

# TRANSPORT MECHANISM IN SOIL†

## METABOLISM AND MOVEMENT OF INSECTICIDES FROM SOILS INTO WATER AND CROP PLANTS

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### ABSTRACT

The persistence, movement and metabolism of insecticides in soils are affected by various environmental conditions. Field data are presented, showing that phorate—after granular band application—moved in both horizontal and vertical directions. Phorate sulphone was the major metabolite recovered. The metabolism and persistence of this insecticide was also affected by its mode of application. Utilizing a soil–plant–water ecosystem, it was demonstrated that the percolation of water through this system did not affect the movement of [<sup>14</sup>C]-phorate through loam soils, but did so with soils of lesser or no sorptive capacity. Water percolated through agricultural soils contained phorate metabolites (phorate sulphoxide and phorate sulphone), while corn greens grown in this system contained in addition phoratoxon sulphoxide and phoratoxon sulphone. With [<sup>14</sup>C]-Dyfonate it was shown that the insecticide did not move to an appreciable extent through an agricultural loam soil and its transport with water through soils was, to a large extent, a function of the soil type. Detergents, having increased the persistence of parathion in soil, indirectly increased the amount of parathion within the percolated water. The presence of salts prevented the appearance of aldrin residues in percolated water and reduced the amount of parathion residues. Movement of insecticides from soils into plants was shown to be dependent on energy supply systems of root cells, soil nutrients and soil insecticide concentrations.

### INSECTICIDE PERSISTENCE

The persistence and metabolism of an insecticide in soils is a function of the chemical nature of the pesticide itself and of a whole variety of environmental factors<sup>1</sup>. Attempts have been repeatedly made to define persistence, yet no clear-cut definition could be obtained. This was the result of the dependence of the persistence of a pesticide on the multitude of environmental factors. However, after the application of several insecticides at the same rate, at the same time, in the same way and to the same soil type in Madison, Wisconsin, strict comparisons about the relative persistence of various insecticides could be made and expressed as percentage of the applied dose

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† To illustrate various principles and points in this presentation, data were used that primarily had been obtained through research in our own laboratory at the University of Wisconsin. This was done for sake of convenience only, although many scientists at various institutions are conducting excellent research in this particular field of interest.

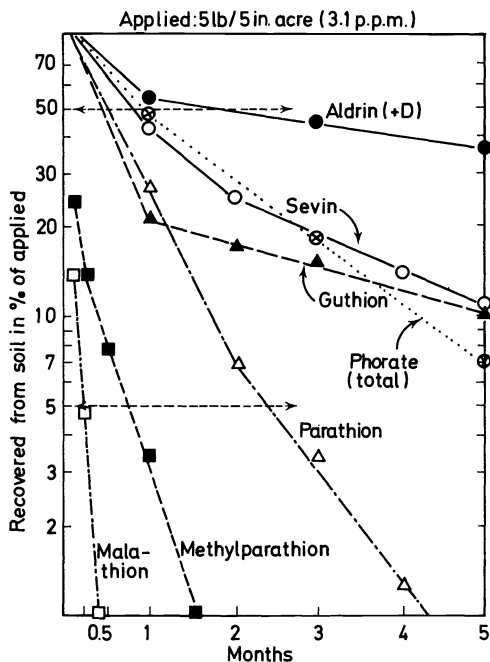


Figure 1. Depletion curves for various insecticides applied at 5 lb/5 in acre to loam soils

that was recovered after a given time from the soil. In these experiments emulsifiable formulations of aldrin, Sevin (carbaryl), phorate (Thimet), Guthion (azinphosmethyl), parathion, methylparathion or malathion had been incorporated at the rate of 5 lb per acre (3.1 p.p.m.) into the upper 5 in layer of a silt loam. These soils were sampled during a 5-month period (May–October) and analysed, thus resulting in typical depletion curves as shown in Figure 1. Aldrin residues include dieldrin, and phorate residues include its sulphone and sulphoxide.

### MOVEMENT AND METABOLISM UNDER FIELD CONDITIONS

The movement and metabolism of phorate in field soils was studied after granular application of the insecticide at 5 and 10 lb per acre. Residues moved in both vertical and horizontal directions. This was determined by analyses of horizontal and vertical soil cores collected 4 months after soil treatment 2 to 4 in away from the original band. Extracts of these soils were all toxic to *Drosophila melanogaster* Meigen, indicating that insects could still be controlled 2 to 4 in away from the place of the original phorate deposit. Contrary to findings with emulsifiable concentrates, phorate persisted for a relatively long period. From 8 to 60% of total residues recovered from soil samples collected through the band was still in the form of phorate. Metabolism of phorate was most pronounced in the 5 lb/acre-treated soil and was relatively slower in the 10 lb/acre-treated soil. Phorate sulphone was the

major component in all soil cores collected from the 5 lb/acre-treated soil, but only in soil cores collected below the original band treated at 10 lb of actual phorate/acre. The relative composition of vertical soil cores collected through the band (5 lb/acre applied) and 2 in away from it was phorate sulphone > phorate sulphoxide > phorate, while in cores from the 10lb/acre-treated soil this composition was phorate > phorate sulphone > phorate sulphoxide<sup>2</sup>.

