterations of parathion had occurred during the period of leaching.

The fact that parathion does not appear in the aqueous effluents until approximately six column volumes of water and electrolytic solutions have passed through the columns together with the low concentration of parathion in the effluents (Figure 2) indicates that something other than water solubility prevents the leaching of parathion in these soils. It is also evident that parathion adsorption is not an ion exchange process, since parathion did not appear in the effluents of the electrolyte leachates until six column volumes of solution had passed through the columns and the concentrations of parathion in the effluents were low. Since 95% ethanol easily extracts parathion from the Katy soil, it appears that part of the parathion may be adsorbed as an organic constituent of the soil as a liquid phase dissolved in the organic fraction of the soil similar to the partitioning process in liquid-liquid extractions. Ethanol and parathion are both polar compounds. The partition coefficient between the soil organic fraction and ethanol is highly in favor of ethanol, since ethanol extracts parathion very efficiently. The partitioning idea is also supported by the results shown in Figure 1. The per cent adsorption of parathion by the individual soils from aqueous solution was the same at all concentrations, indicating that the partition coefficient between the soil organic fraction and water is a constant. The partition coefficients are not the same for different soils, since the compositions of the organic fractions are not the same. Although the amount of adsorption was the same for the Hogan and Harlingen soils, the partition coefficients for the two soils are not necessarily the same since the soils contain different amounts of organic matter and some of the adsorption is associated with other characteristics of the soils.

**Movement of Parathion in Soil Columns.** The foregoing work indicates that parathion is readily adsorbed by soils from aqueous solution, and that the amount in the soil solution is very low. Therefore, laboratory experiments were designed to study the hazard of parathion leaching through soils and the possibility of contaminating underground water supplies.

Fifty-gram soil columns to which parathion had been added were leached with 17.5 cm. of distilled water. The columns were divided into 1-cm. sections and analyzed for parathion.

The movement of parathion in a column of Willacy fine sandy loam soil is shown in Figure 3. The peak concentration of parathion occurred in the 3- to 4-cm. section of the column. If no adsorption has occurred one-half of the parathion should have moved through the 50 grams of soil after 50.1 ml. of water were leached through the column. Even though two pore volumes of water



Figure 2. Parathion concentrations in effluent of Katy silt loam leached with distilled water, 0.01$N$ CaCl$_2$ and 95% ethanol
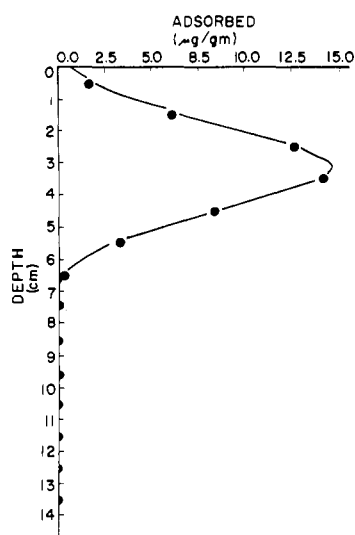
Figure 3. Distribution of parathion in a soil column of Willacy fine sandy loam after leaching with 17.5 ml. of distilled water

were passed through the Willacy soil, no parathion was found below 7 cm. From the data shown in Figure 3, it was calculated that the peak concentration of parathion had moved through 11.9 grams of soil. For the parathion to move completely through the 13.5-cm. column of soil, 422 ml. or 73.8 cm. of water would have to be passed through the column. The amount of parathion leaching in several soils is shown in Table II.

To estimate the movement of parathion which could be expected in a soil in the field from column data it is necessary to know the soil density in the column and the bulk density of the same soil in the field. Then the amount of rainfall, R, required to move parathion to a depth, L, is given by

$$R = \frac{H \rho L}{d\theta} \qquad (2)$$

where H is the height of water used to displace parathion to a depth, d, in a laboratory column. The values ρ and θ are the bulk densities of the soil in the field and columns, respectively. Assuming the bulk density of field soils to

Table II. Movement of [32]P Parathion in Soil Columns Leached with 17.5 Cm. of Water and Calculated Movement in the Field

| Soil[a] | Depth of Leaching, Cm. | Soil Density in Column, G./Cc. | Inches of H₂O Required to Leach Parathion 60 Inches[b] |
|---|---|---|---|
| Willacy f.s.l. | 3.2 | 0.65 | 755 |
| Hoban si.c.l. | 2.1 | 0.59 | 1270 |
| Harlingen c. | 2.1 | 0.58 | 1290 |
| Houston Black c. | 1.6 | 0.57 | 1725 |

[a] 50 grams of soil mixed with 12.5 grams of cellulose powder.
[b] Calculation based on a bulk density of 1.50 grams per cc.

be 1.50 grams per cc., the amount of infiltrating rainfall necessary to leach parathion through 60 inches of several soils was calculated. The results are shown in Table II. The estimated movement of parathion was very small in all soils. Even though the accuracy of these calculations is limited because of the small amount of movement which occurred, it is obvious that an extremely large amount of rainfall would be required to leach parathion below 5 feet.

Since the small amount of movement in these soils in comparison to the size of the column sections taken limits the accuracy in determining the extent of movement, it was decided that better estimates could be obtained by leaching the parathion completely through the columns and subsequently determining the distribution coefficient for parathion from the effluent data. Soil columns containing 30 grams of soil and 10 grams of filter paper pulp were leached with sufficient water to leach the parathion completely through the columns.

