# Behavior of Five Organophosphorus Pesticides in Dust Derived from Several Soil Types

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There is currently great concern for the safety of agricultural workers entering fields and orchards after pesticide applications. Pruners, thinners, and pickers have been made ill by working with some crops after commercial application of certain organophosphorus insecticides, e.g. parathion, azinphosmethyl, ethion, and dioxathion in citrus groves (GUNTHER et al. 1973). As many incidences of reported illnesses involve worker re-entry after the legally prescribed waiting intervals, some circumstance or combination of circumstances not adequately recognized by existing regulations for using pesticides may exist. As workers are exposed to large areas of treated foliage throughout the working day, especially in tree fruits, grapes, cotton, and tobacco, the nature of the foliar residues may be very important with respect to worker safety upon re-entry into insecticide-treated areas. The penetration of pesticides into the waxy and other subsurface layers of plant foliage may be mediated by the strong sorptive properties of dust and other detritus on the plant. The pesticide residues on the leaf surface may be stabilized, converted to more toxic products, or inactivated by sorption onto soil dust and other debris. These residues may be transferred to workers via inhalation of airborne particles dislodged by worker activity and transferred directly to the skin and clothing. An important factor increasing the degree of exposure of workers to dislodgable spray residues is the trend toward concentrated sprays which may leave deposits much higher than those resulting from application of the same amount of pesticide per acre in a more dilute spray mixture (CARMAN et al. 1972). More data on the nature and environmental fate of residues of organophosphorus pesticide chemicals after their application are needed. Evaluation of the stabilizing or destabilizing effects of soil dust on the persistence of some pesticides on citrus trees is under investigation. As the application of microgram quantities of pesticide on milligram quantities of dust results in extremely high concentrations (ppm) of pesticide in the dust, laboratory experiments were conducted to observe the behavior of relatively high (500 ppm) concentrations of five organophosphorus pesticides (azinphosmethyl, dioxathion, ethion, parathion, and phenthoate) in soil dusts obtained from a wide variety of soil types.

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## Experimental

Each soil was passed through a 100-mesh sieve to obtain the dust. Soil characteristics prior to sieving for soils not previously reported (IWATA et al. 1973) are in Table I. Air-dry samples of soil dust equivalent to 150 g of oven-dry dust, in one-qt wide-mouth Mason jars, were fortified with 75 mg of parathion, azinphosmethyl, ethion, phenthoate or dioxathion. Each fortified dust sample was mixed manually, the solvent was allowed to evaporate, and distilled water was added to adjust the moisture content to 40% of maximum retentive capacity as determined from unsieved soils, except for parathion-fortified Windy loam (70%) and Santa Lucia silt loam (60%) dusts. Sample jars, each covered with aluminum foil, were maintained at 30°C and constant overhead illumination with fluorescent tubes.

TABLE I

Soil Characteristics

| Soil[a] | Mechanical analysis, %<br>Sand | <br>Silt | <br>Clay | pH | Saturation percentage | % organic matter |
|---|---|---|---|---|---|---|
| #58 | 53.6 | 31.0 | 15.4 | 6.9 | 26.3 | 0.8 |
| #59 | 12.5 | 50.7 | 36.8 | 7.3 | 48.0 | 2.1 |
| #60 | 22.4 | 34.5 | 43.1 | 7.3 | 57.6 | 2.3 |
| #61 | 56.0 | 33.0 | 11.0 | 7.6 | 22.8 | 1.8 |

[a] #58 = Three Sisters Ranch, fine sandy loam. #59 = B and W Ranch, silty clay loam. #60 = Tulare, clay. #61 = Baer Ranch, sandy loam.

Extraction. Three subsamples, each representing 2.0 g of oven-dry dust, were extracted without drying. Each sample was placed in a two-oz screw-cap bottle and 40 ml of a benzene-acetone (1+1) mixture was added. The bottle, closed with aluminum foil and a Teflon-lined screw cap, was mechanically shaken for one hr. The extraction was repeated twice, each time using 20 ml of fresh solvent mixture and 10 min shaking. Each time, the supernatant liquid was decanted onto a single column of 25 g of anhydrous $Na_2SO_4$ and the eluate was collected in a single flask. The dust, bottle, and $Na_2SO_4$ column were rinsed with two successive 10-ml portions of acetone. The extract after appropriate dilution or concentration to about one μg/ml was analyzed without cleanup by gas chromatography.

