

- Spencer, W. F., Cliath, M. M., *Environ. Sci. Technol.* **3**, 670 (1969).
- Spencer, W. F., Cliath, M. M., *J. Agr. Food Chem.* **18**, 529 (1970a).
- Spencer, W. F., Cliath, M. M., *Soil Sci. Soc. Amer. Proc.* **34**, 574 (1970b).
- Spencer, W. F., Cliath, M. M., *J. Agr. Food Chem.* **20**, 645 (1972).
- Spencer, W. F., Cliath, M. M., *J. Environ. Qual.* **2**, 284 (1973).
- Spencer, W. F., Cliath, M. M., Farmer, W. J., *Soil Sci. Soc. Amer. Proc.* **33**, 509 (1969).
- Spencer, W. F., Farmer, W. J., Cliath, M. M., *Residue Rev.* **49**, 1 (1973).
- Standifer, L. C., Jr., Thomas, C. H., *Weeds* **13**, 302 (1965).
- Weise, A. F., Lavake, D. E., Chenault, E. W., Smith, D. T., *Proc. S. Weed Sci. Soc.* **24**, 365 (1971).
- Wright, W. L., Warren, G. F., *Weeds* **13**, 329 (1965).

Received for review March 4, 1974. Accepted July 26, 1974. Contribution from the Agricultural Research Service, U. S. Department of Agriculture, in cooperation with the California Agricultural Experiment Station, Riverside.

Translocation and Metabolism of [¹⁴C]Phorate as Affected by Percolating Water in a Model Soil-Plant Ecosystem

E. Paul Lichtenstein,* Tom W. Fuhremann, and Ken R. Schulz

A model ecosystem consisting of soils, plants, and water was utilized with corn grown in a [¹⁴C]phorate treated soil layer on top of an insecticide-free soil, while water was periodically percolated through this system. Utilizing different soil types and moist soil through which no water was percolated, the interrelationships of movement and metabolism of [¹⁴C]phorate in soils, the effects of percolating water on these processes, and the penetration, translocation, and metabolism of the insecticides in corn were investigated. Under both percolating and nonpercolating conditions, 12% of the applied radiocarbon had moved into the lower layers of agricultural soils as phorate sulfoxide and phorate sulfone. Phorate still present in the upper layers of all soils moved only in a quartz sand. Water percolated through a quartz sand, a Plainfield sand, and a Plainfield sand-silt loam mixture contained 16.4, 2.8, and 1.8% of the applied radioactivity, respectively, identified as phorate (with

quartz sand only), phorate sulfoxide, and phorate sulfone. Although all soils still contained phorate, only its metabolites were found in plants. Roots contained primarily phorate sulfone and some phorate sulfoxide, while greens also contained phoratoxon sulfoxide and phoratoxon sulfone. It appears that roots of corn plants absorbed phorate from the soil and metabolized it into its sulfoxide and sulfone or absorbed these metabolites directly from the soil, then translocated them into the greens, where their further oxidation into their oxygen analogs (phosphorothiolates) presumably occurred. Roots of plants grown in a quartz sand contained 2.5-5 times more phorate-derived materials than those grown in an agricultural soil. However, the amounts of ¹⁴C-labeled materials that had been translocated into the corn greens were similar with all soils, indicating that the uptake and translocation of chemicals from soil are to a large extent governed by physiological processes of the corn plant itself.

The insecticide phorate (*O,O*-diethyl *S*-(ethylthiomethyl)phosphorodithoate) is often applied to soil for the control of soil insects, such as corn rootworms and wireworms. Its conversion in soils into its sulfoxide and sulfone has been described by Getzin and Chapman (1960) under greenhouse and laboratory conditions, while Lichtenstein (1966) and Suetz (1971) recovered these metabolites under field conditions from soils previously treated with phorate. Lichtenstein *et al.* (1973) also studied the effects of application methods on the persistence and metabolism of the insecticide in an agricultural soil under field conditions. The movement of phorate and/or its metabolites in soils from the application site to other areas has received relatively little attention. Based on bioassay results, Patterson and Rawlins (1968) reported that after the application of insecticide granules to soil columns, "very little phorate was translocated through more than 3-in. of soil." Schulz *et al.* (1973) showed that phorate residues moved under field conditions both vertically and horizontally after band applications of the granular insecticide at the rates of 5 and 10 lb/acre, and that contrary to findings with emulsifiable concentrates, phorate persisted longer.

