LOSS OF PHORATE FROM A GRANULAR FORMULATION APPLIED IN THE SOIL

R. S. PATTERSON AND W. A. RAWLINS[1]
Department of Entomology, Cornell University, Ithaca, New York

ABSTRACT

In experiments conducted out of doors, most of the toxic residue from granular phorate in the soil had disappeared in the summer after 2 months. During the fall the residue persisted longer, and in the winter when the soil was frozen there was almost no loss of the residue. As indicated, phorate degradation or loss in the soil was dependent on the temperature. As the temperature of the soil was increased, the rate of disappearance of the phorate increased.

Moisture does not affect the loss of granular phorate as much as the temperature. Regardless of the soil type, very little phorate translocated through more than 3 inches of soil. By increasing the amount of water added to the soil, an increasing amount of residue was lost by translocation. However, it represented only a small fraction of the total residue. Likewise, barley plants absorbed only a very small percentage of the phorate which was present in either sandy loam or muck.

Systemic insecticides in granular formulations are being used for the control of various insects and mites. Applications are often made to the soil from which the toxicants are absorbed by the roots of plants. Because of the rather slow release of the toxicant from the deactivated carrier, granular formulations usually have a long residual life. To prevent any potential residues from accumulating in the soil which could be picked up by subsequent crops, something must be known about the residual life of the insecticide in the soil. Therefore, a study was made of the rate of loss of the systemic insecticide, phorate, in a granular formulation in the soil.

Several articles have been published on the fate of phorate in the soil under laboratory conditions. Getzin and Chapman (1959, 1960) found that in soil, phorate underwent oxidation to sulfoxides and sulfones at a more rapid rate than hydrolysis except in a quartz sand which was found free of oxidation products over a 32-day period. This difference might be due to the lack of microorganisms in the quartz sand. Ahmed and Casida (1958) found that a number of soil microorganisms were capable of oxidizing and hydrolyzing phorate in nutrient cultures. Later Getzin and Chapman (1959, 1960) discovered that when microorganisms were destroyed by sterilization, phorate was still oxidized in the various soils. They theorized that "agricultural soils provide a catalytic mechanism for phorate oxidation since oxidative derivatives of phorate were not detected in the quartz sand." Hacskaylo et al. (1961) also detected products of hydrolysis from phorate but in larger quantities than found by Getzin and Chapman.

Getzin and Chapman (1959, 1960) showed that there was a direct relationship between the amount of phorate which was bound in the soil and

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[1] Graduate Assistant and Professor of Entomology, respectively. Present address of the senior author is Entomology Research Division, Agr. Res. Serv., USDA, Gainesville, Florida 32601.

the amount of organic matter in the soil. Thus, more phorate was bound in muck than loam and more in loam than sand; none was found to be bound in the quartz sand. More of the insecticide became bound the longer it was in contact with the soil.

The loss of phorate by volatilization and leaching is also dependent on the organic matter content of the soil media as shown by Getzin and Chapman (1959, 1960) and Hacskaylo et al. (1961).

METHODS AND MATERIALS

Four separate experiments were conducted to determine the disappearance of phorate added to soil. The first two experiments were designed to determine phorate loss from barren soil and soil planted to barley during the summer months (May to September) and during the winter months (October to August). Based on the findings of the first two experiments, temperature and moisture seemed to be important factors in determining the rate of phorate loss in the soil. Therefore, the last two experiments were designed to try to determine what effect these two environmental factors had on the residual life of a granular formulation of phorate.

A bioassay technique was employed to measure the level of toxins in the soil samples. The method developed by Parker (1961) employing *Drosophila* was selected. This method gave reproducible results with either extracts or homogenates of plant tissues and soils. Rearing of the *Drosophila* flies and the routine testing were conducted under controlled environmental conditions.

Parker (1961) obtained reproducible results from directly exposing the flies to 20 g portions of soils treated with phorate. When this method was tried with soil treated with phorate granules, variability among replicates was considerable, apparently due to the uneven distribution of granules in the soil. Therefore, the entire soil sample of 100 g was extracted, and the flies were then exposed to dried films of aliquots of the extract.