Analyses. A Trācor MT-220 gas chromatograph equipped with a flame photometric detector was used with inlet and detector temperatures of 233 and 240°C, respectively, and with a nitrogen carrier gas flow rate of 80 ml/min. A 0.61 m x 4 mm i.d. borosilicate column packed with 3% DC-200 on 60/80 mesh Gas Chrom Q and operated at 175°C was used for ethion. A 1.83 m x 4 mm i.d. borosilicate column packed with 3% OV-1 on 80/100 mesh Chromosorb W and operated at 200°C was used for parathion and for phenthoate at 220°C. A 1.83 m x 4 mm i.d. borosilicate column packed with a 1:1 mixture of 10% DC-200 and 15% QF-1, each coated separately on 60/80 mesh Gas Chrom Q, at a temperature of 210°C was used for dioxathion, and a 0.61 m x 4 mm i.d. borosilicate column packed with 3% OV-1 on 80/100 mesh Chromosorb W at a temperature of 200°C was used for azinphosmethyl. Quantitation was by peak height measurements; the amount injected was one to five ng. Samples were generally analyzed within one wk after sampling.

## Results and Discussion

Recovery data for azinphosmethyl, ethion, and parathion from ten soil dusts and for dioxathion and phenthoate from four soil dusts are in Tables II and III. The soils listed in Table II were collected from non-agrarian land and represent diverse soil types; soils listed in Table III were collected from citrus groves having a history of worker poisoning episodes. The soils were sieved (150-μm opening) prior to use. This process changed the characteristics of some of the soils, particularly the sandy ones. Dust #58 (Table III), a fine sandy loam, was obviously still dry when water was added to 40% of saturation based on unsieved soil data. Consequently, this soil exhibited an aberrant behavior due to the effect of the dry condition on soil microorganism activity. Figure 1 illustrates the recovery data obtained for the five pesticides incorporated in a silty clay loam dust and is generally representative of the results obtained in the other dusts.

Parathion. Soils #58 through #61 were freshly collected prior to fortification. In dusts #59 through #61 over 85% of the parathion disappeared within ten days. In the drier dust #58 only 58% disappeared during the first 30 days, but over 99% was gone after an additional 20 days. These results were consistent with an adjustment of parathion-degrading soil microorganisms (LICHTENSTEIN and SCHULZ 1964) to the dry conditions. The soils in Table II were stored in an air-dried condition for several years prior to use and the adjustment of the microorganisms, present in the water added to the dust (and possibly a small residual population in the soil), required at least ten days. Once they were established, the parathion residue levels dropped dramatically regardless of soil type. The Santa Lucia silt loam and Windy loam dusts were moistened at 60 and 70% of capacity, respectively, rather than 40% since IWATA et al. (1973) found that degradation in the unsieved soils proceeded without microbial activity at the lower moisture level.

Phenthoate. The recovery data from four dusts are given in Table III. In dusts #59 through #61, 50% of the pesticide was degraded within ten days, and over 95% within 30 days. A semilogarithmic plot of the data gave slightly curved lines for dust #59 (See Fig. 1) and #60 and a straight line for dust #61. In the drier dust #58, 62% of the pesticide remained after 75 days, but less than 1% remained after an additional 75 days. The