The effects of percolating water on the persistence and movement of a soil-applied insecticide present another problem, since the chemical could be removed with water to areas where it might be unwanted. Another aspect of mobility pertains to the penetration of insecticide soil residues into roots of crop plants and their subsequent translocation and metabolism within the plant system. The metabolism of phorate in some plants was studied by Metcalf *et al.* (1957) with cotton and lemon leaves after topical application of [³²P]phorate to the leaves, or by "cutting stems of mature cotton leaves and placing them into a water dispersion of the compound." Bowman and Casida (1957) treated seeds of cotton and peas with [³²P]phorate and analyzed the foliage of the plants that grew from these seeds. In both studies the major metabolites found were phorate sulfoxide, phorate sulfone, phoratoxon sulfoxide, and phoratoxon sulfone. Corn silage and carrots grown in a phorate treated soil under field conditions contained small residues of phorate sulfone (Lichtenstein *et al.*, 1973). Potato tubers grown in the same soils did not contain measurable amounts of insecticide residues.

This present study was conducted with a model system that consisted of soils, corn plants, and water. With this entity we attempted to investigate the interrelationships of movement and metabolism of [¹⁴C]phorate in different soil types, the effects of water percolating through these

*Department of Entomology, University of Wisconsin, Madison, Wisconsin 53706.

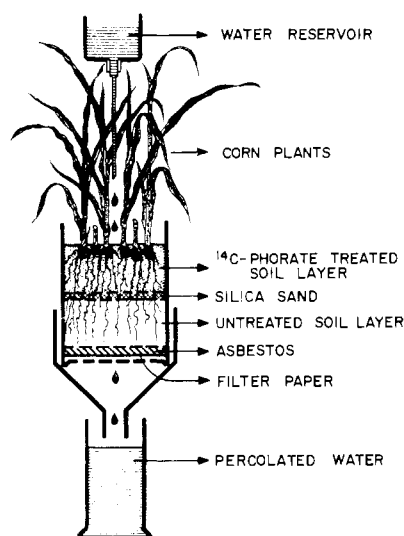


Figure 1. Model ecosystem consisting of ^{14}C -treated and untreated soil layers with corn plants growing therein and water percolating through them.

soils on these processes, and the penetration, translocation, and metabolism of the insecticide in corn plants that grew in these soils under leaching and nonleaching conditions.

MATERIALS AND METHODS

Chemicals. Phorate, [*methylene*- ^{14}C]phorate (specific activity 9.7 mCi/mmol), phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone were obtained through the courtesy of the American Cyanamid Co. [^{14}C]Phorate was diluted with nonradioactive insecticide before its addition to soils. The solvents used were redistilled chloroform, benzene, acetone, and acetonitrile and toluene, methanol, and nitromethane.

Experimental Design. Since previous investigations usually studied only one facet of the objectives mentioned above, a model ecosystem was devised which made it possible to investigate these problems as an entity in which one parameter was related to others. This system is illustrated in Figure 1 and consisted basically of soils, corn plants, and percolating water. A 350-g soil layer—previously treated with a chloroform solution of [*methylene*- ^{14}C]phorate at 1.2–1.7 ppm—was placed within a 1-qt ice cream carton on top of a 350-g untreated soil layer. Seven field-corn seedlings (Funk Hybrid G4444, blight resistant) were then planted in the surface of the top phorate treated soil layer and grown for 17 days in a growth chamber (12-hr light at 28° and 12-hr dark at 20°). The weight of each container was determined and maintained by the daily addition of water which amounted to approximately 600 ml during the 17-day period. In addition, 200 ml of water was added (1 drop/5 sec) to each soil column on days 1, 7, and 14 resulting each time in the collection of approximately 150 ml of water which had passed through each carton. The 200 ml of water added to each soil column for percolation was equivalent to 1.39 in. (3.52 cm) of rainfall.

To study the effects, if any, of percolating water on movement and persistence of the insecticide, identical experiments (controls) were conducted, except that no water was percolated through the soil columns. Soils were kept moist, however, by the daily addition of water (a total of 800 ml during the 17-day period) to maintain their initially determined weight.

Harvest and Preparation of Samples. Seventeen days after planting the corn seedlings, greens were cut, 1 cm above the soil surface, rinsed with tap water, measured

and weighed. Each ice cream carton was then opened vertically by means of a razor blade. The upper soil layer was separated from the lower one by cutting through the quartz (silica) sand separation layer. Roots from each soil layer were removed and rinsed with tap water. Ultimately, two soil layers, corn roots from each layer, corn greens, asbestos filters, and three samples of percolated water were available for extraction and analyses.

Extraction and Analyses. Extraction of soils, crops, and the lower filters as well as cleanup of the extracts were performed as described by Lichtenstein *et al.* (1973). Percolated water was first tested for its insecticidal properties, if any, by placing 20 third instar mosquito larvae (*Aedes aegypti* L.) into each of three 10-ml aliquots of each water sample. After a 48-hr exposure period, mortality counts were performed. The remaining water was then extracted three times with 70-ml portions of benzene which were combined, dried over anhydrous sodium sulfate, concentrated, and adjusted to volume for analyses. These proceedings resulted in benzene and water extraction phases from all materials for subsequent analyses.