A hexane-isopropanol combination was used to extract the phorate residue from soils, a procedure based on the findings of Parker (1961) who tried a number of different solvents for the removal of phorate from soil. This combination had the advantage of not requiring drying of the sample before extraction. This is very important when recovering phorate residues from field samples of moist soil.

The soil sample (100 g) to be extracted was placed in a wide-mouth quart screw-cap jar containing 200 ml of hexane and 100 ml of isopropanol. The jar was put in a shaking machine and shaken for 45 minutes. The mixture of solvents was filtered into a separatory funnel and the filtrate washed four times with approximately 100 ml of distilled water. This washing removed the isopropanol leaving the phorate residue in the hexane.

Extractions of the untreated soil were made in the same way. This filtrate was used in making a standard curve by adding prescribed amounts of phorate that would produce fly mortalities between 0 and 100%. Also, the filtrate was used for diluting any extracts of treated soil suspected of having a toxicity above the upper limits of the standard curve. A standard curve was constructed for each test run.

Five 0.5 ml aliquots were taken from each soil extract; each aliquot was pipetted into an individual 25 X 200 mm rimless test tube. The solution was distributed evenly over the inside of the tube by placing the tubes in a rotating machine. The solvent gradually evaporated leaving a dry film on the lower three-fourths of the tube. A 1.5 inch dental cotton roll, which had been dipped in a sugar-yeast solution and the upper end wrapped in a small piece of cotton, was used to plug the tubes. Into each tube 20 adult fruit flies, 24 hours old or less, were released. The mortality of the flies was recorded about 17 hours later.

EXPERIMENTS 1 AND 2

The first two experiments were conducted in the field. The soil was placed in aluminum cylinders 4 inches in diameter and 12 inches in length, and a 16 mesh screen was placed over the bottom of the cylinder to allow for drainage but prevent soil loss. In the middle of the cylinder, another screen was placed to facilitate separation of the soils in two layers in order to determine the downward movement of the toxicant in the soil. During the filling of the containers, 500 mg of 10% phorate granules were added in a layer at the middle of the upper section. Half of the cylinders in the first experiment were planted with barley seeds to determine the effect of plants on phorate loss. The cylinders were held upright in racks placed out of doors.

Thereafter at monthly intervals, five sets of containers were selected at random from each group. The soil from each can was divided and tagged according to its position, A— top, B— bottom. Each portion was thoroughly mixed to obtain an even distribution of the treated granules in the soil. Small subsamples of approximately 2 to 8 g were taken at random from this mixture to make up the 100 g samples used for determination of phorate.

Two types of soil, a Dunkirk sandy loam and a muck, were included in the first experiment. In the second experiment, four types of soil were studied, a Dunkirk sandy loam, a Dunkirk silty clay loam, a coarse sand, and a muck.

RESULTS AND DISCUSSION

Rapid loss of the toxicant occurred from both the sandy loam and the muck during the test period, May through September. In the sandy loam, the loss was very rapid for the first 2 months, then leveled off (Table 1). This may be a partial explanation for loss of toxicity to insects of potato plants in the field 2 months after being treated with phorate granules (Patterson 1962).

The phorate residue in the muck showed a steady decline for three months before leveling off (Table 2). The sandy loam in each container weighed approximately 1025 g, almost twice as much as the muck, 535 g, on a dry weight basis. Therefore, to compare the residues in the soils, the figures for the sandy loam should be almost doubled. The difference in the residues between the loam and the muck after equilibration is probably due to the binding of the phorate by the organic matter which comprises 90% of the muck.

TABLE 1.—AVERAGE PHORATE RESIDUES IN A BARREN SANDY LOAM AND IN A SANDY LOAM PLANTED WITH BARLEY, AND THE AMOUNT OF TOXICANT THAT TRANSLOCATED INTO THE LOWER HALF OF THE CYLINDER CONTAINING THE SOIL.

Date of soil extraction	Phorate residue (ppm)* in 100 g of soil		
	With barley	Without barley	Amount translocated
May (pretreatment)	23.0	23.0	
June	14.0	13.0	0.34
July	4.0	5.0	.18
August	3.2	2.4	.14
September	.4	1.12	

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

TABLE 2.—AVERAGE PHORATE RESIDUES IN A BARREN MUCK AND IN A MUCK PLANTED WITH BARLEY, AND THE AMOUNT OF TOXICANT THAT TRANSLOCATED INTO THE LOWER HALF OF THE CYLINDERS CONTAINING THE SOIL.