The effects of application methods of phorate at 10 lb/acre on its metabolism, toxicity and translocation into crops were also studied under field conditions. Residues were least persistent when phorate was applied solely to the soil surface; 6 days was required until half of the applied dosage could no longer be detected in the form of phorate and its metabolites. Residues were more persistent after the insecticide had been mixed with the upper 4-5-in soil layer, and 30 days was required until half of the applied dosage could no longer be detected. Less than 1.6% of the applied phorate was measured 14 and 30 days after its application to the soil surface or the upper 4-5-in soil layer, respectively. Highest amounts of phorate sulphoxide (3.2 and 4.88 lb/acre) were recovered from both field soils 6 days after phorate application. Subsequently, the concentration of phorate sulphoxide in these soils declined rapidly, while the amounts of phorate sulphone increased, until they in turn reached their peak (1.44 and 3.5 lb/acre) at 1 month after soil treatment. Residues consisting entirely of phorate sulphone were found 2 months after application of phorate to the soil surface but 5 months after mixing of the insecticide with the upper soil layer. Insect mortalities were obtained with both field soils. Potatoes grown in these soils during 1971 and 1972 did not contain measurable insecticide residues. Corn silage contained phorate sulphone at 0.03 and 0.18 p.p.m. in 1971, but no measurable residues in 1972. Carrots from both field plots contained in 1971 phorate sulphone at 0.12 and 0.50 p.p.m. and in 1972 at 0.04 p.p.m. after growing in the soil whose upper layer had originally been mixed with the insecticide<sup>3</sup>.

### EFFECTS OF PERCOLATING WATER ON TRANSPORT OF INSECTICIDES IN SOILS

The movement and degradation of [<sup>14</sup>C]-Dyfonate, another organophosphorus insecticide, in different soil types was tested in the laboratory under leaching and non-leaching conditions, at different temperatures and various incubation times. Different apparatuses are described which had been especially designed for testing the movement of pesticidal chemicals in soils with and without percolating water. Although Dyfonate did not move to an appreciable extent through an agricultural loam soil, its transport with water through soils was, to a large extent, a function of the soil type. Water after its percolation through a silt loam did not contain measurable amounts of the insecticide, while water after its percolation through a sandy loam soil was toxic to mosquito larvae and contained 4% of the dosage originally applied to the top soil layer. After degradation of [<sup>14</sup>C]-Dyfonate in soils, radiocarbon was lost from the soil by volatilization of the ethoxy moiety and partially by transport of the ring moiety with water. When no water was

percolated, the insecticide also degraded and moved into untreated soil, but to a lesser degree<sup>4</sup>.

In the following study the effects of detergents and inorganic salts in water on the movement and persistence of aldrin and parathion in agricultural loam soils were investigated under leaching and non-leaching conditions. The effect of the detergents ABS (alkyl benzene sulphonate) and LAS (linear alkyl benzene sulphonate) and sodium chloride in water, or of a complete plant nutrient solution, on the movement of the insecticides in the soil also was studied. The water, after its percolation through insecticide-treated soil and through lower insecticide-free soil layers, was analysed for insecticidal residues. Quartz sand of no sorptive capacity and minimal microbiological activity was used as a control. The effects of the sorptive capacities of a loam soil became evident. After its percolation through loam soil, treated at a rate of 2 lb/6 in acre, the water did not contain measurable amounts of aldrin but contained small amounts of parathion. The amount of parathion in percolated water was a function of the concentration of the insecticide in the soil. Detergents, having increased the persistence of parathion in soil, indirectly increased the amount of parathion within the percolated water. Aldrin moved within soils in the absence of percolated water, while parathion moved to a lesser extent. After the percolation of water or water + LAS through insecticide-treated (20 lb/6 in acre) soil and through lower untreated soil layers, small amounts of aldrin (0.1–0.2 p.p.b.) and parathion (0.2–0.8 p.p.b.) were found in the water samples. These amounts were far below the water-solubility of these insecticides and the water was not toxic to mosquito larvae. The presence of salts prevented the appearance of aldrin residues in the percolated water and reduced the amount of parathion residues. It appears unlikely that water in deeper soil strata could be contaminated with insecticidal residues from the upper agricultural soil layers<sup>5</sup>.

#### TRANSLOCATION AND METABOLISM OF [<sup>14</sup>C]-PHORATE AS AFFECTED BY PERCOLATING WATER IN A MODEL SOIL-PLANT ECOSYSTEM

Corn plants were grown in different soils treated with [<sup>14</sup>C]-phorate, while water was percolated through these soils. Seventeen days after soil treatment and planting, soils still contained phorate but also phorate sulphoxide and phorate sulphone; only metabolites of the originally applied insecticide were found in plants. Roots contained primarily phorate sulphone and some phorate sulphoxide, while the corn leaves contained in addition phoratoxon sulphoxide and phoratoxon sulphone. It appears, therefore, that the roots of corn plants either absorbed phorate from the soil and metabolized it into its sulphoxide and sulphone or absorbed these metabolites directly from the soil, then translocated them into the greens. It was here that their further oxidation into their oxygen analogues (phosphorothiolates) presumably occurred. Whole corn plants from a quartz sand contained more <sup>14</sup>C-compounds than those grown in the Plainfield sand, primarily in their roots, which contained 2.5–5 times more phorate-derived materials than those grown in the Plainfield sand. However, the amounts of <sup>14</sup>C-materials that

had been translocated into the corn greens were similar with all soils, indicating that the uptake and translocation of chemicals from soil is to a large extent governed by physiological processes of the corn plant itself<sup>6</sup>.