Analyses of the benzene extraction phases were conducted by gas-liquid chromatography (glc) and thin-layer chromatography (tlc) as described by Lichtenstein *et al.* (1973). Analyses of the benzene and water extraction phases by liquid scintillation counting (LSC) and autoradiography of the thin-layer plates were performed as described by Lichtenstein *et al.* (1972). Unextracted radioactivity ("Bound" in tables and figures) in the previously extracted soil or plant materials was determined by their combustion in a Packard Tri-Carb Model 305 sample oxidizer as described by Flashinski and Lichtenstein (1974).

EXPERIMENTAL SECTION

To test the effects of soil types on the persistence, movement, translocation, and metabolism of [^{14}C]phorate, the described experiments were conducted with Plainfield sand (organic matter 1.2%, sand 89.8%, silt 8%, and clay 1%), with a 1:1 mixture (organic matter 3%, sand 53%, silt 35%, and clay 9%) of a Plainfield sand and a Plano silt loam, and with a pure quartz sand (sand 100%) of no sorptive capacity. The movement and metabolism of [^{14}C]phorate in the absence of biological material were also studied with a quartz sand, but without plants.

With a Plainfield Sand. Six experimental units as shown in Figure 1 were established with a Plainfield sand whose upper layer had been treated with [^{14}C]phorate at 1.7 ppm (3.64 μCi). Three of these units were not percolated with water but were kept moist, while water was periodically percolated through the remaining three. Results obtained under nonleaching conditions are summarized in Table I. Recovery of radiocarbon from the total system was 85% of the amount originally applied to the upper soil layer. Of that 80% were associated with the soil and 3.6% with the corn plants. Although no water had percolated through this soil, some movement of ^{14}C -labeled materials into the untreated lower soil layer had occurred. This layer contained 12% of the applied radioactivity at the end of the 17-day period. The major portion (76% of applied) of the ^{14}C -labeled compounds in the soil was benzene soluble and only 0.5% partitioned into the water extraction phase. This indicated that little or no breakdown of [^{14}C]phorate into water-soluble metabolites had taken place in the soil. Analyses by glc of the benzene extraction phases showed that the upper soil layer still contained phorate (30% of the applied or 0.52 ppm), but also contained phorate sulfoxide (31% of applied phorate or 0.53 ppm) and some phorate sulfone (3.5% of applied phorate or 0.06 ppm). The latter two compounds were the only ones found in the lower soil layer where the more water-soluble phorate sulfone (5.8% of applied or 0.10 ppm) was the major material. These data were qualitatively confirmed by tlc and autoradiography. Neither phoratoxon

Table I. Fate and Metabolism of [¹⁴C]Phorate in a Soil (Plainfield Sand)-Plant Ecosystem^a

Substrates	Recovered from extraction phases							
	In % of applied radiocarbon ^b				Benzene phase, ppm ^c			
	Benzene	Water	Bound ^d	Total	Phorate	P. sulfoxide	P. sulfone	As T % A ^e
Soil (S)								
Upper layer (treated)	65.1 ± 1.5 ^h	0.4 ± 0.04 ⁱ	2.4 ± 0.1	67.9 ^f	0.52 ± 0.03 ^k	0.53 ± 0.01 ^h	0.06 ± 0.00 ^g	64.8 ^h
Lower layer	10.9 ± 0.8	0.1 ± 0.02	1.4 ± 0.3 ^j	12.4	N.D. ^f	0.07 ± 0.01	0.10 ± 0.01	9.9 ^h
Corn (C)								
Greens	1.3 ± 0.2 ^h	1.3 ± 0.2 ^h	0.4 ± 0.1 ^k	3.0 ^h	N.D.	0.36 ± 0.02	0.44 ± 0.03	1.3
Roots								
Upper layer	0.2 ± 0.03	0.1 ± 0.02 ⁱ	0.1 ± 0.02 ^k	0.4 ^k	0.04 ± 0.01	0.30 ± 0.03	0.08 ± 0.02	0.2
Lower layer	0.05 ± 0.02	0.07 ± 0.02 ^j	0.04 ± 0.02	0.2	N.D.	0.08 ± 0.01	0.06 ± 0.01	0.09 ⁱ
Total (S + C)	77.6	2.0	4.3	83.9				76.3
Asbestos (A)	1.1 ± 0.8 ^g	-0.2 ± 0.03		1.3 ^g	N.D.	0.19 ± 0.11 ^g	0.15 ± 0.11 ^h	1.42 ^g
Total (S, C, A)	78.7	2.3	4.3	85.3				77.7