Date of soil extraction	Phorate residue (ppm)* in 100 g of soil		
	With barley	Without barley	Amount translocated
May (pretreatment)	30.0	30.0	
June	17.2	22.0	1.16
July	28.0	14.8	.38
August	13.0	7.0	
September	7.0	5.4	

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

No major difference was noted between the residue found in the barren sandy loam and in the sandy loam planted with barley. This observation indicated that the plants took up a relatively small proportion of the chemical present in the soil. This is in agreement with the work of Hacskaylo (1961) who stated that the cotton plant absorbed less than 5% of the total phorate residue in the soil. Although there was considerable variation among replications of the barley-muck treatment, it showed also the same general decline as the barren muck. This variation was probably caused by the excessive matting of the barley root system in the muck which made it very difficult to obtain a good clear soil sample since the muck particles cling to the root hairs.

Very little of the toxicant was found in the soil in the lower portions of the cylinder with either the muck or the sandy loam. Getzin and Chapman (1959, 1960) also found little leaching from muck soils or soil which contained as much organic matter, 1.3%, as the sandy loam.

A decline in the phorate residue was evident over the 10-month period. The rate of decline of the residue appeared to be governed by temperature.

This was illustrated by the fact that the rate of loss of the phorate was greater during the summer (May - August) than during the fall and winter (October - January). It is noteworthy that no decline in residue occurred in any of the soils during December and January, a period when the soils were frozen.

Comparing the decline of phorate residues in the four types of soil (Table 3) after corrections for the differences in the volume-weight ratio (sand-1600 g, Dunkirk sandy and silty clay loams-1025 g, and muck-535 g), the rates were similar for October to May. By June the toxicant was at a very low level. The muck had a higher phorate residue than the other soils. Getzin and Chapman (1959, 1960) reported that the more phorate that was bound to the organic matter, the longer the toxicant was in the soil.

TABLE 3.—COMPARISON OF THE RATE OF PHORATE LOSS IN FOUR TYPES OF SOIL; SAND, LOAM, CLAY, AND MUCK.

Date of soil extraction	Phorate residue (ppm)* in the top half of the cylinder containing the soil**			
	Sand	Loam	Clay	Muck
Pretreatment on				
15 October	210.0	250.0	250.0	250.0
30 October	330.0	240.0	220.0	
15 November	270.0	220.0	196.0	300.0
15 December	221.0	180.0	168.0	130.0
15 January	222.0	180.0	168.0	130.0
15 May	99.0	70.0	120.0	84.0
15 June		12.0	38.0	64.0
15 July	13.0	2.8	36.0	62.0
15 August	8.4		20.0	66.0

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

** Data have been corrected for the difference in the volume-weight ratio.

As in the previous experiment, very little residue was found in the lower portion of the cylinders (Table 4). However, the amount found varied from soil to soil apparently depending on the organic matter content of the different soils. The highest residues were found in the sand. Following in order of decreasing phorate residues were the sandy loam, silty clay loam, and muck. None of the soil samples taken from the lower portions of the cylinder contained more than a small fraction of the total phorate residue which was originally present in the cylinder.

EXPERIMENT 3

Since the results from the previous experiments indicated that the residual life of the toxicant is influenced by soil temperature, an experiment was designed to study this factor. Small portions, 250 mg of the 10% phor-

TABLE 4.—COMPARISON OF THE PHORATE RESIDUE TRANSLOCATED IN FOUR TYPES OF SOIL; SAND, LOAM, CLAY, AND MUCK OVER A 10-MONTH PERIOD.

Date of soil extraction	Phorate residue (ppm)* in the lower half of the cylinder containing the soil**			
	Sand	Loam	Clay	Muck
Pretreatment on				
15 October	0	0	0	0
30 October	4.8		0	0
15 November	3.75	1.4	0	0
15 December	2.70	.7	.6	0
15 January	4.5	1.5	.6	0
15 May	2.1	2.4	1.2	0
15 June	3.9	1.8	2.5	3.7
15 July	4.5	1.4	1.0	.6
15 August	2.1	1.4	1.5	

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

** Data have been corrected for the difference in the volume-weight ratio.

ate granular formulation, were added to 100 g soil samples of Dunkirk sandy loam and muck. These samples were held at different temperatures, 40°, 70°, 100° F. At monthly intervals five soil samples of each type were selected at random from each temperature series for analyses.