## TABLE II

Recovery Data for Azinphosmethyl, Ethion, and Parathion from Soil Dust

| Soil[a] | Days (ppm) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 4 | 10 | 20 | 30 | 50 | 52 | 60 | 74 | 100 | 150 | 200 |
| | | | | | PARATHION | | | | | | | |
| Mocho silt loam | 460 | 430 | 400 | 4.3 | 2.4 | 1.4 | | | | | | |
| Linne clay | 460 | 370 | 360 | 290 | 8.8 | 1.0 | | | | | | |
| Madera sandy loam | 460 | 430 | 390 | 18 | 11 | 8.6 | | | | | | |
| Laveen loamy sand | 470 | 450 | 420 | 440 | 430 | 0.7 | | | | | | |
| Santa Lucia silt loam | 450 | 410 | 400 | 290 | 21 | 9.4 | | | 7.9 | 6.8 | | |
| Windy loam | 450 | 460 | 440 | 330 | 49 | 25 | | | 19 | 16 | | |
| | | | | | ETHION | | | | | | | |
| Mocho | 460 | 430 | 480 | 450 | 460 | | | 430 | | 420 | 400 | 330 |
| Linne | 450 | 420 | 410 | 430 | 410 | | | 390 | | 400 | 370 | 330 |
| Madera | 440 | 400 | 410 | 410 | 410 | | | 390 | | 410 | 380 | 330 |
| Laveen | 510 | 470 | 470 | 440 | 450 | | | 430 | | 430 | 400 | 340 |
| Santa Lucia | 490 | 450 | 470 | 450 | 450 | | | 430 | | 420 | 370 | 350 |
| Windy | 460 | 440 | 470 | 440 | 450 | | | 420 | | 450 | 360 | 340 |
| | | | | | AZINPHOSMETHYL | | | | | | | |
| Mocho | 420 | 300 | 200 | 140 | 80 | | 36 | | 22 | 9.8 | 4.2 | 1.6 |
| Linne | 420 | 300 | 210 | 120 | 64 | | 20 | | 6.9 | 2.5 | — | — |
| Madera | 430 | 410 | 400 | 350 | 340 | | 290 | | 260 | 190 | 130 | 72 |
| Laveen | 430 | 420 | 420 | 370 | 380 | | 290 | | 230 | 180 | 80 | 39 |
| Santa Lucia | 450 | 370 | 320 | 270 | 230 | | 130 | | 55 | 24 | 9.8 | 5.4 |
| Windy | 410 | 400 | 350 | 320 | 270 | | 250 | | 230 | 160 | 110 | 89 |

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[a] Soil moisture, except for parathion-fortified Santa Lucia silt loam (60%) and Windy loam (70%), adjusted to 40% of maximum retentive capacity, as determined for unsieved soil.

## TABLE III

Recovery Data for Azinphosmethyl, Dioxathion, Ethion, Parathion, and Phenthoate from Soil Dust

| Soil[a] | Days (ppm) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 4 | 10 | 20 | 30 | 50 | 60 | 74 | 100 | 150 | 200 |
| | | | | PARATHION | | | | | | | |
| #58 Three Sisters Ranch | 470 | 450 | 430 | 380 | 200 | 4.0 | | | | | |
| #59 B and W Ranch | 460 | 290 | 7.4 | 1.9 | | | | | | | |
| #60 Tulare | 480 | 390 | 65 | 3.3 | | | | | | | |
| #61 Baer Ranch | 450 | 380 | 21 | 2.2 | | | | | | | |
| | | | | ETHION | | | | | | | |
| #58 | 420 | 440 | 420 | 450 | 400 | | 420 | | 380 | 360 | 370 |
| #59 | 440 | 430 | 420 | 410 | 390 | | 400 | | 340 | 310 | 280 |
| #60 | 430 | 430 | 430 | 380 | 390 | | 370 | | 320 | 260 | 230 |
| #61 | 440 | 460 | 420 | 410 | 400 | | 400 | | 330 | 290 | 280 |
| | | | | AZINPHOSMETHYL | | | | | | | |
| #58 | 450 | 440 | 410 | 370 | 330 | 280 | | 220 | 160 | 100 | |
| #59 | 450 | 400 | 270 | 170 | 110 | 46 | | 14 | 4.8 | — | |
| #60 | 460 | 330 | 250 | 130 | 68 | 26 | | 8.5 | 3.0 | — | |
| #61 | 460 | 420 | 340 | 240 | 200 | 130 | | 78 | 44 | 21 | |
| | | | | PHENTHOATE | | | | | | | |
| #58 | 470 | 440 | 360 | 360 | 340 | 370 | | 290 | 130 | 1.7 | |
| #59 | 460 | 200 | 94 | 38 | 19 | 4.8 | | | | | |
| #60 | 430 | 170 | 100 | 34 | 14 | 3.5 | | | | | |
| #61 | 440 | 260 | 140 | 52 | 19 | 1.0 | | | | | |
| | | | | DIOXATHION | | | | | | | |
| #58 | 490 | 410 | 310 | 210 | 180 | — | 100 | 71 | 47 | 31 | 22 |
| #59 | 480 | 430 | 410 | 340 | 340 | 240 | — | 180 | 130 | 60 | 39 |
| #60 | 480 | 450 | 370 | 320 | 290 | 220 | — | 170 | 100 | 48 | 30 |
| #61 | 480 | 440 | 360 | 290 | 280 | 160 | 130 | 80 | 46 | 12 | 6.0 |

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[a] #58 — fine sandy loam, #59 — silty clay loam, #60 — clay, #61 — sandy loam; soil moisture adjusted to 40% of maximum retentive capacity, as determined for unsieved soil.