^a After 17 days of corn plant growing in the insecticide treated soil. Results are means and standard deviations of triplicate tests. ^b 3.64 μ Ci of [¹⁴C]phorate applied to the upper soil layer of a Plainfield sand (Tables I and II) and 2.2 μ Ci of a quartz sand (Tables III and IV). Determined by LSC of initially extracted soil samples. ^c [¹⁴C]Phorate applied at 1.71 ppm to the upper 350-g soil layer of the Plainfield sand (Tables I and II) and at 1.2 ppm to the upper 350-g layer of the quartz sand (Tables III and IV). Determined by glc of the initially extracted soil samples. ^d ¹⁴C determined after combustion of previously extracted soil or plant material. ^e Total of phorate, phorate sulfoxide, and phorate sulfone in per cent of applied phorate. ^f N.D. = nondetectable; TR = trace. ^{g-k} Results obtained with nonpercolated (Tables I and III) and percolated (Tables II and IV) soils are significantly different at the (g) 0.1%, (h) 1%, (i) 2%, (j) 5%, and (k) 10% levels.

nor its sulfoxide or sulfone was detected in these soils by glc or tlc.

Corn plants grown in these soils, however, contained some of these metabolites in their greens. ¹⁴C-Labeled materials recovered from the total plants (Table I) amounted to 3.6% of the applied insecticide of which the major portion (3% of applied) was associated with the green plant parts. Contrary to results with soils, relatively large amounts of water-soluble ¹⁴C-labeled materials (1.5% of the applied dose) were recovered, representing nearly 50% of the total radioactivity found in plants. In soils, however, the water-soluble ¹⁴C amounted to only 0.6% of the total ¹⁴C that was recovered.

Analyses by glc of the benzene extraction phases of plant material confirmed quantitatively the results obtained by LSC. Although 30% of the applied phorate was still present in the soil, the plants contained only its sulfoxide and sulfone, primarily located in the greens. Analyses of the roots and greens by tlc and autoradiography indicated that roots primarily contained phorate sulfone and some phorate sulfoxide, but no phorate. Greens, however, also contained phoratoxon sulfone and phoratoxon sulfoxide. Removal of the corresponding ¹⁴C-containing areas from the thin-layer plate and quantitative determination of their radioactivity by LSC showed the following: of the total radioactivity recovered from an aliquot of a benzene extract of corn leaves, 26% was attributable to phorate sulfoxide (R_f 0.27), 59% to phorate sulfone (R_f 0.64), 3% to phoratoxon sulfoxide (R_f 0.04), and 12% to phoratoxon sulfone (R_f 0.39). It appears, therefore, that roots of corn plants either absorbed phorate from the soil and metabolized it into its sulfoxide and sulfone or absorbed these metabolites directly from the soil, followed by their translocation into the greens. It was here where their further oxidation into their oxygen analogs (phosphorothiolates) presumably occurred. Although the roots were surrounded by relatively large amounts of insecticides, the amounts of metabolites recovered from roots were relatively small, possibly due to their removal by translocation into corn greens.

Table II summarizes the results obtained from the three Plainfield sand units through which water had been percolated 1, 7, and 14 days after the planting of corn seed-

lings. These results were statistically compared (*t* test) with those obtained under nonpercolating conditions (Table I, footnotes *g-k*). Although the total recovery of radiocarbon (S, C, A in Table I and S, C, A, W in Table II) under nonleaching and leaching conditions was identical, both the upper soil layer through which water had percolated and the corn plants from these soils contained less ¹⁴C-labeled compounds (61.8 and 1.94% of applied, respectively) than under nonleaching conditions. Conversely, the lower asbestos filter contained 4.5 times more ¹⁴C-labeled compounds due to the movement of water through it. Percolation of water through the system caused a movement of insecticide material from the treated soil layer through the untreated soil and the asbestos filter, resulting in the contamination of the percolated water with ¹⁴C-labeled compounds. Phorate, phorate sulfoxide, and phorate sulfone were recovered from these soils, but the amounts in the upper soil layer were smaller than those recovered from the same layer of nonpercolated soil. Due to water movement the concentration of the more water-soluble phorate sulfone was 3.3 times larger in the lower soil layer than in the upper one. This figure was 1.7 under nonpercolating conditions.

Corn plants grown in percolated soil contained phorate sulfoxide and phorate sulfone at concentrations identical with those observed under nonpercolating conditions. The actual amounts of ¹⁴C-labeled materials, however, were smaller under percolating conditions which had resulted in a reduced production of corn greens.