RESULTS

As shown in Tables 5 and 6, as the temperature increased the loss of phorate increased in both the muck and the sandy loam. In the sandy loam at all the temperatures, the most rapid loss of phorate was in the first 8 weeks. Likewise in the muck soil at 100° F the most rapid loss was in the first 8 weeks. At the other temperatures, the phorate residue in the muck fluctuated considerably throughout the test period.

Although an qual amount of granules was mixed in each sample of soil and the entire soil sample was extracted, there were some variations among replicates of the same treatment.

EXPERIMENT 4

Since some of the toxicant, although very little, was found in the lower portions of the cylinders in the first two experiments, some movement of the chemical occurred in the soil. In order to determine if water was the direct cause of this movement, an experiment utilizing the same cylinders as in the first two experiments was set up. Only one type of soil, a sandy loam, was used for this test. Three inches from the top of the cylinder a layer of 500 mg of the 10% granular phorate formulation was added, and the cylinder was filled with soil. Two lots of five cylinders each were pre-

TABLE 5.—COMPARISON OF THE AVERAGE RATE OF DEGRADATION OF GRANULAR PHORATE IN A DUNKIRK SANDY LOAM AT 40, 70, AND 100° F. DURING A 20-WEEK PERIOD.

Weeks after phorate treatment	Phorate residue (ppm)* in the loam held at—		
	40 F.	70 F.	100 F.
Start (pretreatment)	250	250	250
2		210	134
4	240	110	100
8	148	56	40
12	144	80	36
16	148	36	34
20	92	20	36

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

TABLE 6.—COMPARISON OF THE AVERAGE RATE OF DEGRADATION OF GRANULAR PHORATE IN A MUCK HELD AT 40, 70, AND 100° F. DURING A 20-WEEK PERIOD.

Weeks after phorate treatment	Phorate residue (ppm)* in muck held at—		
	40 F.	70 F.	100 F.
Start (pretreatment)	252	252	252
2		108	104
4	184	114	78
8	158	92	80
12	160	180	38
16	170	104	28
20	234	120	30

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

pared and left undisturbed in the greenhouse for a month. At the end of the month three additional lots of cylinders identical to the first ones were set up so that all the treatments could be carried out at one time. Water was added at the rate of 2 and 4 inches per container. Two inches of water were sufficient to completely moisten the soil; when 4 inches of water were applied there was some drainage from the bottom of the cylinder. The water was poured on the surface of the soil in small amounts so that none was lost by spilling. After the cylinders had the required amount of moisture, they were allowed to remain in the greenhouse for 4 days to permit adequate drainage and evaporation in order to facilitate taking soil samples.

RESULTS

As in the previous experiments, the results from experiment 4 clearly showed that only a small fraction of the total residue translocated more than 3 inches through the soil. By comparing the loss of the original residue after the water had been applied, it can be seen that only about 15% of the residue was translocated more than 3 inches. There was a slight relationship between the amount of moisture which was added to the soil and the amount of phorate residue translocated (Table 7). When more water was added to the soil, the amount of chemical being translocated increased slightly.

TABLE 7.—AVERAGE LOSS OF PHORATE RESIDUES IN THE SOIL AFTER ADDING 2 AND 4 INCHES OF WATER.

Inches of water added to the soil	Phorate (ppm)* in 100 g soil sample	
	Top can	Bottom can
At the start		
0 (pretreatment)	12.2	0
2	11.0	.096
4	10.4	.36
After four weeks		
0	.96	0
4	1.56	.072

* Phorate equivalent residue since no distinction can be made of the toxic metabolites in a bioassay when the parent compound is used as the standard.

Although the rate of loss of the phorate residue was tremendous in a month's time, only a slight amount of the residue was found to have translocated. The apparent increase in the toxicity of the phorate residue in the soil after the water had been added possibly was due to the fact the sulfoxides and sulfones are more potent than the parent compound. There was, however, quite a degree of variability among the replicates of the soil samples which had the phorate granules in them for 4 weeks before the water was added.

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