Figure 4 shows the concentration of ^{32}P parathion in the effluent from a column of Nacogdoches soil. The concentration of parathion in the effluent reached a maximum after 104 ml. (18.2 cm.) of water were leached through the column. The void volume, (Vv), or the volume of water necessary to remove half the parathion if no adsorption had occurred, was 35.9 ml. After the effluent concentration reached a maximum, the ^{32}P activity decreased slowly until over 260 ml. were leached through the column. Seventy-three per cent of the added parathion was recovered in 260 ml. of effluents. The maximum concentration in the effluent, 2.02 μg./ml., was well below the solubility of parathion in water. After 330 ml. were passed through the Nacogdoches column, the soil-cellulose mixture was removed from the column and each 1-cm. section extracted with acetonitrile. The amount of ^{32}P activity remaining on the soil was distributed uniformly throughout the column with the average being 0.39 μg. per gram.

The distribution coefficient for the Nacogdoches column was estimated using Equation 1. The value obtained is shown in Table III along with values for several other soils. The values ranged from 2.26 ml. per gram for the Nacogdoches subsoil to 9.97 ml. per gram for Harlingen
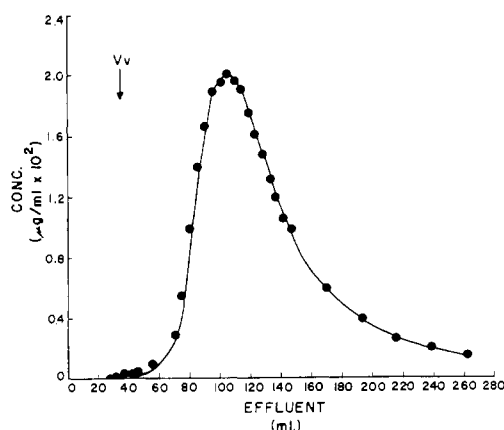


Figure 4. Concentration of parathion in the effluent from a soil column of Nacogdoches clay leached with distilled water

**Table III. Distribution Coefficients and Calculated Amounts of Infiltrating Rainfall Required to Leach Parathion to a Depth of 60 Inches in Five Texas Soils**

| Soil | $K_d$, Ml./G. | Inches of Water Required to Leach Parathion 60 Inches |
|------|------|------|
| Nacogdoches c. | 2.26 | 230 |
| Norwood si. l. | 2.36 | 240 |
| Amarillo f.s.l. | 5.13 | 490 |
| Katy s.l. | 6.05 | 575 |
| Harlingen c. | 9.97 | 930 |

clay. Larger values indicate larger volumes of water required to leach the parathion through the soil. Distribution coefficients calculated from batch experiments were found to be 4.4 ml. per gram for Nacogdoches clay and 13.2 ml. per gram for Harlingen clay. The values obtained by the two experiments are not in exact agreement. However, the methods for calculating the values are derived independent of each other and, therefore, are not necessarily an accurate measure of the same value since the $k_d$ values are extremely dependent on concentration (Swoboda, 1963) and the concentration of solution passing through a column is continually changing.

Equation 1 can be rearranged so that

$$k_d W = Vp - Vc \qquad (3)$$

Since the bulk density, $\rho$, of a soil is its weight divided by the volume it occupies, $V$, then

$$k_d \rho = \frac{Vp}{V} - \frac{Vc}{V} \qquad (4)$$

or

$$\frac{Vp}{V} = k_d \rho + \frac{Vc}{V} \qquad (5)$$

where $\frac{Vp}{V}$ is the number of column volumes of leachate required to displace half the parathion and $\frac{Vc}{V}$ is the porosity of the soil. The term $\frac{Vp}{V}$ is equivalent to the linear ratio $R/L$, where $R$ is the amount of rainfall required to leach parathion to a depth, $L$. Then,

$$R = L \left( k_d \rho + \frac{Vc}{V} \right) \qquad (6)$$

Assuming a bulk density of 1.50 grams per cc. and a porosity of 0.50, the amounts of infiltrating rainfall required to leach parathion to a depth of 60 inches were calculated for five soils and are shown in Table III. The amount of rainfall ranged from 230 inches for Nacogdoches clay to 930 inches for Harlingen clay. In Table II the

estimate for the amount of rainfall to leach parathion 60 inches in Harlingen clay is 1290 inches compared to only 930 inches calculated from the distribution coefficient equation. The discrepancy between the values obtained for the Harlingen soil is believed due to the small amount of movement which limited the results obtained in sectioning the columns in the previous experiment. However, both methods of estimating the extent of parathion movement in these soils indicate that an excess amount of rainfall would be required before leaching could be considered hazardous. The calculated values are used only to indicate that the amount of parathion movement in these soils is very slight; they do not necessarily indicate that similar rainfall values are required to leach parathion 60 inches under natural field conditions. Most soils have profile horizons which differ in pH, mineralogy, texture, organic matter, and many other chemical characteristics which influence the movement of pesticides. However, all the soils used in this study have very uniform profiles except for the Katy and Nacogdoches soils. The 60-inch depth which was used in these calculations was chosen because most soils have a soil profile of at least 5 feet. The thickness of the profile horizons from which the soils used in this study were taken ranged from 50 to 90 inches except for the Katy topsoil which is about 25 inches deep.

The movement of water in the soil columns was under saturated conditions. Since the movement of water through field soils mainly occurs as unsaturated flow, the movement of parathion would be greater under these conditions. However, the amount of evaporation or upward movement of water which occurs in field soils would probably more than offset the increased movement of parathion by unsaturated flow.

From the data presented it is very unlikely that parathion could contaminate underground water supplies beneath any of these soils by leaching under normal rainfall conditions.

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