Water, collected after percolation through the soil, was noninsecticidal as evidenced by bioassays with mosquito larvae. Glc analyses of the benzene extraction phases confirmed that the concentrations of insecticidal materials in the water were below the lethal dose for this type of insecticide (Lichtenstein *et al.*, 1966). The translocation of ¹⁴C-labeled materials from soil with water did not occur at once (Table II) but increased with later percolation. While only negligible amounts of radiocarbon were present in the first percolate, 82% of the total radioactivity recovered from all the percolated water was associated with the third percolate on day 14. Only phorate sulfoxide (1.6% of applied phorate) and phorate sulfone (0.8% of applied) were found in the water. Since the water solubility

Table II. Fate and Metabolism of [¹⁴C]Phorate in a Soil (Plainfield Sand)-Plant-Water Ecosystem^a

Substrates	Recovered from extraction phases							As T % A ^e
	In % of applied radiocarbon ^b				Benzene phase, ppm ^c			
	Benzene	Water	Bound ^d	Total	Phorate	P. sulfoxide	P. sulfone	
Soil (S)								
Upper layer (treated)	60.4 ± 0.82 ^h	0.2 ± 0.07 ⁱ	1.2 ± 0.20	61.8 ^e	0.46 ± 0.02 ^h	0.46 ± 0.00 ^h	0.04 ± 0.00 ^e	56.1 ^h
Lower layer	12.0 ± 0.56	0.1 ± 0.01	0.70 ± 0.16 ^j	12.8	N.D. ^f	0.10 ± 0.02	0.13 ± 0.02	13.4 ^k
Corn (C)								
Greens	0.7 ± 0.02 ^h	0.7 ± 0.05 ^h	0.1 ± 0.03 ^k	1.5 ^h	N.D.	0.38 ± 0.05	0.40 ± 0.04	0.80
Roots								
Upper layer	0.15 ± 0.01	0.07 ± 0.00 ⁱ	0.07 ± 0.01 ^k	0.29 ^k	0.04 ± 0.00	0.27 ± 0.05	0.06 ± 0.02	0.17
Lower layer	0.06 ± 0.00	0.05 ± 0.01 ^j	0.04 ± 0.01	0.15	N.D.	0.24 ± 0.15	0.19 ± 0.12	0.20 ^t
Total (S + C)	73.3	1.1	2.1	76.5				70.6
Percolated water (W)								
Day 1	0.01 ± 0.01	0.05 ± 0.01		0.06	N.D.	N.D.	N.D.	
Day 7	0.23 ± 0.02	0.21 ± 0.02		0.44	N.D.	0.01 ± 0.00	N.D.	0.3
Day 14	1.93 ± 0.34	0.33 ± 0.02		2.26	N.D.	0.05 ± 0.02	0.03 ± 0.8	2.1
Asbestos (A)	5.63 ± 0.31 ^e	0.17 ± 0.00		5.80 ^e	N.D.	1.14 ± 0.02 ^e	0.65 ± 0.05 ^h	7.4 ^e
Total (S, C, W, A)	81.1	1.9	2.1	85.1				80.4

^a After percolation of water through the soil (1, 7, and 14 days after soil treatment with [¹⁴C]phorate) and growing of corn plants in it. Results are means plus standard deviation of triplicated tests. ^{b-k} See corresponding footnotes in Table I.

Table III. Fate and Metabolism of [¹⁴C]Phorate in a Quartz Sand-Plant Ecosystem^a

Substrates	Recovered from extraction phases							As T % A ^e
	In % of applied radiocarbon ^b				Benzene phase, ppm ^c			
	Benzene	Water	Bound ^d	Total	Phorate	P. sulfoxide	P. sulfone	
Soil (S)								
Upper layer (treated)	1.73 ± 0.07 ^e	0.08 ± 0.01 ^h	0.38 ± 0.15 ^k	2.19 ^h	0.01 ± 0.00	0.01 ± 0.00	TR ^f	1.58 ^e
Lower layer	2.02 ± 0.18 ^h	0.10 ± 0.02 ^h	0.18 ± 0.07	2.20 ⁱ	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00 ^h	2.37 ⁱ
Corn (C)								
Greens	0.72 ± 0.16	2.32 ± 0.38 ^h	0.60 ± 0.22	3.64 ^j	N.D. ^f	0.13 ± 0.04	0.14 ± 0.04	0.69
Roots								
Upper layer	0.16 ± 0.02 ^h	0.53 ± 0.05 ^h	0.31 ± 0.01 ^h	1.00 ^e	N.D.	0.30 ± 0.13	0.15 ± 0.03 ⁱ	0.49 ^k
Lower layer	0.26 ± 0.05	0.45 ± 0.02 ^h	0.34 ± 0.01	1.05 ^k	N.D.	0.10 ± 0.01	0.13 ± 0.01 ^k	0.26
Total (S + C)	4.89	3.48	1.81	10.18				5.39
Asbestos (A)	16.72 ± 2.4 ^j	1.09 ± 0.22 ⁱ		17.81 ^j	0.08 ± 0.01 ^e	2.45 ± 0.34 ^k	0.26 ± 0.02	17.16 ^j
Total (S, C, A)	21.61 ^h	4.57	1.81 ^h	27.99 ^h				22.55