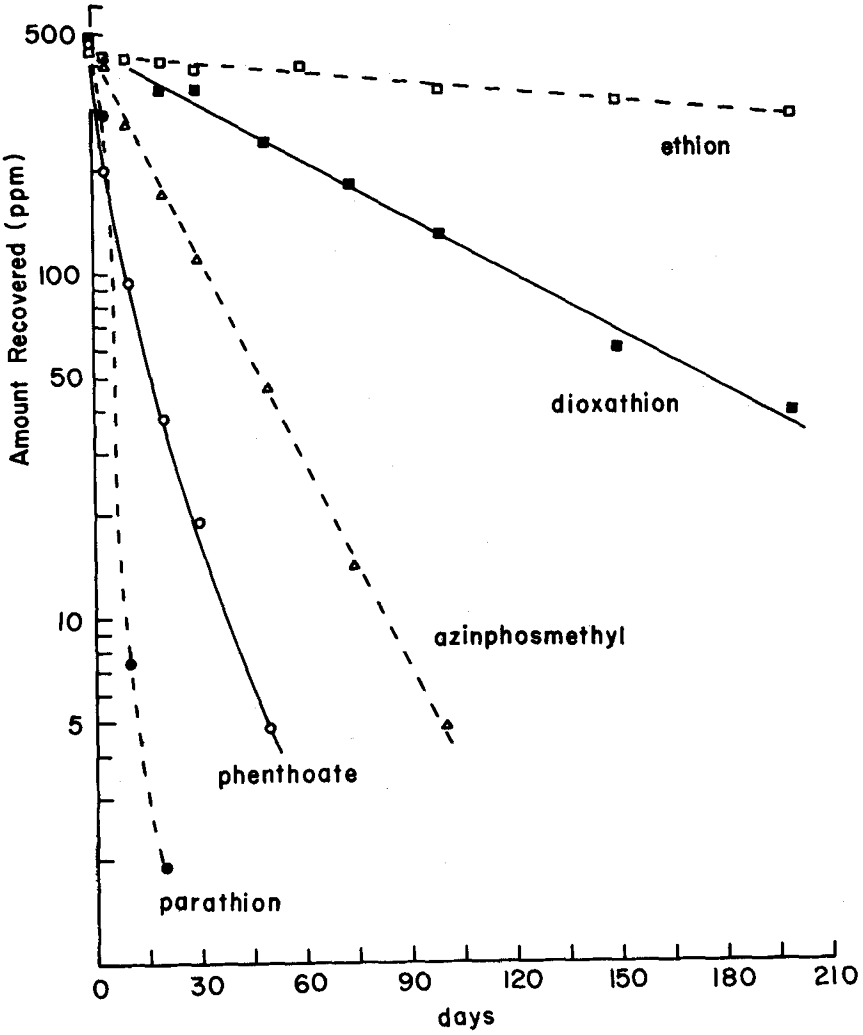

Fig. 1.--Recovery of five organophosphorus pesticides from the silty clay loam dust #59 which was maintained at 30°C with a moisture of 40% of maximum retentive capacity, as determined from the unsieved soil.

results were attributed to the adjustment of soil microorganisms, capable of degrading phenthoate, to the relatively dry conditions. Microbial degradation is thus implicated in all of the dusts. Conditions favoring microbial activity, such as adequate moisture and warm temperatures, make soil type of secondary importance for phenthoate degradation.

Azinphosmethyl. Of the five pesticides, soil type showed its most pronounced effect on the degradation of azinphosmethyl. Semi-logarithmic plots of the recovery data in Tables II and III were either linear (See Fig. 1) or showed slight curvature. For the ten dusts, the approximate half-life (days) was 10 for two clays and a silt loam, 15 for a silty clay loam, 25 for a silt loam, 30 for a sandy loam, 65 for a loamy sand, 70 for a fine sandy loam, and 80 for a sandy loam and a loam. YARON et al. (1974) also reported that azinphosmethyl losses follow first-order kinetics. The half-life in wet (50% of saturation) sterilized soil at 25°C was 29 days while in natural soil it was 13 days; loss through both chemical and biological processes was suggested.