### FACTORS AFFECTING TRANSPORT AND METABOLISM OF INSECTICIDES FROM SOILS INTO PLANTS

Various factors, such as metabolic inhibitors and root aeration, that affect the penetration, translocation and metabolism of insecticides in plants were studied. In this respect, the penetration of lindane from a nutrient solution into pea roots and the translocation of the insecticide into pea greens were investigated. The selective transport of lindane into roots was dependent on energy supply systems of the root cells. The presence of metabolic inhibitors such as KCN ( $5 \times 10^{-4}$  M) and DNP ( $10^{-5}$  M) resulted in an increased penetration of lindane and its decreased translocation into greens. Because of the inhibitory action of rutamycin and atractyloside on some phase of energy transformation, roots were exposed to these inhibitors at concentrations of  $5 \times 10^{-6}$  M and  $2.5 \times 10^{-6}$  M, respectively. This also resulted in an increased penetration of lindane into roots. Similar results were obtained under non-aerating conditions or aeration with nitrogen of the nutrient solutions. In general, a rapid accumulation of lindane was observed on or in roots within 1–2 h after root exposure to the insecticide and a slower but constant increase in the translocation of lindane into greens occurred over a 6-day exposure period. The initial rapid 'penetration' into roots was not dependent on the presence of pea greens, while after a 24 h exposure period excised roots contained less insecticide than those of intact plants. The penetration of lindane into roots was proportional to the insecticide concentration up to 6 p.p.m., while its translocation into greens increased at a much slower rate<sup>7</sup>.

The effects of mineral nutrient deficiencies on the penetration, translocation and metabolism of [<sup>14</sup>C](ethoxy)Dyfonate in pea plants were investigated. With plants grown in nitrogen-deficient nutrient solutions, the penetration of radiocarbon into roots increased by 61%, while the translocation into greens was not affected. Deficiencies of potassium, calcium, and magnesium resulted in reduction of <sup>14</sup>C into the roots by 48, 61 and 58%, respectively, while potassium deficiency caused an 80% increase in translocation. In roots 81–91% of the recovered radiocarbon was associated with organic solvent phase, while in the greens these phases contained only 10–16%. Conversely, only 8–11% of the total <sup>14</sup>C recovered from roots and 48–71% from greens was associated with the water phase. The amounts of unextractable radioactivity in the roots were relatively small (1–6% of the total recovered), while in the greens these figures were 19–47%. Nutrient deficiencies affected the production of water-soluble metabolites and the amounts of unextractable radioactivity. Concentrations of Dyfonate in control roots amounted to 80.2 p.p.m. and of Dyfoxon to 0.87 p.p.m. In the greens these concentrations were considerably lower, but the amounts of Dyfoxon in the greens relative to the amounts of Dyfonate were much larger. A lack of nitrogen or sulphur resulted in the presence of higher concentrations of Dyfonate in the roots, while deficiencies in potassium, calcium or

magnesium caused significant decreases in concentrations of both Dyfonate and Dyfoxon in roots. Concentrations of Dyfoxon in greens were reduced owing to deficiencies of all elements except nitrogen<sup>8</sup>.

### REFERENCES

- <sup>1</sup> E. P. Lichtenstein, in 'Degradation of synthetic molecules in the biosphere', *Proceedings of the National Academy of Science: Washington* (1972).
- <sup>2</sup> K. R. Schulz, E. P. Lichtenstein, T. W. Fuhremann and T. T. Liang, *J. Econ. Ent.* **66** (4), 873 (1973).
- <sup>3</sup> E. P. Lichtenstein, T. W. Fuhremann, K. R. Schulz and T. T. Liang, *J. Econ. Ent.* **66** (4), 863 (1973).
- <sup>4</sup> E. P. Lichtenstein, K. R. Schulz and T. W. Fuhremann, *J. Agric. Fd Chem.* **20** (4), 831 (1972).
- <sup>5</sup> E. P. Lichtenstein, T. W. Fuhremann, K. R. Schulz and R. F. Skrentny, *J. Econ. Ent.* **60** (6), 1714 (1967).
- <sup>6</sup> E. P. Lichtenstein, T. W. Fuhremann and K. R. Schulz, *J. Agric. Fd Chem.* (1974).
- <sup>7</sup> N. S. Talekar and E. P. Lichtenstein, *J. Agric. Fd Chem.* **20** (6), 1260 (1972).
- <sup>8</sup> N. S. Talekar and E. P. Lichtenstein, *J. Agric. Fd Chem.* **21** (5), 851 (1973).