^a After 17 days of corn plant growing in the insecticide treated sand. Results are means and standard deviations of triplicate tests. ^{b-k} See corresponding footnotes in Table I.

of these metabolites is greater than that of phorate (American Cyanamid, private communication), they are more easily leached with water. Their absence in the first and practically also in the second percolate could be indicative of their slow movement in the Plainfield sand or possibly could point to a relatively slow production of these metabolites in soils under percolating conditions.

With Quartz Sand. To determine the effects of an agricultural soil on insecticide persistence and movement, identical experiments as described above were conducted with a quartz sand, a "soil" of no sorptive capacity. In these tests, the upper sand layer had been treated with [¹⁴C]phorate at 1.2 ppm (2.2 μCi) and was separated from the lower one by a thin layer of a Plainfield sand. To prevent excessive volatilization of the insecticide from the sand, a seven-hole perforated plastic sheet was placed on top of the treated sand layer after shoots had emerged. In spite of this partial barrier, the total recovery of ¹⁴C-la-

beled materials under nonpercolating conditions (Table III) amounted to only 28% of the applied dosage, thus indicating an unaccountable loss of over 70%, probably due to volatilization. With Plainfield sand (Table I) a loss of only 15% had occurred. The greater mobility of ¹⁴C-labeled compounds in the quartz sand is also indicated by their relatively high concentrations in the lower asbestos filter where two-thirds of the total radioactivity remaining was recovered.

In contrast to the results with the agricultural soil, the lower originally untreated quartz sand layer contained the same amounts of ¹⁴C-labeled materials as did the upper one. The actual amounts of radioactivity left in the two quartz sand layers, however, were quite small. Even though the quantity of phorate and its metabolites was low, whole corn plants contained more ¹⁴C-labeled compounds (5.69% of applied) than those grown in the Plainfield sand (3.6% of applied). Just as the insecticide mate-

Table IV. Fate and Metabolism of [¹⁴C]Phorate in a Quartz Sand-Plant-Water Ecosystem^a

Substrates	Recovered from extraction phases							As T % A ^e
	In % of applied radiocarbon ^b				Benzene phase, ppm ^c			
	Benzene	Water	Bound ^d	Total	Phorate	P. sulfoxide	P. sulfone	
Soil (S)								
Upper layer (treated)	1.04 ± 0.11 ^f	0.04 ± 0.01 ^h	0.13 ± 0.12 ^k	1.21 ^h	0.01 ± 0.00	0.01 ± 0.00	TR	0.98 ^f
Lower layer	1.39 ± 0.15 ^h	0.04 ± 0.00 ^h	0.14 ± 0.07	1.57 ⁱ	0.01 ± 0.00	0.01 ± 0.00	TR	0.98 ⁱ
Corn (C)								
Greens	0.50 ± 0.15	0.99 ± 0.31 ^h	0.31 ± 0.13	1.80 ^j	N.D. ^f	0.13 ± 0.04	0.12 ± 0.03	0.70
Roots								
Upper layer	0.09 ± 0.02 ^h	0.18 ± 0.06 ^h	0.12 ± 0.05 ^h	0.39 ^e	N.D.	0.15 ± 0.05	0.07 ± 0.03 ⁱ	0.23 ^k
Lower layer	0.29 ± 0.06	0.26 ± 0.05 ^h	0.29 ± 0.05	0.84 ^h	N.D.	0.16 ± 0.05	0.10 ± 0.01 ^k	0.27
Total (S + C)	3.31	1.51	0.99	5.81				3.16
Percolated water (W)								
Day 1	0.02 ± 0.01	0.73 ± 0.12		0.76	N.D.	TR ^f	TR	TR
Day 7	3.32 ± 0.81	0.71 ± 0.39		4.03	0.01 ± 0.00	0.09 ± 0.02	TR	3.51
Day 14	10.84 ± 1.3	0.77 ± 0.15		11.6	0.01 ± 0.00	0.25 ± 0.03	0.01 ± 0.00	10.76
Asbestos (A)	28.42 ± 5.5 ^j	0.47 ± 0.14 ⁱ		28.89 ^j	0.99 ± 0.16 ^e	3.65 ± 0.84 ^k	0.13 ± 0.13	29.29 ^j
Total (S, C, W, A)	45.91 ^h	4.19	0.99 ^h	51.09 ^h				46.62

^a After percolation of water through the sand (1, 7, and 14 days after sand treatment with [¹⁴C]phorate) and growing of corn plants in it. Results are means plus standard deviations of triplicated tests. ^{b-k} See corresponding footnotes in Table I.