SCHULZ et al. (1970) reported considerably faster laboratory degradation at 15 ppm; analytical grade azinphosmethyl incorporated in loam soil at 30°C resulted in 95% disappearance after six days while a diluted emulsifiable concentrate required 22 days. In field experiments, when azinphosmethyl was applied as an emulsion and left on the soil surface, a 50% loss occurred in 12 days, while application in granular form followed by rototilling into the soil required 28 days for a 50% loss.

Dioxathion. The recovery data for dioxathion residues from four dusts are given in Table III. Residues decreased most rapidly from the drier, fine sandy loam-derived dust #58. A semi-logarithmic plot of the data gave a definite curve with a decreasing rate of disappearance with time. A similar plot of the data obtained for the sandy loam-derived dust #61, in contrast, was linear, as were the plots of the data from dusts #59 (See Fig. 1) and #60. The half-lives for the dioxathion residues in dusts #59, #60, and #61 were approximately 55, 45, and 30 days, respectively. Residues disappeared more rapidly from the two sandy loam-derived dusts, in contrast to azinphosmethyl. The mechanism of loss of dioxathion from the drier dust #58 is more complex than the simple hydrolysis mechanism which fits the data obtained from dusts #59 through #61.

Ethion. Of the five pesticides studied ethion was the most persistent in soil dust. In the six dusts in Table II ethion residues decreased in concentration by only 28% in 200 days. In the four dusts in Table III ethion residues decreased an average of 33% in 200 days. A 12% loss of ethion from the drier dust #58 was definitely less than the 36, 23, and 36% losses observed for dusts #59, #60, and #61, respectively. The semi-logarithmic plot of the data for each of the ten dusts was linear. Extrapolating the line obtained by plotting the mean ppm value of the data from all ten dusts, regardless of soil type, predicted a half-life in soil dust of 420 days for ethion.

For parathion and phenthoate microbial degradation was very important, but may not be important on dust adhering to plant surfaces. Dust #58 showed that, under somewhat dry conditions, parathion and phenthoate can be quite persistent. As the effect of sunlight on the sorbed pesticide was neglected, investigations under actual field conditions will be required to supplement the laboratory studies. The dust may facilitate the photochemical conversion of parathion to paraoxon and other compounds such as O,O,S-triethylthiophosphate (GRUNWELL et al. 1973). The persistence of azinphosmethyl, dioxathion, and ethion was moderate to very high at the concentrations used.

The approximate persistence half-life values of parathion, azinphosmethyl, dioxathion, and ethion on and in lemon fruit were 60, 38, 70, and 30 days, respectively, and on and in oranges were >100, 355, >100, and 42 days, respectively (GUNTHER 1969). Parathion, the least persistent in moist dust, was as persistent as dioxathion in citrus fruits; ethion, the most persistent in moist dust, was the least persistent in the fruit. The results obtained approximate the behavior of the pesticides deposited on soil, although probably not of the residues on the plant, and serve primarily as a guide for future field studies.

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## References

CARMAN, G. E., W. E. WESTLAKE, and F. A. GUNTHER: Bull. Environ. Contam. Toxicol. 8, 38 (1972).

GRUNWELL, J. R., and R. H. ERICKSON: J. Agric. Food Chem. 21, 929 (1973).

GUNTHER, F. A.: Residue Rev. 28, 1 (1969).

GUNTHER, F. A., W. E. WESTLAKE, J. H. BARKLEY, W. WINTERLIN, and L. LANGBEHN: Bull. Environ. Contam. Toxicol. 9, 243 (1973).

IWATA, Y., W. E. WESTLAKE, and F. A. GUNTHER: Archives Environ. Contam. Toxicol. 1, 84 (1973).

LICHTENSTEIN, E. P., and K. R. SCHULZ: J. Econ. Entomol. 57, 618 (1964).

SCHULZ, K. R., E. P. LICHTENSTEIN, T. T. LIANG, and T. W. FUHREMANN: J. Econ. Entomol. 63, 432 (1970).

YARON, B., B. HEUER, and Y. BIRK: J. Agric. Food Chem. 22, 439 (1974).