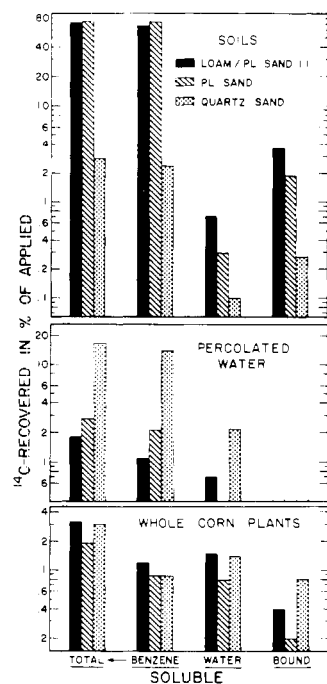


Figure 2. Effects of soil types on the persistence of [¹⁴C]phorate in soils, on the movement of ¹⁴C-labeled compounds with water, and on their translocation into corn plants. Data depict the total ¹⁴C recovered from soils, the total percolated water, and whole corn plants.

rials moved to a larger extent in the quartz sand, they also penetrated the roots at an increased rate: these roots contained 2.5 to 5 times more phorate-derived materials than those grown in the Plainfield sand. However, the amounts of ¹⁴C-labeled materials that had been translocated from roots into the corn greens were similar with both soils. Amounts of water-soluble ¹⁴C-labeled compounds in greens from a quartz sand were about 3 times larger than benzene-soluble compounds, while in plants from the agricultural soil these amounts were equal. Qualitative results obtained by glc were identical with those obtained with corn grown in the Plainfield sand soil.

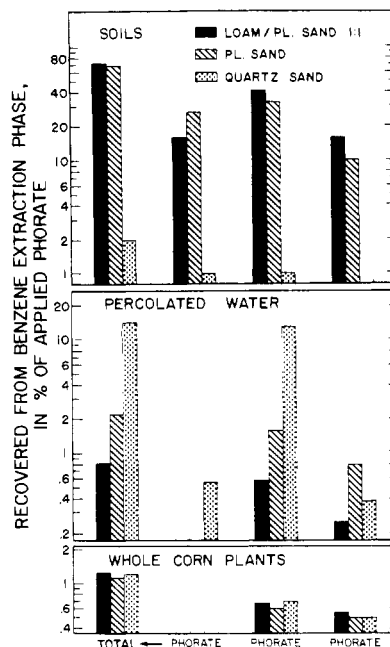


Figure 3. Metabolism of phorate after its application to soils. Data depict the total amounts of metabolites recovered by glc from the benzene extraction phases of soils, all the percolated water, and whole corn plants.

The effects of water percolating through quartz sand are demonstrated by data in Table IV. The most striking feature was the increased recovery of ¹⁴C-labeled compounds (51% of applied) under percolating conditions in comparison to recoveries from the unpercolated units (Table III). Movement of water through the sand resulted in an increased removal of phorate derivatives, as indicated by the smaller amounts left in the quartz sand and the relatively large amounts that were retained by the lower asbestos filter or that percolated with water through the system (56 and 32% of the total recovered radiocarbon, respectively). Since percolating water had removed insecticides from the quartz sand, corn grown therein also contained significantly less ¹⁴C-labeled compounds.

Although the sorptive capacity of the quartz sand is negligible in comparison to agricultural soils, only small amounts of ^{14}C -labeled compounds appeared in the first percolate, while two-thirds of the ^{14}C -labeled compounds that were removed with water from the system appeared in the third percolate on day 14. This seemed to indicate a relatively slow movement with water through the quartz sand or the filters. Phorate sulfoxide was the major insecticidal substance in the water, but some phorate was also present. Phorate sulfone, which was not detected in the quartz sand, appeared in the third percolate (0.01 ppm) and amounted to 0.4% of the applied phorate. The presence of insecticidal substances in the percolated water was also demonstrated by insect mortalities after the exposure of mosquito larvae for 48 hr to 10-ml aliquots of this water. While no insect mortalities were noticed with the first percolate, 22 and 58% of the insects died after exposure to the second and third percolates, respectively.

Experiments as described with a quartz sand and percolated water, but without plants, showed that phorate sulfoxide was the major insecticidal constituent in the percolate. This indicated that the oxidation of phorate to its sulfoxide was independent of the presence of plants.

Data obtained with a 1:1 mixture of a Plano silt loam and Plainfield sand were not too different from those obtained with a Plainfield sand and are, therefore, omitted in tabulated form. However, a summary of the effects of soil types includes data obtained with the soil mixture in Figures 2 and 3. Data utilized in these summaries were selected from soils through which water had been percolated and include only the sum of residues recovered from the upper and lower soil layers, from greens and roots, and the sum of residues from all three water percolations. The effects of soil type on the fate of [^{14}C]phorate under percolating conditions are evident (Figure 2) when comparisons are made between the total or the benzene-soluble ^{14}C -labeled compounds retained by the soils with those that appeared in the percolated water. The amount of benzene-soluble ^{14}C -labeled compounds was smallest in the quartz sand but largest in the water which had percolated through it. The amounts of water-soluble and unextractable radioactivity appeared to be directly related to

the total amounts of radiocarbon in these soils. Residues in corn, primarily concentrated in the greens, were similar with plants from all the soils, indicating that the uptake and translocation of chemicals from soil are to a large extent governed by physiological processes of the corn plant itself.

A summary of the results obtained by glc of the various benzene extraction phases is presented in Figure 3. Water, percolated through the quartz sand, contained the largest amounts of phorate sulfoxide, but also contained phorate, which was not detectable in water that percolated through the two agricultural soils. Based on glc, residues in corn plants consisted of phorate sulfoxide and phorate sulfone and were similar in plants from all soils.

ACKNOWLEDGMENT

The authors are grateful to T.T. Liang for his technical assistance.

LITERATURE CITED

- Bowman, J.S., Casida, J.E., *J. Agr. Food Chem.* **5**, 192 (1957).
 Flashinski, S.J., Lichtenstein, E.P., *Can. J. Microbiol.* **20**, 399 (1974).
 Getzin, L.W., Chapman, R.K., *J. Econ. Entomol.* **53**, 47 (1960).
 Lichtenstein, E.P., *Nat. Acad. Sci. Nat. Res. Council. Publ. No.* **1402**, 221 (1966).
 Lichtenstein, E.P., Fuhremann, T.W., Schulz, K.R., Liang, T.T., *J. Econ. Entomol.* **66**, 863 (1973).
 Lichtenstein, E.P., Schulz, K.R., Fuhremann, T.W., *J. Agr. Food Chem.* **20**, 831 (1972).
 Lichtenstein, E.P., Schulz, K.R., Skrentny, R.F., Tsukano, Y., *Arch. Environ. Health* **12**, 199 (1966).
 Metcalf, R.L., Fukuto, T.R., March, R.B., *J. Econ. Entomol.* **50**, 338 (1957).
 Patterson, R.S., Rawlins, W.A., *Fla. Entomol.* **51**, 143 (1968).
 Schulz, K.R., Lichtenstein, E.P., Fuhremann, T.W., Liang, T.T., *J. Econ. Entomol.* **66**, 873 (1973).
 Suett, D.L., *Pestic. Sci.* **2**, 105 (1971).

Received for review May 17, 1974. Accepted August 9, 1974. Research supported by the College of Agricultural and Life Sciences, University of Wisconsin, Madison, and by a grant from the National Science Foundation (GB-3502). Contribution by project 1387 from the Wisconsin Agricultural Experiment Station as a collaborator under North Central Regional Cooperative Research Project 96, entitled "Environmental Implications of Pesticide Usage."

Further Toxicity Studies with Antimycin, A Fish Eradicant

Erminio Greselin* and Ferenc Herr

Further toxicological studies on antimycin (Fintrol) are presented. Previously reported acute toxicity studies indicated that antimycin has a very low toxicity for mammals and chronic toxicity did not reveal any deleterious effects. These additional studies were designated to determine whether antimycin-treated waters and antimycin-killed fish contained toxic degradation products. Antimycin-treated water was given to dogs and rats as the sole source of drinking water and

antimycin-killed fish were administered to dogs and rats as one-half of their diet. Both tests lasted 3 months. In both studies no toxic effects were noticed in the animal which drank the treated water or which ate fish killed by antimycin. A decrease in food consumption was observed in a few dogs and rats at the beginning of the test. It was not considered toxic manifestation but it was clearly the reaction of the animals to the bitter taste of the compound.

Antimycin (Fintrol) is a compound with antifungal and antibacterial properties (Leben and Keitt, 1948) which has an unusually high toxicity for fish (Derse and Strong, 1963), but a relatively low toxicity for mammals (Herr *et*

al., 1967). Its applications as a piscicidal agent have been reviewed recently by Lennon and Vezina in Pezلمان (1973).

Acute and chronic toxicity studies with this compound previously performed in several species of mammals provide evidence for the safety in its use at concentrations toxic to fish (Leben and Keitt, 1948). In solution, antimycin is rapidly degraded (Derse and Strong, 1963). By

*Ayerst Research Laboratories, Montreal, Quebec, Canada H3C 3J1.